Anti-corrosion properties of coatings with manganese compounds pigmentation

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Abstract. Work investigates properties of corrosion-resistant coatings based on organic-aqueous emulsion and pigmented compounds of manganese, obtained by ceramic method. It is found that the inclusion of synthesized pigments in the composition of the coating increases their ability to inhibit underfilm corrosion of steel.

Introduction
Currently, the exacerbation of environmental problems calls a particular attention to the toxicity of components in composition of paint and varnish material. One of the most pressing issues requiring immediate action is to replace toxic corrosion pigments from the composition of inhibiting type primers.

As a result, researches aimed at developing less toxic compounds that provide high protective properties of the primer coating became highly relevant. In recent years there was a number of works showing that one of the ways to reduce the toxicity of corrosion of primers is the replacement of chromium pigments on manganese compounds [1-4]. Manganese pigments described in these works were obtained by precipitation. The disadvantage of this method is the difficulty of cleaning of the derived pigments from water-soluble salts contained in the mother solution and an adverse effect on the protective properties of pigmented coatings. In this paper, as a corrosion pigments we take barium manganite-sulfate (BMS), calcium manganite (CM), barium manganate (BM) received in a ceramic way [5].

Table 1 lists the properties of the pigment compounds and zinc tetraoxychromate (ZTOH), known as the high-performance corrosion resistant pigment and is used in this work as a reference comparison.

Table 1. The properties of pigments used for filling

| Pigment | Average oxidation state of manganese | Colour | pH of aqueous extract | Oil absorptio n 1 kind, g/100 g | Density, g/cm³ | Coverage rate, g/m² | Content of substances soluble in water,% |
|---------|-------------------------------------|--------|-----------------------|-------------------------------|---------------|------------------|--------------------------------------|
| BMS     | 4                                   | Brown  | 8                     | 14                           | 3.7           | 26               | 0.7                                  |
| CM      | 4                                   | Grey   | 7                     | 21                           | 3.9           | 16               | 0.8                                  |

Protective properties of corrosion resistant coatings depends not only on the characteristics of pigment inhibitor included in its composition, but also on the nature of film-forming one. This work investigated the two classes of film-forming systems: organic- and water-borne. Determining factors when choosing the film-forming coatings are chemical resistant material, its coupling with the protected surface and insulating ability.

As the main factors contributing to corrosive processes behavior under coat, relates moisture, containing electrolytes, particular attention should be paid to the level of the insulating efficiency of the paint film. Also an important part of the protective properties of coatings is inhibiting the ability of compounds extracted from its components by water diffusing through the paint film. To evaluate the barrier and inhibiting properties of coatings based on synthesized pigments were used the results of values of electrical capacitance system of painted metal-electrolyte (C) and steady corrosion potential (E) of steel under cover, as well as a visual assessment of the state of specimens through the 1000 h exposure of 3% aqueous solution of sodium chloride on painted steel.

Experimental technique

Pigment pastes were obtained by dispersion of pigment parts of coating composition. We received degree of grinding 20-30 micron on device "Klin" using the laboratory beaded dispersant DISPERMAT VMA-GETZMANN GMBH D-51580 Reichshof. Coating deposited on previously degreased steel surface 0.8 kp in three layers by centrifuge method. Coating thickness through 7 days drying under natural conditions was 30 ± 3 micron. Capacitance of the system painted metal — electrolyte and electrochemical potential of metal under the coating in process of testing measured using emittance meter FLUK PM6306 and pH-meter pH 340 respectively [6-8]. Potential measured relative to the silver chloride electrode and counted on the scale of normal hydrogen electrode.

Experimental results and discussion

Organic coatings based on film-forming systems

We assumed that as the basis of anti-corrosion primers for domestic purpose widely used alkyd oligomers, and in obtaining industrial primers applied epoxyamine binder. These affects choosing the type of organic aqueous film-forming coatings. Therefore, as objects of study were chosen alkyd binding (Spec 2311-023-4562449-2002) and epoxidiane oligomer (Spec-154 2225-05011907-97), with hardener polyethylenepolyamine (PEPA Spec 2413-357-00203447-99).

![Figure 1. The dependence of electric capacitance values in the system painted metal - electrolyte from time of contact with coatings with 0.5 m aqueous solution of sodium chloride (for E-40 tracks with different levels of filling pigment HCMS% vol.)](image)

Figure 1 presents the typical chronogram of values of capacitance that have the ascending branch due to diffusion of aqueous medium in the amount of paint film which goes into the sloping site,
associated with the completion of the process of swelling. Violation of the integrity of paint coating, caused by exceeding the critical volumetric content of pigment, leads to the formation of direct contact of metal with electrolyte and, as a consequence of a sharp rise in the value of the capacity of the system due to the contribution of electrochemical capacitance (40% of the SWAPS curve in Fig. 1).

Figure 2. Change of values of corrosion potential of system electrolyte - painted metal in time for epoxy compositions with various level of filling of SMES (% vol.)

The nature of chronopotentiometric curves, shown in Figure 2 indicates that the inclusion of manganiferous pigments in the composition of the paint film to a certain level, specific to each filming agent, greatly improves the potential of steel under the coating. The opposite occurs when the filling is above critical, in this case, painted steel capacity begins to decline. That is, the appearance of defects in the paint film causes the destruction of the passive film on the steel surface.

Figure 3. Changing the values of electrical capacitance and corrosion potential of system electrolyte - painted metal from filling level (for E-40 filled HCMs contact time of electrolyte with coating 1000 hours)

It is most clearly seen when presenting the data received in the form of established dependency values of capacitance and potential of volumetric content of pigment in the polymer. Such data for resin e-41 pigmented HCMS are presented in Fig. 3. The beginning of a sharp rise in capacity, corresponding to exceed the critical level filling occurs when filling is more than 35%. Decrease the insulating ability below a certain limit can not be offset by the inclusion in the cover even the most effective pigment-inhibitor.

Results of integrated assessment of coatings and metal substrate beneath it via 1000 h exposure on painted steel 3% aqueous solution of sodium chloride are presented in table 2.
Table 2. Results of integrated assessment

| pigment          | SWAPS, % | C, nF | E, mV | Area of bubbles, % | Area of corrosion % | Adhesion before testing | Adhesion after testing |
|------------------|----------|-------|-------|--------------------|---------------------|-------------------------|------------------------|
|                  |          |       |       |                    |                     |                         |                        |
| Alkyd binding    |          |       |       |                    |                     |                         |                        |
| None             | 0        | 5.95* | -360  | 5                  | 10                  | 2                       | 2                      |
| BMS              | 10       | 0.9   | 40    |                    |                     |                         |                        |
|                  | 20       | 1.1   | 260   | 0                  | 0                   | 1                       | 1                      |
|                  | 30       | 1.3   | 210   |                    |                     |                         |                        |
|                  | 40       | 1.8   | 300   |                    |                     |                         |                        |
|                  | 50       | 8.5   | -300  | 2                  | 10                  | 2                       |                        |
| CM               | 10       | 1.9   | 156   | 0                  | 0                   | 1                       | 1                      |
|                  | 15       | 2.1   | 139   |                    |                     |                         |                        |
|                  | 20       | 2.6   | 127   |                    |                     |                         |                        |
|                  | 25       | 3.2   | -300  | 5                  |                     |                         |                        |
|                  | 30       | 7.3*  | -350  | 25                 | 25                  | 2                       | 2                      |
| BM               | 10       | 0.8   | 114   |                    |                     |                         |                        |
|                  | 20       | 1.0   | 102   |                    |                     |                         |                        |
|                  | 30       | 1.2   | 54    | 0                  | 0                   | 1                       | 1                      |
|                  | 35       | 1.3   | 23    |                    |                     |                         |                        |
|                  | 40       | 1.6   | 36    |                    |                     |                         |                        |
|                  | 50       | 1.6   | 67    |                    |                     |                         |                        |
|                  | 55       | 8*    | -302  | 5                  | 2                   | 2                       |                        |
| Epoxydiane oligomer |          |       |       |                    |                     |                         |                        |
| None             | 0        | 0.4   | -350  |                    | 10                  |                         | 2                      |
| BMS              | 10       | 0.65  | 112   | 0                  | 0                   | 1                       | 1                      |
|                  | 20       | 0.71  | 102   |                    |                     |                         |                        |
|                  | 30       | 0.6   | 52    |                    |                     |                         |                        |
|                  | 35       | 1.2   | 62    |                    |                     |                         |                        |
|                  | 40       | 6.8   | -400  | 20                 |                     |                         | 2                      |
| CM               | 10       | 1.0   | 23    |                    |                     |                         |                        |
|                  | 20       | 1.2   | 6     | 0                  | 0                   | 1                       | 1                      |
|                  | 30       | 1.2   | -67   |                    |                     |                         |                        |
|                  | 40       | 4.2   | -350  | 25                 | 20                  | 2                       | 2                      |
| BM               | 10       | 0.6   | 35    |                    |                     |                         |                        |
|                  | 20       | 0.6   | 39    |                    |                     |                         |                        |
|                  | 30       | 0.7   | 27    |                    |                     |                         |                        |
|                  | 40       | 1.1   | -300  | 5                  |                     | 2                       | 2                      |

The data presented in the table allow you to identify possible filling limits upon receipt of corrosion primers based on synthesized pigments.

2. Coatings based on film-forming systems

The trend towards reducing the use of organic solvents in paint-and-lacquer materials production and application of water-dispersion paints is steadily increasing, expanding their product range. Advantages of water-dispersion paint materials are obvious, they have no odor, dry quickly, easily applied to the surface. As a film-forming system for research has been chosen aqueous styrene-acrylate dispersion Lakroten E-241 (Spec 2241-031-51769913-2004), which, as preliminary studies have shown, suitable as film-forming the basis of anti-corrosion coatings. The formed coatings were analyzed in the same way as the previous ones. The results may be seen in table 3.
Figure 4. Changing the values of electrical capacitance and corrosion potential of system electrolyte — painted metal from filling level (for Lacrotan-E241 filled with HCMs, contact time of electrolyte with coating 1000 hours)

Difference in values of boundary filling of water-dispersion varnish and water-dispersible filmforming systems (see figures 3 and 4) due to the fact that the latter are characterized by more high value relations of particle sizes of filmformer and pigment. In addition, the formation of the interphase boundary pigment — film binders in cover based on the pigmented emulsions is compounded by low mobility of macromolecules of filmformer, which may lead to a reduction in Interfacial adhesion and increase the defectiveness of the paint film.

Comparison of the results leads us to the conclusion that the nonpigmented coating has lower protective properties, since the corresponding values of corrosion capacity are at a lower level and monotonically decreasing. Integrated assessment results are presented in table 3.

Table 3. The results of integrated assessment

| SWAPS,% | C, nF | E, mV | Bubbles, % | Corrosion area,% | Adhesion | before testing | after testing |
|---------|-------|-------|------------|------------------|----------|----------------|--------------|
| BM      |       |       |            |                  |          |                |              |
| 2       | 0.262 | 284   | 0          | 0                | 1        | 1              |              |
| 4       | 0.538 | 117   | 0          | 0                | 1        | 1              |              |
| 6       | 0.345 | 147   | 0          | 0                | 1        | 1              |              |
| 8       | 0.7   | 373   | 0          | 0                | 1        | 1              |              |
| 10      | 1.12  | 342   | 0          | 0                | 1        | 1              |              |
| 12      | 3.44  | -119  | 0          | 0                | 1        | 1              |              |
| BMS     |       |       |            |                  |          |                |              |
| 2       | 1.90  | 170   | 0          | 0                | 1        | 1              |              |
| 4       | 0.36  | 180   | 0          | 0                | 1        | 1              |              |
| 6       | 0.50  | 213   | 0          | 0                | 1        | 1              |              |
| 8       | 1.10  | 210   | 0          | 0                | 1        | 1              |              |
| 10      | 1.50  | 170   | 0          | 0                | 1        | 1              |              |
| 12      | 1.60  | 120   | 0          | 0                | 1        | 1              |              |
| 14      | 8     | -302  | 0          | 0                | 1        | 1              |              |
| CM      |       |       |            |                  |          |                |              |
| 2       | 0.26  | 200   | 0          | 0                | 1        | 1              |              |
| 4       | 0.29  | 211   | 0          | 0                | 1        | 1              |              |
| 6       | 0.32  | 205   | 0          | 0                | 1        | 1              |              |
| 8       | 0.39  | 214   | 0          | 0                | 1        | 1              |              |
Summarizing the results of the comparative evaluation of protective properties of coatings, which are presented in tables 2 and 3, one can conclude that synthesized ceramic pigments HCMs MC and MB with SWAP level below the critical increase anticorrosion efficiency of coatings based on film-formers.

Conclusions
The influence of the manganese-containing anticorrosive pigments’ content and nature on the protective properties of the coating has been studied. It has been shown that when filling below the critical level higher efficiency of anticorrosive coatings is observed. It allows to consider synthetic products alternative to low-toxic chromium-containing pigments.

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