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Waterborne Manganese-Containing Protective Materials*

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Abstract

Properties of anticorrosive coatings based on water-dispersive copolymers pigmented with manganese species were studied. It was found that the inclusion of the synthesized pigments into the composition of coatings elevated their ability to suppress underfilm steel corrosion. The compositions of anticorrosive primers that exceeded industrial analogues according to the efficiency of protective action were proposed.

Keywords: manganese pigments, aqueous dispersions, anticorrosive corrosion inhibitors, protection, protective materials, acrylic dispersions, polymer coatings

INTRODUCTION

Currently, during the development of paint formulations, special attention is being paid to the toxicity of components that are part of their composition. Among the issues that require instant solutions, the replacement of toxic chromium-containing anticorrosive pigments that are part of inhibiting primers is particularly acute [1].

In this regard, research aimed at the development of less toxic compounds that ensure good protective properties of primers is relevant. As demonstrated in a series of publications [2–9], one of the procedures for decreasing the toxicity of anticorrosive primers is related to the replacement of chromium-containing pigments (MPC of 0.01 mg/m^3) by manganese compounds (MPC of 0.3 mg/m^3).

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EXPERIMENTAL

Calcium manganite-phosphate (CMP) and barium magnatite-sulphate (BMS), *i.e.* synthesized manganese (III), (IV), and (V) compounds, were selected as anticorrosive pigments [10]. Table 1 presents the properties of the resulting compounds and zinc tetraoxychromate (ZTO) [11–13].

Protective properties of anticorrosive coatings depend not only on a pigment inhibitor that is part of them but also on film binder. In our case, its selection is determined by the chemical resistance of a material, by its adhesion to the protected surface and insulating capability [14, 15].

Primarily, moisture containing electrolytes contributes to the progression of corrosion processes undercover. Therefore it is worth paying special attention to the insulating capability of the paint film. Furthermore, the insulating capability of compounds extracted with water that diffuses through paint film is crucial. Barrier and inhibiting properties of

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TABLE 1

Properties of pigments used for filling

Pigment	Average degree of manganese oxidation	Colour	pH of aqueous extract	Type I oil absorption, g/100 g	Density, g/cm^3	Coverage, g/m^2	Water-soluble matter, %
CMP	4	Brown	7	51.0	3.41	30	0.5
BMS	3, 5	Purple	8	14.3	4.20	20	0.5
ZTO	–	Yellow	7–8	30–35	3.41– 3.59	160–180	0.1–0.5

coatings based on the synthesized pigments were determined according to the data of the electrical capacitance (C) of the system oxide metal – electrolyte and the formed corrosion potential (E) of steel undercover, as well as to visual assessment of the condition of samples in 1000 h of accelerated electrochemical tests (the impact of a 3 % aqueous solution of sodium chloride onto painted steel) [16, 17].

Pigment pastes were produced by dispersing of the pigment portion of coating compositions to a degree of grinding of 20–30 μm by a wedge device using a laboratory bead type disperser. Coatings were applied onto the pre-defatted surface of 0.8kp steel by three layers *via* the centrifugal method. The thickness of the coatings in 7 days of dying under natural conditions was (30±3) μм.

The electrical capacitance of the painted metal-electrolyte system and the electrochemical potential of the metal undercover during tests were measured using E7-21 impedance measurer and pH-340 pH-meter, respectively.

Against the background of reduction in the levels of utilization of organic solvents in paint and varnish materials, the production and use of waterborne paints are steadily increasing; their range is expanding.

The advantages of water-dispersion paint materials are obvious: they do not have an odour, dry fast, and are readily applied onto the surface. Styrene-acrylate Lacroten E-241 dispersion was selected as a film-forming system. It is optimum as a film-forming basis of anticorrosive coatings, as demonstrated by preliminary studies.

RESULTS AND DISCUSSION

Figure 1 presents representative curves of changes in the electrical capacitance (C) over time for samples with a pigment volume (PV) of less than 9 %. It can be seen that all the curves have a typical rising branch caused by aqueous medium diffusion into the volume of paint film

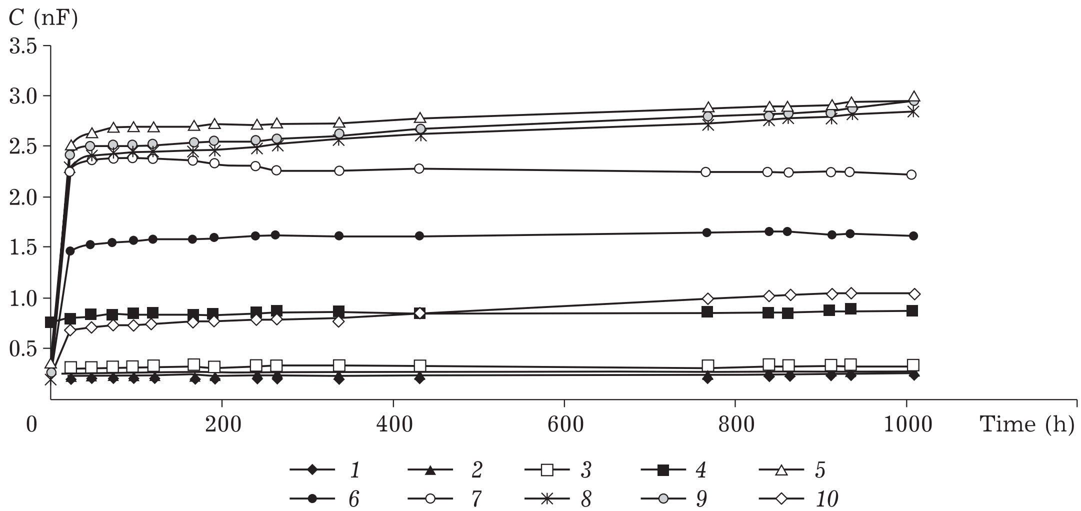

Fig. 1. Kinetics of the electrical capacitance of the painted metal-electrolyte system based on Lacroten E-241 and BMS.

TABLE 2

Results of complex assessment of coatings and metal substrates under them in 1000 h of the impact of a 3 % aqueous solution of sodium chloride onto painted steel

Pigment	PV, %	Bubble area, %	Corrosion area, %	Coating condition, points	Adhesion, points	
					Before tests	After tests
BMS	0	0	2	3	1	1
	1		1	2		
	2–7		0	1		
	8	10	10	4		
CMP	4	0	2	3	1	1
	5–7		0	1		
	8		2	3		
ZTO	3	0	1	2	1	1
	4–7	0	0	1		
	8	0	1	2		

Note. Lacroten E-241 (TU 2241-031-51769913–2004, Orgkhimprom PKF, LLC) was used as film binder.

that later passes into a flat area associated with the completion of the swelling process. As it follows from the data of Fig. 1, all the samples have good barrier characteristics.

The nature of chronopotentiometric curves (Fig. 2) attests to the fact that the inclusion of manganese-containing pigments into paint film composition to PV of 9 % significantly refines the corrosion potential (E) of steel undercover. The shift of E value towards positive values region points to the inhibition of corrosion processes. There is the opposite picture during filling above critical: the potential of painted steel drops. Thus, the violation of paint film uniformity in case of PV > 9 % causes passive film destruction over the steel surface. As it follows from the date of Table 2, non-pigmented Lacroten E-241 coating has poorer protective properties: it is characterized by the minimum values of the corrosion potential.

The findings may be presented most informatively as the steady-state values of the electrical capacitance (C) and the corrosion potential (E) of steel undercover *vs* polymer PV.

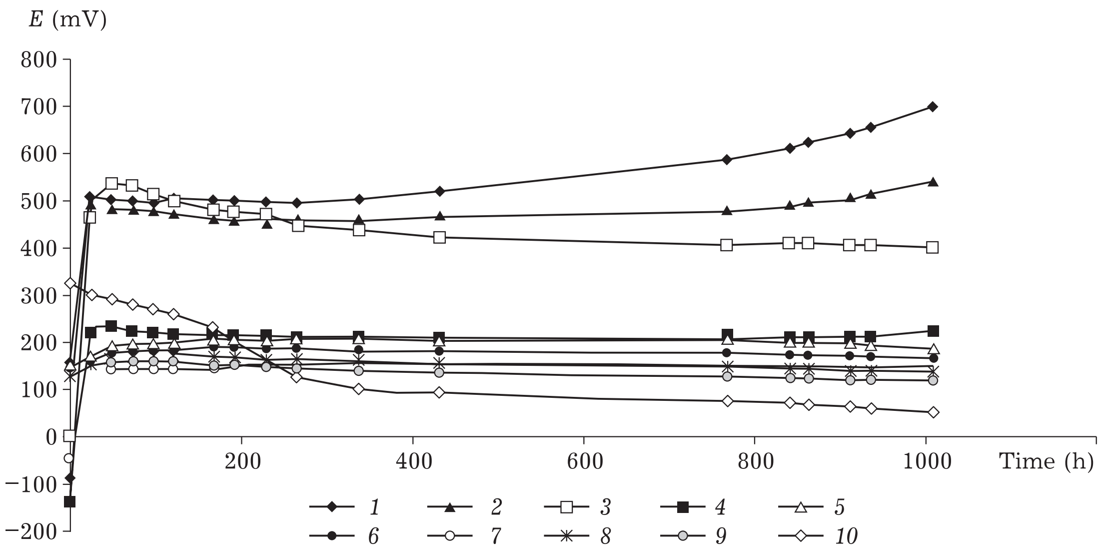

Fig. 2. Chronopotentiometric curves of steel painted with Lacroten E-241 and BMS-based composites.

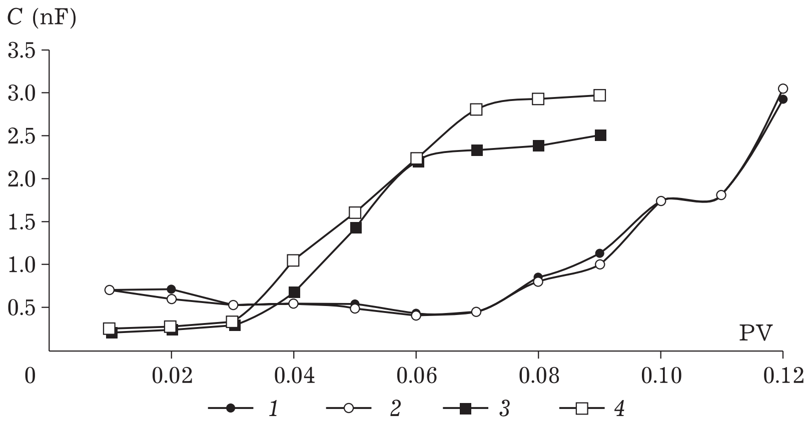

Fig. 3. Electrical capacitance of the steel–coating–electrolyte system *vs* the pigment volume (PV) in Lacroten E-241.

It can be seen that the beginning of a dramatic increase in the capacitance with PV > 9 % depends on the nature of manganese compounds.

Table 2 gives the results of a complex assessment of coatings and metal substrates under them in 1000 h of the impact of a 3 % aqueous solution of sodium chloride onto painted steel.

CONCLUSION

Summarizing the results of comparative assessment of coatings, one may conclude that the synthesized pigments, such as calcium manganite-phosphate (CMP) and magnatite-sulphate (BMS), according to the anticorrosive efficiency, are not inferior to zinc tetraoxychromate (ZTO). On the contrary, according to certain indicators, they are superior to it and wherein are much less toxic (by 30 times or more).

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