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Effects of conductive polymers (type and concentration) in coatings with zinc particles of different shapes

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Abstract

The objective of this work was to compare the anticorrosion effects of organic coatings containing zinc metal consisting of either lamellar particles or isometric particles and to reduce the zinc metal content of the coatings while preserving their high anticorrosion efficiency. The optimisation and Zn metal content reduction can be achieved using zinc with a lamellar particle shape and application of conductive polymers (CP). Conductive polymers are expected to enhance the electrochemical effect of zinc metal in paints. Organic coatings with lamellar zinc particles also exhibit better mechanical properties. Optimisation of the amount of zinc lamellar particles could promote a wider use of this material in anticorrosion paints. The conductive polymers used in this work included polyaniline phosphate, polyaniline benzoate, and carbonised polyaniline. A solvent-based epoxy-ester resin served as the binder. Model paints consisting of this resin and containing different concentrations of polyaniline phosphate, polyaniline benzoate, and carbonised polyaniline were prepared. The paints were tested at the critical pigment volume concentration (CPVC) of Zn dust and at lower Zn dust concentrations, specifically 2% below the CPVC. The paints containing combinations of zinc and a conductive polymer contained the sum of the pigments just below the CPVC of the zinc dust species used. This implies a level of 39% of (PVC_{Zn-lam}) for the systems with lamellar zinc and a level of 61%

of (PVC_{Zn-sf}) for the systems with spherical zinc. The pigment volume concentration (PVC) of the conductive polymers in the zinc-containing paints was (based on results obtained previously) 1%, 5%, and 10% in the systems with lamellar zinc and 1%, 5%, 10%, and 15% in the systems with spherical zinc. The organic coatings were subjected to accelerated cyclic corrosion tests and electrochemical measurements. The sample containing polyaniline carbonate ($PVC=1\%$) and spherical zinc exhibited a significantly lower corrosion rate as compared to that of uncoated steel.

Keywords: conductive polymer, zinc powder, lamellar particle, spherical particle, coating, anticorrosion efficiency

Introduction

Organic coatings with high zinc metal content are used because of their high corrosion resistance. The following two zinc particle shapes are used most frequently: spherical particles and lamellar particles. The latter exhibits a lower tendency to settling than the former.^{1,2} Also, the lamellar zinc particles have a higher binder sorption capacity than the spherical particles, which implies that a lower pigment volume concentration (PVC) can be attained in the paint.³ Additionally, the lamellar pigment particles extend the path length that the diffusing liquid medium must travel from the surface to the substrate; they reflect ultraviolet radiation, thereby protecting the binder from degradation; and they possess a reinforcing capacity, improving the pigmented organic coating's mechanical resistance.⁴

The protective effect of organic coatings pigmented with zinc is based on a cathodic protection mechanism, owing to the position of zinc in the electrochemical metal series or the difference between the potentials of zinc and the protected metal, i.e. steel. Zinc is a common metal with a negative standard electrode potential—more negative than that of iron. The cathodic mechanism can play a protective role only if the zinc particle content of the coating is adequately high, i.e. so high that the zinc particles are in mutual contact and in contact with the

steel substrate.^{3,5,6} This condition, however, is met only during the first stage of contact with the corrosive medium. As the protective mechanism is acting, the pores in the coating get sealed with the zinc corrosion products, such as zinc oxides, zinc hydroxide, and basic zinc carbonates. The zinc metal particles soon get wrapped in the zinc corrosion products, where the electric conductivity of the paint film decreases and the cathodic protection mechanism is hindered (the cathodic protection mechanism is transformed to the barrier protection mechanism). The neutralisation and filtration mechanisms are involved as well.⁵⁻⁹

Although paints with zinc are considerably less toxic than paints with lead or chromate, zinc compounds are categorized as toxic to aquatic organisms and, therefore, standards governing the use of zinc compounds and paints with zinc as the pigment are more and more stringent, striving to minimise the zinc content of paints. For this and other reasons, current efforts focus on zinc content reduction in paints.^{9,10} The use of inorganic particles is one way to achieve this, and carbon/graphite pigments are also promising.¹¹⁻¹³ An alternative concept consists of the use of conductive polymers as the pigments, with a goal of reducing the zinc metal content while attaining the same or even better corrosion resistance. Due to the conductivity of the conductive polymers, they can partly replace zinc metal in the paint, provided that a suitable formula is selected.^{14,15}

Among electrically conductive polymers are polyaniline, polypyrrole, polythiophene, polyphenylene, and poly(p-phenylenevinylene).¹⁶⁻¹⁹ Such polymers owe their conductivity to the regular alternation of single and double bonds (conjugated double bonds) in the molecules. The presence of movable charge carriers providing charge transport along the conjugated chain is another prerequisite for electrical conductivity. Such movable charge carriers are created by doping. The conductivity of polyaniline salts obtained by oxidative polymerisation is 10^{-3} to 10^1 S cm⁻¹ depending on the dopant type.²⁰

It has been demonstrated that the conductivity can also be increased by carbonisation of the conductive polymers (specifically polyaniline) under an inert gas (argon, nitrogen). During the first carbonisation stage, conductivity drops due to the release of the dopant and polyaniline salt transformation to the polyaniline base. However, additional temperature increase is accompanied by conductivity increases up to a level exceeding the initial conductivity of the polyaniline salt due to the formation of cross-linked cyclic hydrocarbons.^{21,22}

Experimental Part

Synthesis of Conductive Polymers

Polyaniline phosphate was prepared by oxidative polymerisation of aniline in acidic medium (diluted phosphoric acid). Ammonium peroxodisulphate was used as an oxidant. Synthesis of polyaniline benzoate (PANI-BENZ) was performed with polyaniline phosphate synthesized previously, which was de-doped by dispersing and stirring in 1 M NH₄OH for 12 h. This de-doped polyaniline was then filtered and dried. Re-doping of polyaniline was done by dispersing the de-doped polyaniline in dilute benzoic acid and stirring for 12 h. The polyaniline benzoate was filtered and washed with dilute benzoic acid and with acetone. The resulting polyaniline benzoate powder was dried for 24 h in air and subsequently in an oven at 60°C. Preparation of carbonised polyaniline was performed with polyaniline phosphate, which was de-doped by dispersing and stirring in 1 M NH₄OH. De-doped polyaniline was subjected to carbonisation in a nitrogen atmosphere. Carbonisation was carried out at 650°C for 6 h.

Pigment Parameter Determination

Pigment density was determined using a Micromeritics AutoPycnometer 1340. Oil absorption was measured by the "pestle-mortar" method based on Czech Standard CSN 67 0531.²³ The data was used to calculate the critical pigment volume concentration (CPVC).²⁴ Microphotographs of the pigment particles were obtained on a JEOL-JSM 5600 LV electron microscope (Japan). Aqueous pigment suspensions (2%) were prepared and their pH and

conductivity levels were measured over 21 days. The particle size was measured on a Mastersizer 2000 (Malvern Instruments Ltd., UK).

Specification of the Binder for Coatings

A solvent-based epoxy–ester resin was used as the binder. The following is a description of the binder: a 60% solution of a medium high molecular weight epoxy resin esterified with a mixture of fatty acids of dehydrated ricin oil and soy oil, trade name WorléeDur D 46, acid number 4, viscosity of 2.5–5.0 Pa s, flow time (DIN 53211-4 200) of 250 s.

Formulation and Preparation of the Organic Coatings

The synthesized conductive polymers, along with spherical zinc (Conmet GmbH, Německo) and lamellar zinc (Eckart GmbH, Germany), were used to prepare the paints (organic coatings).

A solvent-based epoxy–ester resin was used as the binder. The paints prepared from this binder contained the conductive polymers at pigment volume concentrations (PVC_{CP}) of 1%, 5%, 10%, and 15%, with spherical zinc powder at a constant ratio of $PVC/CPVC=0.61$. The next paints prepared from this binder contained the conductive polymers at pigment volume concentrations (PVC) of 1%, 5%, and 10% with lamellar zinc powder at a constant ratio of $PVC/CPVC=0.39$. The organic coating containing spherical zinc only at $PVC_{Zn-sf}=61\%$, 63%, and 65% and the coatings containing lamellar zinc only at $PVC_{Zn-lam}=39\%$, 41%, and 43% served as the reference coatings (paints without conductive polymers). The paints were prepared using a Dissolver type system at 4000 rpm/40 min. Once prepared, the paints were applied to steel panels (standard S-46 low-carbon steel panels, Q-Lab Corporation, ISO Panel Specifications: 1514 Section 3.5.4) and the dry film thickness (DFT) was measured with a magnetic gauge according to ISO 2808. An artificial vertical cut was made through the paint films for the accelerated corrosion tests. The vertical test cut in the organic coating was 80 mm long and 0.5 mm deep and was made in accordance with CSN EN ISO 12944-6 using a cutting tool complying with ISO 2409 (tool for single cuts).

Mechanical Properties of the Paints

Degree of Adhesion of the Coatings by the Cross-cut Test

Determination was made by means of a special cutting blade with cutting edges that were 2 mm apart, and it involved the degree of adhesion of the created 2 mm × 2 mm squares to a base substrate. The test was made according to ISO 2409.

Degree of Adhesion of the Pull-off Test

The pull-off test for adhesion was measured with COMTEST®OP3P (CZ). A circular target with a 20 mm diameter was adhered to the sample by a two part epoxy adhesive. The measurement parameters were the following: tension increased to 152 kPa s⁻¹ and limit force of 15 kN. The test was done according to ISO 4624. The result of this test was the force that was needed to pull-off the layer from a substrate.

Corrosion Test Procedures

Accelerated Cyclic Corrosion Test in NaCl Atmosphere with Water Condensation

The principle of this test was derived from ISO 9227.¹³ The samples were evaluated after 720 h of exposure (60 cycles).

Accelerated Cyclic Corrosion Test in SO₂ Atmosphere with Water Condensation

The test was performed according to ISO 6988.¹³ The samples were evaluated after 2160 h of exposure (90 cycles).

Methods of Corrosion Test Evaluation

The corrosion effects after completion of the tests were evaluated as specified in the ASTM standards. The method classifies the osmotic blisters according to their size, designated by figures of 2, 4, 6, and 8 (2 denotes the largest size and 8 the smallest size). Information on the frequency of occurrence is given. The highest occurrence of blisters is designated as D (dense), and the others are designated as MD (medium dense), M (medium), and F (few).¹³

Selected samples were also examined by electron microanalysis. Electron microanalysis for ascertaining the elemental composition of the paint films was performed on a TESCAN VEGA 5130SB scanning electron microscope and a Bruker Quantax 200 energy dispersive X-ray spectrometer.

Potentiodynamic Polarization Studies

A corrosion cell having a three-electrode geometry with the coated sample as the working electrode (8 cm²), platinum as the counter electrode, and a saturated calomel electrode (SCE; pH Products, Hyderabad, India) as the reference electrode was used. The cell was connected with a Gamry reference system 1000 (Wilmington, USA) for electrochemical measurements. The Tafel extrapolation method was used to determine the corrosion rate of the uncoated sample and the coated samples. In this technique, the polarization curves were obtained by applying a ± 250 mV potential with respect to the open-circuit potential. The resulting Tafel plots contained anodic and cathodic branches. Gamry software was used to determine the corrosion rate. All measurements were carried out five times to check repeatability of the results, and reproducible results are reported in the paper.

Results and Discussion

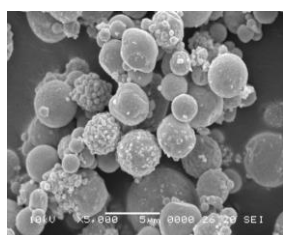
Pigment Specification

Zinc dust consisting of either spherical particles or lamellar particles and the conductive polymers were measured to determine their densities and oil numbers, from which their critical pigment concentrations could be calculated.²⁴ The mean particle sizes of the pigments were also determined. Redistilled water (pH 6.50 \pm 0.01, conductivity=1.5 μ S cm⁻¹) was used to prepare 2% aqueous pigment suspensions, which were allowed to stand for 21 days and then filtered. The filtrate conductivities and pH levels were then measured (**Table 1**). The conductive polymer densities were within the range of 1.42–1.53 g/cm³. Such densities are considerably lower than those of spherical or lamellar zinc (7.14 and 6.44 g/cm³, respectively) and the paints

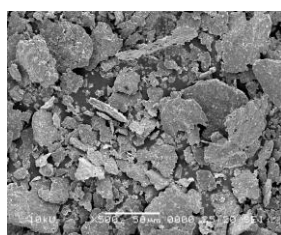
containing the polymers are expected to be more stable than paints containing zinc metal, which possess the tendency to settle down to the bottom of the container (this applies especially to spherical zinc particles). The critical volume concentrations of the polyaniline salts attained similar values, while carbonised polyaniline attained a considerably lower value, presumably due to the higher specific surface area resulting from the carbonisation process. The mean particle sizes of the conductive polymers exhibited a similar tendency: while the polyaniline salts exhibited very similar values, the particle size of carbonised polyaniline was about one-half. As mentioned above, 2% aqueous suspensions of the pigments were prepared, filtered in 21 days, and measured. The filtrates of the polyaniline salt suspensions were highly acidic (pH 1.66 and 1.74), whereas the filtrate of the carbonised polyaniline suspension was nearly neutral. Similarly, the conductivities of the filtrates of the polyaniline salt suspensions were 3 orders of magnitude higher than the conductivity of the carbonised polyaniline suspension. The low pH levels and high conductivities of the polyaniline salt extracts are explained in terms of polyaniline salt deprotonation and release of the acid, which was used for protonation. This mechanism is impossible in carbonised polyaniline because deprotonation had already occurred during the carbonisation process. Microphotographs that served to examine the shapes and surface structures are reproduced in **Figure 1**.

Table 1. Characteristics of the pigments

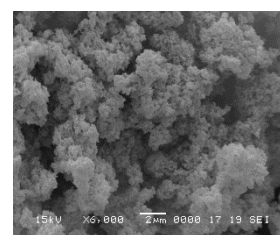
| Pigment | Density [g.cm ⁻³] | CPVC [%] | Particle size [μm] | pH ²¹ | Conductivity [mS.cm ⁻¹] |
|-------------------------------------|----------------------------------|-------------|-----------------------|------------------|--|
| Zn _{sfer.} | 7.14 | 67 | 5.24 | 6.42±0.01 | 7.1×10 ⁻³ ±0.5% |
| Zn _{lam.} | 6.44 | 41 | 13.00 | 8.22±0.01 | 5.3×10 ⁻³ ±0.5% |
| PANI-H ₃ PO ₄ | 1.48 | 51 | 8.20 | 1.74±0.01 | 3.8×10 ¹ ±0.5% |
| PANI-BENZ | 1.42 | 52 | 8.86 | 1.66±0.01 | 4.0×10 ¹ ±0.5% |
| PANI-CAR | 1.53 | 28 | 4.26 | 6.89±0.01 | 5.5×10 ⁻² ±0.5% |



a)



b)



c)

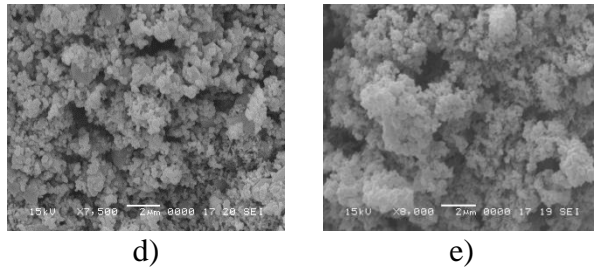


Figure 1. Scanning electron micrographs: a) Zn_{sfer.}, b) Zn_{lam.}, c) PANI-H₃PO₄, d) PANI-BENZ, e) PANI-CAR.

Evaluation of Accelerated Corrosion Tests

Accelerated corrosion tests are designed to intensify the corrosion aggressiveness factors (temperature, humidity or moisture, corrosive component concentration) while preserving the corrosion process mechanism. The accelerated corrosion tests were used to measure the corrosion resistance of the various paint films.

Accelerated Corrosion Tests in a Salt Mist Atmosphere

The pigmented paints were applied to steel panels and subjected to an accelerated cyclic corrosion test consisting of 720 h of exposure to a salt fog atmosphere. The results are listed in **Tables 2–5**. **Table 2** contains the results for the paints with polyaniline phosphate and **Table 5** contains the results for the standard paints with lamellar or spherical zinc. The amount of steel corrosion products in the paint film surface was lower for the paints containing lamellar zinc and polyaniline phosphate than the standard paint film. The extent of film blistering for the above pigmented paints and for the standard paint was similar. The lowest steel substrate corrosion was observed for the paint with polyaniline phosphate at PVC=1%. The paints with spherical zinc and polyaniline phosphate were superior to the standard paint at higher PVC levels. The amount of steel corrosion products on the paint film surface for the paint with polyaniline phosphate at PVC=10% and 15% was one-half that observed with the standard paint. The degree of the steel substrate area corrosion was lower as well. The highest corrosion resistance was attained with the paint containing polyaniline phosphate at PVC=15%. A test cut through the paint film was made on the coated panels. The cut and the area around it are

shown in **Figure 2**. While the cut is protected appreciably by the zinc corrosion products in the presence of polyaniline phosphate, the cut and its neighbouring area exhibit what is called red rust for the standard paint with spherical zinc.

The results obtained with the paints containing zinc and polyaniline benzoate are listed in **Table 3**. The paint with lamellar zinc and polyaniline benzoate at PVC=1% exhibited a lower amount of steel corrosion products on the film surface than the standard paint. Steel panel corrosion attained the same level with those paints. The paints with higher polyaniline benzoate PVC levels exhibited a comparable or slightly lower corrosion resistance. The corrosion resistance was observed for polyaniline benzoate PVC=1%. The paints with spherical zinc and polyaniline benzoate were superior to the standard paint at higher polyaniline benzoate PVC levels: the highest corrosion efficiency was observed at a polyaniline benzoate volume concentration of PVC=15%. The extent of paint film blistering was lower than for the standard film, and both the amount of steel corrosion products on the paint film surface and the extent of steel panel surface corrosion were one-half those observed with the standard paint.

The results obtained with the paints containing zinc and carbonised polyaniline are listed in **Table 4**. A high corrosion resistance was attained with the paint containing lamellar zinc and carbonised polyaniline at PVC=1%. Both the amount of steel corrosion products on the paint film surface and the degree of steel panel surface corrosion were lower when compared with the standard paint, but they grew considerably poorer when increasing the polymer PVC to 5% and 10%. The paints with spherical zinc and carbonised polyaniline were superior to the standard paints at higher PVC levels. The highest corrosion resistance was observed with the paint containing carbonised polyaniline at PVC=15%.

Table 5 includes the results for the standard organic coatings containing lamellar zinc (PVC=39%) and spherical zinc (PVC=61%) for paints with spherical or lamellar zinc at PVC=CPVC and also at PVC by 2% higher than CPVC. Among the paints with lamellar zinc,

the highest corrosion resistance was attained at PVC=39%. The corrosion resistance was lower than that obtained at PVC=CPVC and lowest at PVC>CPVC due to over pigmentation. The tendency was similar with spherical zinc as well. As outlined in the theoretical section, the corrosion resistance is higher if the paints are pigmented with lamellar zinc than if they are pigmented with spherical zinc.

Table 2. Results of the corrosion tests performed in a salt mist chamber of the organic coatings containing PANI-H₃PO₄, with spherical zinc and lamellar zinc after 720 hours of exposure, DFT = 100±10 μm

| Pigment | PVC _{PANI-H₃PO₄} [%] | Rusting On the paint [%] | Blistering | | Corrosion | |
|--------------------------|--|--------------------------------|------------------|--------------------|------------------|-------------------|
| | | | In a cut [dg] | Metal base [dg] | In a cut [mm] | Metal base [%] |
| Zn_{lam} | 1 | 0.01 | 2M | 2F | 0.30 | 1 |
| | 5 | 0.03 | 4M | 4F | 0.36 | 3 |
| | 10 | 0.3 | 4M | 4F | 0.28 | 3 |
| Zn_{sfer} | 1 | 33 | 6M | 6M | 0.24 | 33 |
| | 5 | 33 | 6M | 4M | 0.31 | 33 |
| | 10 | 16 | 6M | 4M | 0.46 | 16 |
| | 15 | 10 | 6M | 4M | 0.34 | 16 |

Table 3. Results of the corrosion tests performed in a salt mist chamber of the organic coatings containing PANI-BENZ, with spherical zinc and lamellar zinc after 720 hours of exposure, DFT = 100±10 μm

| Pigment | PVC _{PANI-BENZ} [%] | Rusting On the paint [%] | Blistering | | Corrosion | |
|--------------------------|---------------------------------|--------------------------------|------------------|--------------------|------------------|-------------------|
| | | | In a cut [dg] | Metal base [dg] | In a cut [mm] | Metal base [%] |
| Zn_{lam} | 1 | 0.1 | 4MD | 4F | 0.14 | 3 |
| | 5 | 3 | 4M | 4M | 0.15 | 10 |
| | 10 | 3 | 6M | 4M | 0.26 | 10 |
| Zn_{sfer} | 1 | 50 | 6MD | 6MD | 0.56 | 33 |
| | 5 | 33 | 6M | 6M | 0.36 | 33 |
| | 10 | 33 | 6M | 6M | 0.45 | 16 |
| | 15 | 16 | 4M | 4M | 0.43 | 16 |

Table 4. Results of the corrosion tests performed in a salt mist chamber of the organic coatings containing PANI-CAR, with spherical zinc and lamellar zinc after 720 hours of exposure, DFT = 100±10 μm

| Pigment | PVC _{PANI-CAR} [%] | Rusting On the paint [%] | Blistering | | Corrosion | |
|--------------------------|--------------------------------|--------------------------------|------------------|--------------------|------------------|-------------------|
| | | | In a cut [dg] | Metal base [dg] | In a cut [mm] | Metal base [%] |
| Zn_{lam} | 1 | 0.1 | 4F | 2M | 0.10 | 1 |
| | 5 | 16 | - | 4MD | 0.10 | 50 |
| | 10 | 33 | 4F | 4MD | 0.10 | 50 |
| Zn_{sfer} | 1 | 33 | 4M | 4M | 0.37 | 16 |
| | 5 | 33 | 4M | 4M | 0.42 | 10 |
| | 10 | 33 | 6M | 6M | 0.51 | 10 |
| | 15 | 16 | 6M | 6M | 0.51 | 10 |

Table 5. Results of the corrosion tests performed in a salt mist chamber of the organic coatings containing spherical zinc and lamellar zinc after 720 hours of exposure, DFT = 100±10 µm

| Pigment | PVC _{Zn} [%] | Rusting On the paint [%] | Blistering | | Corrosion | |
|--------------------------|--------------------------|--------------------------------|------------------|--------------------|------------------|-------------------|
| | | | In a cut [dg] | Metal base [dg] | In a cut [mm] | Metal base [%] |
| Zn_{lam} | 39 | 1 | 4MD | 6F | 0.30 | 3 |
| | 41 | 1 | 4MD | 4F | 0.40 | 3 |
| | 43 | 3 | 2M | 6F | 0.45 | 10 |
| Zn_{sfer} | 61 | 33 | 6M | 6M | 0.50 | 33 |
| | 63 | 33 | 6MD | 4MD | 0.36 | 33 |
| | 65 | 33 | 4MD | 4MD | 0.61 | 50 |

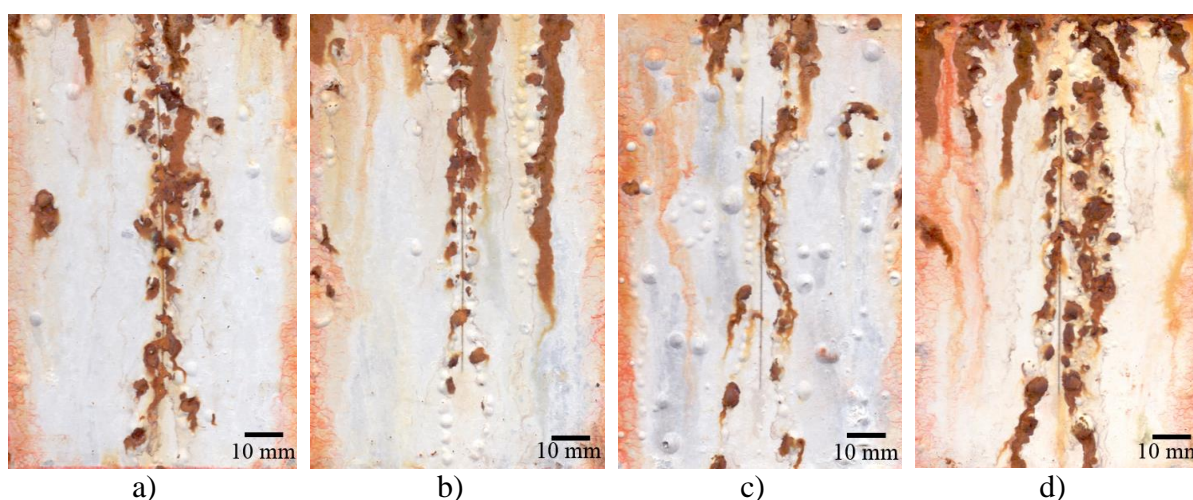


Figure 2. Photographs organic coatings after 720 h exposure to a salt fog atmosphere: a) paint with lamellar zinc and polyaniline phosphate at PVC = 1 %, b) paint with lamellar zinc and polyaniline benzoate at PVC = 1 %, c) paint with lamellar zinc and carbonised polyaniline at PVC = 1 %, d) standard paint with lamellar zinc (PVC = 39 %).

Accelerated Corrosion Tests in SO₂ Atmosphere

This accelerated cyclic corrosion test, during which the coated steel panels were exposed to an SO₂ atmosphere for 2160 h, was applied to all the paints prepared (**Table 6**). Corrosion effects were observed only with those paints containing no polyaniline salts or carbonised polyaniline.

No corrosion products or blisters were observed on the film surfaces of the paints containing polyaniline phosphate, polyaniline benzoate, or carbonised polyaniline. Corrosion in the cut never reached 0.2 mm with those paints. Blisters on the paint film surface were observed for the standard paint with lamellar zinc, and steel corrosion products were found on the film of the standard paint with spherical zinc. **Table 6** demonstrates that the highest

corrosion resistance was attained with the paint containing lamellar zinc at PVC=39%: this was a peak value, decreasing when exceeding that PVC level. The paints pigmented with spherical zinc exhibited the same trend.

Zinc dust conversion to zinc corrosion products proceeded more slowly and was less pronounced in the humid atmosphere with SO₂ than in the salt fog atmosphere. In addition, the sulphate based corrosion products were more soluble than the product forming in the salt fog environment, the particles were less isolated, and the electrochemical mechanism could act longer.

Table 6. Results of the corrosion test performed in a condenser chamber filled with the atmosphere containing SO₂ of the organic coatings containing spherical zinc and lamellar zinc after 2160 hours of exposure, DFT = 100±10 µm

| Pigment | PVC _{Zn} [%] | Rusting On the paint [%] | Blistering | | Corrosion | |
|--------------------------|--------------------------|--------------------------------|------------------|--------------------|------------------|-------------------|
| | | | In a cut [dg] | Metal base [dg] | In a cut [mm] | Metal base [%] |
| Zn_{lam} | 39 | - | - | 8F | - | - |
| | 41 | - | 6F | 8F | - | - |
| | 43 | 0.03 | - | - | 0.1 | - |
| Zn_{sfer} | 61 | 0.03 | - | - | - | - |
| | 63 | 0.03 | - | - | 0.1 | - |
| | 65 | 0.03 | - | - | 0.2 | - |

Potentiodynamic Polarization Studies

The corrosion rates were measured in a 3.5 mass% NaCl solution using Tafel analysis. Tafel curves were generated with a scanning potential from the corrosion potential to 250 mV (cathodic/anodic) for the uncoated low-carbon steel sample and for the tested organic coatings. The Tafel plots for the uncoated low-carbon steel samples and for the organic coatings containing polyaniline carbonate (PVC=1%) and spherical zinc are shown in **Figure 3**. The values of the corrosion rate obtained after Tafel fitting with the help of software are given in **Table 7** and **Table 8**. As observed from these tables, uncoated low-carbon steel had a corrosion rate of ~16.07 mpy and the coating containing carbonised polyaniline (PVC=1%) and spherical zinc exhibited the lowest corrosion rate of ~0.06 mpy. The low corrosive rate of ~0.32 mpy was also determined for an organic coating containing carbonised polyaniline (PVC=5%) and

spherical zinc. The corrosion rates of these coatings containing carbonised polyaniline achieved a lower value compared to standard organic coatings containing only spherical zinc.

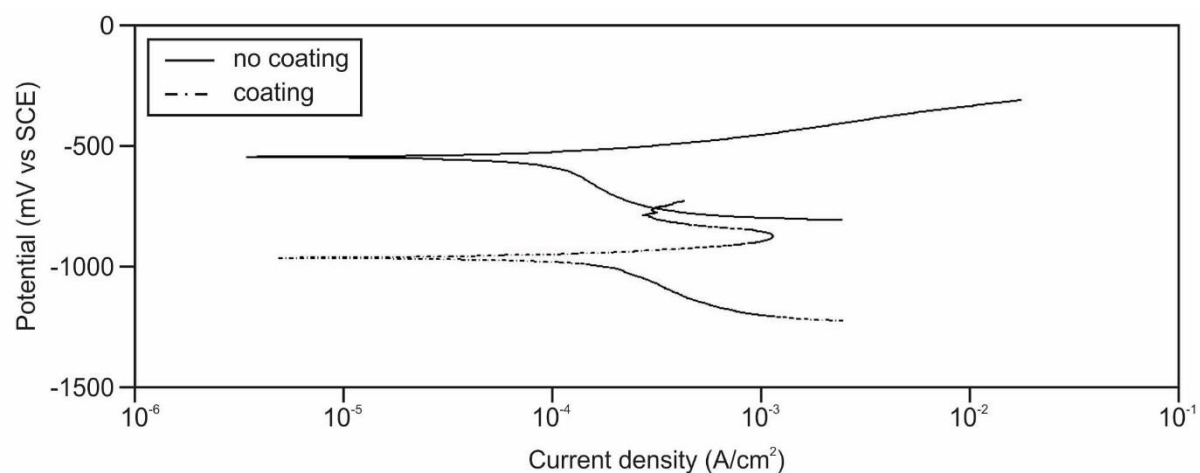


Figure 3. Tafel plot for uncoated low-carbon steel and tafel plot for coating containing polyaniline carbonate (PVC = 1 %) and spherical zinc in 3.5 mass% NaCl solution (DFT = 50 ± 10 μm).

Table 7. Results of the electrochemical test of the organic coatings containing PANI- H_3PO_4 , PANI-BENZ and PANI-CAR, with spherical zinc and lamellar zinc, DFT = 60 ± 10 μm

| Pigment | PVC _{PANI-H3PO4} [%] | Corrosion rate [mpy] | PVC _{PANI-BENZ} [%] | Corrosion rate [mpy] | PVC _{PANI-CAR} [%] | Corrosion rate [mpy] |
|--------------------------|-------------------------------|----------------------|------------------------------|----------------------|-----------------------------|----------------------|
| Zn_{lam} | 1 | 4.53 | 1 | 5.32 | 1 | 8.08 |
| | 5 | 2.17 | 5 | 4.33 | 5 | 7.74 |
| | 10 | 8.37 | 10 | 1.43 | 10 | 10.01 |
| Zn_{sfer} | 1 | 4.28 | 1 | 1.41 | 1 | 0.06 |
| | 5 | 12.00 | 5 | 6.59 | 5 | 0.32 |
| | 10 | 6.92 | 10 | 11.00 | 10 | 2.75 |
| | 15 | 6.00 | 15 | 5.80 | 15 | 3.69 |

Table 8. Results of the electrochemical test of the organic coatings containing spherical zinc, lamellar zinc (DFT = 60 ± 10 μm) and uncoated steel

| Pigment | PVC _{Zn} [%] | Corrosion rate [mpy] |
|--------------------------|-----------------------|----------------------|
| Zn_{lam} | 39 | 4.40 |
| | 41 | 3.21 |
| | 43 | 4.53 |
| Zn_{sfer} | 61 | 2.62 |
| | 63 | 2.36 |
| Uncoated steel | - | 16.07 |

Results of Adhesion Properties of the Protective Organic Coatings

The adhesion measurement results for the paint films before and after the accelerated cyclic corrosion tests are listed in **Tables 9–12** (**Table 12** contains the results for the standard paints containing lamellar or spherical zinc).

The highest pull-off strength was observed for the paint films before the accelerated cyclic corrosion tests (**Figure 4**). The pull-off strength was >0.9 MPa for all paints with lamellar zinc and one of the conductive polymers as compared to the standard paint with lamellar zinc alone, which had a pull-off strength of 0.841 MPa. The pull-off strength values were also >0.9 MPa for the paints with spherical zinc and the conductive polymers as compared to the standard paint with spherical zinc alone, which had a pull-off strength of 0.783 MPa. The pull-off strength was higher if the paints with the conductive polymers contained lamellar zinc than if they contained spherical zinc. The accelerated cyclic corrosion tests reduced the pull-off strength of all the paint films tested. This was due to paint film blistering during exposure to the salt fog atmosphere: the pull-off strength was poorer the higher the number and size of the blisters on the paint film surface (**Figure 5**). Pull-off strength reduction was observed after the accelerated cyclic corrosion tests. The adhesion score was 0 and 1 for all the paint films with the conductive polymers and 1 for the standard paint with spherical zinc, which were all obtained prior to the accelerated corrosion tests. This high score (0–1) was retained after the accelerated corrosion test in the atmosphere containing SO_2 and not the salt fog atmosphere, which caused appreciable adhesion reduction due to paint film blistering. Lamellar zinc was superior to spherical zinc in the standard paints for pull-off strength and adhesion. Both the pull-off strength and adhesion were poorer if the zinc dust (both spherical and lamellar) concentration was increased to $\text{PVC}=\text{CPVC}$ or $\text{PVC}>\text{CPVC}$.

Table 9. Adhesion properties of the paints containing polyaniline phosphate, before and after the accelerated cyclic corrosion tests.

| Pigment | $\text{PVC}_{\text{PANI-}}\text{H}_3\text{PO}_4$ | Before corrosion tests | After exposure to neutral salt mist | After exposure in an atmosphere containing SO_2 |
|---------|--|------------------------|-------------------------------------|--|
|---------|--|------------------------|-------------------------------------|--|

| | [%] | Cross-cut test [dg.] | Pull-off strength [MPa] | Cross-cut test [dg.] | Pull-off strength [MPa] | Cross-cut test [dg.] | Pull-off strength [MPa] |
|--------------------------|-----------|----------------------|-------------------------|----------------------|-------------------------|----------------------|-------------------------|
| Zn_{lam} | 1 | 0 | 1.492 | 2 | 0.564 | 0 | 0.662 |
| | 5 | 0 | 1.328 | 2 | 0.523 | 1 | 0.610 |
| | 10 | 0 | 1.277 | 2 | 0.554 | 1 | 0.601 |
| Zn_{sfer} | 1 | 1 | 1.003 | 4 | 0.411 | 1 | 0.602 |
| | 5 | 1 | 1.028 | 4 | 0.293 | 1 | 0.553 |
| | 10 | 1 | 1.047 | 4 | 0.349 | 1 | 0.558 |
| | 15 | 1 | 1.106 | 4 | 0.498 | 1 | 0.579 |

* Fracture type: cohesion in the coating > 95 %

Table 10. Adhesion properties of the paints containing polyaniline benzoate, before and after the accelerated cyclic corrosion tests.

| Pigment | PVC _{PANI-BENZ} [%] | Before corrosion tests | | After exposure to neutral salt mist | | After exposure in an atmosphere containing SO ₂ | |
|--------------------------|------------------------------|------------------------|-------------------------|-------------------------------------|-------------------------|--|-------------------------|
| | | Cross-cut test [dg.] | Pull-off strength [MPa] | Cross-cut test [dg.] | Pull-off strength [MPa] | Cross-cut test [dg.] | Pull-off strength [MPa] |
| Zn_{lam} | 1 | 0 | 1.298 | 3 | 0.576 | 0 | 0.741 |
| | 5 | 0 | 1.178 | 3 | 0.513 | 1 | 0.675 |
| | 10 | 0 | 1.235 | 2 | 0.504 | 1 | 0.701 |
| Zn_{sfer} | 1 | 1 | 0.958 | 4 | 0.342 | 1 | 0.692 |
| | 5 | 1 | 0.951 | 4 | 0.331 | 1 | 0.675 |
| | 10 | 1 | 0.936 | 4 | 0.393 | 1 | 0.643 |
| | 15 | 1 | 0.970 | 3 | 0.485 | 1 | 0.696 |

* Fracture type: cohesion in the coating > 95 %

Table 11. Adhesion properties of the paints containing carbonised polyaniline, before and after the accelerated cyclic corrosion tests.

| Pigment | PVC _{PANI-CAR} [%] | Before corrosion tests | | After exposure to neutral salt mist | | After exposure in an atmosphere containing SO ₂ | |
|--------------------------|-----------------------------|------------------------|-------------------------|-------------------------------------|-------------------------|--|-------------------------|
| | | Cross-cut test [dg.] | Pull-off strength [MPa] | Cross-cut test [dg.] | Pull-off strength [MPa] | Cross-cut test [dg.] | Pull-off strength [MPa] |
| Zn_{lam} | 1 | 0 | 0.987 | 2 | 0.588 | 1 | 0.642 |
| | 5 | 0 | 0.982 | 3 | 0.366 | 1 | 0.376 |
| | 10 | 0 | 0.953 | 3 | 0.462 | 1 | 0.532 |
| Zn_{sfer} | 1 | 1 | 0.933 | 3 | 0.376 | 1 | 0.502 |
| | 5 | 1 | 0.922 | 3 | 0.479 | 1 | 0.553 |
| | 10 | 1 | 0.939 | 4 | 0.424 | 1 | 0.528 |
| | 15 | 1 | 0.943 | 4 | 0.497 | 1 | 0.416 |

* Fracture type: cohesion in the coating > 95 %

Table 12. Adhesion properties of the zinc-pigmented paints before and after the accelerated cyclic corrosion tests.

| Pigment | PVC _{Zn} [%] | Before corrosion tests | | After exposure to neutral salt mist | | After exposure in an atmosphere containing SO ₂ | |
|-------------------------|-----------------------|------------------------|-------------------------|-------------------------------------|-------------------------|--|-------------------------|
| | | Cross-cut test [dg.] | Pull-off strength [MPa] | Cross-cut test [dg.] | Pull-off strength [MPa] | Cross-cut test [dg.] | Pull-off strength [MPa] |
| Zn_{lam} | 39 | 0 | 0.841 | 2 | 0.642 | 1 | 0.662 |

| | | | | | | | |
|--------------------------|-----------|----------|--------------|----------|--------------|----------|--------------|
| | 41 | 1 | 0.895 | 3 | 0.478 | 1 | 0.501 |
| | 43 | 2 | 0.735 | 3 | 0.475 | 2 | 0.595 |
| | 61 | 1 | 0.783 | 4 | 0.436 | 1 | 0.523 |
| Zn_{sfer} | 63 | 1 | 0.718 | 4 | 0.447 | 1 | 0.574 |
| | 65 | 2 | 0.675 | 5 | 0.422 | 2 | 0.546 |

* Fracture type: cohesion in the coating > 95 %

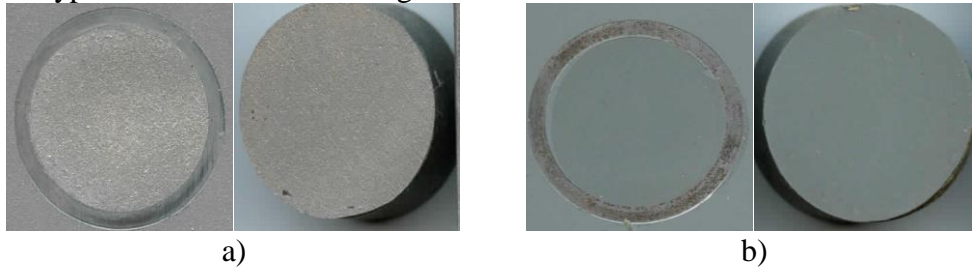


Figure 4. Photograph of the standard paint films and roller after the pull-off test: a) paint with lamellar zinc (PVC = 39 %), b) paint with spherical zinc (PVC = 61 %).

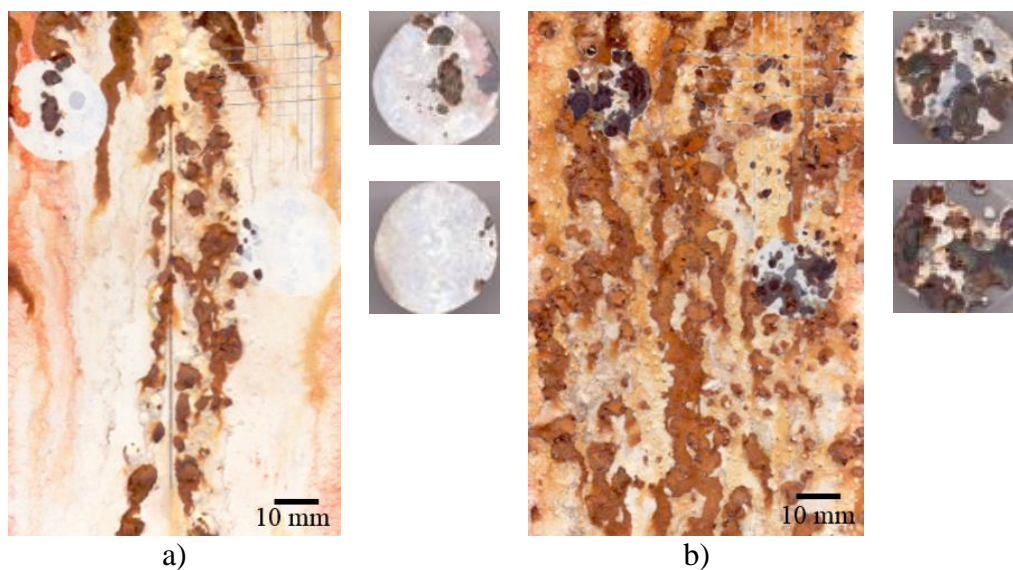


Figure 5. Photographs of the standard paint films and rollers after the pull-off test performed after the accelerated cyclic corrosion test in the salt fog atmosphere: a) paint with lamellar zinc (PVC = 39 %), b) paint with spherical zinc (PVC = 61 %).

Characterising the Organic Coating Composition

After exposure to the salt fog atmosphere for 240 h, the paints were examined by scanning electron microscopy and energy dispersive spectroscopy to obtain information on the paint composition in areas far from the test cut (**Figure 6**) and in a close vicinity to the test cut (**Figure 8**).

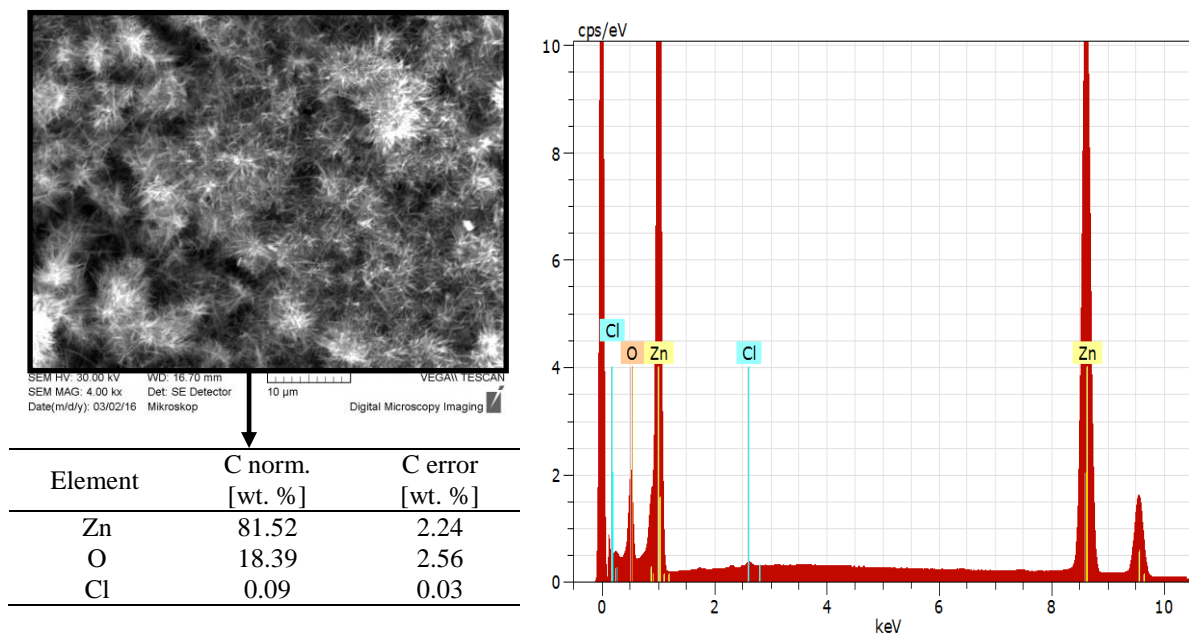
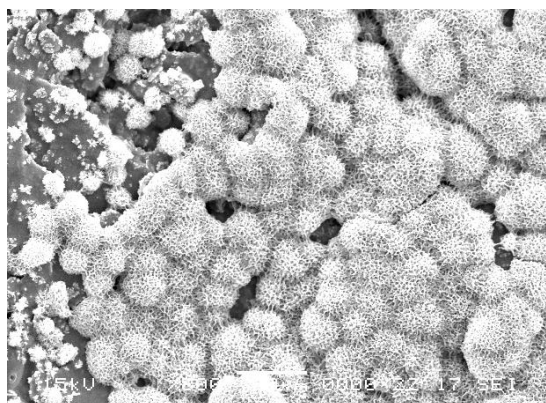
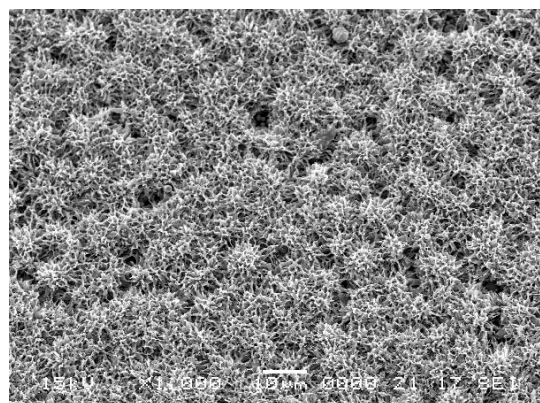


Figure 6. Scanning electron micrographs and energy-dispersive X-ray analysis results of the standard organic coating containing spherical zinc (PVC = 61 %), DFT = $50 \pm 10 \mu\text{m}$.

X-ray diffraction analysis (XRD) gave evidence that zinc had been present in the paint in the metal dust form only prior to the accelerated corrosion test, and energy dispersive spectroscopy showed that the pores in the paint films had been sealed by the zinc corrosion products (ZnO) due to the action of the cathodic protection mechanism (this conclusion is supported by the XRD data). No substrate steel corrosion products were found after the 240-h exposure, which attests to a high degree of corrosion protection provided by the paint films. Microphotographs of the surfaces of the standard paints are given in **Figure 7**.



a)



b)

Figure 7. Microphotographs of the surfaces of the standard paints following 240 h exposure to the salt fog atmosphere: a) standard paint containing lamellar zinc particles, b) standard paint containing spherical zinc particles

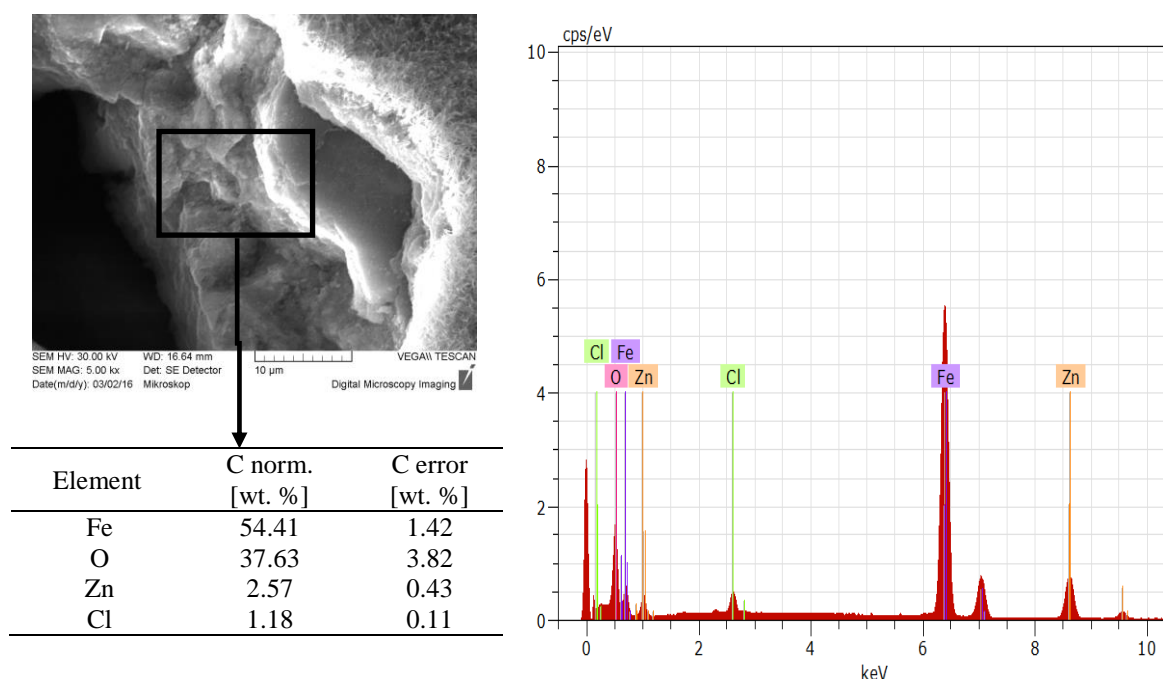


Figure 8. Scanning electron micrographs and energy-dispersive X-ray analysis results of the standard organic coating containing lamellar zinc (PVC = 39 %), DFT = 50 ± 10 μm .

Energy dispersive spectroscopy (**Figure 9**) demonstrated that the test cut had been partly sealed by the zinc corrosion products (ZnO) due to the effect of the cathodic protection mechanism. The presence of iron corrosion products, however, indicates that the sealing effect was not rapid enough to prevent corrosion of the steel substrate. The energy dispersive spectroscopy results are given in **Figure 9**, showing that in the case of the organic coating containing PANI-CAR particles (PVC=1%) and lamellar Zn particles, electrochemical protection was enhanced compared to the standard organic coating containing lamellar Zn particles (PVC=39%, **Figure 8**). These results are in line with the results given in **Table 4**, where for the organic coating containing PANI-CAR particles (PVC=1%) and lamellar Zn particles corrosion in the cross section was achieved for a distance of only 0.1 mm, whereas in the case of the standard organic coating containing lamellar Zn particles (PVC=39%), the corrosion in the cross section was extended to a distance of 0.3 mm.

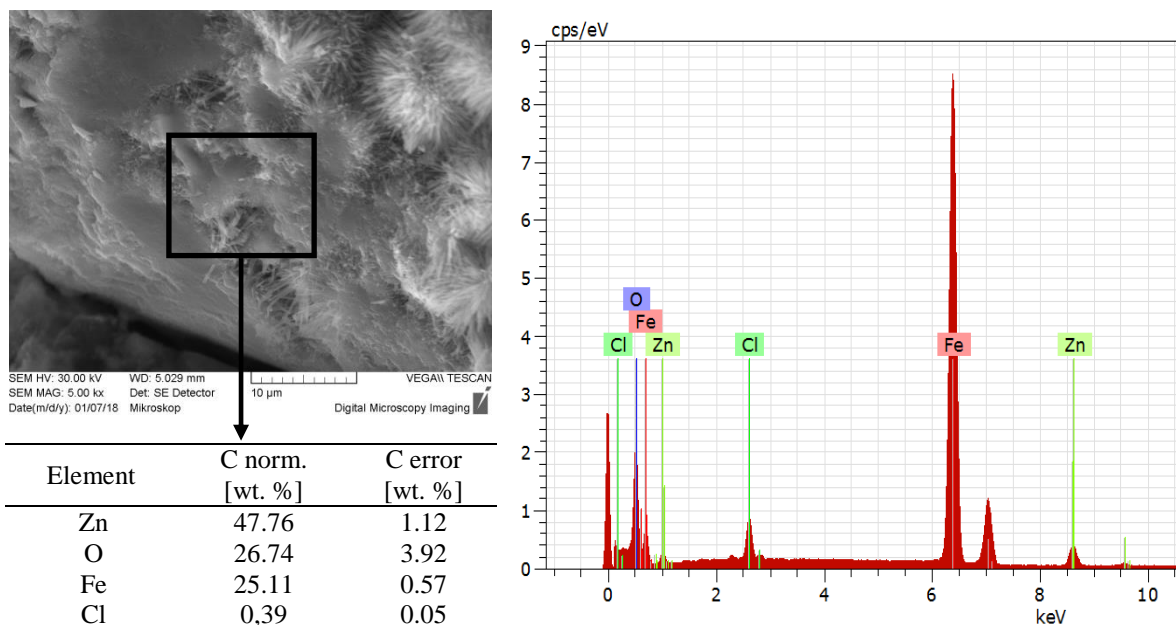


Figure 9. Scanning electron micrographs and energy-dispersive X-ray analysis results of the organic coating containing PANI-CAR (PVC = 1 %) and lamellar zinc, DFT = $50 \pm 10 \mu\text{m}$.

Summary of the Results of the Adhesion Properties and Accelerated Corrosion Tests

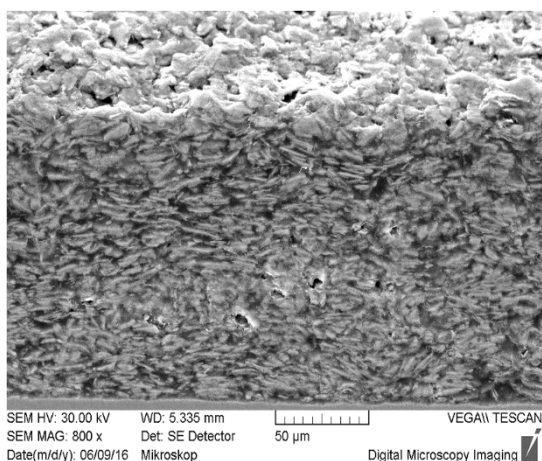
The results of the adhesion tests indicate that the addition of the conductive polymers as pigments to the paints with lamellar zinc or with spherical zinc had a favourable effect at any of the PVC levels applied. Furthermore, zinc possessing the lamellar particle shape was superior to zinc possessing the spherical particle shape in regards to corrosion protection provided by the organic coatings containing either of the two zinc species. As for the standard paints with no conductive polymer added, the highest corrosion resistance was attained at a PVC that was 2% lower than the CPVC: the resistance in the adhesion tests was poorer if the PVC was increased to $\text{PVC} = \text{CPVC}$ or further to $\text{PVC} > \text{CPVC}$.

The corrosion resistance attained in the accelerated cyclic corrosion test in the salt fog atmosphere was higher for the paints containing lamellar zinc than for the paints containing spherical zinc. The optimum volume concentration of the conductive polymer was $\text{PVC} = 1\%$ in the presence of zinc possessing the lamellar particle shape and 15% in the presence of zinc possessing the spherical particle shape.

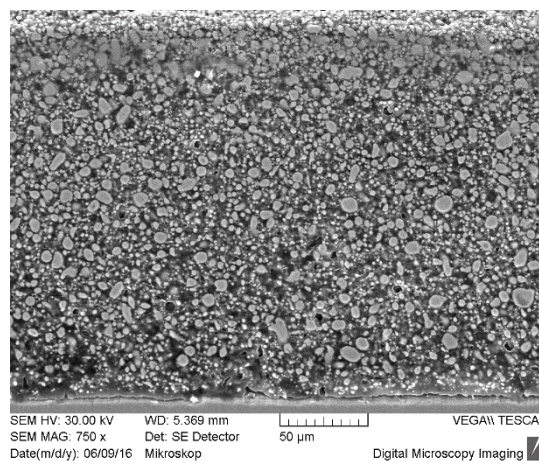
The addition of a conductive polymer to the paint system had a favourable effect on the accelerated cyclic corrosion test in the SO₂ atmosphere at any PVC level and in the presence of lamellar zinc, as well as in the presence of spherical zinc. The zinc particle shape had no appreciable effect on the resulting corrosion resistance.

Organic coatings with high spherical zinc content protect the steel substrate against the effect of the corrosive medium by the electrochemical mechanism. Contact of the zinc-containing paint film with the corrosive medium results in the formation of zinc corrosion products (Zn²⁺), which are less electrically conductive and, therefore, reduce the conductivity of the paint film, whereupon the electrochemical mechanism ceases to act and the barrier mechanism starts to play a role. If a conductive polymer is present in the paint, zinc (Zn⁰) is in contact not only with its corrosion products (Zn²⁺) but also with the conductive polymer, therefore, the conductivity within the paint film is higher and the electrochemical protection mechanism is supported/enhanced. Carbonised polyaniline was most efficient in this respect because this polyaniline species provides a higher conductivity than the polyaniline salts due to the formation of cross-linked cyclic hydrocarbons during the carbonisation process. Furthermore, the conductive polymers added to paints rich in zinc metal enhance the heterodisperse arrangement of the particles, whereby the adhesive properties of the paint film are supported. The presence of conductive polymers in zinc-pigmented paints brings about zinc dissolution reduction, particularly in acidic corrosion atmospheres (such as atmospheres with SO₂) by virtue of the barrier protection mechanism. The mechanism of action of the organic coatings rich in zinc consisting of lamellar particles is similar to that of the coatings containing zinc with spherical particles. The former are superior to the latter due to the longer path travelled by the diffusing liquid medium from the film surface to the substrate metal. Also, such paints protect the binder from degradation by reflecting ultraviolet radiation. The lamellar zinc particles also have a reinforcing effect on the paint structure and, hence, improve the paint's

mechanical resistance. These facts can also be seen in the microphotographs of sections of organic coatings containing either spherical or lamellar zinc particles (**Figure 10**). In zinc-pigmented paints, conductive contact must be ensured between the particles themselves as well between the particles and the substrate metal. This can be achieved only by preparing paint formulas with high zinc particle contents.



Standard organic coating pigmented with lamellar zinc (PVC = 39 %)



Standard organic coating pigmented with spherical zinc (PVC = 61 %)

Figure 10. Microphotographs of sections of organic coatings containing either spherical or lamellar zinc particles.

Conclusion

The first objective of this work was to compare the anticorrosion efficiency of paints containing zinc with the lamellar particle shape and zinc with the spherical particle shape. The former proved to be superior to the latter in an accelerated corrosion test in an atmosphere with neutral salt fog, whereas no appreciable differences between the two zinc species were observed in an accelerated cyclic corrosion test in an atmosphere with SO_2 . The second objective consisted of determining the optimum concentration of a conductive polymer added to the paint so as to reduce the zinc content while preserving the high corrosion resistance. It was found that this goal could be achieved by using paints containing lamellar zinc particles and one of the conductive polymers at PVC=1%. The highest corrosion efficiency was attained by using carbonised polyaniline at PVC=1%. When the lamellar zinc particle form was replaced with

the spherical form, a high corrosion resistance was attained by using the carbonised polyaniline species at a considerably higher pigment volume concentration (PVC=15%).

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