Enhancing corrosion resistance of zinc-filled protective coatings by using conductive polymers

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Abstract

Organic coatings containing zinc are amply used for the protection of metals, particularly steel structures. Ways to reduce the zinc content in the coating materials are sought for environmental and financial reasons. Our previous work (Kohl et al., 2014; Kohl & Kalendová, 2015a) suggested that one of the options consists in the use of conductive polymers in the formulation of the zinc coatings. The benefits of conductive polymers include nontoxicity, high stability, electric conductivity and redox potential. Previously we focussed on the effect of conductive polymers added to the organic coatings so as to complete the zinc volume concentration to 67%. The anticorrosion efficiency of the organic coatings was found to improve with increasing polyaniline phosphate (Kohl et al., 2014) or polypyrrole (Kohl & Kalendová, 2015a) concentrations. Zinc content reduction in the system, however, did not attain more than 5%. The present work focusses on systems where the organic coatings are prepared with zinc having a pigment volume concentration PVC = 50%. Zinc content reduction in the system attains up to 20%. This work examines the mechanical and anticorrosion properties of the organic coatings with reduced zinc contents. The present work was devoted to the feasibility of using of conductive polymers in the formulation of coatings with reduced zinc contents. The conductive polymers included polyaniline, polypyrrole and poly(phenylenediamine); these were synthesized and characterized by using by using physico-chemical methods.

Polyphenylenediamine as a potential corrosion inhibitor has not been paid adequate attention so far. Subsequently, organic coatings with reduced zinc contents and containing the pigments at 0.5 %, 1 % and 3 % volume concentrations were formulated. The coatings were subjected to mechanical tests and accelerated corrosion tests in order to assess their mechanical and corrosion resistance. The corrosion resistance of the organic coatings was also studied by linear polarisation. The results of the mechanical tests, accelerated corrosion tests and linear polarisation measurements indicate that the organic coating properties get affected by the conductive polymer type as well as by the pigment volume concentration. The important finding is that the use of conductive polymers in coatings with reduced zinc contents was beneficial in all cases.
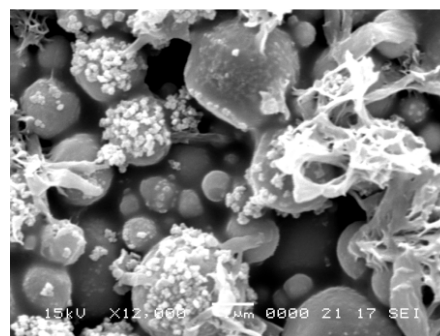
Keywords: coating, corrosion, conductive polymers, zinc

Introduction

Zinc powder as an anticorrosion pigment is used in paints in which zinc acts as sacrificed electrode. High anticorrosion efficiencies of zinc coatings are attained mainly at high pigment volume concentrations (PVC) (Kalendová, 2003; Havlík et al., 2007). A high zinc concentration in the coating provides electric contact between the zinc particles themselves and between the zinc particles and the substrate metal to be protected. 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. The system provides active protection because the electrochemical cathodic protection mechanism is resumed on any mechanical paint film damage (Havlík et al., 2007; Schaefer & Miszczyk, 2013; Shreepathi et al., 2010; Armelin at al., 2010).
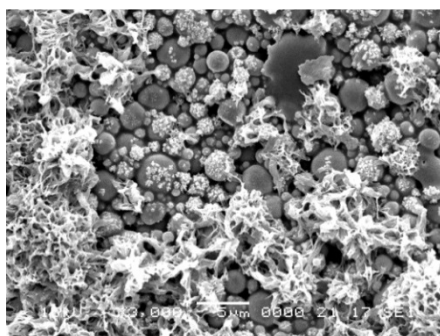
a) Magnification 3000x   b) Magnification 12000x

Fig. 1. Corrosion changes in the surface of a zinc-pigmented coating on exposure to moisture (humidity).

Although zinc coatings are considerably less toxic than chromate or lead coatings, zinc compounds are categorised as toxic to aquatic organisms. Standards covering zinc compounds and zinc coatings are more and more stringent, aiming to reduce the zinc contents of the paints. Furthermore, high-zinc paints must be made adequately fluid by adding considerable volumes of diluents (Armelin at al., 2010). Current trend is towards reducing the use of organic solvents, compelled by more and more stringent environmental legislation taking into account their toxicity and environmental pollution by evaporation (Vliet, 1998). Also, mechanical resistance of high-zinc paints is not ideal because the high degree of pigmentation detracts from the paint's mechanical parameters. A next issue, playing a role during zinc paint storage, is pigment sedimentation in the binder due to the high density of zinc metal. And since no aqueous system with zinc that is stable for a reasonable period of time can be formulated, no water-based paints with zinc can be manufactured (Kalendová, 2003; Kalendová et al., 2015). The above reasons and some others too, stimulate research aimed at reducing the zinc content of the paints. The use of conductive polymers in the paints is one of the options (Armelin et al., 2007a, 2007b).

Conductive polymers (CP) have been attracting interest during the past years. As the name suggests, they differ from conventional polymers by being electrically conductive: their conductivity is 10 orders of magnitude higher than that of conventional polymers and so they can be classed as semiconductors. It is beneficial that conductive polymers are able to change their chemical as well as physical properties, depending on their redox state which, in turn, is dependent on the environment (Schultze & Karabulut, 2005; Xie & Wang, 2016). As a next advantage, most of the conductive polymers are rather easy and inexpensive to prepare. Conductive polymers are of interest in various branches of science and technology owing to their low density as compared to metals or inorganic materials (Somboonsub et al., 2010; Király & Ronkay, 2015). Among prominent conductive polymer species are polyaniline (PANI), poly(phenylenediamine) (PPDA) and polypyrrole (PPy) (AL-Oqla et al., 2015; Balinta et al., 2014; Guimard et al., 2007). Such conductive polymers can be subjected to an oxidation-reduction reaction during which they lose or gain electrons from the surrounding environment, and this property may be made use of to enhance the anticorrosion efficiency of paints containing them (Abu-Thabit & Makhlouf 2014; Armelin et al., 2009; Akbarinezhad et al., 2010; Stejskal, 2015; Vernitskaya & Efimov 1997).

PANI is prepared by oxidative polymerisation of aniline. Closely related to aniline is phenylenediamine, which can also be oxidised to the oligomer or polymer (Kang et al., 1998;

Li et al., 2002). Phenylenediamine contains two primary amino groups, which serve to interconnect the monomeric molecules during the oxidative polymerisation reaction (Huang et al., 2006; Nascimento et al., 2010). Although PPDA is considerably less conductive than PANI, the two species have many similar properties owing to their similar structures (Stejskal, 2015). PPy, which is more conductive than either PANI or PPDA, is prepared by oxidative polymerisation of pyrrole (Blinová et al., 2007).

Experimental part

Conductive polymer synthesis

The conductive polymers: polyaniline phosphate (PANI-H_3PO_4) (Kohl & Kalendová, 2015b), polypyrrole phosphate (PPy-H_3PO_4) (Kohl & Kalendová, 2015a), and poly(p-phenylenediamine) (PPDA-H_3PO_4) (Kohl & Kalendová, 2015c) were prepared by oxidative polymerisation in dilute phosphoric acid by using ammonium peroxodisulphate as the oxidant. The syntheses are depicted in Fig. 2.
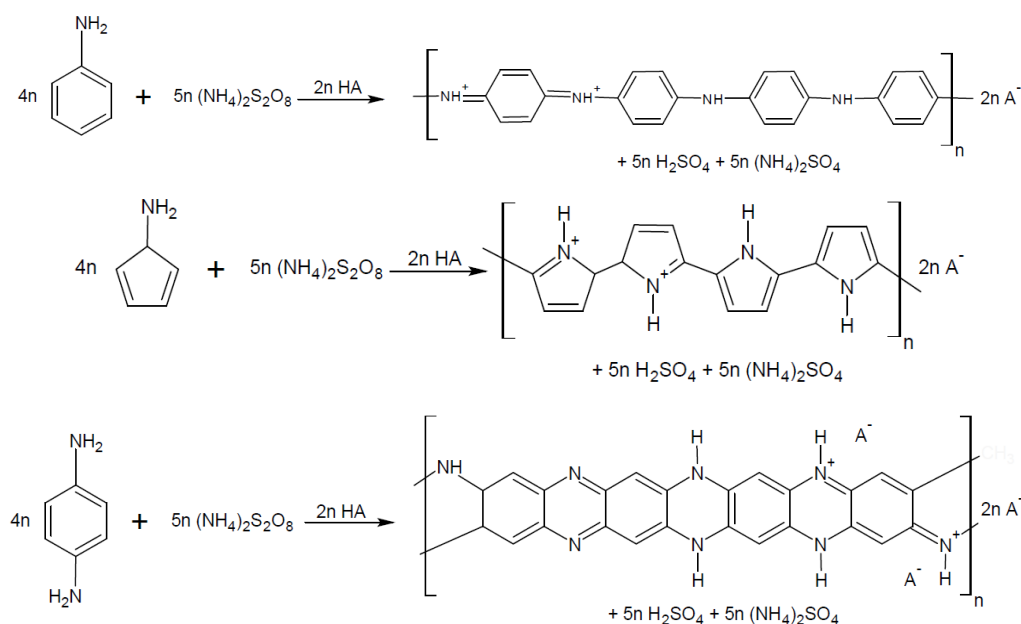

Fig. 2. Syntheses of the conductive polymers: a) PANI-H_3PO_4, b) PPy-H_3PO_4, c) PPDA-H_3PO_4.

Pigment parameter determination

Pigment density (ρ) was determined by using a Micromeritics AutoPycnometer 1320. Oil absorption (oil. abs.) was measured by the "pestle – mortar" method based on Czech

Standard CSN 67 0531 (Veselý et al., 2012). The data were used to calculate the critical pigment volume concentration (CPVC) (Kalendová & Veselý, 2009). Microphotographs of the pigment particles were obtained on a JEOL–JSM 5600 LV electron microscope (Japan) and used to deduce the pigment particle shape. Suspensions (2%) of the pigments in redistilled water were prepared and their pH and conductivity (χ) levels were measured during 21 days. The mean particle size (d_{50}) was determined on a Mastersizer 2000 (Malvern Instruments Ltd., UK).

Formulation and preparation of the organic coatings

The conductive polymers along with zinc 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 = 0.5%, 1% and 3%, and zinc at PVC = 50%. The organic coating containing zinc only at PVC = 50% served as the reference coating. The paints were prepared by using a Dissolver type system at 4000 rpm/40 minutes. Once prepared, the paints were applied to steel panels (standard S-36 low-carbon steel panels, Q-Lab Corporation) and the dry film thickness (DFT) was measured with a magnetic gauge as per 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 by using a cutting tool complying with ISO 2409 (tool for single cuts).

Mechanical properties of the paints

The paints were subjected to tests providing information on the paint film elasticity and strength. Surface hardness of the paint films was also measured, viz. with a Persoz pendulum system in accordance with ISO 1522. Adhesion of the films to the substrate was assessed on cutting a lattice into the films as per ISO 2409, by using a special cutting blade with cutting edges 2 mm apart. The impact strength of the paint films applied to steel panels was determined by letting a 1000 g weight fall onto the panels from different heights and recording the largest height (in mm) at which the film integrity remained undisturbed (ISO 6272). The paint film resistance to cupping was evaluated by measurement on an Erichsen cupping tester. The result is the steel ball indentation depth (in mm) at which the film integrity remained undisturbed, as specified in ISO 1520. The test aimed at evaluating the paint film resistance to bending consists in bending the painted panels over mandrels of different diameter and recording the largest diameter (in mm) at which the paint film integrity is disturbed, as specified in ISO 1519 (Goldschmidt & Streitberger, 2007).

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Corrosion test procedures

The steel panels coated with the organic coatings were subjected to accelerated cyclic corrosion tests in 3 different environments: in an NaCl spray atmosphere with steam condensation (ISO 9227) (Kohl & Kalendová, 2015b), to which the panels were exposed for 1152 hours; in an SO_2 atmosphere with water condensation (ISO 6988) (Kohl & Kalendová, 2015b), to which the panels were exposed for 1200 hours; and in a condenser chamber with continuous condensation (ISO 6270-1) (Kohl & Kalendová, 2015b), to which the panels were exposed for 2640 hours. The corrosion effects after completion of the tests were evaluated as specified in the above ISO standards. Blistering on the paint film surface and in the test cut was assessed by comparing with the photographs of standards included in the ASTM D 1654–92 standards. Corrosion on the metal plane was evaluated (after stripping the paint film down) by comparison with the photographs of standards included in the ASTM D 610-85 standard. Corrosion in the test cut was evaluated by measuring the distance to which corrosion propagated from the cut to its sides (Kohl & Kalendová, 2014). 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. Electron microanalysis allows information on the concentrations of the elements to be obtained based on comparison of their spectral lines in the X-ray region with those of the standards.

Furthermore, the organic coatings were subjected to the electrochemical test of linear polarisation by using a VSP-300 multichannel potentiostat/galvanostat (Bio-Logic, France). In the three-electrode setting, 1 cm^2 of the sample was submerged in a 3.5 wt.% NaCl solution and polarized across the range from -10 mV E_{OC}^{-1} to $+10$ mV E_{OC}^{-1} at and rate of 0.166 mV sec^{-1}. The spontaneous corrosion potential (E_{corr}), corrosion current density (I_{corr}), polarisation resistance (Rp) and corrosion rate (υ_{corr}) were measured when the polarisation procedure was over (Kohl & Kalendová, 2015b)

Results and discussion

Pigment specification

The basic properties of the pigments prepared are summarised in Table 1. The densities (ρ) of the three pigments – PANI-H_3PO_4, PPy-H_3PO_4 and PPDA-H_3PO_4 – lie within the range of 1.56–1.81 g cm^{-3}. This is considerably less than the density of zinc (7.14 g cm^{-3}), and so it

is reasonable to expect the pigment particles to have a markedly lower tendency to settle to the bottom of the container with the paint than the zinc powder in a zinc-containing paint.

The oil absorption (oil abs) capacity of the pigments was also determined because this parameter provides information on the pigment's specific surface area, particle size distribution and porosity. The densities and oil absorptions served to calculate the critical volume concentration (CPVC) for each pigment. Knowledge of the CPVC is a prerequisite for proper formulation of a pigmented organic coating (Kalendová & Veselý, 2009).

Pigment suspensions (2 % w/w) in redistilled water whose pH was 6.50±0.01 and conductivity (χ) 1.5 μS cm^{-1} were prepared and their pH and conductivities were measured in 21 days. During that time, the acidity and conductivity of the suspensions increased appreciably (ultimate pH 1.75–2.05, conductivity 3.1–9.2 mS cm^{-1}). The highest acidity and conductivity were found for the suspension with PPy. For polyaniline salts, the acidity and conductivity increase is explained in terms of polyaniline salt deprotonation and release of the acid used for protonation (Kalendová et al., 2008). It is the released acid that is responsible for the higher suspension acidity and conductivity. Analogous behaviour can also be expected for the suspensions with the pigments $PANI\text{-}H_3PO_4$ and $PPDA\text{-}H_3PO_4$. The suspension with zinc powder did not exhibit any marked changes in the pH or conductivity levels.

The mean particle size (d_{50}) of the pigments lay within the range of 8.20–8.65 μm, that of the zinc particles was 5.20 μm. The microphotographs from which the shapes and surface structures were studied are shown in Fig. 2. The microphotographs demonstrate that the zinc particles were spherical whereas the pigments possessed an isometric shape.

Table 1. Characteristics of the pigments

Pigment	ρ/g cm^{-3}	oil abs/g 100g^{-1}	CPVC/%	pH^{21}	χ^{21}/mS cm^{-1}	d_{50}/μm
Zn	7.14	6.4	67	6.42±0.01	7.1×10^{-3}±0.5%	5.20±0.1
$PANI\text{-}H_3PO_4$	1.56	170.9	26	1.81±0.01	8.3±0.5%	8.20±0.1
$PPy\text{-}H_3PO_4$	1.81	188.5	21	1.75±0.01	9.2±0.5%	8.65±0.1
$PPDA\text{-}H_3PO_4$	1.69	142.2	29	2.05±0.01	3.1±0.5%	8.45±0.1

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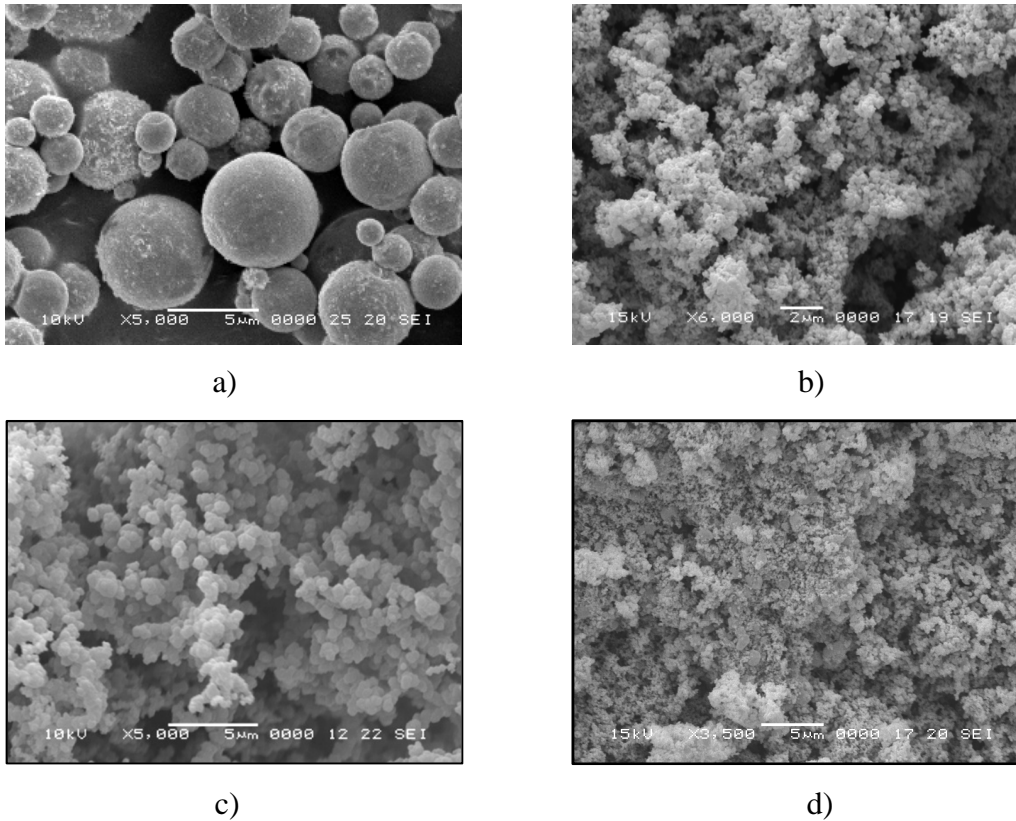<tr><td>c)</td><td>d)</td></tr>
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Fig. 2. Scanning electron micrographs: a) zinc metal; b) PANI-H_3PO_4; c) PPy-H_3PO_4; d) PPDA-H_3PO_4.

Assessment of the physico-mechanical tests

The resulting relative surface hardness data of the organic coatings are listed in Table 2, the mechanical test results are summarised in Table 3. The mechanical tests provided information on the paint film elasticity, adhesion and strength and served to judge if the use of a specific pigment in the paint was favorable or unfavorable (Kalendová et al., 2010).

Relative surface hardness of the protective organic coatings

The relative surface hardness values of the paint films was measured during 90 days and were found to increase during that time (Table 2). The final relative surface hardness was highest for the paint with zinc. The addition of the pigments to the organic coatings brought about a negligible relative surface hardness reduction, similar for all of the pigments used.

Table 2. Relative surface hardness of protective organic coatings containing PANI-H_3PO_4, PPy-H_3PO_4, PPDA-H_3PO_4 pigments with PVC 0, 0.5, 1, 3 % together with zinc metal (PVC/CPVC = 0.50), DFT = 80±10 µm

Sample	PVC/%	Relative surface hardness/%								
		Day of measurement								
		1	2	4	7	14	21	42	60	90
PANI-H$_3$PO$_4$	0	8	9	10	13	20	26	35	40	45
	0.5	6	7	8	11	17	22	31	38	43
	1	7	8	9	13	20	26	35	39	44
	3	7	8	9	12	19	24	31	35	39
PPy-H$_3$PO$_4$	0	8	9	10	13	20	26	35	40	45
	0.5	7	9	10	13	19	24	33	40	44
	1	7	8	9	12	17	22	32	38	42
	3	7	8	9	11	16	21	31	35	39
PPDA-H$_3$PO$_4$	0	8	9	10	13	20	26	35	40	45
	0.5	8	9	10	15	20	25	33	36	40
	1	6	7	8	13	19	24	33	36	40
	3	7	8	9	14	19	24	32	35	39

Results of the mechanical properties of the protective organic coatings

Four mechanical test types were used to assess the paint films' mechanical properties. The results are presented in Table 3. In the adhesion (cross-cut) test, the lattice-pattern film surface remained intact for all the films with the pigments, while the surface of the film with zinc powder was damaged to ≤ 5 %. In the bending test, all the films remained intact even if the mandrel diameter was mere 4 mm. (Lower diameter mandrels were not used.) The films also remained undamaged in the free drop test where a 1 kg weight was dropped from 1 m height. The cupping test provided different results for the different paint films: the organic coating with zinc was poorest in this test, the coatings with PANI-H$_3$PO$_4$ and PPDA-H$_3$PO$_4$ provided good results, similar at any of the PVC levels applied, and the best results were obtained with the coating containing the pigment PPy-H$_3$PO$_4$. For all of the pigments – PANI-H$_3$PO$_4$, PPy-H$_3$PO$_4$ and PPDA-H$_3$PO$_4$ – resistance to this test increased with increasing PVC. Hence, pigmentation of the zinc coatings with these pigments was favorable as far as the mechanical properties are concerned.

Table 3. Mechanical properties of the organic coatings containing PANI-H$_3$PO$_4$, PPy-H$_3$PO$_4$, PPDA-H$_3$PO$_4$ pigments with PVC 0, 0.5, 1, 3 % together with zinc metal (PVC/CPVC = 0.50), DFT = 80±10 µm

Sample	PVC/%	Adhesion test/dg	Bend test/mm	Impact test/cm	Cupping test/mm

	0	1	< 4	> 100	4.32
PANI-H$_3$PO$_4$	0.5	0	< 4	> 100	4.98
	1	0	< 4	> 100	5.24
	3	0	< 4	> 100	5.68
	0	1	< 4	> 100	4.32
PPy-H$_3$PO$_4$	0.5	0	< 4	> 100	5.24
	1	0	< 4	> 100	5.55
	3	0	< 4	> 100	6.82
	0	1	< 4	> 100	4.32
PPDA-H$_3$PO$_4$	0.5	0	< 4	> 100	4.89
	1	0	< 4	> 100	5.17
	3	0	< 4	> 100	5.81

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 steel panels coated with the paints were exposed to the salt mist atmosphere for 1152 hours and the occurrence of blisters on the film surface and in the surroundings of an artificial cut in the film was evaluated. Subsequently, the paint films were removed and corrosion on the bare steel panels was examined. The results are listed in Table 4.

No blisters were found on the surface of any of the paint films. The occurrence of blisters near the cut was similar for all of the paint films and was classed as MD. The blister size, however, was different for the different pigment concentrations: it was 4 for the paint film with zinc and for the paint films with the pigments at PVC = 0.1 %. The blisters were classed as 6MD for all of the paint films with the conductive polymers at PVC = 1 % and 3 %. The paint with PANI-H$_3$PO$_4$ at PVC = 3% was an exception where the blisters were classed as 8MD.

Occurrence of blisters near the cut has direct impacts on corrosion near the cut. Corrosion reached a distance of 1.5−2 mm from the cut for the paint with zinc and 1−1.5 mm for the remaining paints. The shortest corrosion distance, 0.5−1 mm, was observed for the paint with PANI-H$_3$PO$_4$ at PVC = 3 %. Fig. 3 shows photographs of the corrosion of the paint film cuts following 240 hours exposure in the salt mist atmosphere. The corrosion was most pronounced for the paint with zinc and less pronounced for the paints with the conductive

polymers at PVC = 3 %. The extent of corrosion was lowest for the paint with PANI-H_3PO_4 at PVC = 3 %.

The last parameter examined was corrosion on the steel panel surface. The corrosion was most extensive, viz. 0.3 %, on the panel initially coated with the paint with zinc, and considerably less extensive, viz. from 0.1 % down to 0.03 %, on most of the remaining panels. And no corrosion at all was found on the panel initially coated with the paint with PANI-H_3PO_4 at PVC = 3 %.

Table 4. Results of the corrosion tests performed in a salt mist chamber for coatings after 1152 hours of exposure, DFT = 85±10 μm

Sample	PVC/%	Blistering	Corrosion	
		In a cut/dg	In a cut/mm	Metal base/%
PANI-H_3PO_4	0	4MD	1.5–2	0.3
	0.5	4MD	1–1.5	0.1
	1	6MD	1–1.5	0.03
	3	8MD	0.5–1	0
PPy-H_3PO_4	0	4MD	1.5–2	0.3
	0.5	4MD	1–1.5	0.1
	1	6MD	1–1.5	0.03
	3	6MD	1–1.5	0.03
PPDA-H_3PO_4	0	4MD	1.5–2	0.3
	0.5	4MD	1–1.5	0.1
	1	6MD	1–1.5	0.03
	3	6MD	1–1.5	0.03

a)   b)
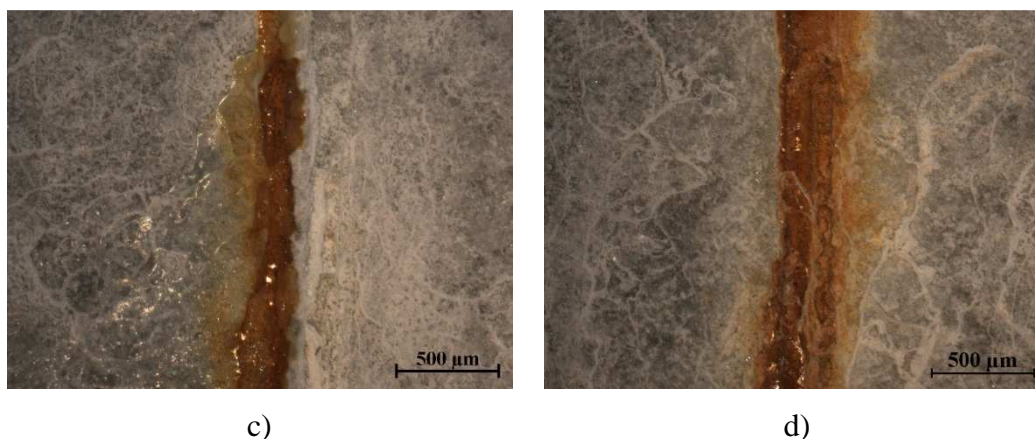
| c) | d) |

Fig. 3. Photographs of corrosion in the cuts in the paints following 240 hours' exposure in the salt mist atmosphere. Organic coating containing: a) Zn; b) PANI-H_3PO_4 at PVC = 3 %; c) PPy-H_3PO_4 at PVC = 3 %; d) PPDA-H_3PO_4 at PVC = 3 %.

Accelerated corrosion tests in atmosphere with SO_2

The steel panels coated with the paints were exposed to the atmosphere with SO_2 for 1200 hours and the occurrence of blisters on the film surface and in the surroundings of an artificial cut in the film was evaluated. Subsequently, the paint films were removed and corrosion on the bare steel panels was examined. The results are listed in Table 5. No blisters were found on the surface of any of the paint films or in the area surrounding the test cut. Corrosion on the panel near the cut reached a distance of 0.5–1 mm from the cut for the majority of paints, except for the paints with the conductive polymers at PVC = 3 %, where the distance was only 0–0.5 mm. Photographs of the cuts in the paint films following 240 hours' exposure to the atmosphere with SO_2 are shown in Fig. 4. The photographs demonstrate that the paint with zinc was inferior to the paints with the conductive polymers at PVC = 3 %. The last parameter examined was corrosion on the steel panel surface. The corrosion was most extensive, viz. 0.3 %, on the panel initially coated with the purely zinc paint, considerably less extensive, viz. about. 0.1 %, on the majority of the remaining panels, and lowest, 0.03 %, on the panels initially coated with the paints containing the conductive polymers at PVC = 3 %.

Table 5. Results of the corrosion test performed in a condenser chamber filled with the atmosphere containing SO_2. The coated panels were exposed for 1200 hours, DFT = 85±10 µm

Sample	PVC/%	Corrosion	
		In a cut/mm	Metal base/%
PANI-H_3PO_4	0	0.5–1	0.3
	0.5	0.5–1	0.1

	1	0.5–1	0.1
	3	0–0.5	0.03
	0	0.5–1	0.3
PPy-H$_3$PO$_4$	0.5	0.5–1	0.1
	1	0.5–1	0.1
	3	0–0.5	0.03
	0	0.5–1	0.3
PPDA-H$_3$PO$_4$	0.5	0.5–1	0.1
	1	0.5–1	0.1
	3	0–0.5	0.03

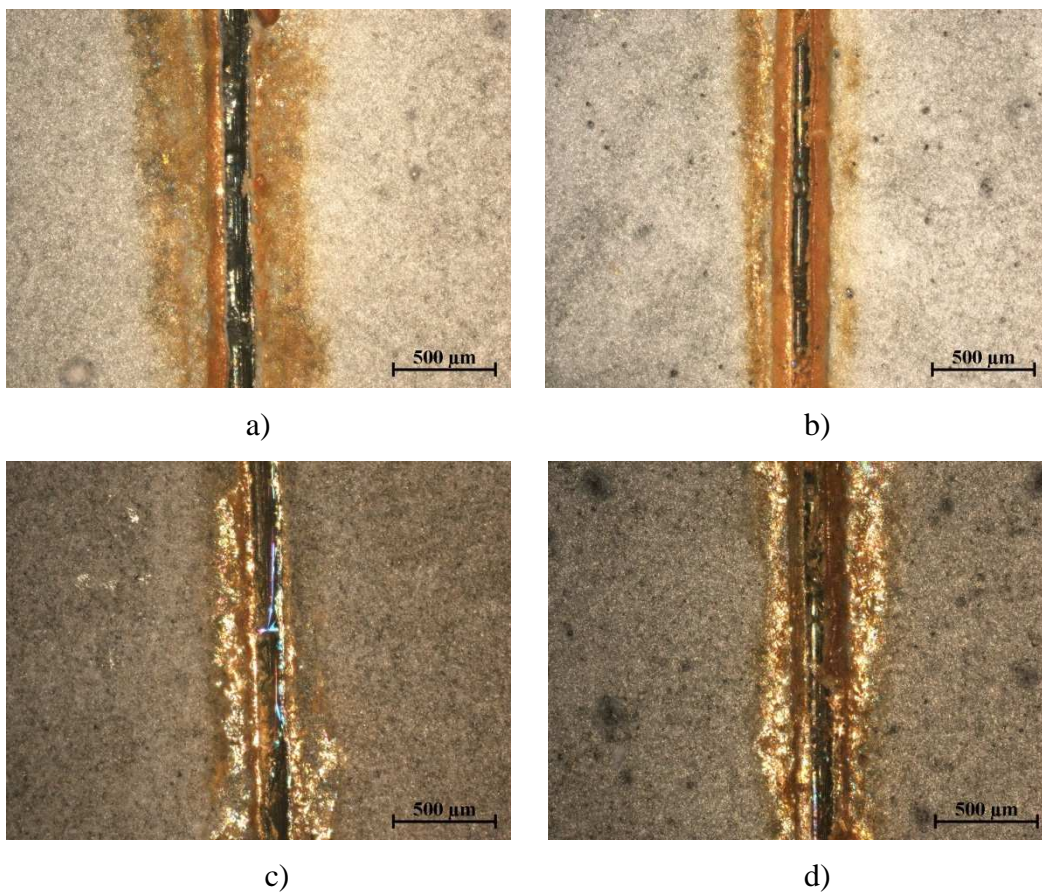**Fig. 4.** Corrosion in the cut through the paint films after 240 hours' exposure to the atmosphere with SO$_2$. Paint containing: a) Zn; b) PANI-H$_3$PO$_4$ at PVC = 3 %; c) PPy-H$_3$PO$_4$ at PVC = 3 %; d) PPDA-H$_3$PO$_4$ at PVC = 3 %.

Accelerated corrosion tests in a chamber with continuous water condensation

The steel panels coated with the paints were exposed in the chamber with continuous water condensation for 2460 hours and the occurrence of blisters on the film surface and in the surroundings of the test cut in the film was evaluated. Subsequently, the paint films were

removed and corrosion on the bare steel panels was examined. The results are listed in Table 6. No blisters were found on the paint film surface after this accelerated corrosion test. Blisters in the cut were classed 8M–8MD for all of the paints. Occurrence of blisters near the cut has direct impacts on corrosion near the cut, which propagated to a distance of 0–0.5 mm on all of the panels. Corrosion on the steel panel surface amounted to 0.03–0.01 %.

Table 6. Results of the corrosion test performed in a condenser chamber with continual condensation for coatings after 2640 hours of exposure, DFT = 85±10 μm

Sample	PVC/%	Blistering	Corrosion	
		In a cut/dg	In a cut/mm	Metal base/%
PANI-H$_3$PO$_4$	0	8MD	0–0.5	0.03
	0.5	8MD	0–0.5	0.01
	1	8M	0–0.5	0.01
	3	8M	0–0.5	0.01
PPy-H$_3$PO$_4$	0	8MD	0–0.5	0.03
	0.5	8MD	0–0.5	0.01
	1	8M	0–0.5	0.01
	3	8M	0–0.5	0.01
PPDA-H$_3$PO$_4$	0	8MD	0–0.5	0.03
	0.5	8MD	0–0.5	0.01
	1	8M	0–0.5	0.01
	3	8M	0–0.5	0.01

***Results of the electrochemical method of linear polarisation***

The results of the electrochemical method of linear polarisation are included in Table 7. The target values included polarisation resistance and corrosion rate measured with the organic coatings studied, i. e. parameters providing information on the coating resistance to corrosion. The zinc paint provided polarisation resistance 4×10^6 Ω while all of the paints with the conductive polymers exhibited higher polarisation resistance levels. Polarisation resistance invariably increased with increasing PVC. The highest polarisation resistance, 4×10^7 Ω (hence, one order of magnitude higher than for the zinc paint), was observed with the paint containing PANI-H$_3$PO$_4$ at PVC = 3 %. The corrosion rate was 8×10^{-5} mm year^{-1} for the zinc paint, was lower for all of the paints with the conductive polymers, and decreased with increasing conductive polymer PVC. The lowest corrosion rate, 4×10^{-6} mm year^{-1}, was observed with the paint containing PANI-H$_3$PO$_4$ at PVC = 3 %.

Table 7. Results of the electronic measurement of linear polarization of the prepared coatings in 3.5 wt. % NaCl, DFT = 75±10 μm

Sample	PVC/%	E_{corr}/mV	I_{corr}/μA	β_a/mV	β_c/mV	R_p/Ω	$\upsilon_{corr.}$/mm year^{-1}
PANI-H$_3$PO$_4$	0	−920	8×10^{-1}	21	22	4×10^{6}	8×10^{-5}
	0.5	−684	4×10^{-2}	38	32	2×10^{7}	6×10^{-6}
	1	−761	4×10^{-2}	33	32	3×10^{7}	5×10^{-6}
	3	−854	3×10^{-2}	12	17	4×10^{7}	4×10^{-6}
PPy-H$_3$PO$_4$	0	−920	8×10^{-1}	21	20	4×10^{6}	8×10^{-5}
	0.5	−928	7×10^{-1}	20	21	6×10^{6}	8×10^{-5}
	1	−759	1×10^{-2}	37	32	2×10^{7}	6×10^{-6}
	3	−739	1×10^{-2}	42	42	2×10^{7}	5×10^{-6}
PPDA-H$_3$PO$_4$	0	−920	8×10^{-1}	21	20	4×10^{6}	8×10^{-5}
	0.5	−851	5×10^{-1}	19	17	5×10^{6}	4×10^{-5}
	1	−848	3×10^{-1}	17	17	8×10^{6}	2×10^{-5}
	3	−808	1×10^{-1}	26	28	9×10^{6}	1×10^{-5}

Organic coating composition measurements

The composition of the organic coatings following 240 hours' exposure to the salt spray environment was examined by scanning electron microscopy and energy-dispersive X-ray spectroscopy. Sites far from the test cut (Fig. 5) as well as sites close to the test cut (Fig. 6) were examined.
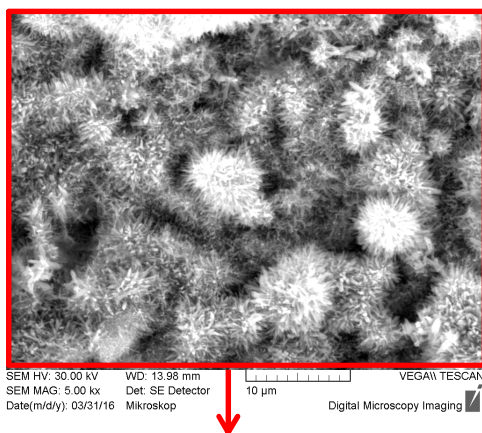
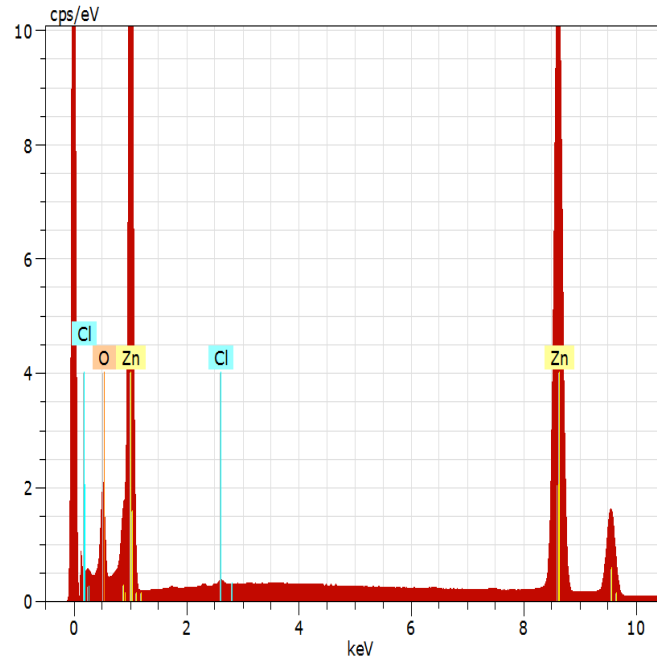| Element	C norm./ wt. %	C error/ wt. %
Zn	80.31	2.26
O	19.57	2.52
Cl	0.12	0.03

Fig. 5. Scanning electron micrographs and energy-dispersive X-ray analysis results of an organic coating area containing zinc (PVC = 50 %).

X-Ray diffraction analysis (XRD) of the organic coatings before exposure to the salt spray environment contained zinc metal only. The energy-dispersive X-ray spectroscopy results indicate that the cathodic protection mechanism sealed the pores in the coating with the zinc corrosion products (white corrosion) (Kalendová, 2003). This deduction is corroborated by XRD. The zinc corrosion products reduced the organic coating's conductivity, whereupon the corrosion protection effect transformed from the electrochemical mechanism to the barrier mechanism. No substrate steel corrosion products were detected in the organic coating after 240 hours of exposure, which attests to a high corrosion protection provided by the coating. Corrosion observed on the steel panel surface after 1152 hours of exposure to the salt spray atmosphere (Table 4) was found to diminish with increasing PVC.
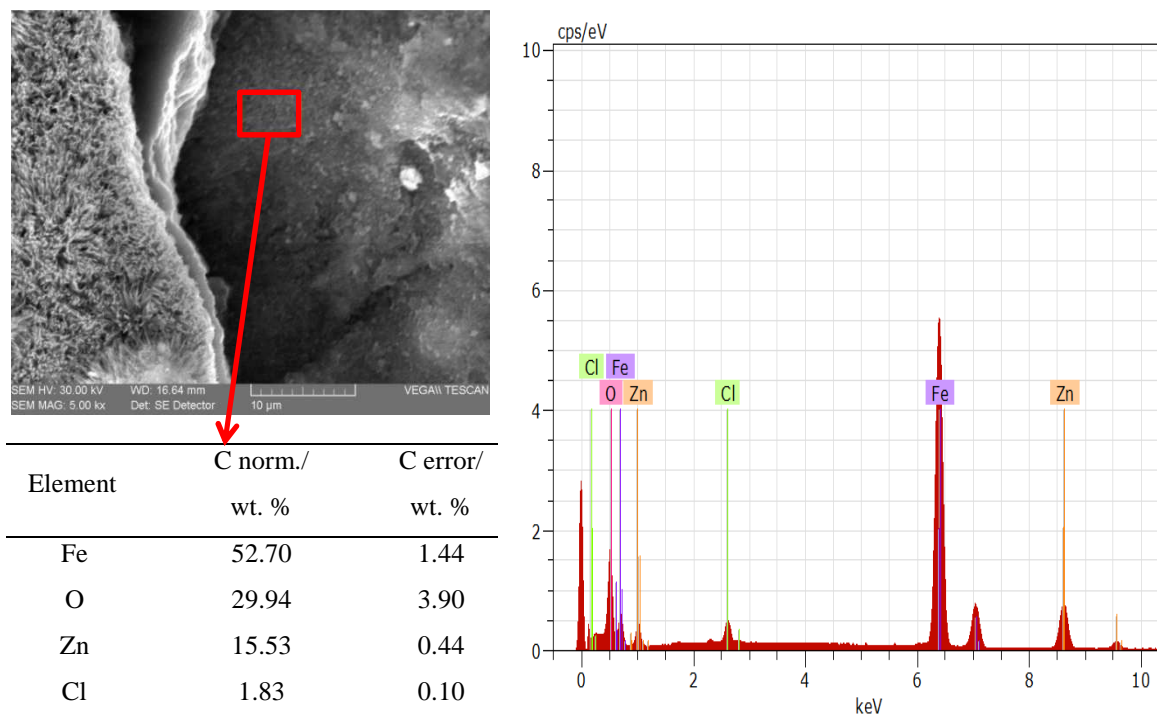
Element	C norm./ wt. %	C error/ wt. %
Fe	52.70	1.44
O	29.94	3.90
Zn	15.53	0.44
Cl	1.83	0.10

Fig. 6. Scanning electron micrographs and energy-dispersive X-ray analysis results of the test cut area of an organic coating containing zinc (PVC = 50 %).

The energy-dispersive spectroscopy results indicate that the test cut was partly sealed by the zinc corrosion products (white corrosion) due to the cathodic protection mechanism (Kalendová, 2003). The presence of iron corrosion products, however, suggests that the sealing effect was not rapid enough. As evidenced by photographs of corrosion in the test cut after 240 hours of exposure to the salt spray atmosphere (Fig. 3) as well as by the results of corrosion in the test cut after 1152 hours of exposure to the same atmosphere (Table 4), corrosion in the test cut diminishes with increasing PVC in the organic coating.

Summary of the results of the physico–mechanical tests and accelerated corrosion tests

The results of the mechanical tests demonstrate that the use of conductive polymers as the pigments was beneficial – the overall mechanical resistance was thereby improved. This effect was observed at any of the PVC values used and increased with increasing conductive polymer PVC.

The use of the conductive polymers was also beneficial in the accelerated corrosion test in the salt mist atmosphere. The favorable effect occurred at any PVC. The best results were observed with the pigment PANI-H_3PO_4 at PVC = 3 %, where all the corrosion phenomena investigated were lowest.

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The accelerated corrosion test in the atmosphere with SO_2 also gave evidence that the use conductive polymers (at any of the PVC levels applied) is beneficial to the paint's anticorrosion efficiency. This effect was similar for all of the conductive polymers added. The use of conductive polymers improved the anticorrosion properties of the paints very slightly in the accelerated corrosion test in the chamber with constant water condensation, irrespective of the conductive polymer type or PVC.

The favorable effect of pigmentation with the conductive polymers (at any PVC) was also borne out by the results of the electrochemical linear polarisation method. The best results – highest polarisation resistance and lowest corrosion rate – were obtained with the paint containing the pigment PANI-H_3PO_4 at PVC = 3 %. These results are in accordance with the results of the accelerated corrosion test in the salt mist atmosphere.

Role of the conductive polymers in the zinc-containing protective coatings

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 conductive polymers, specifically PANI-H_3PO_4, PPy-H_3PO_4 and PPDA-H_3PO_4, at volume concentrations 0.5 %, 1 % and 3 %. The volume concentration of zinc in the organic coatings was 50 %. The conductive polymers used in this work served as auxiliary anticorrosion ingredients that also improved adhesion and elasticity of the organic coating. The improved adhesion and elasticity were contributed to by the anions derived from phosphoric acid, making up for the positive charge on the conductive polymer, increasing paint film coating adhesion to the steel surface. One of the functions of the conductive polymer 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. This zinc oxide then creates a layer protecting the substrate metal from contact with the corrosive environment. Oxidation from Zn^0 to Zn^{2+} is associated with the release of two electrons, which can migrate through the paint film (Armelin et al., 2008, 2010). Conductive polymers in the paint have the capacity to capture the electrons (Nguyen 2004). Specifically, when using the doped polyaniline form (PANI-ES), the electrons are captured and the conductive polyaniline is transformed to the neutral form, called polyaniline base (PANI-EB). If the paint film is exposed to a corrosive environment, e.g. with chloride ions, the Cl^- ions, readily passing through the ZnO crystal

structure, are captured by the polyaniline base (PANI-EB) and used for PANI-EB transformation to the polyaniline salt (PANI-ES). This 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) (Armelin et al., 2008, 2010). A similar protection mechanism is assumed for other conductive polymers as well. This protective mechanism is shown schematically in Fig. 7b.
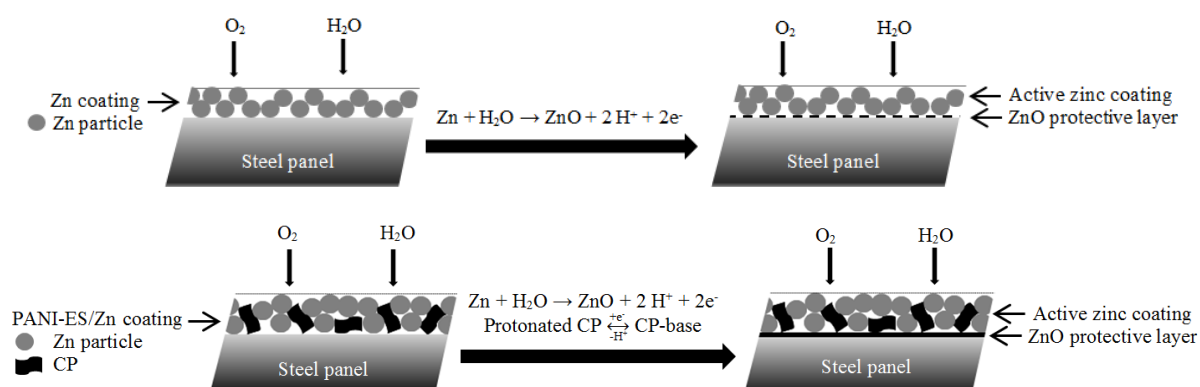

Fig. 7. Schematic representation of the protective mechanism: a) Zn coating; b) CP/Zn coating.

Conclusion

This work was devoted to the examination of the mechanical and anticorrosion properties of paints with conductive polymers and a reduced zinc content. The mechanical tests gave evidence that the use conductive polymers in the formulation of paints with a reduced zinc content improves the paint films' mechanical resistance. The particular conductive polymer type played a minor role in this compared to the pigment volume concentration: a higher PVC was accompanied by better mechanical properties of the coating. As to the anticorrosion protection provided by the paint film, this is affected both by the conductive polymer type and by its volume concentration in the paint. Generally, increasing PVC of any of the conductive polymer is accompanied by improved corrosion protection provided by the paint. Although each of the conductive polymers improved the anticorrosion efficiency of the paint, the best results were obtained with PANI-H_3PO_4 at PVC = 3 %.

Symbols

ASTM   American Standard for Testing and Materials

CP   conductive polymers

CP-base	conductive polymers – base	
CPVC	critical pigment volume concentration	%
CSN	czech state norm	
d_{50}	mean particle size	
DFT	dry film thickness	
e^-	electron	
e.g.	exempli gratia	
E_{corr}	spontaneous corrosion potential	mV
EDX	Energy-Dispersive X-ray spectroscopy	
E_{OC}	potential value reached at the end of the previous open circuit period	mV
Fe	iron	
H	hydrogen	
i.e.	id est	
I_{corr}	current density	mV
ISE	ion-selective electrode	
ISO	International Organization for Standardization	
norm	normed	
oil abs	oil absorption	g $100g^{-1}$
PANI	polyaniline	
PANI-EB	polyaniline base	
PANI-ES	polyaniline salt	
PANI-H_3PO_4	polyaniline phosphate	
PPDA	poly(phenylenediamine)	
PPDA-H_3PO_4	poly(p-phenylenediamine) phosphate	
PPy	polypyrrole	
PPy-H_3PO_4	polypyrrole phosphate	
PVC	pigment volume concentration	%
R_p	polarisation resistance	Ω
SEM	Scanning Electron Microscope	

Greek Letters

ρ	density	g cm^{-3}
υ_{corr}	corrosion rate	mm $year^{-1}$
χ	conductivity	mS cm^{-1}

Subscripts

corr   corrosion

oc   open circuit period

p   polarization

21   21st Day

Reference

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