

The Effect of Silicate Fillers on Adhesion and Adhesion Strength Properties of Water-Based Coatings

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Abstract. The properties of coatings largely depend on the nature of the interaction of the film material with the substrate – the type of bonds between them. The degree of this interaction, associated with the nature of the paint and varnish material, mineral fillers and the nature of the surface to be protected, may be a criterion for evaluating the protective and operational properties. Therefore, an urgent scientific and practical task is to study the silicate fillers effect on the nature of adhesive interactions at the interface of water-based coatings with a steel substrate and to establish the relationship of adhesion strength properties with the thermodynamic adhesion work. It is shown that the adhesion strength in the paint systems for steel is significantly affected by the thermodynamic adhesion work, in which the dispersed component of the surface free energy makes the greatest contribution when the degree of filler content changes.

Introduction

The properties of coatings largely depend on the nature of the interaction of the film material with the substrate – the type of bonds between them. Adsorption interaction is established already at the time of application of the liquid paint material on a solid surface. The degree of this interaction, associated with the nature of the paint and varnish material and mineral fillers and the nature of the surface to be protected, determines the completeness of its wetting, which is manifested in many indicators of coatings: hiding power, water absorption, adhesion and protective and decorative properties.

By adhesion of coatings is understood the phenomenon of establishing a bond between the film and the substrate on which it is applied. Adhesion is usually judged by adhesion strength, i.e. the work that needs to be spent on breaking the adhesive bond. Adhesion is the most important property of paint coatings. Many properties of coatings substantially depend on the value and stability of adhesion, including durability and protective ability under operating conditions.

Adhesion work W_α can conditionally be represented as the product of the average energy of the bond unit \overline{W} the number of bonds N per unit surface of the adhesive contact:

$$W_\alpha = \overline{W} \cdot N. \quad (1)$$

It follows that the adhesion strength of the coatings depends on the nature and density of the adhesive bonds. Between dissimilar bodies, bonds of various nature can arise: chemical (ionic, covalent, coordination) with energies from 65 to 1000 kJ/mol, hydrogen and van der Waals (induction, dispersion, dipole, etc.), whose energy in most cases does not exceed 50 kJ/mol. When applying coatings, the interaction with the substrate is established already at the moment of contact of the liquid paint material. However, the values of the adhesion work of liquid paint and the

finished hard coating, as a rule, are not equal to each other. In the process of film formation, the chemical composition, structure and properties of the material change, conformational changes in macromolecules occur, activation of the surface of the substrate and the appearance of stresses in the contact layer are possible. All this affects the nature of the adhesive interaction, and the more significant, the greater the difference in the conditions of film formation and the application of coatings.

Therefore, an urgent scientific and practical task is to study the effect of silicate fillers on the nature of adhesive interactions at the interface of water-based coatings with a steel substrate and to establish the relationship of adhesion strength properties with the thermodynamic adhesion work [1-6].

Materials and Methods

Styrene acrylic dispersion (non-volatile 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.

Hollow aluminosilicate microspheres and silicates based on hydrophobic 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 00.61 m²/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 [7-10].

To control the rheological properties, a hydrophobic AEROSIL filler (specific surface area 200 m²/g and average density 0.051-0.059 g/cm³) 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 [11-14].

To assess the effect of silicate fillers on the nature of the adhesive interactions at the water-based coatings interface with a steel substrate, the contact angle was determined from the parameters of a small droplet lying on the plane. The droplet size of the coating composition deposited on the defatted surface of the substrate was determined with an interval of 1 minute until it became clear that the droplet size did not change, this moment will become the exposure time of the sample. Measurement of droplet size was carried out using a Cathetometer; the accuracy of measuring the contact angles was 2.5 degrees. The calculation of the contact angle was carried out according to the formula for a spherical head at $\theta < 90^\circ$:

$$\cos \theta = (r^2 - h^2)/(r^2 + h^2), \quad (2)$$

where r – drop radius; h – maximum drop height.

Free surface energy (σ), its polar (σ_p) and dispersion (σ_d) components for the hardened samples of coatings and steel substrate were determined by the two-fluid Owens-Wendt-Kabl (OWK) method behind the angle of wetting with test liquids, measured by the method of a lying drop [15-24]. The characteristics of the test liquids and the steel substrate are given in Table 1.

Table 1. Characteristics of test fluids and steel substrates

Name	σ , [mJ/m ²]	σ^d , [mJ/m ²]	σ^p , [mJ/m ²]
Water	72.2	21.8	51.0
Dimethyl Sulfoxide	43.6	34.9	8.7
Steel	35.4	4.6	30.8

The OWK method is based on the fact that free surface energy (FSE) is the sum of the polar and dispersion components (Equation 3-5) and is determined by linear regression, based on the results of determining the contact angles of contact with liquids with known polar and dispersion components:

$$\sigma_l \cdot (1 + \cos \theta) = 2 \cdot ((\sigma_l^d \cdot \sigma_s^d)^{0.5} + (\sigma_l^p \cdot \sigma_s^p)^{0.5}), \quad (3)$$

$$\sigma_l = \sigma_l^d + \sigma_l^p, \quad (4)$$

$$\sigma_s = \sigma_s^d + \sigma_s^p, \quad (5)$$

$$\sigma_l \cdot (\cos \theta + 1) / 2 \cdot (\sigma_l^d)^{0.5} = (\sigma_s^p)^{0.5} \cdot (\sigma_l^p)^{0.5} / ((\sigma_l^d)^{0.5} + (\sigma_s^d)^{0.5}), \quad (6)$$

where σ_l – liquid surface tension; σ_s – FSE of solid body; σ_s^p – polar component of the FSE of the liquid and solid, respectively, which is determined by the electrostatic interaction, hydrogen bonds, and the acid-base Lewis interaction; σ_l^d , σ_s^d – dispersion component of the FSE of the liquid and solid, respectively, determined by the Van der Waals interaction; θ – contact angle of a solid.

The quantitative value of coating adhesion to concrete was determined by the tear-off method (ISO 4624:2002), which consists in measuring the tear-off strength of the coating from the surface to be protected using a metal stamp glued to the coating and a dynamometer (tearing device). As an adhesive, a two-component epoxy composition was used, which has higher adhesion to the test coating and to metal disks as compared with the value of adhesion of the coating to the concrete surface.

Discussion

Wetting is the initial stage of the formation of the interface in the composite material and one of the most important conditions for good adhesion of the polymer matrix to the filler. Yu.S. Lipatov [1] has repeatedly noted the significant influence of wetting processes on the possibility of strengthening polymers with reinforcing elements. It is known that wetting a solid surface with a liquid depends on the nature of the interaction between the liquid and the solid. It is characterized by the equilibrium contact angle θ and is described by the Young equation:

$$\cos \theta = (\sigma_s - \sigma_{s/l}) / \sigma_l, \quad (7)$$

where θ – contact angle, σ_s – solid surface energy, $\sigma_{s/l}$ – energy of interfacial interaction of a solid surface with a liquid, σ_l – liquid surface energy.

Thus, to increase wetting (an increase in $\cos \theta$), the surface tension of the wetting fluid (σ_l) has to be minimal, and this is possible only if the molecular nature of the surface and the liquid is related. That is, a decrease in free energy is achieved by changing the wetting.

Fig. 1.a shows the curves of changes in the contact angle θ depending on the content of aluminosilicate microspheres (10, 20, 30 wt.%) and AEROSIL (0.5, 1.0, 1.5 wt.%) and with their compatible introduction to the coating composition (Fig. 1.b).

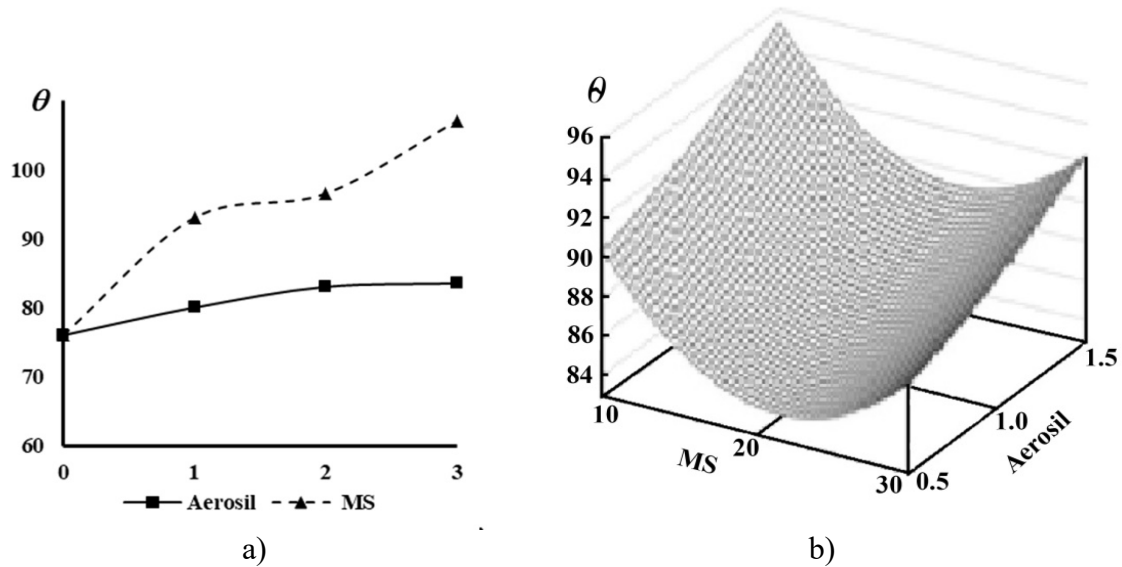


Fig. 1 The dependence of the contact angle based the aluminosilicate microspheres and AEROSIL (a) content and when they are combined into the coating composition (b)

As can be seen from Fig. 1(a), as the AEROSIL content in the paint composition increases, there is no significant increase in the contact angle, since the dispersed component of surface energy in steel is minimal, and when AEROSIL is introduced, there is a significant decrease in the dispersed component of surface energy at the same level polar component. The introduction of aluminosilicate microspheres, compared with AEROSIL, leads to a significant increase in the contact angle (by 10-20 degrees). But, the introduction of more than 30 wt.% microspheres is impractical, since, along with an increase in the viscosity of the composition, the growth of the contact angle begins (more than 90 degrees), which will lead to technological difficulties when applying the paintwork to the surface to be protected.

Good wetting of the substrate is a necessary but not sufficient condition to ensure a strong adhesive bond, moreover, during film formation, the liquid binder can undergo significant changes due to chemical reactions, reorientation of macromolecules in space and in the surface layer, due to defects at the interfacial limit, and changes in composition phases. Therefore, in order to predict the adhesion properties, a thermodynamic approach was used, namely, the study of the relationship between free surface energy (FSE) and its components, and the thermodynamic adhesion work W_a of the cured paint with its adhesion strength to steel

The calculation of the adhesion work was carried out through a series of expressions based on different approximations of the equations of the molecular theory of adhesion:

$$W_a = 2 \cdot \left(\sqrt{\sigma_i^d \cdot \sigma_s^d} + \sqrt{\sigma_i^p \cdot \sigma_s^p} \right), \quad (8)$$

where indices (*d*) and (*p*) refer to the dispersion and polar components of the free surface energy of the paint coating σ_i and substrates σ_s .

Based on the results of the studies, the values of the FSE and the adhesion work W_a for the hardened paint coating were calculated, which are listed in Table 2.

Table 2 – The calculated and experimental FSE values, the adhesion work and the adhesion strength of coatings

Coating composition wt.%	σ^d , [mJ/m ²]	σ^p , [mJ/m ²]	σ , [mJ/m ²]	W_a , [mJ/m ²]	Adhesion, [MPa]
No fillers (Paint Coating (PC))	67.3	25.0	92.8	112.5	0.61
PC+AEROSIL 0.5	67.2	22.2	89.4	111.2	0.50
PC+AEROSIL 1.0	60.8	21.3	82.1	106.3	0.51
PC+AEROSIL 1.5	50.8	20.4	77.2	98.5	0.56
PC+MS 10	60.6	24.5	85.1	107.6	1.23
PC+MS 20	56.9	23.8	80.7	104.7	1.28
PC+MS 30	55.6	20.5	76.1	102.2	1.25
PC+MS+AEROSIL 10/0.5	55.4	22.7	78.1	103.1	1.12
PC+MS+AEROSIL 10/1.0	52.3	21.9	74.2	100.3	1.10
PC+MS+AEROSIL 10/1.5	50.8	21.3	72.1	98.9	1.14
PC+MS+AEROSIL 20/0.5	50.4	22.0	72.4	98.9	1.17
PC+MS+AEROSIL 20/1.0	50.6	20.5	71.1	98.4	1.19
PC+MS+AEROSIL 20/1.5	49.5	21.6	71.1	98.0	1.16
PC+MS+AEROSIL 30/0.5	51.8	19.8	71.6	98.9	1.10
PC+MS+AEROSIL 30/1.0	49.9	20.8	70.7	97.9	1.15
PC+MS+AEROSIL 30/1.5	49.2	20.9	70.1	97.5	1.13

The analysis of the calculated and experimental values of the FSE, the adhesion work (Table 2) show that the introduction of fillers significantly affects the dispersed component of the surface energy (7-18 mJ/m²). At the same time, the polar component remains almost unchanged (1.0-4.5 mJ/m²). This is due to the fact that the amount of polar groups used by the fillers used is not significant. Accordingly, the total surface energy changes by 8-22 mJ/m².

Based on the fact that the steel substrate is characterized by a large part of the polar component of the surface energy, and the surface energy of the studied paint coatings is more dependent on the dispersed component, the adhesion work will depend more on the total surface energy, which will allow predicting the adhesive interaction on the surface of the distribution of paint coatings to steel.

Therefore, it was of considerable scientific interest to correlate the data on the adhesion strength of the studied paint coatings with the value of the adhesion work theoretically calculated for them according to formula (8), in which the place of the test fluid is occupied by polymer adhesive, and the solid is a metal substrate.

The results obtained (Table 2) show that despite the decrease in the thermodynamic work of the adhesion W_a , for the studied paint coatings with the introduction of aluminosilicate microspheres, an increase in the adhesion strength (by 2.1-2.4 times) is observed. This effect can be justified by the colloid-chemical approach, which explains the increase in adhesion strength [1] in systems with different surface energies. As a result, the redistribution of coating components between these surfaces occurs and, as a result, the migration of low molecular weight adhesive fractions to the filler surface occurs. In the boundary layer of the defect, the defectiveness decreases and its homogeneity increases to the limit of filler concentration (30 wt.% MS). At the same time, the introduction of hydrophobic AEROSIL does not significantly reduce the adhesion strength of the paint coating (by 10-15%), which is apparently due to the formation of hydrophobic areas at the adhesive-substrate interface, as evidenced by an increase in the contact angle when AEROSIL is introduced into the paint coating by 3-5 degrees.

With the joint introduction of silicate fillers in paint coatings, the adhesion strength increases by 1.8-2 times, which allows them to be used as protective-decorative coatings.

Conclusions

As a result of studying the effect of silicate fillers on the nature of adhesive interactions with a steel substrate, it was found that the introduction of aluminosilicate microspheres into a water-based coating allows to increase the adhesive strength by 2.1-2.4 times. The introduction of small additives of water-repellent AEROSIL does not have a significant effect on the adhesive strength of the paint coating. It is shown that the adhesion strength in the paint-steel system is significantly affected by the thermodynamic adhesion work, in which the dispersed component of the surface free energy makes the greatest contribution when the degree of filler content changes.

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