ANTICORROSION EFFICIENCY OF EPOXY-RESIN BASED COATINGS DEPENDING ON PVC OF CONDUCTING POLYMER

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Abstract
Polyaniline phosphate—emeraldine was prepared by reaction in an aqueous solution in the environment of ammonium peroxodisulfate and phosphoric acid. The epoxy resin based coatings containing 2, 4, 10, 14, 20 and 23 vol. % of PANI as a corrosion inhibitor were tested for their mechanical properties and corrosion resistance. The testing of the anticorrosion efficiency of emeraldine as a corrosion inhibitor was based on the accelerated corrosion tests in the environment of NaCl mist, and condensing water and SO2. The synthesized emeraldine provides good anticorrosion efficiency in an epoxy-ester coating.

Keywords: coating, anticorrosion, polyaniline, emeraldine, conducting polymer

1. INTRODUCTION
The last three decades have seen a significant development of materials based on conducting polymers. [1]. Electrically-conducting polymers can change their structure depending on the reaction of the surrounding environment. One of the conducting polymers is polyaniline. According to currently available studies, this substance displays propitious applications when used as a corrosion-inhibition pigment in the organic binders of paints [2-5]. The electrical conductivity of polyaniline, which is comparable to that of common semi-conductors, was known as early as the 1960’s. General interest in conducting polymers did not develop until the late 1970’s when it was discovered that following the halogenation of trans-polyacetylene, the specific conductivity of this polymer increases to the conductivity level of inorganic semiconductors. Despite its high conductivity, the limited stability of polyacetylene directed attention at much more stable polymers, polyaniline PANI [6-11] and polypyrrole.

2. EXPERIMENTAL
2.1. The formulation of organic coatings with emeraldine content

Model paints were formulated to test the properties of the studied polyaniline as an anticorrosion component. A solvent-borne epoxy-resin was selected as the binder of the tested coatings. In this binder the green conductive form of polyaniline remains stable, i.e. it does not deprotonate to PANI base. We formulated a number of model epoxy-rein based paints with an increasing volume concentration of emeraldine as a pigment. The content of emeraldine in a coating was set to the value of pigment volume concentration (PVC) that was equal to 2 %, 4 %, 10 %, 14 %, or 20 %, and to the value of critical pigment volume concentration (CPVC = 23 %).

![Fig. 1 SEM images and morphology of emeraldine particles: a) 5 000x and b) 500x](image-url)

2.2. Preparation of test coatings
To carry out corrosion tests of the formulated organic coatings, paint films on steel panels were prepared (Q-panel, England; size: 150×100×0.9 mm). Samples on 150×75×0.6 mm steel panels were also prepared for mechanical tests. Paints were applied onto the steel panels by an applicator with a 150 μm slit. In order to determine the gloss, and surface hardness of the paint, paints were also
applied onto glass panels (210 × 100 × 2.9 mm) by a hexagonal applicator with a 200 μm slit. A magnetic thickness gauge was used to measure the dry thickness of the coatings according to ISO 2808. A 7 cm long trial cut that was applied to the samples used in the corrosion tests was executed in the lower part of the steel panel.

2.3. Mechanical properties of the coatings
The following physical-mechanical properties were identified in the prepared coatings: the surface hardness of the paint film, the gloss of the paint film, adhesion of the film to the base, and the hardness, resilience and strength of the film. The applied standardized tests simulate mechanical stress in the external environment, such as the impact of objects falling onto the surface (impact test), or deformities caused by bending and by elongation (bending strength test, cupping test).

2.4. Corrosion tests
Accelerated cyclic corrosion test in an atmosphere of SO₂ with water condensation
The test was carried out in accordance with standard ISO 6988. The exposure of the samples in a testing chamber was performed in 24-h cycles: 8 h of exposure to SO₂ at a temperature of 35°C followed by exposure to the condensation of humidity for a period of 16 hours and at a temperature of 21°C. The condition of the samples was evaluated after 2 500 h of exposure.

Accelerated cyclic corrosion test in the atmosphere of NaCl with water steam condensation
The principle of this test is derived from standard ISO 9227. The exposure of the samples in a testing chamber was performed in 12-h cycles divided into three parts: 6 h of exposure to the mist of 5 % solution of NaCl at a temperature of 35 °C; 2 h of exposure at a temperature of 23 °C; and 4 h of humidity condensation at a temperature of 40 °C. The samples were evaluated after 2 000 h of exposure.

3. RESULTS AND DISCUSSION
3.1. Evaluation of physical tests
The measurement of the surface hardness of epoxy-resin based paint films on glass panels took 60 days. The time-dependence of coating hardness is shown in Figure 2. The maximum values of surface hardness and the rate of drying were displayed by the epoxy-ester paints pigmented with polyaniline (emeraldine) at lower PVC values: i.e. at PVC_emeraldine = 2 %. With this lower PVC value surface hardness is higher than that of a non-pigmented coating. The values of the volume concentration of polyaniline (PVC_emeraldine) = 4 – 10 % exhibited a steep reduction in hardness. The coatings containing more conducting polymer than PVC_emeraldine = 10 % were affected by markedly retarded drying, during which hardness increased by some tenths of one percent, and was generally extremely low.

Tab 1 Evaluation of the mechanical tests of epoxy-resin based coatings in dependence on PVC_emeraldine (DFT = 60±5 μm)

<table>
<thead>
<tr>
<th>PVC_emeraldine (vol.%)</th>
<th>Bend (mm)</th>
<th>Impact – reverse (cm)</th>
<th>Cupping (mm)</th>
<th>Adhesion (deg)</th>
<th>Total resistance (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>&lt;4</td>
<td>95</td>
<td>5,1</td>
<td>1</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>&lt;4</td>
<td>98</td>
<td>&gt;10</td>
<td>0</td>
<td>99</td>
</tr>
<tr>
<td>10</td>
<td>&lt;4</td>
<td>100</td>
<td>&gt;10</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>14</td>
<td>&lt;4</td>
<td>&gt;100</td>
<td>&gt;10</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>20</td>
<td>&lt;4</td>
<td>&gt;100</td>
<td>&gt;10</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>23 (CPVC)</td>
<td>&lt;4</td>
<td>&gt;100</td>
<td>&gt;10</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

Fig.2 Time course of the surface hardness of epoxy-resin based paint films depending on PVC_emeraldine

3.2. Corrosion tests
The condenser chamber with SO₂ content
The evaluation of blistering identified some interesting facts, specifically, that the increasing value of PVC is accompanied by a decreasing number of blisters near the cut. Furthermore, it was observed that an increasing PVC_PANI value is connected with increasing resistance against corrosion in the cut. The lowest corrosion degree under the paint was detected to be within a range of PVC_PANI of 10–14%. The highest resistance against blistering in the cut was displayed by the samples of epoxy-ester paint films with PVC_PANI = 14%. With regard to total anticorrosion efficiency, the best efficiency was clearly achieved with an epoxy-ester coating pigmented with PANI at PVC = 14 % (Figure 3).
The ability of conducting polymer (PANI, emeraldine) to provide the most efficient protection of a metal surface in the place of coating disturbance (cut) indicates that its active function is facilitated by an electrochemical mechanisms. It belongs to the anodic type of inhibitors that suppress this following anodic reaction: Fe → Fe^{2+} + 2 e⁻; i.e. the anodic oxidation of iron to ferrous cations. If the emeraldine PVC value increases, then:
1. The occurrence of blisters in the cut decreases, reaching a minimum at PVC_{PANI} = 14 \%.
2. The extent of corrosion in the cut decreases, reaching a minimum at PVC_{PANI} = 14 \%.
3. The extent of corrosion on the surface of the metal base is lowest at PVC_{PANI} = 14 \%.

The condenser chamber with salt mist
The samples of epoxy based coatings were exposed to a chamber with salt mist for 2 000 hours. The test results, depending on emeraldine PVC following a test taken in a chamber with salt mist, are given in Table 2. The greatest efficiency against blistering in the cut was displayed by the samples of epoxy-ester coatings at PVC_{PANI} = 14–23 \%. The increasing value of PVC_{emeraldine} is accompanied with increasing resistance against the spread of corrosion in the cut, reaching as far as zero corrosion (0–0.5 mm). The extent of surface corrosion in the base was lowest at PVC_{PANI} = 10 \%; in general, corrosion connected with a PVC_{PANI} range of 10–20 \% exhibited low occurrence. Coating surface blistering was zero at PVC_{emeraldine} = 14–23 \%.

Tab. 2 Results of coating exposure in dependence on PVC_{PANI} in a chamber with salt mist (DFT=80 ±5\mu m)

<table>
<thead>
<tr>
<th>PVC_{PANI} (%)</th>
<th>Blistering in the cut</th>
<th>Surface blistering</th>
<th>Corrosion in the cut (mm)</th>
<th>Corrosion in the base (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>6M</td>
<td>2F</td>
<td>1–2</td>
<td>16</td>
</tr>
<tr>
<td>4</td>
<td>4M</td>
<td>2F</td>
<td>1–2</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>8F</td>
<td>8F</td>
<td>0.5–1</td>
<td>1</td>
</tr>
<tr>
<td>14</td>
<td>-</td>
<td>-</td>
<td>0–0.5</td>
<td>1</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>-</td>
<td>0–0.5</td>
<td>1</td>
</tr>
<tr>
<td>23</td>
<td>-</td>
<td>-</td>
<td>0.5–1</td>
<td>100</td>
</tr>
</tbody>
</table>

With regard to total anticorrosion efficiency, the best efficiency was clearly achieved with an epoxy-ester coating pigmented with PVC_{PANI} = 14 \%. It can be claimed that a relatively low PVC value is required for the anticorrosion effects of PANI in the NaCl environment. Unlike in the SO2 environment, the spread of corrosion in the cut is not so fast in a chamber with salt mist since chloride ions are less mobile than sulfate ions. The anticorrosion efficiency of coatings with PANI is higher in the NaCl environment than in the SO2 environment.

If the polyaniline PVC value increases, then:
1. The occurrence of blisters in the cut decreases, reaching a minimum at PVC_{PANI} = 14–23 \%.
2. Corrosion in the cut decreases, reaching a minimum at PVC_{emeraldine} = 14–20 \%.
3. Corrosion on the surface of the metal increases steeply at PVC_{emeraldine} ≥ 14 \%.
4. CONCLUSION

This aim of this paper was to report a study of the properties of organic coatings containing emeraldine as an efficient corrosion-inhibiting pigment. Polyaniline phosphate - emeraldine was obtained by chemical oxidative polymerization. In order to study the effects of polyaniline volume concentration on the mechanical and corrosion resistance of the coatings, a number of paint films with the increasing values of emeraldine volume concentration were prepared. Epoxy based resin (medium molecular weight) was chosen as a binder; this resin exhibited very good adhesion-barrier properties on a base metal panel. The results of the laboratory tests of the physical resistance of the tested samples with the emeraldine content revealed that the resilience and strength of the paint films increases along with increasing values of volume concentration.

Analyses of results of the laboratory tests of corrosion resistance concluded that the best anticorrosion efficiency was displayed by an epoxy resin based coating pigmented with emeraldine to PVC_{emeraldine} = 14 vol. %. This concentration facilitates the best anticorrosion effects of emeraldine in all the applied corrosion environments and approximately corresponds to the percolation threshold of conducting polyaniline – emeraldine dispersed in the non-conducting matrix.

References: