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PIGMENT WITH ANTICORROSIVE PROPERTIES BASED ON TRANSITION METAL COMPOUNDS

Pigments for corrosion-resisting paint and varnish materials were synthesized. Physicochemical properties (water solubility, oil-absorption power I and type II, pH of the aqueous extract) of the obtained pigments were determined. Corrosion stability of the synthesized pigments are studied by electrochemical method (in sodium chloride NaCl solutions). It is established that the pigments are cathodic corrosion inhibitors. Corrosion current density decreases by 2–3 times and protective effect of 37–68% is observed in the suspension of synthesized pigments in a solution of sodium chloride.

Introduction. It is known, that the destruction of metals is due to their chemical or electrochemical interaction with the corrosive environment. Electrochemical and chemical processes occurring on the surface of the metals lead to the destruction of metal equipment. Consequently, the corrosion brings about great damage to the industry, as it requires a significant investment for repairing the equipment, various designs and constructions made of metal. In industrialized countries, the loss of corrosion makes up from 2 to 4% of GDP.

Protection of metal surfaces against corrosion can be achieved by spreading protective coatings on them: lacquer, paint, coatings, enamels, and other metals.

The advantages of paint and varnish coatings compared to others include low gas and vapor permeability, water repellency, preventing access of water, oxygen, and aggressive components containing in the atmosphere to the metal surface. Paint and varnish materials have a protective function on the one hand and a decorative one on the other hand. Due to the combination of these two functions they are in great demand. The efficiency of both functions depends on the composition of the resulting materials and of process parameters for their production. Chromaticity of any material is achieved by introducing into its structure of dyes. Among the coloured compounds are compounds of transition metals, due to the electronic structure of atoms in their structure. Pigments anticorrosive effect is stipulated by their ability to create a certain concentration of passivating ions diffusing to the metal surface and forming protective films. Previously, for protection against corrosion the main emphasis was placed on paint and varnish materials containing lead pigments. At present, due to toughened environmental requirements, preference is given to non-toxic anticorrosive pigments.

However, as to the analysis of the scientific and the technical literature, currently known inorganic pigments suitable for use in anti-corrosion paint and varnish materials, either contain toxic components, or provide very scarce colour palette (yellow, red, brown or black). Thus, the development of alternative paint and varnish coatings based on non-toxic materials is an important task. Moreover addition of transition element compounds into the pigments allows to expand the colour spectrum of employed paint and varnish coatings [1, 2].

The aim of this work is to produce the pigments that contain compounds of transition elements providing anticorrosive properties of paint and varnish coatings, and their study.

Main part. Based on the literature data, some transition metal compounds were chosen for the composition of pigments. The basic requirements that guided the choice of the components were: their low solubility in water, preventing their spread in the environment, low oil absorption I and II.

The high water solubility limits the application of paint and varnish coatings in corrosive environments. At a high content of water-soluble substances in the pigment the insulating properties of coatings are reduced. The less is the pigment oil absorption, the lower is the cost of paint and varnish coatings.

The requirement of environment neutrality is connected with the fact that at the decrease of pH solution, the activity of H^+ ions increases, and, as a rule, the rate of corrosion grows, except for cases where the aggressive environment has passivating effect and leads to the formation of the protective film on the metal surface.

The compositions were produced by mixing the individual substances listed in Table 1 (the exact composition of the pigments is not specified). Such components of pigments, as $Ni_3(PO_4)_2$, $Zn_3(PO_4)_2$, were synthesized by known methods [3].

The prepared mixtures were milled in a planetary mill, sifted through copper sieves, and the fraction less than 0.2 mm were selected. The residue was re-ground and re-sifted.

Oil absorption of pigments I and II were determined by the standard method (GOST 21119), pH of 10% aqueous suspension was found by titrating apparatus TitroLineEasy.

Table 1

The composition and the oil absorption of pigments

Index	Pigment			
	2	3	4	5
Content Cr_2O_3, wt %	30–40	10–20	40–50	–
Content NiO, wt %	30–40	30–40	–	–
Content $CaTiO_3$, wt %	–	–	–	33.3
Content $Ni_3(PO_4)_2$, wt %	–	–	20–30	–
Content ZnO, wt %	–	–	20–30	–
Content $Zn_3(PO_4)_2$, wt %	–	–	–	33.3
Content WC, wt %	10–20	30–40	–	33.3
Oil absorption I, g/100 g	11	12	16	16
Oil absorption II, g/100 g	42	38	42	31

Corrosive properties of the pigments were investigated electrochemically by anodic and cathodic polarization curves of steel in the pigment suspension in sodium chloride solution of 0.5 mol/l. Potentiostatic polarization curves were taken in a standard three-electrode electrochemical cell with a platinum auxiliary electrode. A saturated silver chloride electrode was used as a reference electrode. All potentials were converted to the scale of the standard hydrogen electrode. The steel plate St3 with surface area of 1 cm^2 was used as the working electrode.

The content of obtained compositions and their physical and chemical properties are given in Table 1. On the basis of the research results it was found that all pigment compositions have low water solubility and oil absorption I and II. pH of pigment aqueous suspensions ranges from 6 to 8.

Fig. 1 shows the polarization curves taken in the suspension of pigments 2, 3, 4, and Fig. 2 – in the pigment slurry 5.

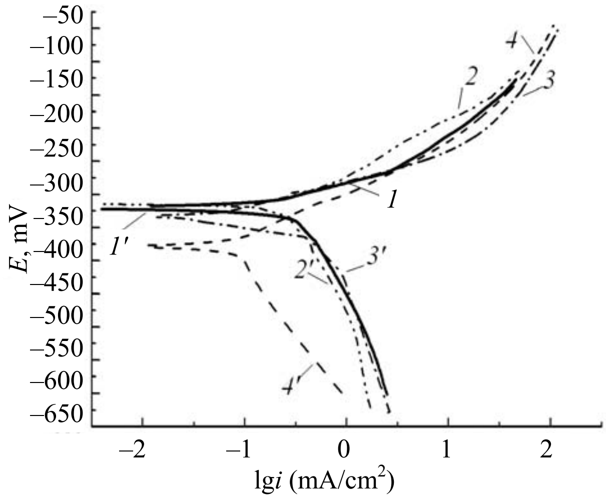

Fig. 1. Anode (*1*, *2*, *3*, *4*) and cathode (*1′*, *2′*, *3′*, *4′*) polarization curves, taken without inhibitor (*1* and *1′*) and in suspensions of pigments

Curves *1* and *1′* – anodic and cathodic polarization curves were obtained for sodium chloride solution without inhibitor.

It is obvious from the dependencies that in solutions containing pigments, drainless potential shifts to negative values. It seems to be the result of pigment adsorption on the surface of the corroding metal and, as a consequence, leads to a change in the physical and chemical properties of the surface.

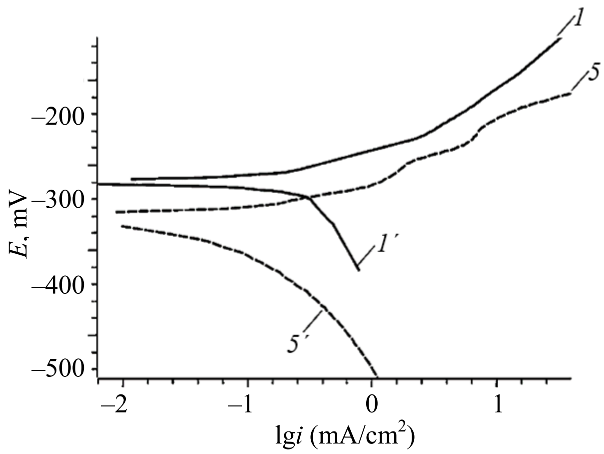

Fig. 2. Anode (*1*, *5*) and the cathode (*1′*, *5′*) polarization curves, taken without inhibitor (*1* and *1′*) and in the presence of the inhibitor (*5* and *5′*)

The presence of the pigment particles adsorbed on the metal surface causes a change in the kinetics of the partial electrochemical reactions. As seen from the given relation (Fig. 1 and 2), the introduction of pigments into aqueous solutions NaCl increases the polarizability of cathodic partial process, while the course of the anodic polarization curves only slightly varies.

Therefore we can conclude that the resulting pigments are cathodic inhibitors of the process of iron corrosion [4, 5]. The corrosion rate was determined by the intersection of the linear parts of the anodic and cathodic polarization curves near the stationary potential of the corroding metal. Quantitative effect of inhibitors on the rate of the corrosion process is characterized by the weight and depth indicators, size of the protective effect and coefficient of protective action. The calculated corrosion parameters are given in Table 2.

Table 2

Anti-corrosion properties of the pigments

Sample	Equilibrium potential corrosion – E, mv	Corrosion current density, mA/cm^2	The corrosion rate		The effectiveness of protection against corrosion	
			Weight indicator, g/(m$^2 \cdot$ h)	Depth indicator, mm/year	Protective effect, %	Factor of protective activity
1	318	0.126	1.31	1.46	–	–
2	315	0.079	0.82	0.92	37	1.59
3	333	0.039	0.41	0.46	68	3.16
4	378	0.044	0.46	0.51	51.63	2.07
5	365	0.008	0.084	0.093	93.62	15.75

To assess the anti-corrosion properties of the pigments Table 2 represents the characteristics of the corrosion process of steel in sodium chloride medium without pigment (sample 1). As to the data in (Table 2), the studied pigments possess anticorrosion properties, as they bring down the density of corrosion current by several times and have a protective effect from 37 to 94%.

When comparing the samples of pigments 2, 3 and 5, which contain tungsten carbide, it follows that the minimum corrosion current and the maximum inhibition efficiency were recorded for samples 3 and 5, with a higher content of tungsten carbide in their composition. For the pigment having a lower content of WC (sample 2), the density of corrosion current is higher. Results of electrochemical studies correlate with the results of the research of physical and chemical properties of investigated pigments presented above.

Conclusion. It has been found that all of the obtained pigments are cathodic corrosion inhibitors. Pigments containing tungsten carbide, nickel and zinc phosphates are characterized by low corrosion current and high protection effectiveness.

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