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ENVIRONMENTALLY FRIENDLY ANTI-CORROSION PIGMENTS BASED ON PLANT RAW MATERIALS

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The paper dials with the using of corrosion-resistant environmentally friendly pigments by "dry" and "wet" surface modification of pyrolysis products of rice hulls. The article considers the high corrosion protection activity of the synthesised pigments in the acrylic urethane primer.

Introduction

Nowadays, most corrosion protection pigments used in coatings are environmentally hazardous and contain lead and other heavy metal compounds [1]. The use of such pigments in various products pollutes the environment and is harmful for human health [2].

Today, ion exchange pigments based on silicon dioxide are widely used abroad. They have no toxic components such as chromium, lead, strontium and others in their composition [3]. In particular, ion exchange anti-corrosion pigments such as Shieldex™, Dowex™ and Activox™ slow down the rate of corrosion processes in coatings without harming the environment [4]. However, the high cost of these products and the exchange rate of the dollar are holding back the use of these anti-corrosion, environmentally friendly pigments in domestic production.

Therefore, obtaining domestic laboratory samples of ion-exchange pigments based on non-toxic raw materials, determination of their physical-technical and anticorrosive properties, evaluation of the possibility of using them in anticorrosive paintwork materials is an urgent problem of import substitution.

There is a large amount of rice processing waste in Russia and abroad - rice hulls, pyrolysis products of which are amorphous silicon dioxide. This product can be used to produce a domestic environmentally friendly, low-cost corrosion protection pigment.

This study presents material on the production of environmentally friendly anti-corrosion pigments, their physical and technical properties and the possibility of using them in filled paintwork materials in order to obtain anti-corrosion coatings.

Experimental part

The production of ion-exchange pigments consists of the mechanochemical treatment [5-7] of silicon dioxide with calcium compounds. There were used two ways of production of anticorrosive pigment of ion-exchange mechanism of action: "wet" method consisting in treatment of pyrolysis product of rice husk with saturated aqueous solution of calcium hydroxide in a laboratory disolver and "dry" method including treatment of natural amorphous silicon dioxide with calcium hydroxide in a vibrating mill.

The calcium ions in the pigment particles can occur both in the capillaries of the silica aggregates and on their surface, primarily in the form of silicate. To incorporate calcium compounds into the pigment is not easy because of the low solubility of calcium hydroxide in water. The use of other calcium compounds as a source is not advisable. It is associated with the formation of electrolyte in the mother solution and in the pigment composition, which reduces the corrosion resistance of the coating.

The concentration of calcium hydroxide in its saturated solution was determined by potentiometric acid-base titration. The resulting value of 0.018 mol/l, corresponding to 1.338 g/l, agrees well with the reference solubility value [8].

Experimental samples of ion-exchange pigments were obtained from the maximum sorption capacity of natural silica to calcium ions when treating the substrate surface with a saturated aqueous solution of $Ca(OH)_2$.

The mechanochemical treatment of silica with saturated calcium hydroxide solution was carried out for 40 minutes by H-302 dissolver equipped with a disc agitator. The average speed of the agitator was measured by PM10-R tachometer. Dispersing was carried out at a cutter speed of 75–83 s^{-1} (equal to a linear speed of 9.4-10.4 m/s). Cutter speed control was carried out by a frequency-controlled motor rotor controller.

After dispersion we washed the pigment paste with distilled water and separated from the mother solution for 10 minutes by centrifuge at 50 s^{-1} rotor speed. After centrifugation, we dried the ion-exchange pigment in a desiccator at 105–110 °C for 5 hours.

The "dry" method of producing an environmentally friendly anti-corrosion pigment consisting in processing a mixture of silicon dioxide powders and a formulated amount of calcium hydroxide in a Vibratory Ball-Mill, with the container filled with the reaction mass and steel grinding media at a vibration frequency of 50 Hz. The resulting product was separated from the grinding media by sieving through a vibrating screen with mesh No. 100.

Table 1 shows the results of the study of the physical and technical properties of the pigments.

Table 1. Physical and technical properties of the resulting environmentally friendly pigments

Appearance	"Wet" method of producing ion exchange pigment	"Dry" method of producing ion exchange pigment
	White powder	White powder
Average particle size, μm	1.89	12.5
pH of the aqueous extract	8.19	10.54
Density, kg/m^3	1940	2100
Oil capacity, g/100 g	60.0	25.0
Water-soluble salt content, %	1.16	-
Corrosion current density, $\mu A/cm^2$	82.2	88.2
Corrosion potential, mV	-550.0	-557.7

The "dry" method of treating silica with calcium hydroxide in a vibrating mill is not effective to produce a highly dispersed powdery material. The average particle size of the produced pigment (12.5 μm) is significantly higher than the same for the "wet" one. The "dry" modification sample is also characterised by a very high pH value in the aqueous extract. The anti-corrosive pigment obtained by "dry" treatment of silicon dioxide with hydroxide can be used in filled paintwork materials.

During the experiment, a 5% "wet" or "dry" synthesised anti-corrosion pigment was added to the two-component organically-dilutable acrylic-urethane light grey primer.

Paintwork materials with anti-corrosion pigments were applied to the plates in two coats by air spraying. The coatings were dried at 60 °C for 30 minutes. Before testing the coatings were cured for 7 days at (20±2) °C and a relative humidity of (65±5)%. The coated plates were then placed in a 3% sodium chloride solution and kept for 10 days at (20±5) °C.

a ***b*** ***c***

Fig. 1. Appearance of coatings formed of acrylic-urethane primer after curing in 3% sodium chloride solution for 10 days (20±5) °C: *a* - coating without the synthesised anti-corrosion pigment; *b* - coating with "wet" synthesised anti-corrosion pigment; *c* - coating with "dry" synthesised anti-corrosion pigment

The coatings with "wet" synthesised corrosion protection pigment show good anti-corrosion properties.

Conclusion

The environmentally friendly pigments derived from pyrolysis products of rice hulls have anti-corrosive properties. The sample obtained by "wet" modification of the surface of natural silicon dioxide shows the best anti-corrosion properties.

The resulting corrosion protection pigments can be used for coatings to protect steel structures against corrosion

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