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**Effect of Conductive Polymers and Other Substances on Corrosion-
Inhibiting Properties of Zinc-Filled Epoxyester Coatings**

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Abstract

The research part of this work was aimed at examining the feasibility of using conductive polymer salts in epoxy-ester resin based paints and the feasibility of reducing the zinc content in paints pigmented with zinc possessing either the spherical particle shape. In view of the fact that conductive polymer salts are currently investigated by many branches of science and technology, the feasibility of their use in the paint industry appears promising, not only owing to their electrical conductivity (reaching the levels observed in semiconductors) but also owing to their redox capacity. Conductive polymer salts were synthesized and used for the preparation of paints for organic coatings, whose mechanical and anticorrosion properties were studied by using mechanical tests, corrosion tests and electrochemical measurements. Options for using the conductive polymer salts in the paints were identified and ways to reduce the zinc contents (using zinc powder with either spherical particle shape) while preserving or enhancing the mechanical resistance and corrosion resistance were found by using the conductive polymer salts at the optimum pigment volume concentrations.

Abstrakt

Výzkumná část disertační práce byla zaměřena na studium využití solí vodivých polymerů v nátěrových hmotách na bázi epoxyesterové pryskyřice a dále na hledání možností snížení obsahu zinku v nátěrových hmotách pigmentovaných zinkem se sférickým tvarem částic. Vzhledem ke skutečnosti, že právě soli vodivých polymerů, jsou v současné době studovány v řadě technických oborů, hledá se i možnost jejich využití v oboru nátěrových hmot, kde se jeví jako perspektivní materiály nejen z důvodu jejich elektrické vodivosti, která dosahuje vodivosti polovodičů, ale i z důvodu jejich redoxních schopností. V rámci této práce byly syntetizované soli vodivých polymerů použity pro přípravu nátěrových hmot, kdy mechanické a antikorozi vlastnosti připravených organických povlaků byly studovány pomocí mechanických, korozních a elektrochemických testů. V rámci disertační práce byly nalezeny možnosti využití solí vodivých polymerů v těchto nátěrových hmotách a dále byly nalezeny možnosti snížení obsahu zinku se sférickým tvarem částic při využití solí vodivých polymerů při optimálních hodnotách objemové koncentrace pigmentu při zachování či zvýšení mechanické i korozní odolnosti.

Keywords

organic coating

corrosion

zinc

conductive polymer

polyaniline salt

Klíčová slova

organický povlak

koroze

zinek

vodivý polymer

polyanilinová sůl

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1. Introduction

Powdered zinc has been used for preparation of paints for many years as the so-called "sacrificed electrode". The first-stage protection is cathodic protection, during which zinc corrosion products are formed in the coating pores (Fig. 1) and seal the pores, thereby reducing the coating's conductivity. As the conductivity is reduced, the electrochemical mechanism is transformed into the barrier mechanism. [1-3]. An active protection is required since the function of electrochemical cathodic protection takes place upon mechanical damage to the coating. These coatings are used to protect steel structures, for example structures immersed in water or protective coatings on ships. The high corrosion resistance of the coating is due to the high content of zinc. For environmental and economic reasons options are looked for aiming at reducing the content of zinc in these films [3-5]. One of the options is using a combination of zinc with conductive polymers. When a zinc powder is combined with conductive polymers, the volume concentration of the zinc metal is reduced while a high anticorrosive efficiency is preserved [6].

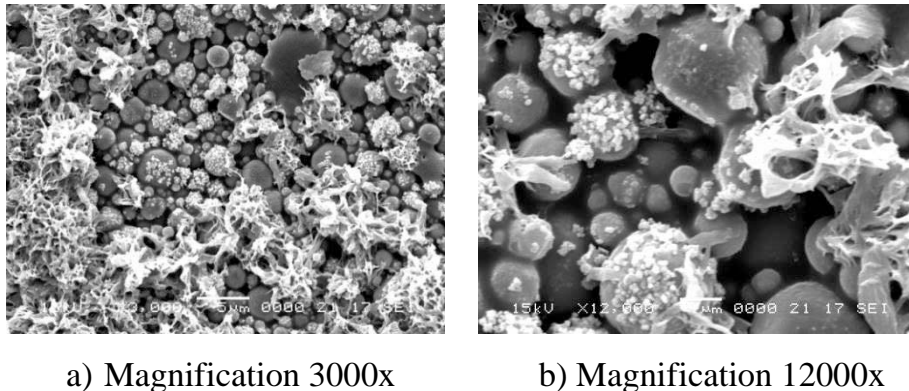


Figure 1: Corrosion changes in the surface of a zinc-pigmented coating on exposure to moisture (humidity) [7].

Conductive polymers are substances that possess a conductivity similar to that of semiconductors [8]. The benefits of conductive polymers include nontoxicity, high stability, electric conductivity and redox potential. This conductivity is due to the system of alternating single and double bonds (conjugated system) in the polymers' molecular structure. In addition to such a system of conjugated bonds, the presence of movable charge carriers providing transport along the conjugate chain is a prerequisite for conductivity [9, 10]. Very important representative of conductive polymers is polyaniline, polypyrrole and polyphenylenediamine [8].

Polyaniline, which can be prepared in five different forms, constitutes a very important representative of conductive polymers. Its individual forms differ in the extent of oxidation or the extent of protonation and also in chemical structure, stability, colour and electrical characteristics [11-13]. The anion present in the polyaniline structure offsets the positive charges present in the chain. The anion present depends on the protonating acid employed [14]. Both the type and concentration of the acid substantially affect the conductivity of the polyaniline conductive form (emeraldine salt) [15].

2. The Aim of the Thesis

Conductive polymers find use, among other things, as substances exerting a corrosion-inhibiting effect on steel substrates. They are used at various – low or higher – concentrations and are frequently combined with other substances, e.g. pigments, corrosion inhibitors or other polymers in order to enhance the performance of the protective layer, polymeric paint, organic and composite coating on contact with a corrosive atmospheric environment. In the coating they can act synergistically with other ingredients or pigments to provide a beneficial effect. In fact, conductive polymers represent an interesting option for anticorrosion protection of metals. In this domain of metal protection against corrosion, considerable attention is paid, e.g., to polyaniline as the historically oldest conductive polymer, as well as to its salts, frequently in the carbonised form.

Zinc-filled paints, also, have been attracting considerable interest lately, particularly owing to their high efficiency in very aggressive corrosive environments. The properties of paints that are based on diverse binder types, with different zinc particle shapes and with different zinc concentrations in the binder are studied. Since the high efficiency of zinc is associated with some shortcomings, lowering its concentration or replacement of a fraction of this metal with equally electrochemically noble pigments is desirable. The use of zinc dust with a different zinc particle morphology is among the options.

The aim of this thesis was to study the properties of the synthesised conductive polymer salts as ingredients in protective organic coatings to substitute certain existing toxic pigments, their effects on the coatings' anticorrosion capacity and physical resistance. The use of such conductive polymer salts as pigments is a way to novel non-toxic materials possessing anticorrosion properties.

Study of the properties of zinc-pigmented paint films in dependence on the polyaniline salt type (PANI-H₃PO₄, PANI-H₂SO₄, PANI-HCl, PANI-PTSA and PANI-CAS) and concentration, i.e. study of the usability of the polyaniline salts for reducing the zinc content.

- Synthesis of five polyaniline salt types: PANI-H₃PO₄, PANI-H₂SO₄, PANI-HCl, PANI-PTSA and PANI-CAS.
- Study of the structure and physico-chemical properties of the polyaniline salts.
- Formulation and preparation zinc-pigmented paints containing polyaniline salts. Preparation of paints with reduced zinc contents by using conductive polymer salts while preserving or enhancing the initial paints' anticorrosion efficiency.
- Study of the effect of the polyaniline salts on the corrosion resistance of the zinc-pigmented paint films through corrosion tests and electrochemical measurements – relation between the use of the polyaniline salts and feasibility of reducing the zinc content.
- Study of the effect of the polyaniline salts on the mechanical properties of zinc-pigmented paint films through mechanical tests.
- Identification of the mechanism of action of the polyaniline salt in the zinc-pigmented paint film.

3. Experimental Part

3.1. Preparation of Polyaniline Salts by Polymerisation of Aniline

To prepare polyaniline salts, aniline was oxidised by potassium peroxydisulphate in an acidic medium. Phosphoric acid (H_3PO_4), sulphuric acid (H_2SO_4), hydrochloric acid (HCl), p-toluenesulphonic acid (PTSA), or 5-sulphosalicylic acid (CAS) was used as the doping acid. The synthesis is depicted in Fig. 2.

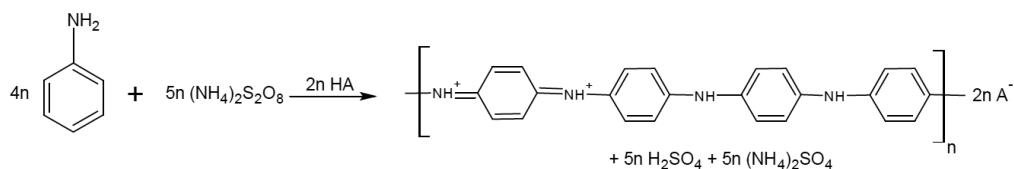


Figure 2: Syntheses of the polyaniline salts

3.2. Pigment Specification

The thermogravimetric analyses were performed using a DMA, D047 (RMI). The measurements were carried out in air between 30 and 600°C at a heating rate of 5 °C.min⁻¹.

The calorimetric measurements were performed by calorimeter (Mettler DSC 12E) in perforated alumina pans using heating rate 5 °C.min⁻¹ in the temperature range 30–525 °C. The calorimeter was calibrated with indium and sapphire. Samples were weighed (Sartorius R 160 P) before and after DSC measurements.

X-ray diffraction (XRD) data were obtained with D8-Advance (Bruker AXE) diffractometer with Bragg–Brentano θ – θ geometry using CuK_α radiation. XRD data were collected at room temperature from 5 to 70° (2θ) in 0.02° steps with a counting time of 3 s per step.

Transmission IR spectra were recorded in the 4000–400 cm⁻¹ region on a Nicolet 6700 FTIR spectrometer in KRS-5 pellets. Pellets were dried in a desiccator over P_2O_5 for 3 days before measurements.

Gel permeation chromatography for measurement of molecular mass of the polyanilines was performed on a Calc 100 chromatograph equipped with a PLgel mixed-C column using *N*-methylpyrrolidone containing 0.005 g.cm⁻³ of lithium bromide (to prevent aggregation) as the eluent at the flow rate of 0.70 ml.min⁻¹. Samples were dissolved in mobile phase containing 0.005 g.cm⁻³ of triethanolamine. The system was calibrated with polystyrene standards. Samples were detected spectrophotometrically at 340 nm.

Conductivity was determined by a four-point van der Pauw method using a Keithley 237 High-Voltage Source Measurements Unit and a Keithley 2010 Multimeter equipped with a 2000-SCAN 10 Channel Scanner Card on samples compressed into pellets, 13 mm in diameter and ca. 1 mm thick.

Determination of particle size and the distribution of pigment particle size were identified by means of Mastersizer 2000, which is able to measure the distribution of particles sized from 0.01 to 2000 μm.

Pigments were subjected to the measurement of density by a Gas Pycnometer. Further on the oil absorption value was determined for these pigments using „the pestle-mortar”

method. These results were used to calculate the critical pigment volume concentration (CPVC).

The shape of pigments has been studied using microphotography that had been taken by electron microscope. The resulting micrographs used to follow the shape and the surface structures of pigments.

3.3. Paint Formulation and Preparation

After the specification of pigments the formulation of organic coatings had been made. As a binder epoxyester resin of solvent type was selected. Polyaniline salts and zinc were used as pigments. The paints prepared from this binder contained the polyaniline salts at pigment volume concentrations $PVC = 0.1\%$, 0.5% , 1% , 2% , 3% , 5% , 10% and 15% and zinc at $PVC/CPVC = 0.67$. Dispergation of the formulated organic coatings took place in a Dissolver at operating speed $10-15\text{ m/s}$ for $45-60$ minutes. Nuodex Combi HS was added as a siccative. Prepared organic coatings were applied to steel and glass panels using an applicator with a slit. Subsequently dry film thickness was determined using magnetic gauge.

3.4. Mechanical Properties of the Paints

The prepared organic coatings containing conductive polymers and zinc were subjected to tests providing information on the paint film elasticity and strength.

The surface hardness of the paints by a pendulum apparatus.

The hardness of the paint film was determined by means of a Persoz pendulum. The results are indicated as percentages related to the hardness of glass standard.

The degree of the adhesion of the coatings by a lattice method (ISO 2409).

Determination was made by means of a special cutting blade with cutting edges 2 mm apart and involved the degree of adhesion of the created $2\text{ mm} \times 2\text{ mm}$ squares to a base substrate.

Impact resistance (ISO 6272).

The test revealed the height of the free fall of a weight (1000 g) at which the paint film still resists damage. The test was performed on the reverse of the panel with a coating.

The resistance of the coating against cupping in an Erichsen cupping tester (ISO 1520).

The objective of this test is to identify the resistance of the paint film against on-going deformation of a coated steel panel with a pressed-in 20 mm steel ball. The result of the test gives the so-called cupping in mm during which the first disturbance of the coating occurred.

The resistance of the coating during bending on a cylindrical spindle (ISO 1519).

The result of this test indicates the diameter of the spindle (in mm) on which the cohesion of the paint film became disturbed.

Degree of Adhesion of the Pull-off Test (ISO 4624).

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 result of this test was the force that was needed to pull-off the layer from a substrate.

3.5. Corrosion Test Procedures

Accelerated corrosion tests are based on the intensification of the effects of natural forces that have a decisive influence on the protective properties of the paints, their degradation, and primarily on the extent of corrosion under the paint film on a protected base.

Accelerated cyclic corrosion test in an atmosphere of NaCl with water steam condensation (ISO 9227).

The exposure of the samples in a testing chamber was performed in 12-h cycles divided into three parts: 10 h of exposure to a mist of 5 %-solution of NaCl at a temperature of 35 °C; 1 h of exposure at a temperature of 23 °C; and 1 h of humidity condensation at a temperature of 40 °C.

Accelerated cyclic corrosion test in an atmosphere of SO₂ with water condensation (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 38 °C followed by exposure to the condensation of humidity for a period of 16 hours and at a temperature of 21 °C.

Methods of Corrosion Test Evaluation.

The degree of blistering on the surface of the coatings (ASTM D 714-78), the degree of corrosion at the test scribe (ASTM D 1654-92) and the degree of steel surface corrosion (ASTM D 610-85) were evaluated after the exposure in the corrosive environments

Electrochemical method linear polarisation.

This technique enables the polarization resistance (R_p), corrosion potential (E_{cor}), corrosion current density (I_{cor}) and corrosion rate (CR) to be determined. The corrosion potential and corrosion current density were determined by analysis of Tafel curves.

4. Results and Discussion

4.1. Thermogravimetric Analysis

All polyaniline salts exhibited three regions where weight loss took place. The first weight loss amounting to 2–6.3 %, taking place at temperatures up to 175 °C, was attributed to the loss of moisture and of adsorbed low molecular weight substances. A next, very small weight change (≤ 1 %) was observed within the temperature region from 175 °C to 250 °C. The third weight loss, very marked (>76 %), was observed within the temperature region from 250 °C to 600 °C, where the sample underwent thermo-oxidative degradation [16, 17]. The weight loss observed at 600 °C was > 83 % for all of the polyaniline salts synthesized.

4.2. Differential Scanning Calorimetry

All samples exhibited an endothermic change within the region from 75 °C to 175 °C. This endothermic change can be linked to the weight loss observed in thermogravimetry and attributed to the loss of moisture and adsorbed low-molecular-weight substances. This is supported by the enthalpy data. An exothermic change which is attributed to crosslinking or recrystallization was observed in the DSC spectra within the range from 175 °C to 275 °C [18]. This interpretation is also supported by the thermogravimetry data, where a negligible weight change occurred within that temperature range. A marked exothermic change was observed within the temperature range from 275 °C to 525 °C on the DCS traces of all the polyaniline salts examined; this was attributed to thermo-oxidative degradation [16]. Once again, this is in accordance with the results of the thermogravimetric analysis, where a marked (>76 %) weight loss was observed within the temperature range in question.

4.3. X-ray Diffraction Analysis

None of the XRD diffractograms of salts conductive polymers contain any sharp diffraction peaks, thus confirming the amorphous state of the prepared samples [19].

4.4. Infrared Spectroscopy

The compounds were studied by FTIR spectroscopy in the range of 4000-600 cm^{-1} . All prepared PANI samples showed medium bands at 3449, 3231, 3060 cm^{-1} corresponding to stretching vibrations of OH, NH and aromatic CH bonds, respectively.

Fig. 3 shows the spectra of PANI salts in the region of 1800–600 cm^{-1} , where bands characteristic for polyaniline salts are present. The observed bands, together with their assignment (based on the comparison with reported data) are listed in the Table 1. The vibrational pattern in this region was similar for all the studied PANI samples and, upon comparing the IR spectra, we could distinguish the bands corresponding to anions (sulfate, sulfonate or dihydrogen phosphate) incorporated into the PANI salts during synthesis [20, 21].

In the PANI- H_3PO_4 and PANI-CAS, weak absorption at 1373 cm^{-1} was found, typical of the PANI base (C–N stretching in the neighborhood of a quinonoid ring). The presence of this band indicates that the PANI salt was not fully protonated, which also correlates with the lower conductivity observed for these two samples [22].

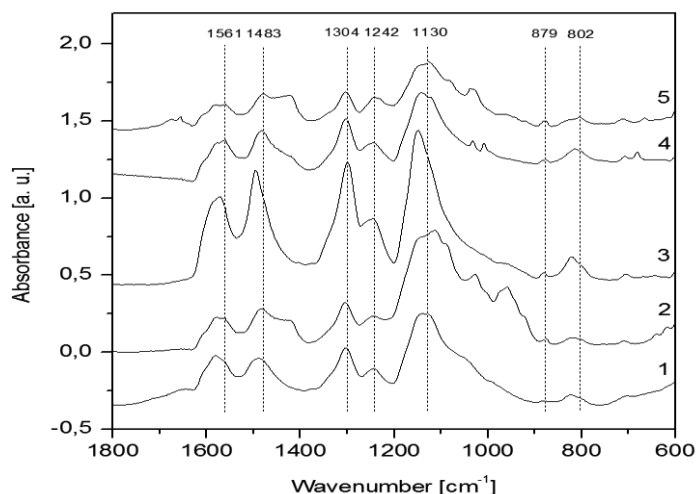


Figure 3. FTIR spectra of the polyaniline salts (1. PANI-H₃PO₄, 2. PANI-H₂SO₄, 3. PANI-HCl, 4. PANI-PTSA, 5. PANI-CAS).

Table 1: The assignment of FTIR bands for the studied polyaniline salts [23, 24].

Mode	Wavenumber [cm ⁻¹]				
	PANI-H ₃ PO ₄	PANI-H ₂ SO ₄	PANI-HCl	PANI-PTSA	PANI-CAS
Quinonoid (Q) ring stretching	1567	1557	1556	1556	1574
Benzenoid (B) ring stretching	1484	1472	1471	1473	1477
(C–N) of secondary aromatic amine	1298	1295	1289	1295	1299
(C–N ⁺) in the polaron lattice of PANI	1242	1240	1236	1228	1225
Q=NH ⁺ –B or B–NH ⁺ –B	1109	1105	1105	1112	1109
γ (C–H) 1,2,4-trisubstituted ring /B ring deformation	879	878	878	878	878
γ (C–H) (1,4-disubstituted ring)/Q ring deformation	795	788	791	792	802
ν (S–O)	–	1090, 1026, 1006	–	1142, 1033, 1008	1126, 1084, 1034
ν (P–O)	1048, 1092	–	–	–	–

B: benzenoid ring; Q: quinonoid ring; γ: out-of-plane deformation.

4.5. Molecular Weight

The PANI-PTSA salt dissolved completely during the determination, whereas the remaining polyaniline salts dissolved only partially. The polyaniline salts that were prepared in mineral acid solutions exhibited polydispersity index levels from 3.2 to 3.9 and molecular weights from 7000 to 14000, whereas the polyaniline salts that were prepared in organic acid solutions exhibited polydispersity index levels from 4.0 to 4.8 and molecular weights from 13000 to 25000.

4.6. Conductivity

The electrical conductivity of PANI-H₃PO₄ (0.13 S.cm⁻¹) was markedly lower than the conductivities of the remaining polyaniline salts. This can be explained in terms of incomplete protonation of the salt in question, as found by FTIR spectroscopy. Incomplete protonation was also observed for PANI-CAS, whose conductivity was also lower (0.78 S.cm⁻¹) than the conductivities of the fully protonated polyaniline salts.

Differences between the electrical conductivity levels were also observed between the fully protonated polyaniline salts: conductivity decreased in the order PANI-PTSA (5.85 S.cm^{-1}) > PANI-HCl (1.75 S.cm^{-1}) > PANI-H₂SO₄ (1.48 S.cm^{-1}). This order may be linked to the molecular weight (M_w), which increased in that order. The observed electrical conductivity values were within the range found for polyaniline salts prepared by oxidative polymerization. Note that the electrical conductivity of the non-conductive polyaniline species (emeraldine base) is $1 \times 10^{-8} \text{ S.cm}^{-1}$ [25].

4.7. Particle Size

The mean particle size, identified with the diameter of an equivalent sphere, i.e. a sphere that scatters laser radiation to the same extent as the particle measured of the polyaniline salts was from $6.3 \mu\text{m}$ to $6.5 \mu\text{m}$. Densities, oil absorption and CPVC levels of the polyaniline salts.

Table 2: M_w , M_w/M_n , conductivity and particle size of the polyaniline salts.

Polyaniline salt	M_w	M_w/M_n	Conductivity [S.cm^{-1}]	Particle size [μm]
PANI-H ₃ PO ₄	7000	3.2	0.13	6.4 ± 0.1
PANI-H ₂ SO ₄	10000	3.5	1.48	6.4 ± 0.1
PANI-HCl	14000	3.9	1.75	6.5 ± 0.1
PANI-PTSA	25000	4.8	5.85	6.3 ± 0.1
PANI-CAS	13000	4.0	0.78	6.4 ± 0.1

4.8. Particle Morphology

Microphotographs of the polyaniline salts are shown in Figure 4. The photographs were primarily used to examine the shape and surface of the substances studied. The microphotographs demonstrate that the polyaniline salts had an isometric shape and formed clusters of particles.

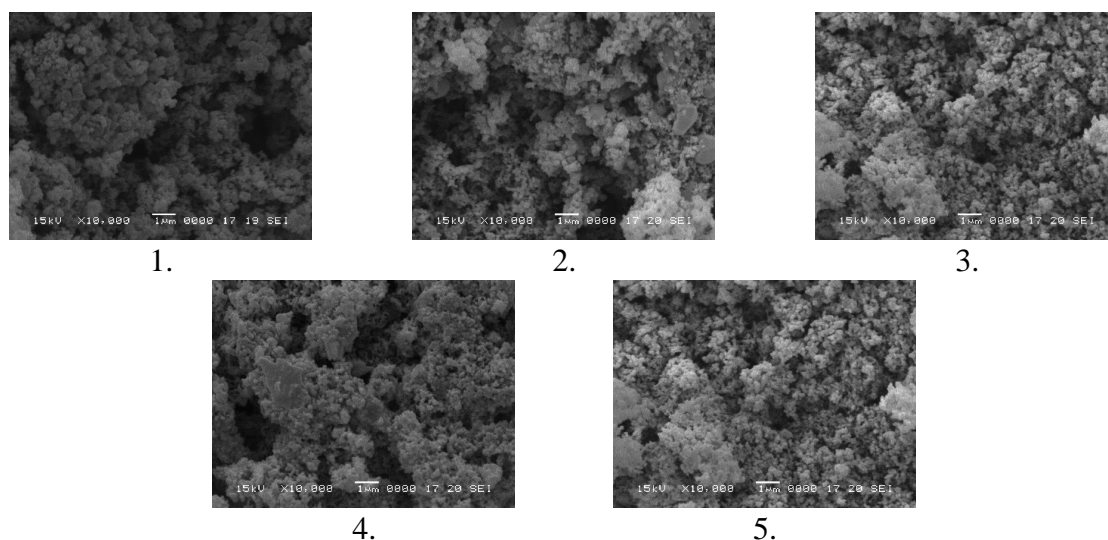


Figure 4: Microphotographs of the polyaniline salts (1. PANI-H₃PO₄, 2. PANI-H₂SO₄, 3. PANI-HCl, 4. PANI-PTSA, 5. PANI-CAS).

4.9. Density, Oil Absorption and Critical Pigment Volume Concentration (CPVC) of the Polyaniline Salts

The basic parameters of the polyaniline salts are provided in Table 3. The densities of the salts were within the range of 1.37-1.57 g.cm⁻³. The relatively low densities suggest that the sedimentation rate in organic coating materials will not be high. The CPVC values of the polyaniline salts lay within the range from 28 % to 31 %. The CPVC depends on density and on the oil absorption, the latter providing indirect information on the pigment's specific surface area, particle size distribution and porosity. Knowledge of the CPVC is a prerequisite for appropriate formulation of the pigmented organic coating material.

Table 3: Densities, oil absorption and CPVC levels of the polyaniline salts.

Polyaniline salt	Density [g.cm ⁻³]	Oil absorption [g.100 g ⁻¹]	CPVC [%]
PANI-H ₃ PO ₄	1.47 ± 0.02	152	29
PANI-H ₂ SO ₄	1.48 ± 0.02	159	28
PANI-HCl	1.37 ± 0.02	153	30
PANI-PTSA	1.37 ± 0.02	152	31
PANI-CAS	1.57 ± 0.02	156	27

4.10. Summary of the Results of the Physico-Mechanical Tests

The mechanical test results show that the resulting mechanical resistance of the zinc-pigmented organic coating is unaffected by the polyaniline salt type but it is affected by the pigment volume concentration applied. In particular, the mechanical resistance of the organic coatings increased with increasing pigment concentration at PVC > 1%. High-zinc organic coatings are known to attain a lower mechanical resistance (because of the too high zinc content). The enhanced mechanical resistance of organic coatings containing the polyaniline salts can be explained in terms of the slowly increasing heterodisperse arrangement of the particles in the system due to the decreasing zinc content and increasing polyaniline salt content. High mechanical resistance parameters were observed for organic coatings with polyaniline salts at PVC ≥ 2%, where only increasing resistance to cupping was observed with increasing PVC.

4.11. Summary of the Results of the Accelerated Corrosion Tests

The results of the accelerated cyclic corrosion tests as well as of the electrochemical linear polarisation measurements demonstrate that the volume concentration of the polyaniline salt affects appreciably the corrosion resistance of the zinc-pigmented organic coatings. The optimum volume concentration of the polyaniline salt in the organic coatings as derived from the accelerated cyclic corrosion tests and electrochemical linear polarisation measurements was between 1% and 5% depending on the corrosive environment type. Outstanding mechanical resistance data and the highest corrosion resistance data in all the accelerated cyclic corrosion tests and electrochemical linear polarisation measurements were obtained with the zinc-pigmented organic coating containing the pigment PANI-H₃PO₄ at PVC = 3%.

The organic coatings exhibiting the highest corrosion resistance are suitable for use in corrosive environments category C5-I, where their service life will be medium. Specifically, they are organic coatings containing PANI-H₃PO₄ at PVC = 2% and 3%,

and also the organic coating containing PANI-PTSA at PVC = 2% and 3%. This conclusion was derived from the facts that the surfaces of such organic coatings exhibited no blisters or signs of corrosion of the substrate, their adhesion was scored 0 or 1, and corrosion in a test cut was not broader than 1 mm following 720 hours of exposure to neutral salt fog atmosphere. The remaining organic coatings with $PVC \leq 5\%$ (including the conventional organic coating) are suitable for use in category C5-I environments, where their service life will be short. This conclusion was derived from the facts that the surfaces such organic coating exhibited no blisters or signs of corrosion of the substrate, their adhesion was scored 0 or 1, and corrosion in a test cut was not broader than 1 mm following 480 hours of exposure to neutral salt fog atmosphere. Organic coatings with $PVC > 5\%$ are unsuitable for use in corrosive environments C5-I because they exhibited blisters even before the 480-hour exposure to the neutral salt fog atmosphere.

The results suggest that the option of reducing the zinc content in zinc-pigmented organic coatings by using polyaniline salts is feasible. Specifically the use of the polyaniline salts PANI-H₃PO₄, PANI-HCl or PANI-PTSA at their optimum concentrations (PVC = 2% to 3%) brought about higher mechanical resistance and higher corrosion resistance than the conventional organic coating. In particular, the highest corrosion resistance and highest mechanical resistance parameters were obtained with PANI-H₃PO₄ at PVC = 2% and 3% in the zinc-pigmented paint formulations. The use of this polyaniline salt in the zinc-containing paint formulation results in up to 2.5 wt.% zinc savings compared to the conventional organic coating.

It is well-known that in paints containing zinc, this metal constitutes what is called a sacrificed electrode provided that the condition of contact existing between the zinc particles is satisfied. To meet this condition, zinc must be present in a high amount in the formula. However, too high pigmentation degrades the paint's mechanical properties. The present work was devoted to the investigation of the anticorrosion properties of zinc coatings containing small amounts of polyaniline salts. The parameter PVC/CPVC of zinc in the organic coatings was 0.67. One of the functions of the polyaniline salts in the paint is to provide electric contact between the zinc atoms, thus supporting the electrochemical reactions of the zinc, primarily resulting in the formation of zinc oxide. The method of protection is then based on the autocatalytic cycle controlled via reversible transformation between the doped polyaniline form (PANI-ES) and the neutral polyaniline form (PANI-EB).

5. Conclusion

Polyaniline salts were used in order to achieve the goal of this work. The salts were described by means of a number of instrumental methods. They were also characterised with respect to their physico-chemical properties and parameters used in the paint industry. The results were used when formulating model zinc dust-containing paints. Specifically, the polyaniline salts included PANI-H₃PO₄, PANI-H₂SO₄, PANI-HCl, PANI-PTSA and PANI-Zinc dust with spherical particles was used and the paints were prepared by dispersing operations. Subsequently, the paints were applied to steel panels by using an applicator with a slit. The organic coatings so prepared were subjected to mechanical tests and cyclic corrosion tests. Their mechanical resistance and corrosion resistance of the films were examined and compared to those of the reference salt-free zinc-pigmented paint film. The electrochemical method of linear polarisation was also used to examine the corrosion resistance of the coatings.

The results gave evidence that the use of polyaniline salts is a feasible way to reduce the zinc content of zinc-pigmented organic coatings. Specifically, the use of the polyaniline salts PANI-H₃PO₄, PANI-HCl or PANI-PTSA at their optimum concentrations (PVC = 2% to 3%) brought about higher mechanical resistance and higher corrosion resistance than as measured for the conventional organic coating containing zinc only. The highest corrosion resistance parameters as well as highest mechanical resistance parameters were obtained with PANI-H₃PO₄ at PVC = 2% and 3% in the zinc-pigmented paint formulations. The use of this polyaniline salt in the zinc-containing paint formulation results in up to 2.5 wt.% zinc savings compared to the conventional organic coating. Furthermore, organic coatings with the above polyaniline salt types at the optimum concentrations are suitable for use in corrosive environments category C5-I and their service life will be medium in such circumstances.

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