Improving the technology of repair painting with powder-coated paints in agro-industrial complex

Andrey Bodrov, Anton Panichkin, Denis Lomakin*, and Andrew Simushkin

Orel State University named after I.S. Turgenev, Russia

Abstract. The article presents the results of studies to determine the dependence of the degree of adhesion and the separation force of the powder coatings layer on the roughness parameter of the substrate, as well as the contact angle of wetting for various methods of preparing the painted surface by chemical methods. In addition, practical tests for stain resistance were carried out, which showed the absence of corrosion damage, as well as a slight change in color, gloss of coatings, chalking and dirt retention on the studied coating samples.

Knowledge of the surface tension coefficient and the work of adhesion allows us to obtain information about the energy state of individual near-surface molecules, which is especially important to consider when developing new methods for diagnosing interphase boundaries, as well as methods for studying the interaction of molecules at these boundaries [1, 9].

One of these methods can be based on measurements of the contact angle of wetting, which can be carried out either directly or using capillary phenomena [13].

Based on the equilibrium condition of interface (G) of three phases, one of which is gas (Figure 1) [15], it is easy to show that the surface tension coefficient σ_{12} is related to the contact angle θ by the following expression [14]:

$$\sigma_{12} = \sqrt{\sigma_1^2 + \sigma_2^2 - 2\sigma_1\sigma_2 \cos \theta} . \quad (1)$$

In this case, the work of adhesion:

$$w_{12} = \sigma_1 + -\sigma_2 \sqrt{\sigma_1^2 + \sigma_2^2 - 2\sigma_1\sigma_2 \cos \theta} . \quad (2)$$

Given the fact that both of these values are expressed in terms of the corresponding molecular interaction energies, it should be recognized that the measurements of the coefficients σ_1 and σ_2 , as well as contact angle of wetting θ , do indeed make it possible to judge the energy state of the interface between substances 1 and 2 and the interaction of the surface molecules of these substances. In particular, using these data, using formulas (1) and (2) and expressing the average distance between the molecules of substances in terms of their density, it is possible to determine the average energy U_{12} of the interaction of the surface molecule of substance 2 with the near-surface layer of the molecules of substance 1 [16]:

* Corresponding author: forstudentwork@mail.ru

$$U_{12} = \pi \cdot \left(\frac{\mu_2}{\rho_2 N_A} \right)^{2/3} \left(\sigma_1 + \sigma_2 - \sqrt{\sigma_1^2 + \sigma_2^2 - 2\sigma_1\sigma_2 \cos \theta} \right), \quad (3)$$

as well as the average energy V_{12} of the pair interaction of molecules of these substances at the interface:

$$V_{12} = \pi \cdot \left(\frac{\mu_1}{\rho_1 N_A} \right)^{2/3} \left(\sigma_1 + \sigma_2 - \sqrt{\sigma_1^2 + \sigma_2^2 - 2\sigma_1\sigma_2 \cos \theta} \right). \quad (4)$$

Fig. 1. Interface (G) of three phases, one of which is gas

Here ρ_1 and ρ_2 are the densities of substances 1 and 2, respectively, μ_1 and μ_2 are their molar masses, N_A is Avogadro's number.

Formulas (1) and (2) are simplified when the inequation is satisfied $2\sigma_1\sigma_2 \ll \sigma_1^2\sigma_2^2$:

$$\sigma_{12} \approx \sigma_1 + \sigma_2 - \frac{\sigma_1\sigma_2}{\sigma_1 + \sigma_2} \cdot (1 + \cos \theta), \quad (5)$$

$$w_{12} \approx \frac{\sigma_1\sigma_2}{\sigma_1 + \sigma_2} \cdot (1 + \cos \theta). \quad (6)$$

When a more stringent condition is met $\sigma_2 \ll \sigma_1$

$$\sigma_{12} \approx \sigma_1 - \sigma_2 \cos \theta \quad (7)$$

$$w_{12} \approx \sigma_2 \cdot (1 + \cos \theta). \quad (8)$$

The latter case corresponds to the solid-liquid interface. For a liquid, the surface tension coefficient σ_2 at the “liquid-gas” interface can be expressed through the density of the liquid ρ_2 and its specific heat of vaporization q_2 :

$$\sigma_2 \approx \frac{q_2}{2\pi} \cdot \left(\frac{\mu_2 \rho_2^2}{N_A} \right)^{1/3}. \quad (9)$$

Therefore, the adhesion work, the average energy U_{12} of the interaction of a surface liquid molecule with a near-surface layer of solid molecules, as well as the average energy V_{12} of the pair interaction of the molecules of these substances at the interface, can be found by measuring the critical wetting angle θ , the density of the liquid ρ_2 and its specific heat of evaporation q_2 :

$$w_{12} \approx \frac{q_2}{2\pi} \cdot \left(\frac{\mu_2 \rho_2^2}{N_A} \right)^{1/3} (1 + \cos \theta), \quad (10)$$

$$U_{12} = \frac{q_2 \mu_2}{2N_A} \cdot (1 + \cos \theta), \quad (11)$$

$$V_{12} = \frac{q_2}{2N_A} \cdot \left(\mu_1^2 \mu_2 \cdot \frac{\rho_2^2}{\rho_1^2} \right)^{1/3} (1 + \cos \theta). \quad (12)$$

The above equations are applied in an equilibrium system. When wetting real solids, wetting hysteresis is observed, which is understood as the ability of a liquid to form contact angles other than equilibrium angles when in contact with a solid. For example, the contact angles depend on the order of contact with the solid surface of the contacting phases (the so-called ordinal hysteresis): maximum contact angles formed when a liquid drop is applied to a solid surface, as a rule, are larger than the outflow angles formed when an air bubble is brought to the same surface submerged into liquid. Hysteresis of contact angle can be caused by surface contamination, its chemical and geometric heterogeneity, the formation of wetting films on the surface, and other reasons [5, 6, 7, 8, 10, 11, 12].

The microgeometry of the solid surface and its roughness have a significant effect on the measured contact angles. Surface roughness is characterized by a roughness factor K equal to the ratio of the actual surface area S_{REAL} to the area of its projection onto a horizontal plane (S_{IDEAL}) [3, 4]:

$$\frac{S_{IDEAL}}{K} = \frac{S_{REAL}}{S_{IDEAL}} \quad (13)$$

The relationship of the contact angle on a rough surface $\Theta_{EFFECTIVE}$ with the equilibrium contact angle Θ on a smooth surface is given by the Wenzel–Derjaguin equation:

$$\cos \Theta_{EFFECTIVE} = K \cdot \cos \Theta_{IDEAL}. \quad (14)$$

Thus, the value of the hysteresis coefficient has a significant effect on the contact angle. Since $K > 1$, then $|\cos \Theta_{EFFECTIVE}| > |\cos \Theta|$. Thus, surface roughness improves wetting ($\Theta_{EFFECTIVE} < \Theta$, if $\Theta < 90^\circ$) and worsens non-wetting ($\Theta_{EFFECTIVE} > \Theta$, if $\Theta > 90^\circ$).

Determination of the equilibrium contact angle is carried out by the formula:

$$\cos \Theta = \frac{\sigma_1^2 + \sigma_2^2 - \sigma_{12}^2}{2\sigma_1 \cdot \sigma_2}. \quad (15)$$

Since steel 3 (GOST 380-88), which has a surface tension coefficient $\sigma_1 = 1850 \text{ MJ/m}^2$, was used as a substrate during the research. Epoxy-polyester and polyester coatings with low surface tension values $\sigma_2 = 55 \text{ MJ/m}^2$ were used as paint coatings. In turn, the surface tension at the boundary is $\sigma_{12} = 1819 \text{ MJ/m}^2$

Then:

$$\cos \Theta = \frac{1850^2 + 55^2 - 1819^2}{2 \cdot 1850 \cdot 55} = 0,57.$$

Thus, the equilibrium wetting edge angle for a given substrate material and type of powder coatings is 55° .

The value of the effective contact angle is expressed from the formula (2), considering adhesion, determined as a result of experimental studies by the formula:

$$\cos \Theta_{EFFECTIVE} = \frac{\sigma_1^2 + \sigma_2^2 - (\sigma_1 + \sigma_2 - w_{12})^2}{2 \cdot \sigma_1 \sigma_2}. \quad (16)$$

Comparing the obtained data of effective and equilibrium contact angles of wetting, the influence of one or another method of surface preparation was determined.

As noted earlier, the wetting angle of a drop of a paint and varnish material (in the liquid phase) is of great importance for the adhesion of paints and varnishes, which in turn depends on the roughness of the substrate surface on which the paint and coatings are applied [2].

Therefore, the purpose of this study is to determine the optimal roughness parameter at which the best adhesion will be achieved.

When conducting research on the effect of roughness on adhesion, samples with different surface roughness were examined. In this case, the roughness parameter decreased. With a decrease in the roughness of the substrate, the force of separation of the paintwork material from the substrate surface also changed (Figure 2).

Fig. 2. Dependence of the degree of adhesion and the paint coating pull-off force on the parameter of the substrate roughness

It should be noted that with a decrease in the substrate roughness, the roughness of the paint coating applied to it also decreases. Reducing the substrate roughness leads to a decrease in the thickness of the operational-capable coatings.

In accordance with formula (16), based on the determination of the adhesion of powder coatings to the substrate surface, we determine the value of the effective contact angle of the surface.

When determining the effective contact angle of wetting of the surface, it was noted that when using various methods of surface preparation by chemical methods, the following results were obtained (Figure 3).

Fig. 3. Effective contact angle of wetting for various methods of surface preparation by chemical methods

When determining the effective contact angle of wetting, the following values were obtained (Fig. 4).

Fig. 4. Effective contact angle of wetting at various values of the roughness parameter Ra

The roughness factor indicating the effect of the roughness parameter on the contact angle of wetting is shown in Figure 5.

Fig. 5. Dependence of the hysteresis coefficient on the roughness parameter Ra

One of the most important properties of paint coatings, which characterize their applicability for cars repair painting, is the corrosion resistance of coatings. As a result of tests for corrosion resistance, the following results were obtained (Table 1-2).

Table 1. Assessment of external appearance of coatings according to GOST 9.407-85

Sample number	Types of destruction			
	Tarnishing	Color change	Dirt retention	Chalking
Epoxy Polyester (red RAL 3002)	T1	C1	D1	CH1
Epoxy-polyester (white RAL 9016)	T1	C1	D1	CH1
Polyester (red RAL 3002)	T1	C1	D1	CH1
Polyester (white RAL 9016)	T1	C1	D1	CH1

Table 2. Assessment of protective properties of coating according to GOST 9.407-85

Sample number	Assessment of protective properties by the size of coating destruction		
	Depth of cracks, airing, flaking, dissolution	Bubble diameter, mm, depth of destruction	Diameter of corrosion centers, mm
Epoxy Polyester (red RAL 3002)	No destruction	No destruction	0
Epoxy-polyester (white RAL 9016)	No destruction	No destruction	0
Polyester (red RAL 3002)	No destruction	No destruction	0
Polyester (white RAL 9016)	No destruction	No destruction	0

Operational tests of the samples under study for a year and a half showed the absence of coating damage, as well as violations of texture and gloss. From the above, it is possible to draw a conclusion about the possibility of using powder-coated paints for repair painting of equipment in the agro-industrial complex.

As a result of the conducted theoretical studies, it is established:

1. The process of forming coatings from powder paints is associated with the transition of powder paint from a solid to a liquid state by heating.

2. To ensure the adhesion of powder paints melt to the substrate, it is necessary to ensure that the substrate is wetted with the melt.

3. It was found that the value of the effective contact angle of wetting differs from the equilibrium one by the value of the hysteresis coefficient.

As a result of the conducted theoretical studies, it is established:

1. The values of the minimum hiding power for paints of various colors and the corresponding thickness of the paint coating are established. Black and gray paints have the highest hiding power (the thickness of the paint layer is 40 and 45 microns, respectively), red (65 microns), blue (60 microns) and green (65 microns) colors occupy an intermediate position, and light colors (white) (75 microns) have the lowest hiding power.

2. Experimental studies on the influence of the chemical surface preparation method have shown that chemical etching of the substrate surface with Ferrofos increases the adhesion of the obtained powder-coated paints by 3 times, due to an increase in the hydrophilicity of the substrate (the pull-off force of the powder-coated paints is 500 N). When using DuPont preparations 3920S and 3911W compositions, the pull-off force of the powder-coated paints is reduced to 450 N. The lowest adhesion values were obtained when using Henkel preparation – the pull-off force of the powder-coated paints is 150 N.

3. It was found that with an increase in the roughness parameter R_a from 0.4 to 1.175 microns, the pull-off force of powder-coated paints increases from 167 N to 195 N, due to a decrease in the effective contact angle. On the basis of the conducted experimental studies, it was revealed that the value of the roughness parameter $R_a = 1.1 \mu\text{m}$ is optimal, since its further increase leads to the appearance of the "orange peel" effect on the surface of the powder paint.

4. Practical tests for corrosion resistance showed the absence of corrosion damage, as well as a slight change in color, gloss of coatings, chalking and dirt retention on the test samples of paint coatings in comparison with the reference sample, regardless of the type of film forming substance used in them.

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