Development of an epoxy inhibiting primer using barium manganate (IV) as a pigment

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Abstract
The properties of anticorrosive coatings based on epoxy resin pigmented with barium manganate (IV) produced by ceramic method have been investigated. Electrochemical tests of coatings based on the developed primer showed inhibiting properties with respect to corrosion processes and also demonstrated that the coatings retain a high adhesion even after exposure to an electrolyte solution for 1000 hours. It has been established that the inclusion of the synthesized pigment in the coatings increases their ability to inhibit sub-film corrosion in steel.

1. Introduction
One of the most common methods of protecting metals against corrosion is the use of polymer anticorrosion coatings [1-3]. The main role in ensuring the protective properties of such coatings is played by anticorrosive pigments [4]. The disadvantages of pigments that give modern metal primers high anti-corrosion properties include toxicity due to the highly oxidised content of chromium [5]. The search for low-toxicity pigments comparable in protective effect to those of chromate pigments, such as strontium and zinc chromates, remains a current challenge [6-11]. Many substances may act as substitutes for chromate pigments, but zinc phosphate and related compounds [12] are currently the most common, but they are not without their disadvantages and do not provide the necessary level of anticorrosive protection at similar concentrations. For this reason, less toxic manganese (IV) compounds with oxidative and complex-forming properties, as well as chromium (VI), are of great interest from the point of view of protective action similar to chromate pigments.

In a number of previous works [13,14] we have shown that the regulation of the chemical composition of manganese pigments, including nanoscale pigments [15,16], and the correct selection of formulations for paints and coatings allow us to obtain coatings with high protective properties.

The aim was to develop and optimise the composition of an epoxy primer to protect metals using synthetic barium manganate (IV) as an anticorrosive pigment.

2. Experimental part
The application compositions were dispersed in a laboratory bead mill to a grinding degree of 25 μm, which was determined using a grindometer. The development of the primer was based on the pigment part of EP-0191 primer (TU 6-10-16-92-86) containing zinc tetraoxychromate, zinc oxide, talcum and calcite. E-41 epoxy-diane resin (TU 6-10-1316-84) cured with hardener No. 11 (TU 2332-098-21743165-97), which is a polyamide resin solution in a mixture of organic solvents, was used as a film forming base. The calculation of the composition of the primer (MiniTab programme) is presented in Table 1, and a diagram of the calculation results is shown in Figure 1.
Figure 1 - Schematic presentation of the results of the primer composition calculation

### Table 1. Compositions of E-41 resin-based primers received

| Number | Barium manganate | Zinc oxide | Talc | Calcit | E-41 | Hardener |
|--------|------------------|------------|------|--------|------|----------|
| 1      | 4                | 20         | 3.2  | 12.8   | 134.7| 47.15    |
| 2      | 40               | 0          | 0    | 134.7  | 47.15|
| 3      | 20               | 0          | 4    | 16     | 134.7| 47.15    |
| 4      | 10.8             | 13.6       | 3.12 | 12.48  | 134.7| 47.15    |
| 5      | 18.8             | 15.6       | 1.12 | 4.48   | 134.7| 47.15    |
| 6      | 18.8             | 5.6        | 3.12 | 12.48  | 134.7| 47.15    |
| 7      | 4                | 16         | 4    | 16     | 134.7| 47.15    |
| 8      | 10.8             | 15.6       | 2.72 | 10.88  | 134.7| 47.15    |
| 9      | 20               | 20         | 0    | 0      | 134.7| 47.15    |
| 10     | 17.6             | 11.2       | 2.24 | 8.96   | 134.7| 47.15    |
| 11     | 28.8             | 5.6        | 1.12 | 4.48   | 134.7| 47.15    |

Coatings from the obtained primers were applied in three layer on 08kp steel samples in accordance with GOST 1050-2013 and cured for 72 hours without heat supply. The thickness of the formed coating was 30±5 microns. Primer samples in the form of free films were applied to a fluoroplastic sheet with subsequent delamination from it after the films were cured under similar conditions as described above.

Extracts of filled epoxy films were studied by linear polarization. To carry out electrochemical tests on coatings according to the method described in [17,18], an electrochemical cell was formed on their surface by gluing a glass cylinder into which a 3% aqueous sodium chloride solution was poured. Electrical capacity and corrosion potential were monitored during electrochemical tests. Coating adhesion was determined by the stripping method in accordance with GOST 32299-2013 (ISO 4624: 2002).

3. Results and discussion

In parallel, corrosion studies of water extracts from calculated compositions were carried out using the method of low linear polarization. The data obtained is shown in Figure 2, according to which the curves obtained for some compositions were close.
The data presented in Figure 2 also confirms the inhibitory effect of the synthesized pigment. The formed coatings were electrochemically tested for 1000 hours in 3% aqueous sodium chloride solution. Contour diagrams were drawn based on the results obtained (Figure 3).

In selecting the optimal pigment part composition for further research, we proceeded from the need to minimize the content of the most expensive component - the anti-corrosion pigment. The contour diagram of electrical capacitance (Figure 3a) and corrosion potential (Figure 3b) shows the optimum areas in the form of an increase in the grey color intensity corresponding to the improvement of these characteristics.

The analysis of the results shows that the optimum areas of the investigated characteristics do not coincide with each other. For the convenience of determining the optimum composition of the pigment part, values of electrical capacitance and corrosion potential have been superimposed within given limits. The results of approximation for the compositions under study are shown in Figure 4.
Figure 4. Areas of optimal ratio of pigment part components in E-41 epoxy resin after 1000 hours tests

The area of proportions of the pigment part, in which the pigment content is minimal but the protective properties of the coatings are preserved, is highlighted in white. Following these tests, a comprehensive assessment of the condition of the samples was carried out, the results of which are shown in Table 2.

Table 2. Comprehensive evaluation of samples after testing within 1000 hours

| Number | Capacity C, nF | Corrosion potential E, mV | Corrosion area, % | Adhesion by separation, MPa before the tests | Adhesion by separation, MPa after the tests |
|--------|----------------|---------------------------|-------------------|----------------------------------------------|---------------------------------------------|
| 1      | 1.282          | 17                        | 1                 | 4.810                                        | 4.249                                        |
| 2      | 0.938          | 150                       |                   | 3.873                                        | 3.124                                        |
| 3      | 1.153          | 123                       |                   | 5.061                                        | 4.157                                        |
| 4      | 1.215          | 99                        |                   | 6.370                                        | 4.499                                        |
| 5      | 1.261          | 110                       |                   | 6.685                                        | 4.813                                        |
| 6      | 0.955          | 93                        | 0                 | 7.250                                        | 4.249                                        |
| 7      | 1.369          | 25                        |                   | 4.186                                        | 3.937                                        |
| 8      | 1.196          | 100                       |                   | 6.216                                        | 4.651                                        |
| 9      | 1.411          | 126                       |                   | 5.435                                        | 4.300                                        |
| 10     | 1.454          | 120                       |                   | 5.373                                        | 5.373                                        |
| 11     | 1.411          | 141                       |                   | 4.155                                        | 3.524                                        |

The corrosion potential values for all compositions given in Table 2 are in the positive area, which also confirms the inhibitory properties of the obtained pigment.

4. Conclusion

Studies have shown that synthetic barium manganate (IV) can be used as an anti-corrosion pigment in primers to protect metals. Electrochemical tests revealed the high barrier and inhibitory properties of coatings containing the synthesized pigment. In addition, no corrosion damage was detected under the coatings after the tests, and the adhesion for some formulations remained almost unchanged. The optimum ratio between pigments and fillers was determined during the formulation of the pigment part of the primer.

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