

ANTICORROSIVE PROPERTIES OF SETTLED AND COPRECIPITATED METAL MANGANATES

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Introduction

In the modern industrialized society, anti-corrosive protection of metals is one of the most important scientific, technical and economic problems. Its solution can save huge material and financial resources. In the course of time, the problem of preserving the metal fund, primarily steel objects, becomes more acute due to the increasing use of corrosive environment, high temperatures and pressures in industry. Carbon steel being the most commonly used structural material also belongs to corrosion-sensitive metals.

Dyeing, including the application of anti-corrosion pre-coatings belongs to the most economically viable and effective methods of metal corrosion damage prevention [1]. The mechanism of pre-coatings' protective effect is diverse, but almost in all cases it is determined by the nature of the anti-corrosive pigments that are included in them.

It should be noted that the most effective anticorrosive pigments (chromate, lead containing), that have maintained high protective properties of pre-coatings for a long time, are toxic. That fact has led to the restriction and even prohibition of their use in some countries [2-4]. That is why one of the urgent tasks of researchers developing modern anti-corrosive paint materials is the creation of inhibitory-type pigments characterized by low toxicity.

This group of anticorrosive pigments (generally they are divided into three groups: barrier-type, protective and inhibiting [5]) is distinguished by the diversity of both the chemical composition and the mechanisms of anti-corrosion action. This group, in particular, includes the above-mentioned chromium and lead pigments, as well as phosphates, molybdates, borates, etc. [6].

For a long time, mixed metal oxides have been in the inhibiting pigments' developers' field of vision [7]. It is possible to use complex (mixed) metal oxides, forming stable crystalline structures, that can be considered as solid solutions as anticorrosive pigments. Therefore, first of all, the attention of anti-corrosion pigments' developers was drawn to compounds with spinel and rutile structures, that are characterized by high thermal and chemical stability of the oxide lattice. In [5] the results of the study of rutile and spinel structure complex oxides' anticorrosive properties showing their clear advantages are presented. Therefore, the main development vector of the direction associated with the use of complex oxides in the field of anticorrosive protection is synthesis, research and practical use of ferritic pigments [8].

The passivating effect of ferrites, which can be considered as salts of weak ferrous acid, is associated with a high pH value, that aqueous environment acquires in contact with this type pigments as a result of their hydrolysis [9, 10]. In coatings based on binders containing free organic acids (alkyds, vegetable oils), polyvalent ions extracted by water from ferrites form soaps with the latter. The soaps increase the coatings' insulating properties and, as a result of interaction with the steel surface, passivating layers.

In our opinion, the group of complex oxides, based on manganese oxide - manganites (salts of manganic acid H_2MnO_3), is unfairly overlooked by the anti-corrosion pigments' developers. The proximity of chromium and manganese properties testifies to their use as anti-corrosion pigments. Manganese also exists in several degrees of oxidation, in +2, +3 and +4 oxidation degrees it has a complexing ability, substances containing manganese with oxidation degree 3+ and higher have got high oxidation potential. These very properties give chromium compounds, used as anti-corrosion pigments, high inhibitory ability.

Experimental

Syntheses of settled and co-settled manganates

Literature references indicate that pure manganites may be settled from aqueous solutions with a neutral or alkaline environment by reducing permanganates in the presence of salt-forming metal ions [11]. Calcium and barium were chosen as the latter, by analogy with ferritic anticorrosive pigments. Nitrates of the named metals, potassium nitrite (reducing agent) and potassium permanganate (manganese compound in the highest oxidation state) served the starting materials in the synthesis. The precipitation of the product was observed as a result of redox reactions proceeding according to the following scheme (1):



In the case of obtaining coprecipitated manganite phosphates, potassium phosphate was added to the reaction environment, and as a result of that the reaction scheme acquired the following form:



Synthesized products were brown precipitates of various shades. After the products had been separated from the mother solution, thoroughly repulvably washed and dried at 120° C, the composition and main pigment properties of the highly dispersed powders were investigated.

Synthesis products' identification

To identify the synthesis products, they were studied using IR spectroscopy and thermogravimetry. IR spectra were recorded using a Tensor 27 Ft-IR spectrometer. Shooting mode TR, resolution 4 cm⁻¹, scanning speed 10 KHz. The thermoanalytical study of permanganites was carried out on a OD-3425-1500 derivatograph in the range of 20-1000° C with a heating rate of 15 degrees / minute. Elemental analysis was performed using x-ray fluorescence analysis (external standard method). The fluorescence intensity of the tested and standard samples was measured using a VRA20L spectrometer.

Physicochemical properties the resulting products as pigments.

Determination of oil absorption according to ISO 787-5-80. The density of pigments was determined by the pycnometric method according to GOST 21119.5-75. The mass fraction of substances soluble in water was determined by the method of hot extraction according to ISO 787-3-79. The reaction of the pigment's aqueous extract was determined according to GOST 21119.4-75.

Methods for testing pigments' anticorrosive properties

The pigments' inhibiting ability was evaluated by the values of the potential and the corrosion current of steel in an aqueous extract containing 3% sodium chloride.

The corrosion potential of steel was measured using a pH-340 potentiometer. A three-electrode electrochemical cell was used to determine the corrosion current. It was prepared by gluing a hollow glass cylinder with 3 cm inner diameter onto the steel sample surface. The section of steel surface forming the bottom of the resulting glass was used as working electrode. 20 ml of electrolyte was poured in the resulting cell. The platinized platinum auxiliary electrode was lowered into the electrolyte solution. A silver chloride electrode that was placed in Luggin served as the reference electrode.

The electrochemical cell was connected to a PI-50-1 potentiostat with a PR-8 programmer. After the stationary potential had been established the cathode polarization of the steel sample was carried out for 15 min at minus 30 mV. Polarization curves (current versus potential) required for current calculation were recorded in the sphere of slight potential deflections from the stationary value (from minus 30 to 30 mV) using the small linear polarization method. This method guarantees minimal perturbations introduced into the metal dissolution process during electrochemical measurements. The corrosion current according to the results of polarization measurements was calculated using a computer program based on the Stern - Geary equation solving [12].

Results and Discussion

The synthesis products' identification

According to literature data, Mn (IV) compounds are characterized by the presence of typical effects on their thermograms [13]: the effect of water removal, the exothermic effect corresponding to crystallization, and the endothermic manganite effect - decomposition. On the differential thermal analysis' and thermogravimetry curves derived from the study of the products obtained in full accordance with [13], the effects typical of manganites were got: four endothermic and an exothermic one. In the temperature range of 20-570° C, dehydration is observed, and its most active phase goes to temperatures of 400-425° C. This endothermic transformation extended in a wide temperature range is caused by the release of weakly bound crystallization water (dehydration) and the removal of structural water of OH-groups (dehydroxylation). In the temperature range of 570-750° C, a complex exothermic transformation is observed with two exothermic effect maxima (640° C and 710° C). They correspond to the superposition of two processes, i.e., the crystallization of manganite and oxygen release during the decomposition of manganese dioxide impurity present in the sample. In the temperature range of 885-920° C, manganite decomposes (permanganite effect) with a new compound formation. The next effect at the temperature of 920-965° C probably indicates the presence of β-kurnakite formed as a result of the dissociation of MnO₂ impurity compound. With further heating, a slow mass loss is observed on the DTG curve, which may indicate the beginning of the manganite's gradual decomposition, the active phase of which begins above 1000° C. The data obtained allow us to consider the studied substances as manganites.

This is confirmed by IR spectra analyses of the studied substances that indicates the absorption spectra have bands characteristic of manganites in the area of 940, 840, 570, and 460 cm⁻¹ wavenumbers [14].

General physicochemical properties of synthesized manganites as anticorrosive pigments.

Table 1 presents the main characteristics of calcium and barium manganites, that allow to make a conclusion about the possibility of their use as anti-corrosive pigments.

Table 1

The results of the physicochemical properties of the synthesized manganites evaluation			
Studied object	Barium manganite	Calcium manganite	3% NaCl water solution
<i>The content of substances</i>			
<i>soluble in water, %</i>	5,25	5,75	-
<i>pH, aqueous extract</i>	7,0	7,1	7,0
<i>Oil absorption, g / 100g</i>	43	28	-
<i>Density, g/sm³</i>	2,91	4,1	-
<i>Corrosion potential of steel, mV</i>	125	87	-
<i>Corrosion current density, ImcA / cm²</i>	0,26	6,26	4,5

Lower oil absorption, that is, the specific amount of oil absorbed by barium manganite, indicates a higher packing density of pigment particles, which corresponds to a higher marginal filling of coatings, quantified by the value of the critical volume content of pigments. This makes it possible to introduce a greater amount of fillers into the coatings' composition with the minimum required content of an anticorrosive pigment. This is done to reduce the cost and, often, to increase the barrier properties of the paint film. High density of barium manganite can cause problems with the sedimentation stability of pre-coatings containing this pigment.

The values of steel set potential in contact with manganites' water extract containing 3% sodium chloride indicate its considerable refinement, and in both cases, taking into account almost neutral reaction of water extract, according to the Purba diagram [8], steel is in passive state. This is evidenced by the comparison of the corrosion current density values obtained by contacting steel with water extract containing 3% sodium chloride and a 3% aqueous solution of the latter.

The content of substances soluble in water is an important characteristic of pigments. Such substances are always contained in inhibiting type pigments, since water-extractable substances inhibit metals' corrosion. However, too rich content of water-soluble impurities in the pigment can lead to coagulation of the binder during storage and the formation of bubbles as a result of osmotic phenomena when polymer coating is exposed to moisture or water. According to the literature references data, the amount of water-soluble substances up to 1% is considered optimal in pigment [15]. From the data in the table, it follows that the content of water-soluble substances in the synthesized calcium and barium manganites significantly exceeds the specified critical value.

In order to eliminate this drawback, manganite and calcium phosphate were coprecipitated according to reaction (2). Calcium manganite was chosen for further experiments because of the better anti-corrosion characteristics in comparison with barium manganite (Table 1). The choice of phosphate ion for coprecipitation was based on information about the fairly wide use of phosphate pigments in anti-corrosion coatings.

When calculating the ratio between the starting materials, we proceeded from the need to obtain mixed pigments containing 20, 30, 50 and 80% of the phosphate component. A high percentage of yield (up to 98%), as well as X-ray fluorescence analysis data, made it possible to conclude that the synthesized pigments' composition is close to the desired one. The results of the synthesized manganite phosphates' properties' study are shown in Table 2.

Table 2

The results of physicochemical properties' evaluation of the synthesized calcium manganite phosphates				
Phosphate content, %	20	30	50	80
The content of water soluble substances, %	1,75	0,95	0,5	0,35
pH, aqueous extract	7,0	7,0	6,9	7,5
Oil absorption, g / 100g	47	49	51	55
Corrosion potential of steel, mV	131	122	118	87
Corrosion current density, ImcA / cm ²	0,5	0,25	0,3	0,9

Their analysis showed that coprecipitation with calcium phosphate had a slight effect on the pH of aqueous extract and oil absorption of calcium manganite. Inhibiting properties also remain almost unchanged up to 50% phosphate content, while the content of water-soluble substances decreases by more than 5 times. This confirms the correctness of the chosen modification of manganites and opens up broad opportunities in anticorrosive pigments development, the active principle of which are manganites of various metals.

Conclusion

In order to eliminate this drawback, co-precipitated calcium manganite phosphates with different phosphate contents were synthesized. The inclusion of up to 50% of the phosphate component in the pigment practically does not reduce the inhibiting efficiency of aqueous extracts, and that confirms the correct choice of manganites' modification and opens up wide possibilities for expanding the range of anticorrosive pigments.