ANTICORROSION PROPERTIES OF PEROVSKITES SURFACE-MODIFIED WITH CONDUCTING POLYMERS IN ALKYDE COATINGS

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Abstract
The effect of pigment particle surface treatment with polyaniline and polypyrrole on the corrosion inhibiting properties of organic paints was investigated. Mixed oxides possessing the spinel and perovskite structures were synthesised for the study. Coatings based on an alkyde resin were prepared for the investigation of the corrosion protection properties of the pigments, the surfaces of which had been provided with a polyaniline and polypyrrole layers. Laboratory corrosion tests were applied to the paint films. Polyaniline phosphate was found preferable to polypyrrole as the modifying agent of the pigment surface regarding the pigment’s corrosion inhibiting efficiency.

Keywords: conducting polymer, polypyrrole, polyaniline phosphate, organic coating, anti-corrosion efficiency

1 Introduction
Conductive polymers are promising materials that are beneficial in protective anti-corrosion paints [1-6]. It is hoped that conductive polymers may replace corrosion inhibitors containing heavy metals. They are classed as electrochemically active corrosion inhibitors [7-9]. Examples of conductive polymers include polyacetylene, polypyrrole, polythiophene, polyaniline, polyphenylene and poly (p-phenylenvinylene), which are all systems containing conjugated double bonds with charge carriers providing charge transfer along the chain [10-12]. Polyaniline is probably the oldest synthetic conductive polymer [13]. The green protonated emeraldine is a conductive form of polyaniline [14]. Polypyrrole is appealing owing to its simple preparation in the form of a powder, film or composite [15-17]. Organic-inorganic composites containing inorganic nanoparticle fillers exhibit both improved electrical and mechanical properties. Inorganic nanoparticles in the composites are coated with a conductive polymer layer, which improves the physical properties of the material [18].

The potential of using polyaniline in inorganic paints as an anti-corrosion agent is the subject of extensive studies. In powder form, in which it is used most frequently as a pigment, polyaniline is prepared by chemical polymerisation by the oxidation of aniline [19]. Pigments that are coated deliberately with a thin layer of polyaniline have also been used in many studies aimed at creating a new anti-corrosion pigment that could provide the highest level of protection to metallic surfaces coated with it [20, 21]. In a number of applications into organic paints, it is convenient to apply composite particles formed by a layer of a conductive polymer on an
inorganic particle, as a corrosion protection element. Hence, the systems comprise pigment or filler particles, which are provided with a layer of an active compound; a conductive polymer and a suitable substance (pigment substrate) that provides an additional active effect [22-24]. The inner core should determine the paint’s physical properties at the substrate metal/paint film interface, such as its adhesion to the substrate [25]. However, the polymer’s conductive property must be preserved. With polyaniline phosphate (PANI), such a particle must not be appreciably alkaline in order to preserve its conductive form for polymerisation on the particle surface. Also, the particle structure must not undergo change during the conductive polymer preparation process. In view of the specific properties of paint fillers and of the different corrosion conditions, it is necessary to find pigment particles with morphological and physicochemical properties that would not affect adversely the stability of the film-forming component of the paint binder or the physical properties of the cross-linked polymeric paint [26].

2 Material and experimental methods
2.1 Synthesis of mixed-metal-oxide-based pigments possessing the perovskite structure
Perovskites can be described generally by the formula $\text{ABO}_3$ where atom A is in the oxidation state 2+ and atom B is in the oxidation state 4+ [27].

2.2 Laboratory synthesis of the pigments:
The weights of the starting materials for the synthesis of $\text{CaTiO}_3$, $\text{SrTiO}_3$ were calculated based on the stoichiometry of equations (1) with respect to the total amount of pigment.

$$\text{MeCO}_3 + \text{TiO}_2 \rightarrow \text{MeTiO}_3 + \text{CO}_2$$

where: Me = Ca, Sr

The first calcination phase was conducted at 1000 °C and the second phase, at 1180 °C. In each phase, the holdup time at the respective temperature was 2 hours, ramp 5 °C/min. The temperatures were chosen based on experience from previous studies and were confirmed by X-ray analysis. After cooling, the calcined products were removed from the furnace and subjected to the subsequent operation, i.e., grinding to particle size within the range of 100–101 μm. The wet grinding process was conducted in ethanol in a Pulverisette 6 (Netzsch, Germany) planet ball mill at 400 rpm for 4 hours with a reverse mode after 2 hours. The milling container was made of zirconium oxide, 500 mL volume. The 10-mm–diameter milling balls were made of zirconium silicate. The milling procedure was followed by pigment rinsing with a multiply larger volume of distilled water followed by drying at 110 °C in a hot-air dryer for 10 hours.

2.3 Preparation of pigments with conductive polymer surface layers
The surface of the pigments was modified by treatment with polyaniline phosphate and polypyrrole. The anti-corrosion efficiency was evaluated both for the untreated pigments and for the pigments with surfaces modified with polyaniline or PPy.

2.3.1 Laboratory preparation of pigments modified with a surface layer of polyaniline phosphate (PANI)
The pigment (100 g) was suspended in 250 mL of 0.2 M aniline (C6H7N, Fluka, Switzerland) solution in 0.4 M ortho-phosphoric acid (Lachema, Czech Republic) and 250 mL of 0.5 M ammonium peroxydisulfate (Lach-Ner, Czech Republic), also in 0.2 M ortho-phosphoric acid,
was added to initiate the aniline polymerisation process at room temperature. The suspension was stirred for one hour during which the aniline polymerised on the surface of the pigment particles. The following day, the solids were filtered out and rinsed with 0.2 M phosphoric acid followed by acetone. The pigment particles coated with the PANI over layer were dried in air and then at 60 °C in a laboratory dryer. The composite particles contained about 10 wt.% PANI (emeraldine) phosphate.

**2.3.2 Laboratory preparation of pigments modified with a surface layer of polypyrrole (PPy)**

The pigment (20 g) was suspended in 250 mL of distilled water and pyrrole (C4H5N, Fluka, Sigma-Aldrich Co.) (3.56 mL) was added. The system was stirred vigorously by using a glass stirrer and an oxidant solution consisting of ammonium peroxodisulfate (14.25 g) ((NH4)2S2O8, Lach-Ner, Czech Republic) in 250 mL of distilled water was added. Stirring continued for approximately 1 hour and then it was allowed to stand overnight. The following day, the modified pigments were filtered out, rinsed with distilled water and acetone and dried at room temperature in air and then at 60 °C in a laboratory dryer.

**2.3.3 Characterisation of the pigments in the powder form**

The pigment particles’ surface and shape were examined with a JEOL-JSM 5600 LV (Japan) scanning electron microscope (SEM). The pH of the aqueous extracts was determined as described in ISO 789-9. Suspensions (10 wt.%) of the pigments in redistilled water were prepared and their pH was measured continually for 21 days until a steady value was observed. The suspension was then filtered off and the final filtrate pH (pH21) was measured with a WTW pH 320 Set-2 multiprocessor pH-meter fitted with a measuring glass electrode (WTW Wissenschaftliche Werkstätten, Germany). The specific electric conductivity ($\chi$) of the aqueous suspensions was measured conductometrically with a Handylab LF1 conductometer (Schott–Geräte GmbH, Germany) in combination with a measuring Pt cell. The measurements were performed in 10% pigment suspensions in redistilled water in accordance with ISO 787/14. The samples were measured for 21 days until the conductivity levels remained nearly constant. Subsequently, the suspension was filtered off and the final conductivity of the filtrate (in $\mu$S/cm) was measured.

**2.3.4 Corrosion-inhibiting efficiency of the pigments**

The corrosion inhibiting properties of the pigments with a surface layer of conductive polymer (pigment/PPy, pigment/PANI) in comparison with those of the untreated pigments were examined following the application of the coating materials on the organic binder.

**2.3.5 Organic coating formulations containing the pigments**

The pigments were added to a solution of a water-based medium-molecular-weight epoxy resin used frequently in the manufacture of coating materials intended for the protection of metals. All coating materials were model formulations, i.e., they contained no additional fillers or additives that might affect appreciably the formulations’ efficiency. The pigment volume concentration (PVC) was invariably 10 vol.%. The critical pigment volume concentration (CPVC) (an important parameter in the formulation of coating materials) was calculated from the density, determined with a Micromeritics Autopycnometer 1320 instrument (Micromeritics Instrument Corp., USA) and from linseed absorption by the pigment (oil consumption).
The model coating materials (paints) were prepared by dispersing the liquid binder and the powder ingredients in a Dispermat CV pearl mill (WMA Getzmann GmbH, Verfahrenstechnik, Germany). Immediately prior to making the coat, the pigmented coating material was homogenised with the polyamide hardener in a 100:27 resin-to-hardener weight ratio.

2.3.6 Preparation of test samples of the paint films
The paint films on steel panels (Q-panel, UK) with dimensions 152 × 102 × 0.8 mm were prepared by means of an applicator for the corrosion tests. Paint films were prepared on a polyethylene sheet, which was removed when dry, cut into 1 × 1-mm pieces and used for the preparation of 10 wt.% aqueous suspensions of the free films, which were treated in the same way as the powder samples for pH measurement and for corrosion loss determination. The samples were allowed to dry and conditioned on the test panels in normal conditions (air-conditioned laboratory, 20 °C, 50% RH) for 6 weeks. The dry film thickness (DFT) was measured with a Minitest 110 magnetic thickness gauge combined with an F16 type probe (Elektrophysik, Germany) in accordance with ISO 2808. A 7-mm-long test cut was made on the bottom of all steel panels for completing the corrosion tests.

2.4 Laboratory corrosion tests
The cyclic corrosion test with water condensation in the presence of sulphur dioxide was performed in line with EN ISO 3231. The exposure in the corrosion environment was conducted in 24-hour cycles: 8 hours of condensation of distilled water containing SO2 (SO2 concentration = 0.2 L) at 36 °C (SO2 =0.2 l), followed by 16 hours of sample drying at 23 °C. The outcome was evaluated following 720 hours’ exposure.

The cyclic corrosion test in an NaCl solution spray environment was derived from ISO 7253. The paint films were exposed to the mist of a 5% NaCl solution at 35 °C for 10 hours (1st cycle stage), followed by 1 hour of water condensation at 40 °C (2nd cycle stage) and 1 hour of drying at 23 °C (3rd cycle stage). The outcome was evaluated following 504 hours’ exposure.

2.4.1 Corrosion test outcome evaluation
The following parameters were evaluated to assess the corrosion effects in the tests: site and frequency of occurrence of blisters on the paint film, degree of corrosion of the metallic substrate surface and degree of corrosion of the substrate near the cut. Methods as per ASTM D 714-87, ASTM D 610, and ASTM D 1654-92 were used. The corrosion effects were rated on a 100–0 scale. The total anti-corrosion efficiency was obtained based on the arithmetic mean of the degree of corrosion of the metallic substrate, degree of blister formation on the paint film surface and the degree of corrosion of the metallic substrate near the cut. In other words, the total anti-corrosion efficiency E [20] from the corrosion tests (EH2O, ENaCl, ESO2, EMS) was calculated by using Equation 2:

\[ E = \frac{A + B + C}{3} \]  

where:  
A - the degree of blistering in the paint film area,  
B - the substrate metal corrosion,  
C - corrosion in the paint film cut.
2.5 Determination of the corrosion-induced steel mass loss
This test measures the mass loss of steel submerged in the test solutions. This corrosion test was conducted both in the aqueous filtrate (extract) of a 10% suspension of the pigment powder and in aqueous extracts of 10% suspensions obtained from the free paint films containing the pigment tested. Suspensions in which the pH and specific electric conductivity levels had attained their steady states (i.e., after 21 days) were used. The defined steel panels were used and were submerged in aqueous extracts obtained by filtration of 10% suspensions of the pigments studied. The steel panels were exposed to the test conditions for 21 days. The metal mass loss values relative to those in water (in %) were calculated for the steel panels submerged in the filtrate of the pigment powder suspension (Xp), as well as for the steel panels submerged in the filtrates obtained from the free paint films (Xf).

3 Results and discussion
3.1 Pigment particle morphology
The pigment particle morphology was examined by an SEM using an SEI detector. The SEM photographs showing the particle shapes are shown in Fig. 1 – Fig.6.

![Fig. 1 SEM photographs CaTiO₃](image1)

![Fig. 2 SEM photographs CaTiO₃/PANI](image2)

![Fig. 3 SEM photographs CaTiO₃/PPy](image3)

![Fig. 4 SEM photographs SrTiO₃](image4)
3.2 Physicochemical properties of the pigments

Parameters describing the properties of the powdered pigments, including density, oil consumption, particle shape and CPVC, are given in Table 1.

### Table 1 Physicochemical parameters of the pigments

<table>
<thead>
<tr>
<th>Pigment type</th>
<th>Particle morphology</th>
<th>Specific weight [g/cm³]</th>
<th>Oil consumption [g/100 g]</th>
<th>CPVC [%]</th>
</tr>
</thead>
</table>
| Mixed oxides and iron oxides
| CaTiO₃       | Isometric           | 3.98                    | 30.05                     | 43.76    |
| CaTiO₃/PANI  | Isometric           | 3.51                    | 51.82                     | 33.86    |
| CaTiO₃/PPy   | Isometric           | 3.31                    | 57.92                     | 32.68    |
| SrTiO₃       | Isometric           | 4.69                    | 23.79                     | 45.47    |
| SrTiO₃/PANI  | Isometric           | 3.81                    | 39.88                     | 38.00    |
| SrTiO₃/PPy   | Isometric           | 3.69                    | 40.65                     | 38.28    |

3.3 pH, electric conductivity, and corrosion-induced mass loss in aqueous extracts of the powdered pigments

The pH levels measured after 21 days’ exposure of the steel panel to the aqueous extracts of the powdered pigments (pH21) and the simultaneously measured specific conductivity levels (χ21) are given in Table 3. The calculated corrosion-induced mass loss data (Xp) measured in filtrates of the aqueous extracts of the pigments, corrosion-induced mass loss data measured in filtrates of PANI, PPy and the reference anti-corrosion pigment and corrosion-induced mass loss in drinking water are also given in Table 2.

### Table 2 Values of pH21 and specific conductivity (χ21) of aqueous extracts of the powder pigments and calculated corrosion-induced mass loss data (Xp) for aqueous extracts of the powder pigments.

<table>
<thead>
<tr>
<th>Pigment type /PANI, PPy</th>
<th>pH21</th>
<th>χ21 [g/m²]</th>
<th>Xp [%]</th>
</tr>
</thead>
</table>
| Mixed oxides and iron oxides
| CaTiO₃                 | 7.73 | 129.1      | 74.60  |
| CaTiO₃/PANI            | 6.55 | 590.0      | 118.72 |
| CaTiO₃/PPy             | 5.75 | 1307.0     | 77.40  |
| SrTiO₃                 | 11.56| 984.0      | 18.54  |
| SrTiO₃/PANI            | 6.51 | 379.0      | 52.86  |
| SrTiO₃/PPy             | 5.78 | 621.0      | 81.36  |
| Reference anti-corrosion pigment | 6.02 | 103.0 | 31.74  |
| Water                  | 7.64 | 351.0      | 100.00 |
3.4 Corrosion-induced mass loss of steel in aqueous extracts of the paint films

Changes in the pH levels during corrosion of steel panels exposed in aqueous extracts of the paint films (pH1 a pH21) and the observed specific electric conductivity levels (χ1 and χ21) are given in Table 3. This table also includes the calculated mass loss data for the steel panels following 21 days’ exposure to extracts of the free paint films (Xf).

Table 3 Specific conductivity data of aqueous extracts observed after 21 days’ exposure of steel panel to aqueous extracts of the paint films (pH21, χ21). Calculated corrosion-induced mass loss data for aqueous extracts of the paint films (Xf) in 21 days’ exposure to extracts of the free paint films.

<table>
<thead>
<tr>
<th>Pigment type / PANI, PPy</th>
<th>pH21</th>
<th>χ21 [μS/cm]</th>
<th>Xf [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed oxides and iron oxides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaTiO3</td>
<td>7.36</td>
<td>240.0</td>
<td>29.45</td>
</tr>
<tr>
<td>CaTiO3/PANI</td>
<td>7.45</td>
<td>183.1</td>
<td>64.62</td>
</tr>
<tr>
<td>CaTiO3/PPy</td>
<td>7.14</td>
<td>324.0</td>
<td>39.43</td>
</tr>
<tr>
<td>SrTiO3</td>
<td>7.78</td>
<td>178.7</td>
<td>30.18</td>
</tr>
<tr>
<td>SrTiO3/PANI</td>
<td>6.66</td>
<td>149.2</td>
<td>30.84</td>
</tr>
<tr>
<td>SrTiO3/PPy</td>
<td>5.81</td>
<td>214.0</td>
<td>31.79</td>
</tr>
<tr>
<td>Binder without pigment</td>
<td>7.23</td>
<td>96.8</td>
<td>77.36</td>
</tr>
<tr>
<td>Water</td>
<td>7.64</td>
<td>351.0</td>
<td>100.00</td>
</tr>
</tbody>
</table>

3.5 Accelerated corrosion tests

Table 4 contains data for SO2. Table 5 includes the results for atmosphere with NaCl. These tables display observations of paint blistering (blister size and frequency of occurrence), extent of corrosion changes of the metal substrate propagating from the cut (in mm), corrosion of the metal substrate (in % affected area) and calculated overall anti-corrosion efficiency in atmosphere with condensed humidity (EH2O), atmosphere with SO2 (ESO2), environment with NaCl (ENaCl) and in a chemically aggressive environment (EM-S).

3.5.1 Corrosion tests of paint films in an atmosphere with SO2

Table 4 Anti-corrosion efficiency of pigmented paint films following 720 hours’ exposure to atmosphere with SO2 (DFT = 80 ± 5 μm)

<table>
<thead>
<tr>
<th>Pigment type</th>
<th>Surface blistering (+) ASTM D714-87</th>
<th>Corrosion in a cut (mm) ASTM D1654-92</th>
<th>Surface corrosion (%) ASTM 610-85</th>
<th>Anticorrosion efficiency ESO2 (dg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed oxides and iron oxides</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaTiO3</td>
<td>8M</td>
<td>7.0-10.0</td>
<td>0.3</td>
<td>58</td>
</tr>
<tr>
<td>CaTiO3/PANI</td>
<td>-</td>
<td>10.0-13.0</td>
<td>16</td>
<td>53</td>
</tr>
<tr>
<td>CaTiO3/PPy</td>
<td>-</td>
<td>13.0-16.0</td>
<td>100</td>
<td>37</td>
</tr>
<tr>
<td>SrTiO3</td>
<td>8F</td>
<td>3.0-5.0</td>
<td>10</td>
<td>62</td>
</tr>
<tr>
<td>SrTiO3/PANI</td>
<td>8M</td>
<td>7.0-10.0</td>
<td>16</td>
<td>42</td>
</tr>
<tr>
<td>SrTiO3/PPy</td>
<td>-</td>
<td>13.0-16.0</td>
<td>100</td>
<td>37</td>
</tr>
<tr>
<td>Binder without pigment</td>
<td>-</td>
<td>5.0-7.0</td>
<td>16</td>
<td>60</td>
</tr>
</tbody>
</table>
3.5.2 Corrosion tests of paint films in a chamber with a mist of neutral NaCl and humidity

Table 5 Anti-corrosion efficiency of pigmented paint films following 504 hours’ exposure to a mist with NaCl (DFT = 80 ± 5 µm)

<table>
<thead>
<tr>
<th>Pigment type</th>
<th>Surface blistering</th>
<th>Corrosion in a cut</th>
<th>Surface corrosion</th>
<th>Anticorrosion efficiency E_{NaCl} (dg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(-)</td>
<td>(mm)</td>
<td>(%)</td>
<td></td>
</tr>
<tr>
<td>ASTM D714-87</td>
<td>ASTM D1654-92</td>
<td>ASTM D610-85</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Mixed oxides and iron oxides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaTiO₃</td>
<td>6M</td>
<td>5.0-7.0</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>CaTiO₃/PANI</td>
<td>4F</td>
<td>3.0-5.0</td>
<td>0.1</td>
<td>70</td>
</tr>
<tr>
<td>CaTiO₃/PPy</td>
<td>6F</td>
<td>5.0-7.0</td>
<td>0.3</td>
<td>67</td>
</tr>
<tr>
<td>SrTiO₃</td>
<td>6M</td>
<td>3.0-5.0</td>
<td>0.3</td>
<td>63</td>
</tr>
<tr>
<td>SrTiO₃/PANI</td>
<td>6MD</td>
<td>3.0-5.0</td>
<td>0.1</td>
<td>58</td>
</tr>
<tr>
<td>SrTiO₃/PPy</td>
<td>-</td>
<td>5.0-7.0</td>
<td>0.1</td>
<td>78</td>
</tr>
<tr>
<td>Binder without Pigment</td>
<td>-</td>
<td>3.0-5.0</td>
<td>0.3</td>
<td>80</td>
</tr>
</tbody>
</table>

3.6 Pigment particle morphology

As the SEM photographs demonstrate (Fig.1-6, Table 1), the pigment particles exhibit a lamellar or isometric shape depending on their structure. Isometric particles are found for magnetite, the perovskites and spinel. The surface treatment with a conductive polymer did not change the basic shape of the pigment particles.

3.7 Physicochemical properties of the pigments

The first information on the pigments is obtained from the physicochemical properties of the pigment powders (Table 1). The pigment particle surface treatment with the conductive polymers brought about, naturally, a change in their specific weight. Surface modification with PPy resulted in a lower specific weight than the modification with polyaniline did. Oil consumption is an indicator providing indirect information on the pigment’s specific surface area, particle size distribution and porosity because oil consumption increases with increasing specific surface area, decreasing particle diameter and an increasing fraction of smaller particles. Pigment surface modification with PANI or PPy brought about a higher linseed oil consumption, which was more pronounced with PPy than with PANI. Presumably, this difference between the effects of the two polymers is due to a larger total specific surface area of PPy compared with polyaniline. The oil consumption data serve to calculate the critical volume concentration of the pigments and fillers (CPVC), the knowledge of which is a prerequisite for the formulation of paints. The critical volume concentration of the pigments and fillers (CPVC) expresses the amount of binder in the system, which fills the void space between the pigment of filler particles coming in mutual contact.

3.7.1 Corrosion-induced mass loss in aqueous extracts of the pigments

Corrosion-induced mass loss data relative to pure water can be used to characterise the protective effect of the pigment extracts on the steel surface (Table 3). Corrosion of the steel panels also depends on the aqueous extract pH. Specific conductivity decreased during the measurement due to the formation of a layer of insoluble compounds on the steel surface accompanied by a decrease of the conductive ion content of the filtrate.

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3.7.2 pH, specific electric conductivity and corrosion loss in aqueous extracts of free paint films

The pH levels of extracts of the paint films (Table 3, 4) all lay within the range of 3.5–10.0. The suspensions of paints with pigments modified with PPy exhibited pH 3.6–6.7, extracts of paints with pigments modified with polyaniline exhibited pH 6.9–7.3 and extracts of paints with the untreated pigments exhibited pH 7.4–10.0. This may be due, for instance, to the fact that PPy has more open pores in the paint films, which facilitates its solvation and transfer to solution and so extracts of pigments modified with PPy were more “acid” than extracts of pigments modified with PANI.

When comparing the pH levels of extracts of pigments and of suspensions of the paint films, it is clear that addition of pigments to the water-based epoxy resin brought about pH increase in the extracts, due to the slightly basic nature of the pure binder extract (-OH, -NH₂ groups). The conductivity values (Table 4) exhibited the same trend during the measurement for all samples. The highest specific electric conductivity was observed in extracts of the conductive polymers (about 2200 µS/cm for PANI and one-third that value for PPy). For the perovskites, surface modification with PPy (CaTiO₃/PANI, SrTiO₃/PPy) resulted in paints exhibiting higher conductivities than if polyaniline were used for the modification. The lowest specific conductivities were observed for extracts from films of the paint of the reference pigment and of the non-pigmented epoxy resin.

3.7.3 Corrosion-induced mass loss in aqueous extracts of the paint films

Specific conductivity, pH, and mass loss of the steel panels were measured in three weeks (Table 4).

The effects of PANI and PPy were nearly identical only for paint films with the perovskite SrTiO₃ (SrTiO₃/PANI – SrTiO₃/PPy – SrTiO₃), in other words, the ability of the two polymers to inhibit corrosion was virtually identical.

3.8 Accelerated corrosion tests of the pigmented organic coatings

3.8.1 Exposure of the coatings to an atmosphere with SO₂

The pigmented paint samples were put into a test chamber and exposed for 720 hours to an atmosphere containing sulphur dioxide gas (Table 6). When PANI or pigments modified with PANI had been added to the epoxy resin, the green conductive emeraldine salt had transformed to the blue non-conductive emeraldine base due to the basic nature of the binder and exposure to the acid environment in the chamber (pH about 2) brought about back transformation to the green conductive species.

The formation of osmotic blisters on the film was suppressed by using paints containing perovskite (CaTiO₃) modified with either of the conductive polymers (PANI, PPy). Although paints containing perovskite modified with polyaniline (SrTiO₃/PANI) provided favourable results, their efficiency was lower than that with the untreated pigments because the values differed by as little as 5 degrees Heubach. The overall conclusions from the exposure of the paints to an atmosphere with sulphur dioxide are as follows:

- The anti-corrosion efficiencies of paints containing pigments modified with PANI and with PPy are comparable.
- For all pigments, their modification with PANI resulted in higher resistance to the acid environment of SO₂ than did their modification with PPy.
3.8.2 Exposure of the coatings to an atmosphere with NaCl

The paints were exposed to a neutral salt mist in a salt chamber for 504 hours. Modification of CaTiO$_3$ and SrTiO$_3$ (CaTiO$_3$/PANI, SrTiO$_3$/PANI, and CaTiO$_3$/PPy, SrTiO$_3$/PPy) improved the paints’ overall anti-corrosion efficiency. Modification of particles of the perovskite SrTiO$_3$ with PPy (SrTiO$_3$/PPy) gave rise to a form that exhibited an anti-corrosion efficiency that was higher than that of untreated perovskite (SrTiO$_3$). Perovskite itself possesses a relatively low electric conductivity, which was increased to an optimum level for use in paints by modification with PPy.

The overall conclusions from the exposure of the paints to an atmosphere with NaCl are as follows:

- Modification of the pigments with PANI resulted in higher anti-corrosion efficiency of the paints than did modification with PPy.
- The anti-corrosion efficiencies of paints with CaTiO$_3$ were comparable with those of paints with the pigments modified with PPy and in both cases, were higher than those of paints with the untreated pigments.
- The anti-corrosion efficiencies of paints with SrTiO$_3$ decreased in the following order: pigment modified with PPy > untreated pigment > pigment modified with PANI.
- The anti-corrosion efficiencies of paints with pigments modified with the conductive polymers were higher than those of the respective paints with the untreated pigment.

4 Conclusions

The aim of this work was to assess the effect of pigment surface modification with conductive polymers on the corrosion-inhibiting capacity of the coating materials. The paint films applied to steel substrates were subjected to resistance testing by physicomechanical and corrosion tests.

1. The overall conclusions from the exposure of the paints to the corrosion atmospheres are as follows:
2. In many cases, this treatment enhanced the anti-corrosion efficiency of the paint films significantly.

References


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