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PAINT COATINGS WITH HIGHER HYDROPHOBICITY FOR PROTECTION AGAINST ICE ACCRETION

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ABSTRACT

The application of hydrophobic paint coatings is one of the ways to reduce ability to ice accretion. The properties of painted surfaces largely depend on the paint formulation and they are determined by the volume loading of ingredients. The study carried out in this field made it possible to classify the coatings into the surface hydrophobic and volume hydrophobic coatings as well as to elaborate scientific approaches to their development. Some paint coatings were found to increase hydrophobic properties due to the change in their surface polarity with time. The hydrophobic properties of the coatings can also be changed by the use of pigments and extenders with high surface energy in their compositions. The investigations have led to the development of the anti-icing enamel EP-439.

The issues of fighting against icing of ships, waterside structures, oil and gas facilities, especially in connection with the Arctic shelf development attract sound attention of experts engaged in solving this problem.

Of special interest out of many methods used in the fight with ice accretion, i.e. thermal, mechanical, physical and chemical methods [2], is the application of anti-icing paint coatings that must meet a number of specific requirements the main of which is the lower ice adhesion.

The exposure of the ice ships underbody and waterside structures to ice has been well explored [6, 8] as well as the paint products forming the coatings with the properties desired and protecting against its impact have been developed, e.g. the paint “EP-437”, which is a Russian prototype of well-known Inerta-160. However, the paint products designed for forming weather-resistant anti-icing coatings are practically not available.

Ice deposited on the coatings passes through a liquid state phase, therefore, the theoretical backgrounds to develop anti-icing coatings are to be considered from the

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viewpoint of the surface phenomena occurring at the liquid-solid interface [7, 10]. When such coatings are formulated, the most important matters are the free specific surface energy, which is determined by the surface tension (γ_s, mJ/m^2), the wettability determined by the interfacial angle (θ), the adhesion defined by the adhesion strength (A, MPa) and some others.

The surface properties of the lacquer films based on hydrophobic filmformers and those of the paint products containing pigments and extenders as a solid phase differ sharply, as the most of solid ingredients specified have high γ_s. Some of their values are given below:

Pigment	γ_s, mJ/m^2
Titanium dioxide	
rutile	143
anatase	91
Iron oxide	107
Silicon oxide	123
Carbon black	9

In this connection the study to determine the θ variations depending on the loading degree of epoxy resins by rutile TiO_2 (% by volume) was carried out (see Fig.1).

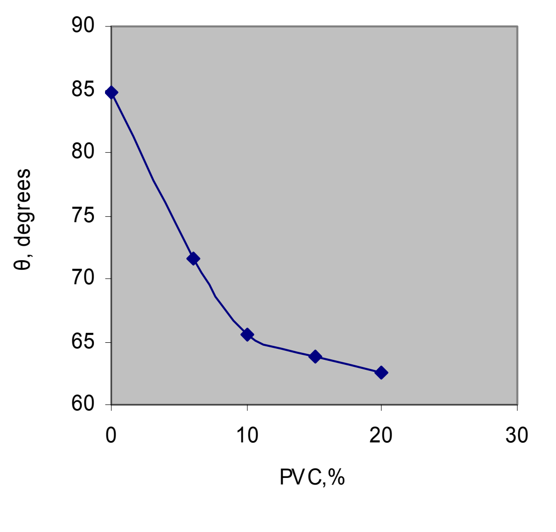

Fig.1. θ versus Pigment Volume Concentration

As seen from Fig.1, the loading greatly influences upon the value of the wetting angle, in particular, when up to 10% TiO_2 (by volume) is introduced, thereafter the influence is sufficiently decreased. The loading influence was evaluated by the average degree of change in the wetting angle depending on the 1% by volume change in loading. In a range of 0% to 10% of TiO_2 loading that value amounts to 2°/%, and in a range of 10 to 20% of TiO_2 it accounts for 0.4°/%.

The statistical treatment of the experimental data by the least-squares method has shown that the relationship between the coating wetting angle and the TiO_2 volume content in the coating is described with a polynomial function in the best way.

So, it can be considered that the decrease in the wetting angle is the result of a complex action of the hydrophilic TiO_2 introduction that, being statistically distributed in an epoxy binder, causes in addition the surface energy change as a consequence of its interaction with a binder. Thus, the paint materials designed for anti-icing coatings must comprise of pigments and extenders having low surface energy. In this case the total surface tension of the formulation can be expressed as:

$$\gamma_t = \frac{c_1\gamma_r + c_2\gamma_{\text{solv}} + c_3\gamma_{\text{pigm}}}{c_1 + c_2 + c_3}, \tag{1}$$

where $\gamma_r = \gamma$ of resin; γ_{solv} = that of solvent; γ_{pigm} = that of a pigment or an extender; c = concentration.

At the same time the additive formula given above is not sufficient to describe a system resulted from the ingredients interaction.

As a result of the coating exposure to atmospheric factors (UV-radiation, moisture, oxygen) and the influence of the mechanical alternating stresses, its surface is destructed and becomes rough. In this case the value of roughness R_a for various coatings can be varied in a range of 1.4 to 4.5 μm [3, 4].

According the Wenzel-Deryagin equation the link between rough and smooth surfaces is established:

$$\cos\theta_{\text{rough}} = K\cos\theta\ . \tag{2}$$

The K value shows how much the bonding strength of liquid with a surface is changed, when the roughness increases.

According to the existing concepts [10], the roughness of the hydrophobic surface decreases its wettability, as the liquid is not able to penetrate into the surface cavities, and the θ value becomes higher than that for a smooth surface. On the contrary, the θ value for the hydrophilic surface is decreased. When the hydrophobic coating based on the multi-ingredient paint formulation is being decomposed, the influence of pigments and extenders having high surface energy is enhanced and the surface becomes hydrophilic.

That's why some deviation can be observed between the equation for hydrophobic surfaces:

$$\cos\theta_{\text{rough}} < \cos\theta,\ \theta_{\text{rough}} > \theta \tag{3}$$

and the equation for multi-component formulations which can be represented as follows:

$$\cos \theta_{rough} > \cos \theta, \theta_{rough} < \theta \,. \quad (4)$$

Thus, the filmformers, which are resistant to mechanical stresses and climatic factors in the Northern latitudes and which do not change the coatings roughness during their service life, should be used in the paint compositions for anti-icing applications.

The epoxy filmformers having the molecular weight of 360 to 20,000 (phenoxy resins) most absolutely comply with these requirements, that affords to formulate coatings with a wide range of properties.

The epoxy compounds are polar and have high dissolving power. The solubility parameters of epoxy oligomers (e.g. of ED-20 type) have the values, $(mJ/m^3)^{1/2}$ as follows:

Before curing	After curing
$\delta_d = 17.3$	$\delta_d = 16.72$
$\delta_p = 11.2$	$\delta_p = 6.73$
$\delta_h = 11.2$	$\delta_h = 6.93$

Where δ_d, δ_p, δ_h are solubility parameters due to the interaction energies of dispersive, polar and hydrogen bonds.

According to [9], $\gamma_c \sim \delta^{4/3}$, and hence, it can be assumed that a kind of the coating "self-hydrophobization" is taking place in the process of curing.

However, for such coatings θ is equal to 75 – 80° [4] depending on the type of a hardener and the temperature.

So, in this paper silicone adhesion promoters and silazane curing agents were used to enhance the hydrophobicity of epoxy resins.

The compounds having a common formula of X-R-Si(OR^1)$_3$, where X = reactive group; R = aliphatic radical; OR^1 = a hydrolyzable group of C_2H_5O-, have been used as adhesion promoters.

If the moisture is present at the surface of an epoxy coating, silanol groups interact with each other and with hydroxyl groups of the epoxy oligomer located at the surface according to the mechanism as follows:

$$XRSi(OR^1)_3 + 3H_2O \xrightarrow{-2R^1OH} XRSi(OH)_3$$

$$XRSi(OH)_3 + \underbrace{OHOH}_{\text{coating}} \rightleftharpoons \underbrace{XRSi(OH)_2 + XRSi(OH)_2}_{\text{coating}}$$

The ice adhesion strength has been determined by the technique based on the tearing-out of a rod located in a cylinder from the ice mass [4].

The cylinder made of stainless steel and having the internal diameter of 39 m is filled with 70 ml of tap water. Afterwards the painted rod is immersed into it and the cylinder is covered with a cylinder head. Then it is placed into a cooling chamber where it is conditioned at $(40 \pm 2)°C$ for 1.5 h until firm ice is formed. Thereafter the cylinder is taken out of the cooling chamber, fixed in the clamps of the tearing machine and the force (P) is determined at which the rod is pulled out from the ice thickness. The adhesion strength A (MPa) is calculated by the below formula:

$$A = 0.1\ P/2\pi rl\ , \tag{5}$$

where P = force to tear out a rod, kg; r = radius of a rod, cm; l = length of a rod in contact with ice.

The results given below show that the addition of the adhesion promoter into the epoxy formulation leads to a sharp decrease in the ice adhesion to the coating.

Substrate	Adhesion strength, MPa
Non-coated rod	2.27
Epoxy coating	2.13
Epoxy coating with an adhesion promoter	0.92

The hydrophobic coatings can be obtained if siliceous curing agents (based on silazane) are used that are capable of interacting with hydroxyl groups of an epoxy filmformer, thus forming a space structure with built-in Si, for instance:

$$\begin{array}{c} -CH_2\text{-}CH\text{-}CH_2- \\ | \\ O \\ | \\ -Si- \\ | \\ O \\ | \\ -CH_2\text{-}CH\text{-}CH_2- \end{array}$$

The experiments carried out, while hydrophobic coatings were developed, gave the opportunity to classify the latter into the surface-hydrophobic and volume-hydrophobic coatings according to the principle of imparting the properties required [5]. The surface-hydrophobic coatings are obtained when the surface is treated by water-repellent agents, when hydrophobic filmformers or coatings having the absolute hydrophobicity effect are used [1]. The volume-hydrophobic coatings are obtained by the usage of hydrophobic modifiers (promoters), chemical modification (the addition of curing agents), completely hydrophobic compositions (see equation 1).

Based on the research carried out the NIPROINS company has developed the anti-icing enamel EP-439 (Specifications 2312-123-05034239-99) designed for anti-icing coatings that is recommended by the Vedeneev VNIIG for application on floodgates of hydropower plants and by CNII KM Prometey for marine structures.

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