Research of inter-phase interaction in ZOL-silicate paints

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Abstract

It was suggested to use polysilicate solutions obtained by mixing liquid glass and silicic acid sol as a binder in the manufacture of silicate paints. Information is provided on the mechanism for increasing the operational properties of coatings based on sol silicate paint. It has been revealed that polysilicate solutions form membranes characterized by higher tensile strength due to an increase in the fraction of high-polymer fractions of silicic anions in the structure of the polysilicate binder in comparison with liquid glass. The results of a study on the interphase interaction between the pigment and the film-forming agent are given. It is shown that potassium polysilicate solutions form a smaller contact angle on the surface of the pigment (filler) and are characterized by greater work of wetting and adhesion to the filler (pigment).

Keywords: Liquid Glass; Polysilicate Solutions; Interfacial Interaction; Paint.

1. Introduction

For finishing of exterior and interior walls of buildings, silicate paints, which are a suspension of pigments and fillers in liquid glass, have found wide application [1]. Considering the increasing requirements to the quality of the finish, it is actual to develop methods for modifying the liquid glass, which will allow obtaining coatings with higher protective and decorative properties. The analysis of patent and scientific-technical literature indicates that one of the means of modification is the introduction of silicone com- pounds, furl alcohol, a solution of polystyrene and other polymer compounds into the binder [2], [3]. It is of interest to use silicate paints of polysilicates as film formers, which provide higher per-formance properties of coatings [4], [5]. Film-forming agents and auxiliary substances, adsorbed on the surface of pigments and fillers, form boundary interfacial layers, differing in structure and properties from the initial film former. These interphase layers affect many properties of paint and varnish materials.

Like any colloidal system, the PVM have a reserve of surface energy Gibbs, determined by the surface tension of the pigment σ and the area of the interfacial surface S: The surface Gibbs energy pigment phase affects the surrounding molecules of the film former both in liquid systems and in coatings. The most common case of this effect is the adsorption interaction of the surface opf pigments with film-forming agents, which plays a decisive role in creating highly, disperse and stable color systems.

The measure of the adsorption interaction is the work of adhesion between phases, quantitatively determined by the Dupre-Young thermodynamic equation:

\[ W_A = \sigma (1 + \cos \theta) \]  

Where \( W_A \) - adhesion work; 
\( \sigma \) - Interfacial tension; 
\( \theta \) - Equilibrium wetting contact angle.

2. The research methods

In view of the foregoing, the cohesive properties and the ability of the polysilicate binder to wet the surface of the pigment (filler) were also investigated. In the work, polysilicate solutions were obtained by the interaction of stabilized solutions of colloidal silica (sols) with aqueous solutions of alkaline silicates (liquid glasses). The sol of the silicic acid Nanosi 20 and Nanosi 30, manufactured by the PC "Promeklassecenter" was used. A sodium liquid glass with a modulus M = 2.78 was used, a potassium liquid glass with a modulus M = 3.29. As the filler used microcalcite brand MK-2 (TU 5743-001-91892010-2011) and t alc of MT-GShM (GOST 19284-79), as a pigment - titanium dioxide230 rutile form (TU 2321-001-1754-7702- 2014).

Determination of cohesive strength was carried out according to GOST 18299-72 * on a tearing machine IR 5057-50 at a deformation rate of 1 mm / min

We was calculated the work of adhesion of liquid glass and polysilicate solution to the pigment (filler). The research was carried out using equipment on the basis of the Center of High Technologies of BSTU. V.G. Shukhov. The contact angle of wetting was determined on the KRUSS DSA-30.

To determine the wetting contact angle, tablets were mixed from the mixture of pigment and filler with the automatic hydraulic press Vanex-40 automatic, with a pressure of 18 tons for 11 seconds. The powder was compressed in a dry state, without fur- ther processing. The surface tension of the solutions was deter- mined by the stalagmometric method. The stalagmometric method is based on measuring the number of droplets formed when a liquid flows out of a vertical tube of a small radius. The relation- ship between the work of adhesion and the work of wetting is determined by the relationship:
\[ W_A = W_{cm} + \sigma_{\text{ж} - \text{r}} \]  

It was found, that coatings based on polysilicate solutions are characterized by faster curing. Figure 1 shows the kinetics of coating curing, which is characterized by a change in the relative hardness. At the age of 24 hours, the relative hardness of the film based on the control composition (without sol) is 0.28, and with the addition of the Nanosil 20 sol in an amount of 5, 10, 15% of the mass of the liquid glass, respectively, 0.38; 0.43, 0.47. The curing process ends after 7 days (Fig. 1).

\[ \text{Fig. 1: Kinetics of the Change in the Relative Hardness of Films Based on Polysilicate Solutions 1 - Potassium Liquid Glass; 2 Potassium Liquid Glass.} \]

+ 5% Nanosil 20, 3 - potassium liquid glass + 10% Nanosil 20; 4 - potass- sium liquid glass + 15% Nanosil 20

It has been established, that membranes based on polysilicate solutions have a higher cohesive strength [6]. It was found that the tensile strength of a membrane based on potassium liquid glass is \( \sigma_p = 0.392 \text{MPa} \), and the tensile strength of a membrane based on a polysilicate solution (15% Nanosil 20) is 1.1345 MPa. The increase in strength, in our opinion, is due to an increase in the proportion of high-polymer fractions of silicic anion (CCA) in the structure of the polysilicate binder in comparison with liquid glass [7]. To study the structure of liquid glasses, a molybdate method was used, based on the different rates of interaction of monomeric, oligomeric, and polymer KCA with molybdic acid.

We have established that with increasing sol content the fraction of the polime fraction of silica increases. In the potassium polysili- cate solution, the content of the polymer form of \( \gamma \)-SiO2 is 19.93% with a 15% sol content, and 2.51% in potassium silica liquid glass. Analysis of the data (Table 1) shows, that for the potassium polysilicate solution, a large work of adhesion to the filler (pig- ment) is characteristic. Thus, the work of adhesion of the potas- sium polysilicate solution to the filler (pigment) is 103.85 mN / m, while the work of adhesion of potassium liquid glass is 87.74 mN / m. Similar regularities are observed when using sodium liquid glass and sodium polysilicate solution. A potassium polysilicate so- lution is also characterized by a large wetting work of 39.786 mN / m.

In determining the wetting contact angle, it was found that the sod- ium glass droplets on the surface of the sample formed an angle much larger than that of the potassium and for 5 minutes re- mained unchanged on the surface, while the drops from the potas- sium half a second remained in shape and then blurred. Drops based on the sodium polysilicate solution were quickly absorbed into the mate- rial, forming a pyramidal shape. Drops based on the potassium pol- ysilicate solution are more stable and retained on the sample for up to two minutes.

\[ \begin{array}{|c|c|c|c|c|}
\hline
\text{Name of film-form- } & \text{Surface} & \text{Angle of} & \text{Adhesion} & \text{Wetting} \\
\text{ing} & \text{tension,} & \text{wetting,} & \text{work, mN /} & \text{op-}
\\
\text{mN / m} & \text{m} & \text{m} & \text{m2} & \text{eration, mN} \\
\hline
\text{Water} & 72.8 & 46.2 & 123.18 & 50.38 \\
\text{Potassium liquid glass} & 55.22 & 53.9 & 87.74 & 32.52 \\
\text{Potassium polysilicate solution} & 64.064 & 51.6 & 103.85 & 39.786 \\
\text{Sodium liquid glass} & 51.66 & 74.7 & 65.3 & 13.64 \\
\text{Sodium pol-} & 55.22 & 62.5 & 80.73 & 25.51 \\
\text{ysilicate solution} & (15% Na-} & & & \\
\text{niosil 20) } & & & & \\
\hline
\end{array} \]

The availability of more complete wetting of the surface of the filler and the pigment in the case of use a potassium polysilicate solution promotes the formation of a denser coating structure and an increase in the physico-mechanical properties. This is evi- dence by data on the change in the tensile strength of films on the basis of colored compositions. It was found, that the cohesive strength of membranes based on zol- silicate paint is 2.65 MPa, and on the basis of silicate paint - 1.8 MPa (Fig. 2). An increase in the relative deformations is ob- served, which is 0.06 mm/mm for membranes based on zol- silicate paint, and 0.033 mm/mm on the basis of silicate paint. Higher de- formations of coatings based on zol-silicate paint char- acterize coatings as more resistant to cracking.

\[ \text{Fig. 2: Change in the Relative Deformations When Tensile Samples Based On [1] - Zol-} \]

\text{silicate Paint 2-Silicate Paint.}

Based on the polysilicate solution, the formulation of the composi- tion designed for finishing the external and internal walls of build- ings has been developed [8,9]. The viscosity of the colorful com- positions is 17-20s according to VZ-4, the degree of drying to a degree of 5 - 70-90 min, the adhesion to the substrate solution is 1 point, the washability is no more than 2 g/m2. The paint forms a coating characterized by an even, uniform matte surface. Resist- ance to the static action of water at a temperature of 20 °C is not less than 24 hours.

3. Conclusions

The study found that the increase in the physical-mechanical prop- erties of coatings based on polysilicate binders is due to a change in the structure of the film formed itself, caused by an in- crease in the fraction of high-polymer fractions of silicic anions (SA), as well as an increase in the adhesion of the film-forming agent to the filler (pigment).
References


