

Effect of concentration of zinc-powder in epoxy-ester based anticorrosive coatings

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The present work is directed to study the effect of zinc powder concentration on anticorrosive efficiency of epoxy ester resin-based anticorrosive coatings. A high performance of zinc coating for metal protection is of vital importance depending on the concentration of zinc incorporated into coating formulation. Zinc pigment gives protection against corrosion by cathodic protection and barrier protection mechanism; however, it is necessary to keep adequate dosage of zinc. A lower dosage of zinc is insufficient to obtain sufficient cathodic protection while much higher concentration leads to the pores in the film which may influence corrosion. Therefore, this study was focused on the development of highly effective zinc coatings for excellent anticorrosion protection, as well as mechanical performance, when using standardized tests on corrosion, mechanical and chemical properties.

Keywords: Anticorrosive pigment; Zinc dust; Corrosion; Protective organic coating

Introduction

Metals and alloys are the basis of the engineering sector. Due to their high tensile strength, ease of availability, low cost, and other desirable properties, metals — and especially mild steels — are extensively utilized in various areas of industry, including the food, power generating, petroleum, chemical and electrochemical branches [1,2]. However, mild steel surfaces exposed to more aggressive environments are prone to corrosion and one of the most frequent reasons for the failure of metal components is a damage due to corrosion. Major economic and

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industrial losses can result from the absence of mitigation measures or techniques for such electrochemical processes [3,4]. The economic effect of corrosion is underestimated and, for example and according to a report in 2001, the cost estimated due to corrosion in United States has been around \$278 billion dollars annually. Recently, in 2016, the annual cost in the U.S. was estimated to be over \$1.1 trillion [5]. Despite the impossibility of completely eliminating the corrosion processes, various protective methods are employed in a variety of industries, such as construction of pipelines or marine machinery. Most preferable protections against corrosion are hot dip galvanization, cathodic protection, and coatings. The latter for coating of the basic material is one of the best ways of how to stop corrosion. By creating a barrier between the metal and its surroundings and/or by inserting a corrosion inhibitor, the resultant coatings can provide effective protection for a substrate. Such a coating must be uniform, well adherent, pore-free, impermeable, and hard in order to provide appropriate corrosion protection [6,7]. Liquid medium in which coatings are made is known as binder/resins. These materials are considered to be a core of coatings, when the performance of resins is based on their "chemistry", i.e., chemical properties.

Different chemistry of resins used in industrial coatings for excellent corrosion protection offer the products like Epoxy 1K, Epoxy 2K, Polyaspartic, Polyurethane 1K, Polyurethane 2K, silicone-based and chlorinated rubber binders. Selection of a resin for coatings depends on various factors, such as application area, environment character, substrate, performance, overcoats application, drying methods and conditions. The most used epoxy binder is a kind of polymeric matrix with a number of distinctive qualities, such as excellent thermal stability and low thermal expansion coefficient. These favorable features, along with epoxy's strong interface adhesion to diverse metal substrates, have motivated to use epoxy as an anti-corrosion coating on mild steel substrates [8].

Film-forming materials that are also resistant at high pH must be chosen for zinc-containing contact-type materials because the reactions of the zinc-steel corrosion cell close to the steel surface are accompanied by an increasing pH in water that has diffused through the coating. Due to the impact of the zinc particles with own alkaline reaction products, the binder must not produce soap. Possible binders include epoxy resins, epoxy-ester resins, polyurethanes, silicates, and ethyl silicates [8,9].

High-pigment coating materials suffer from issues that arise during production, application, and storage, which reduces their usefulness. During storage, zinc particles tend to settle because of their high specific weight (7 g/cm^3). Such systems' rheology is particularly unfavorable for the common application techniques used to cover metal surfaces since the coating ingredients are difficult to employ and have poor flow characteristics. Some specific requirements are placed on zinc-pigmented coating materials and rheological additives are required for stabilizing the coating substance [9].

The inability of aqueous environments to generate long-term stable systems of the conventional zinc type suggests that water-based coating materials are less used. Solvent based Epoxy anticorrosive coatings rich in zinc offer a very high anticorrosive effectiveness. By year of 2026, it is predicted that the global market for zinc-rich anticorrosive coatings will increase to 9.5 billion USD. The zinc metal particles have presented an anticorrosive pigment frequently used for the coating compositions destined to heavy corrosion protection of metals already for many years [10–12]. The action mechanism of zinc has always been explained based on the electrochemical theory as a cathodic protection [13], when a continual electrical connection inside the coating is required to be capable of providing such a kind of protection.

To ensure that zinc particles come into touch with one another and form a seepage pathway for corrosive media, the ratio of pigment volume concentration (PVC) to critical pigment volume concentration (CPVC) is always greater than 1, when giving rise to zinc-rich primers (ZRP). Based on this, it is essential to have a zinc content of 60 wt. % or more (dry film weight \geq 90 wt. %). Currently, there are opinions that the effective action of this pigment takes place at a concentration between 94 to 96 %, related to the coating composition [14]. Even with 90 wt. % zinc concentration, long-term and sustainable protection cannot be assured. This is due to various disadvantages of using high concentration of zinc pigments such as increased permeability of film, toxicity of zinc and higher cost of paints. In addition, as zinc corrosion products are formed, the electrical connection between the zinc particles or between metal substrate and zinc particles steadily weakens, when the cathodic protection can be totally lost. And really low volume concentration of the binder makes such a system hardly to be produced. A further obstacle is logically because of rather poor physico-mechanical properties of such coating compositions. Therefore, it becomes important to study the concentration of zinc by keeping in mind improvement in both anticorrosive and physio-mechanical properties of zinc rich coatings [15–19].

Figure 1 depicts SEM images of the surface of coatings with different zinc PVC. It is quite evident from images that at a low PVC (30–40), there is continuous film of binder and particles of zinc pigment are separated from each other. PVC (50–60) shows that zinc particles in the film are closely attached and in tight contact with the film of binder. As PVC (60–70) approaches PVC = CPVC and more than that in which the film possesses pores and voids due to less binder and excess zinc pigment forming agglomerates.

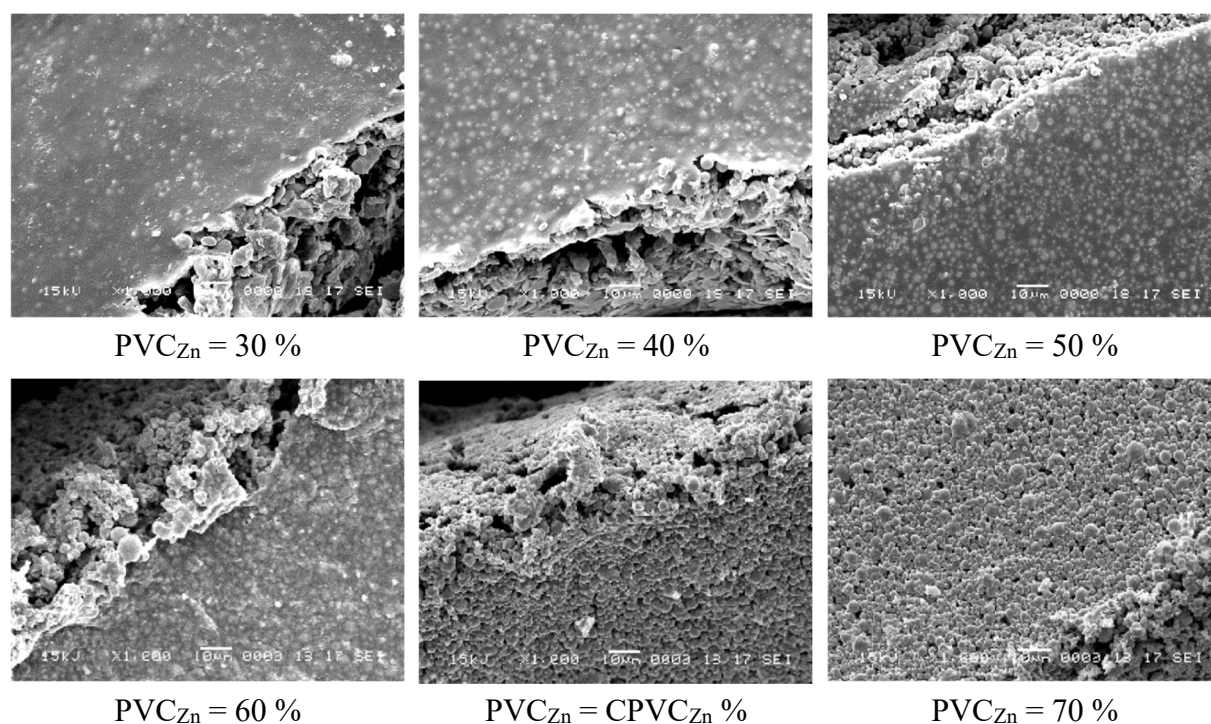


Fig. 1 Coatings containing zinc at different PVC

Experimental part

Characterization of the pigments studied

Morphology of the zinc metal particles was mapped by electron microscopy (LYRA 3, Tescan, Brno, Czech Republic), when the resulting micrographs reflected the shape and the surface structures. The critical volume concentration of the pigments (CPVC) was calculated from the density determined using Autopycnometer Micromeritics 1340 and oil absorption was measured according to the Czech State Standard (CSN) 67 0531 using the "pestle – mortar" method.

Formulation and preparation of the organic coatings

The study of zinc concentration in the coatings requires to select a suitable binder in which the metal is sufficiently protected. Such a binder is epoxy ester resin desiccating due to an oxidative process induced by atmospheric oxygen. Using this binder, the model coating compositions were prepared, in which the zinc content had been varied as PVC_{Zn} 0–45 %. The formulations of the organic coatings studied are shown in Table 1. A series of coating compositions surveyed was studied with respect to corrosion and physicomechanical tests. The respective coating compositions were prepared by dispersing in a dissolver unit operated at 2000 rpm for 30 min.

Table 1 Formulation of organic coatings containing zinc (PVC = 0–45 %) and CaCO₃ (PVC/CPVC = konst. = 0.6)

PVC _{Zn} [%]	Zn [wt. %]	CaCO ₃ [wt. %]	Epoxy ester resin [wt. %]
0	–	54.3	45.7
1	1.3	53.3	45.4
3	3.8	51.5	44.7
5	9.6	47.4	43.0
10	19.0	40.6	40.4
15	28.3	34.0	37.7
20	37.3	27.5	35.2
25	46.2	21.0	32.7
30	55.0	14.8	30.2
35	63.5	8.7	27.8
40	72.0	3.0	25.0
45	77.5	–	22.5

For corrosion tests, the coating compositions were spread on the steel panels (type S46, low-carbon steel panels, Q-Lab Corporation, ISO Panel Specifications: 1514 section 3.5.4). The experimental coatings were prepared under standard conditions (at a temperature of 22 °C and a relative humidity of 55 %) using a box-type applicator when the resulting thickness of the dry coating film was set to a value of 90–100 µm. Dry film thickness (DFT) of the prepared coating films was measured by magnetic gauge (Byko-test 8500 premium Fe/NFe, BYK Additives & Instruments, Wesel, Germany) according to ISO 2808. All the corrosion tests were performed in parallel and three times. After 30 days of conditioning at a temperature of 22 °C and a relative humidity of 55 %, a vertical cut in the organic coating was made (to study it by accelerated cyclical corrosion tests) when being 100 mm long and 1 mm wide and corresponding to three CSN EN ISO 12944-6. For this, a cutting tool was used (Elcometer 1538, DIN scratching tool with 1 mm Cutter, Manchester, UK) complying with ISO 2409. Subsequently, cyclic corrosion tests could be started.

Corrosion test of coatings

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

In a testing chamber (SKB 400 A-TR-TOUCH, Gebr. Liebisch GmbH & Co. KG, Bielefeld, Germany), test was performed in 12h cycles divided into three parts: (i) 10 h of exposure to a mist of 5% NaCl at a temperature of 35 °C; (ii) 1 h of exposure

at a temperature of 23 °C; and (iii) 1 h of humidity condensation at a temperature of 40 °C. The samples exposed to these conditions were evaluated after 120 h, 240 h, 480 h, and 960 h.

Evaluation of the corrosion tests

The test panels after the exposure were evaluated from the point of view of the formation of osmotic blisters (ASTM D 714-87), the degree of subsurface corrosion (ASTM D 610-85), and the corrosion in the vicinity of cutting (ASTM 1654-92) points of view.

The evaluation of tests used to detect the corrosion resistivity of coating can be done by defects formed in the coating film. These coating defects are formed by diffusion of the surrounding medium through the film into the substrate metal. The defects can be osmotic blisters, loss of adhesion, and corrosion formation. For osmotic blisters, adhesion of the film onto substrate is of prime importance. If adhesiveness is sufficient, blisters are less pronounced and vice versa. Anticorrosion pigments and fillers may also affect formation of blisters in the coating film. If the fillers are water soluble, they tend to form blisters in the film.

A further result of accelerated tests concerns the corrosion in cut scribe of artificially prepared mechanical disturbance in the film by a cross section. The corrosion and a distance of corrosion traces from the section indicated the electrochemical action of anticorrosive pigment used in the coating. If there do not appear the traces of corrosion in the vicinity of the section; then, the anticorrosive pigment acts in the cathodic or anodic corrosion region.

Electron microanalysis for ascertaining the elemental composition of the paint films was performed on a TESCAN VEGA 5130SB scanning electron microscope (Tescan, Brno, Czech Republic) and a Bruker Quantax 200 energy dispersive X-ray spectrometer (Bruker, Rheinstetten, Germany).

ASTM D 714-87 method

The method classifies the osmotic blisters to the groups according to their sizes designated by figures 2, 4, 6, and 8 (the lowest denoting the largest size and vice versa, the highest the smallest one). Regarding the blister size, an information on the frequency of occurrence is given. The highest occurrence density of blisters is designated as D (dense), the lower ones then as MD (medium dense), M (medium), and F (few). In such a way, a series from the surface area attacked at least by the osmotic blisters up to the heaviest occurrence can be formed as follows: 8F-6F-4F-2F-8M-6M-4M-2M-8MD-6MD-4MD-2MD-8D-6D-4D-2D.

ASTM D 1654-92 method

This method evaluates the degree of corrosion along the section and of coating sub-corroding in the vicinity of the section. Table 2 surveys the analysis of corrosion at a distance from scribe in mm. Rating is done from 10 to 0, where 10 means 0 mm of corrosion in the scribe and 0 is 16 mm of corrosion at the scribe.

Table 2 Evaluation of corrosion in the test cut according to ASTM D 1654-92 [20]

Evaluation [–]	Distance [mm]	Distance [inch]
10	0	0
9	0–0.5	0–1/64
8	0.5–1	1/64–1/32
7	1–2	1/32–1/16
6	2–3	1/16–1/8
5	3–5	1/8–3/16
4	5–7	3/16–1/4
3	7–10	1/4–3/8
2	10–13	3/8–1/2
1	13–16	1/2–5/8
0	16 and more	5/8 and more

ASTM D 610-85 method

The results obtained by means of this method are compared with the standards given in the Annex related to the degree of corrosion in the area under the protective coating. The result is thus a definite corrosion degree of the substrate surface expressed in the percent scale (0 – 0.03 – 0.1 – 0.3 – 1 – 3 – 10 – 16 – 33 – 50 – 100 %) according to Figure 2 (see overleaf).

Linear polarization

Furthermore, a VSP-300 multichannel potentiostat / galvanostat (Bio-Logic, Seyssinet-Pariset, France) was used to electrochemically assess the linear polarization of the organic coatings. 1 cm² of the sample was polarized in the range from –10 mV/EOC to +10 mV/EOC at a rate of 0.166 mV/s in the three-electrode configuration (see Figure 3). After the polarisation, spontaneous corrosion potential (E_{corr}), corrosion current density (I_{corr}), polarisation resistance (R_p), and corrosion rate (v_{corr}) were all measured and/or evaluated.

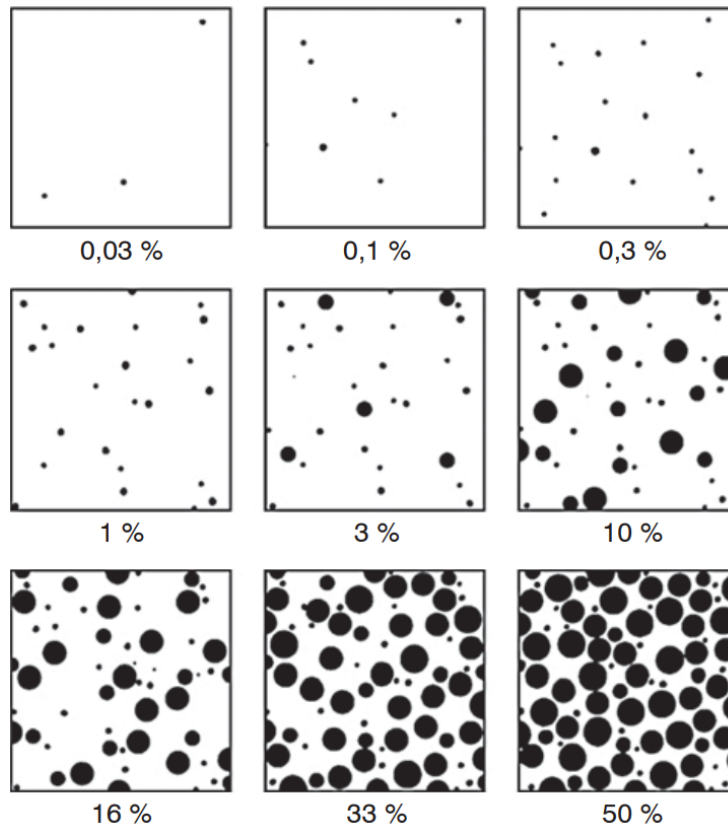


Fig. 2 Photographic standards for the assessment of panel surface corrosion (ASTM D 610–85) [21]

The corrosion potential and corrosion current density were obtained by analysis of Tafel curves (Figure 4), the polarization resistance calculated from Stern–Geary equation (1):

$$I_{\text{corr}} = \frac{B}{R_p} \quad (1)$$

where the R_p is polarization resistance and B is a constant for the particular system which is calculated from the slopes of the anodic (β_a) and cathodic (β_c) Tafel regions (2):

$$B = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \quad (2)$$

Corrosion rate was calculated using the following equation (3), where K is constant that defines the units of the corrosion rate, EW is equivalent weight, ρ is density and A is sample area [22].

$$CR = \frac{I_{\text{corr}} K EW}{\rho A} \quad (3)$$

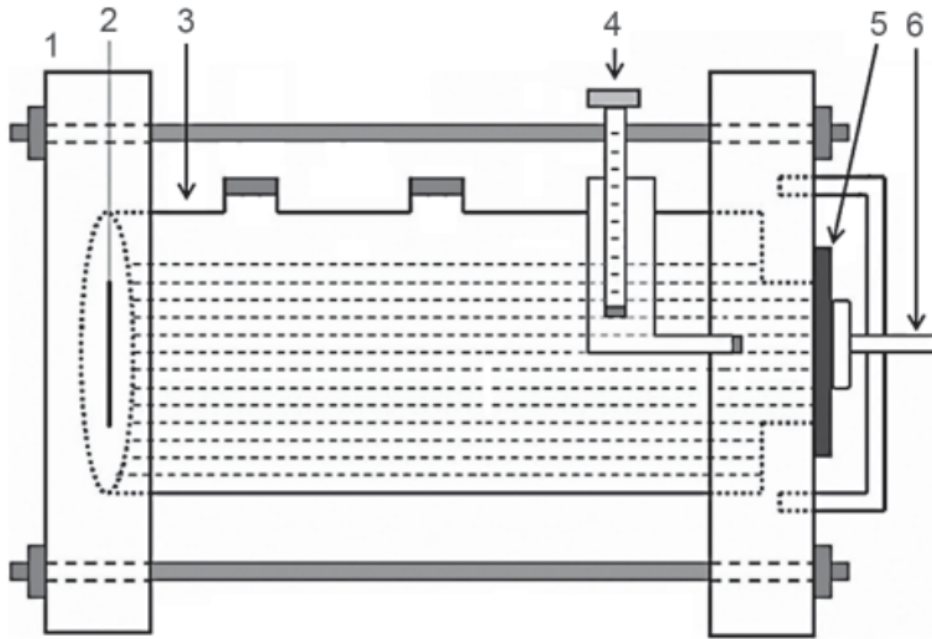


Fig. 3 Electrochemical cell (1 – PTFE plate, 2 – platinum electrode, 3 – cylindrical glass 250 mL reservoir (with 1 M NaCl solution), 4 – reference electrode (saturated calomel electrode, SCE), 5 – working electrode (steel panel with organic coating), 6 – screw (to fix the working electrode) [21]

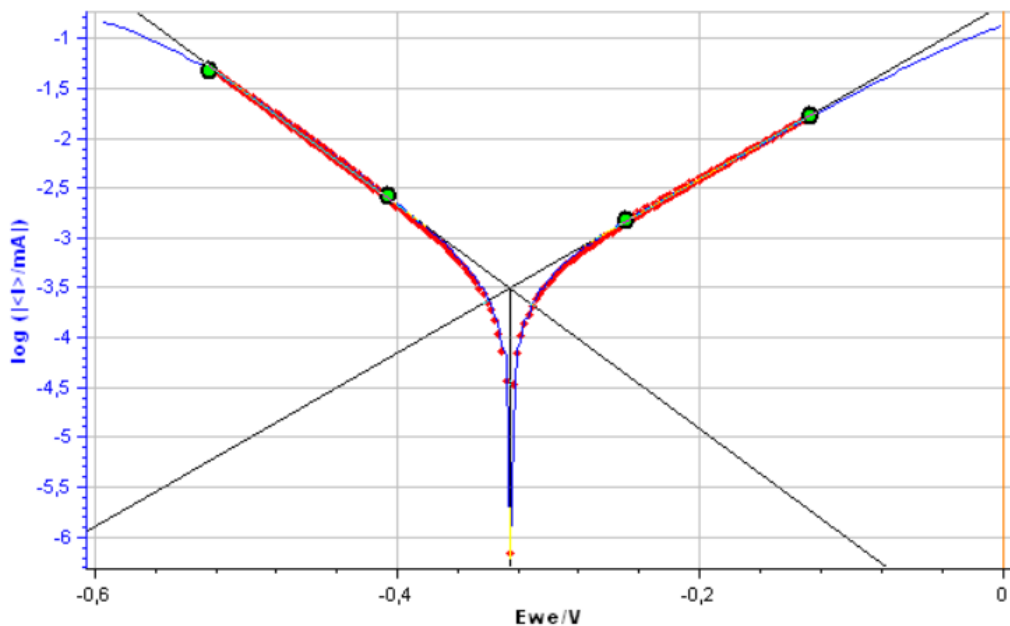


Fig. 4 Tafel fit analysis

Mechanical properties of coatings

Testing of mechanical qualities included the flexibility and strength of paint. When using a specialized cutting blade with cutting edges spaced 2 mm apart, the adhesion of the films to the substrate was evaluated by cutting a lattice into

the films in accordance with ISO 2409. The largest height (in mm) at which the film integrity remained unaffected after a 1000 g weight was dropped onto steel panels was recorded to determine the impact strength of the paint films (ISO 6272). Measurements on a cupping tester were used to evaluate the cupping test. As per ISO 1520, the result is the depth of the steel ball indentation (in mm) at which the integrity of the film was not compromised. The painted panels were bent over mandrels of different diameters to test the flexibility of the material and to record the largest diameter (in mm) at which the paint film had not been cracked, as specified in ISO 1519. The pull-off test for adhesion was measured after ISO 4624 with COMTEST®OP3P (Roklan – electronic s.r.o., Prague, Czech Republic).

Results and discussion

Pigment specification

The pigments studied were subjected to measurements of typical paint parameters, i.e. density and oil number that are used to calculate the critical pigment volume concentration (CPVC) of each pigment. The results of the respective pigments are summarized in Table 3.

Table 3 Physical characteristics data of pigments

Sample	Density [g/cm ³]	Oil absorption [g/100g]	CPVC
Zn	7.09±0.02	7.0	65.2
CaCO ₃	2.73±0.02	18.7	65.5

The representative SEM scans of studied pigments are then shown in Figure 5. Zinc pigment formed large spherical particles with 0.5–5 µm in diameter.

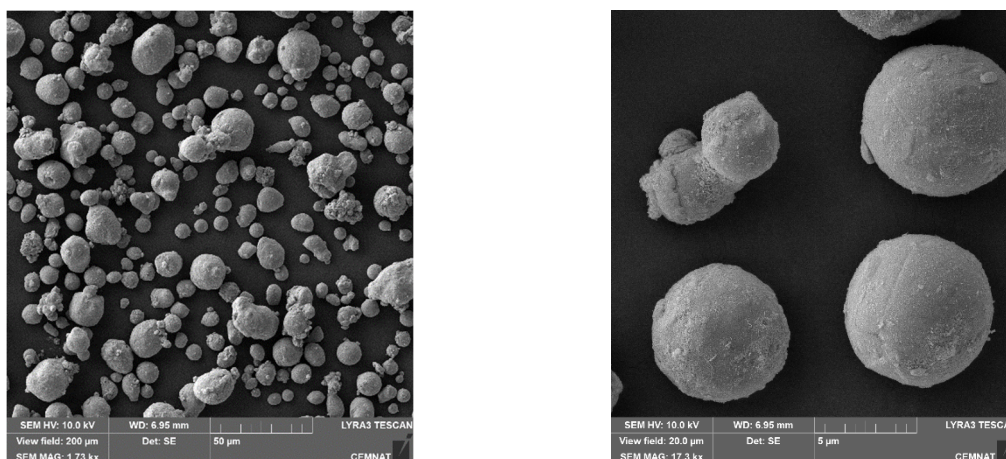


Fig. 5 Scanning electron micrographs of the zinc

The figures bring graphical representations of the corrosion-testing results obtained both in the salt and condensation chambers for all the types of formulated coating compositions. The dependence courses show clearly that the protective function of the coatings pigmented with zinc indicates improvements with the increases in the concentration of zinc up to a respective PVC value (*ca.* 35–45 % PVC). After this concentration limit ($PVC_{Zn} = 45 \%$) has been exceeded the deterioration, i.e. a reduction of the anticorrosive protection of substrate metal takes place. For illustration, some testing panels are represented in Figure 6 and Figure 7 and the trend commented above is clearly evident therein. The initial value at a zero concentration of zinc pigment gives substantially the barrier capacity of the binder to protect the substrate material. As a result with Zn concentration of 0–5 % PVC, the anticorrosive efficiency is high and almost similar.

Relative surface hardness of studied organic coatings.

The results of a test on Pendulum hardness after 60 days of application of coatings on glass panels is shown in Table 4. It shows that after application as days passing coatings becomes harder as the coating dries by solvent evaporation. It is also observed that as zinc PVC has increased, when the hardness of coatings increases too as the presence of metallic zinc pigments gives strength to coating because of its spherical shape and close packing inside the coating film. Lower concentration of zinc in films has only binder and $CaCO_3$ in high quantity, which does not provide toughness to the film.

Sufficient hardness of the film is very important for coating's corrosion protection ability, as the corresponding studies have revealed that high-strength coatings are likely to be less permeable and less susceptible to mechanical damage. Also, the test results show that maximum hardness was achieved with coating having Zn PVC 45 %.

Corrosion test

Coatings with Zn PVC (0–45 %) were exposed in SST under accelerated corrosive environment for 500 h. Results obtained can be explained as follows: coatings with Zn PVC 0 % show no blistering in the area and a minimal corrosion at the surface. However, coatings without zinc fails in blistering at scribe and corrosion at scribe. Blisters size observed at cut was large (6F) and corrosion around 2–3 mm. Such results can be explained only by the presence of binder and $CaCO_3$, because the absence of zinc pigment does not give inhibitor protection at cut of coating and thus corrosion propagates in the film. Coatings with Zn PVC 1–10 % shows slightly improved results than coating with Zn PVC 0 % in terms of corrosion at the scribe.

Table 4 The results of relative surface hardness of epoxy-ester coatings; DFT = $95 \pm 5 \mu\text{m}$

PVC _{Zn} [%]	Relative surface hardness [%]								
	3. day	5. day	8. day	10. day	15. day	20. day	25. day	30. day	60. day
0	8	21	27	31	31	34	35	38	39
1	8	21	27	30	31	34	36	39	41
3	10	21	25	25	32	37	37	40	43
5	11	22	30	31	34	39	39	42	43
10	13	24	29	32	33	39	40	42	42
15	13	24	25	29	30	34	36	39	40
20	11	23	21	21	29	31	35	35	39
25	11	22	21	22	29	31	35	36	39
30	13	25	24	30	32	34	37	39	40
35	13	25	24	25	30	32	34	37	39
40	17	27	28	35	37	38	40	41	42
45	17	27	28	26	28	30	32	34	45

The presence of Zn pigment gives inhibitor protection by blocking the cut and thus, it does not allow corrosion to propagate. While corrosion protection in the surface is mainly because of barrier protection by binder in these coatings (Zn PVC 0–10 %). Coatings with Zn PVC 15–25 % shows good results in terms of corrosion and blisters at scribe; nevertheless, these coatings fail to protect corrosion and blisters in the surface as documented in Table 5.

Table 5 The results of exposure of epoxy-ester coatings to the conditions governing the medium of Salt Spray cabinet with 500 hour run; DFT = $95 \pm 5 \mu\text{m}$

PVC _{Zn}	Blistering in scribe [dg.]	Blistering in area [dg.]	Failure at the section [mm]	Corrosion in the surface [%]
0	6F	–	1–2	0.3
1	2MD	–	0.5–1	0.3
3	2MD	–	0.5–1	0.3
5	2F	–	1–2	1
10	2F	–	0.5–1	1
15	2M	8F	0.5–1	1
20	8MD	8F	0.5–1	10
25	8M	6M	0.5–1	33
30	8M	8F	0.5–1	1
35	4M	8F	0.5–1	1
40	8M	8F	0.5–1	0.3
45	8M	8F	0.5–1	0.3

These results can be observed because of insufficient zinc pigment present in the film and due to less concentration of binder. Coatings with Zn PVC (30–45 %) shows excellent results of anticorrosion in all aspects. At scribe, blistering and corrosion both are less observed, because of sufficient amount of zinc. Zinc pigment present gets in contact with environment and converts into zinc corrosion products like ZnO that penetrates into the scribe or cut in the coating filling it, thus making an impermeable barrier. Best corrosion protection was obtained with Zn PVC 45 % coatings. Blisters and corrosion at surface were scarcely observed, as well as blisters and corrosion at scribe was almost negligible.

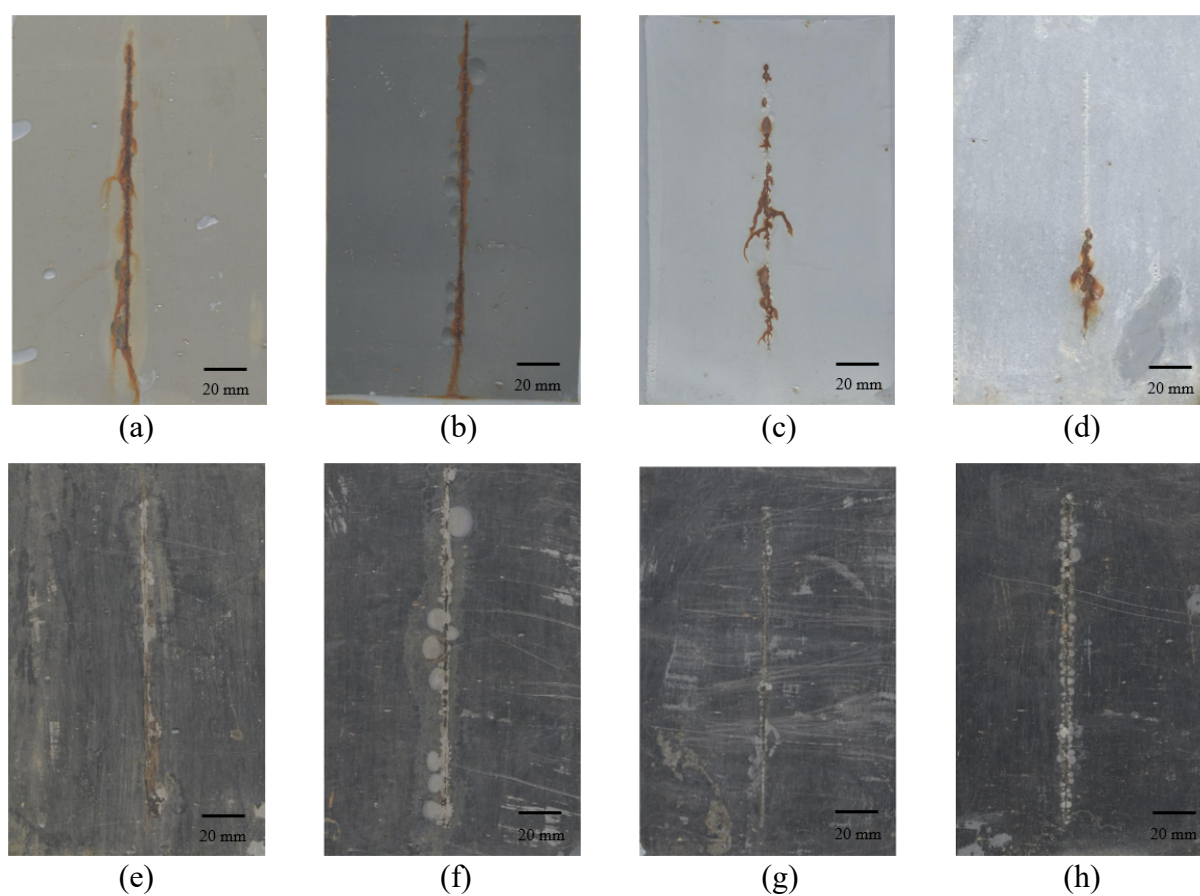


Fig. 6 Organic coating after 500 h of exposure in a salt mist atmosphere and steel panel before removing the organic coating

Organic coating with zinc at PVC: (a) PVC = 0 %, (b) PVC = 5 %, (c) PVC = 25 %, (d) PVC = 45 %; steel panel after removing the organic coating with zinc at PVC: (e) PVC = 0 %, (f) PVC = 5 %, (g) PVC = 25 %, (h) PVC = 45 %

Condensation test – Humidity chamber exposure (ISO 6270)

When the samples had been exposed in a testing chamber, a special test machine was used to evaluate the moisture resistance of the coating system in the environment with high humidity.

This device simulates rain and dew damage to the coating by producing continuous condensation on the surface of the sample under test. It was observed that, under testing of all the coatings for 3500 h, there was no damage on the film, as well as no observable corrosion. Therefore, it can be stated that all the samples have exhibited an excellent moisture resistance irrespective of Zn PVC.

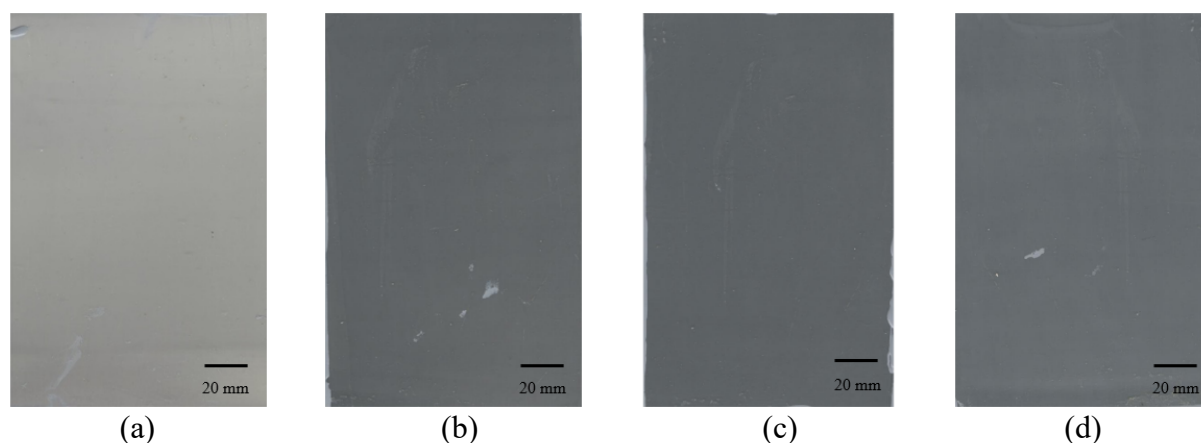


Fig. 7 Organic coating after 3500 h of exposure in condensation chamber

Organic coating with zinc at PVC: (a) PVC = 0 %, (b) PVC = 5 %, (c) PVC = 25 %, (d) PVC = 45 %

Linear polarization

Potentiodynamic polarization studies are surveyed in Table 6. The data on corrosion rate shows that the coatings with Zn PVC 45 % offer excellent corrosion resistance. It possesses the lowest corrosion rate of $9.04 \cdot 10^{-6}$ mm/year as compared to other samples. Values of corrosion rate give clear understanding of the importance of concentration of zinc in the coatings. As zinc pigment concentration is added in more extent, the corrosion rate decreases which proves the inhibition of the corrosion protection of zinc pigment. Thus, polarization resistance can be used to determine the resistance of the metal under investigation against corrosion. Values from table indicate that coatings with Zn PVC 45 % offer the highest values of polarization resistance and therefore also a high corrosion resistance.

Table 6 Results of the electronic measurement of the studied coatings; DFT = $95 \pm 5 \mu\text{m}$

PVC _{Zn}	E_{corr} [mV]	I_{corr} [μA]	β_a [mV]	β_c [mV]	R_p [Ω]	v_{corr} [mm/year]
2	-180	$8.70 \cdot 10^{-2}$	25.2	29.4	$6.77 \cdot 10^4$	$1.29 \cdot 10^{-3}$
1	-225	$7.58 \cdot 10^{-2}$	26.2	28.7	$7.84 \cdot 10^4$	$1.12 \cdot 10^{-3}$
3	-250	$6.99 \cdot 10^{-2}$	25.8	27.8	$8.31 \cdot 10^4$	$1.03 \cdot 10^{-3}$
5	-300	$6.48 \cdot 10^{-2}$	26.0	28.3	$9.08 \cdot 10^4$	$9.57 \cdot 10^{-4}$
10	-580	$5.47 \cdot 10^{-2}$	26.4	28.7	$1.09 \cdot 10^5$	$8.08 \cdot 10^{-4}$
15	-620	$4.68 \cdot 10^{-2}$	25.9	26.5	$1.22 \cdot 10^5$	$6.91 \cdot 10^{-4}$
20	-650	$2.11 \cdot 10^{-2}$	25.7	26.3	$2.67 \cdot 10^5$	$3.12 \cdot 10^{-4}$
25	-700	$7.80 \cdot 10^{-3}$	24.7	25.6	$6.99 \cdot 10^5$	$1.15 \cdot 10^{-4}$
30	-735	$2.71 \cdot 10^{-3}$	24.3	24.8	$1.97 \cdot 10^6$	$4.00 \cdot 10^{-5}$
35	-780	$1.02 \cdot 10^{-3}$	24.4	24.7	$5.23 \cdot 10^6$	$1.51 \cdot 10^{-5}$
40	-820	$8.42 \cdot 10^{-4}$	24.2	24.4	$6.27 \cdot 10^6$	$1.24 \cdot 10^{-5}$
45	-850	$6.12 \cdot 10^{-4}$	24.1	24.2	$8.57 \cdot 10^6$	$9.04 \cdot 10^{-6}$

Mechanical properties

These characteristics of coatings are usually studied by five tests as shown in Table 7. Cross-cut adhesion tests have led to almost the same results for coatings with all PVC values. Flexibility mandrel test then shows that all the coatings have remained undamaged after bending with a mandrel of 5 mm.

Table 7 Results of the mechanical properties of the studied coatings; DFT = $95 \pm 5 \mu\text{m}$

PVC _{Zn}	Adhesion test [dg.]	Bend test [mm]	Impact test [cm]	Cupping test [mm]	Pull-off strength [MPa]	Fracture type [%]
0	0	< 4	> 100	> 10	1.61	A/B-100
1	0	< 4	> 100	> 10	1.59	A/B-100
3	0	< 4	> 100	> 10	1.57	A/B-100
5	0	< 4	> 100	> 10	1.54	A/B-100
10	0	< 4	> 100	> 10	1.51	A/B-100
15	0	< 4	> 100	> 10	1.50	A/B-100
20	0	< 4	> 100	> 10	1.48	A/B-100
25	0	< 4	> 100	> 10	1.48	A/B-100
30	0	< 4	> 100	> 10	1.50	A/B-100
35	0	< 4	> 100	> 10	1.45	A/B-50, B-50
40	1	< 4	> 100	9.90	1.42	A/B-70, B-30
45	1	< 4	> 100	9.85	1.38	A/B-90, B-10

A/B – adhesion fracture between the substrate and the coating; B – cohesive fracture in the coating

The samples subjected to the impact test provide similar results after all coatings withstand drop of weight of 1000 g at 100 cm. Testing coatings with cupping tests displayed tolerance of indentation of more than 10 mm in all coatings without any damage of the film.

Pull-off test gave a value of force in MPa by which film is pulled, the respective results document that coatings with lower Zn PVC value shows higher pull off strength as binder is present in excess and zinc is low. However, as Zn PVC increases in coatings, the pull off strength is slightly decreased because of the presence of more zinc and lesser amount of binder. Fracture type noted in almost all types of coatings was an adhesive failure between the coating and substrate, while in some of the coatings, a fracture of cohesion in coatings and an adhesive failure were observed.

Organic coating composition measurements

Selected samples were examined by electron microanalysis (Figure 8). These observations for ascertaining the elemental composition of the paint films were performed on a scanning electron microscope (model TESCAN VEGA 5130SB) connected to a dispersive X-ray spectrometer (Bruker Quantax 200 energy). Prior to being exposed to the salt spray environment, the organic coatings' examined by X-Ray diffraction (XRD) revealed that only zinc metal was present. The results from energy-dispersive X-ray spectroscopy showed that the coating's cathodic protection mechanism filled the pores with the white corrosion (zinc corrosion) byproducts.

Such an interpretation was supported by SEM. The organic coating's conductivity was decreased by the zinc corrosion products, which caused the corrosion protection effect switched from electrochemical principles to a barrier mechanism. After 500 h of exposure, no substrate from steel corrosion products could be found in the organic coating, demonstrating the high level of corrosion protection.

According to the findings from energy-dispersive spectroscopy, the cathodic protection caused that the test cut was partially sealed by zinc oxidation products (white corrosion). Nevertheless, the simultaneous presence of iron corrosion products indicates that the sealing is not quick enough. Corrosion in the test cut decreased with more PVC in the organic coating, as shown by images of the corrosion in the test cut after 500 hours of exposure to the salt spray atmosphere. Figure 9 shows XRD data after exposing coatings for 500 h to salt spray where (a) depicts the coatings with Zn PVC 35 % and (b) coatings with Zn PVC 45 %.

It can be evaluated from the coating composition that corrosion products of iron are more frequent in coatings with Zn PVC 35 %, expressing corrosion occurrence. However, in case of Zn PVC 45 %, zinc corrosion products are more

abundant than one could expect from corrosion of zinc into white oxidized product and hence, the corrosion process is almost negligible. This has proved the theory that the increase of zinc PVC helps in the prevention of corrosion.

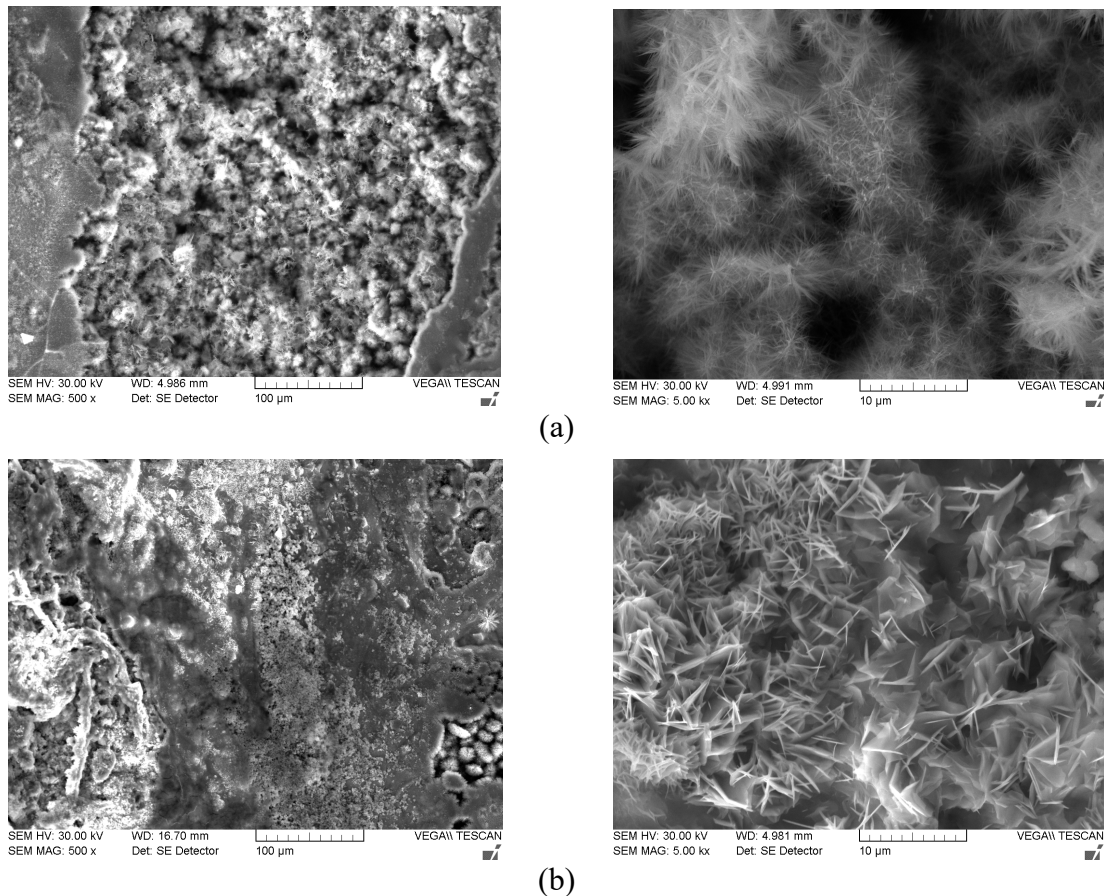


Fig. 8 SEM images of coatings after 500 hrs of salt spray exposure: (a) Images of coatings with Zn PVC 35 %, (b) Images of coatings with Zn PVC 45 %

Corrosion protection mechanism

Zinc-rich epoxy coatings are distinctive in that they protect the metal surface even after flaws like scratches, pinholes, voids, and other minor damages if the coating system start to show up them. The complicated corrosion protection in ZRE coating comprises the formation of a physical barrier on the metal surface by an epoxy binder separating the metal from the corrosive environment. The zinc particles "sacrifice themselves" to ensure cathodic protection of the underlying substrate when the coating is destroyed by an external force, which, in result, delays the initiation of corrosion processes. When the coating is damaged, the electrolyte invariably penetrates along the coating layer. At the zinc-electrolyte interface, metal particles undergo oxidation while reduction processes take place at the metal substrate. Finally, when the cathodic protection phase has run out, the substrate is protected for a considerable amount of time only by the barrier action.

This is accomplished either by zinc corrosion compounds plugging the pores inside the coating or by the zinc by-products with inhibition activity, which lowers the coating's electrical conductivity. Mechanism is shown in Figure 10 [23–25].

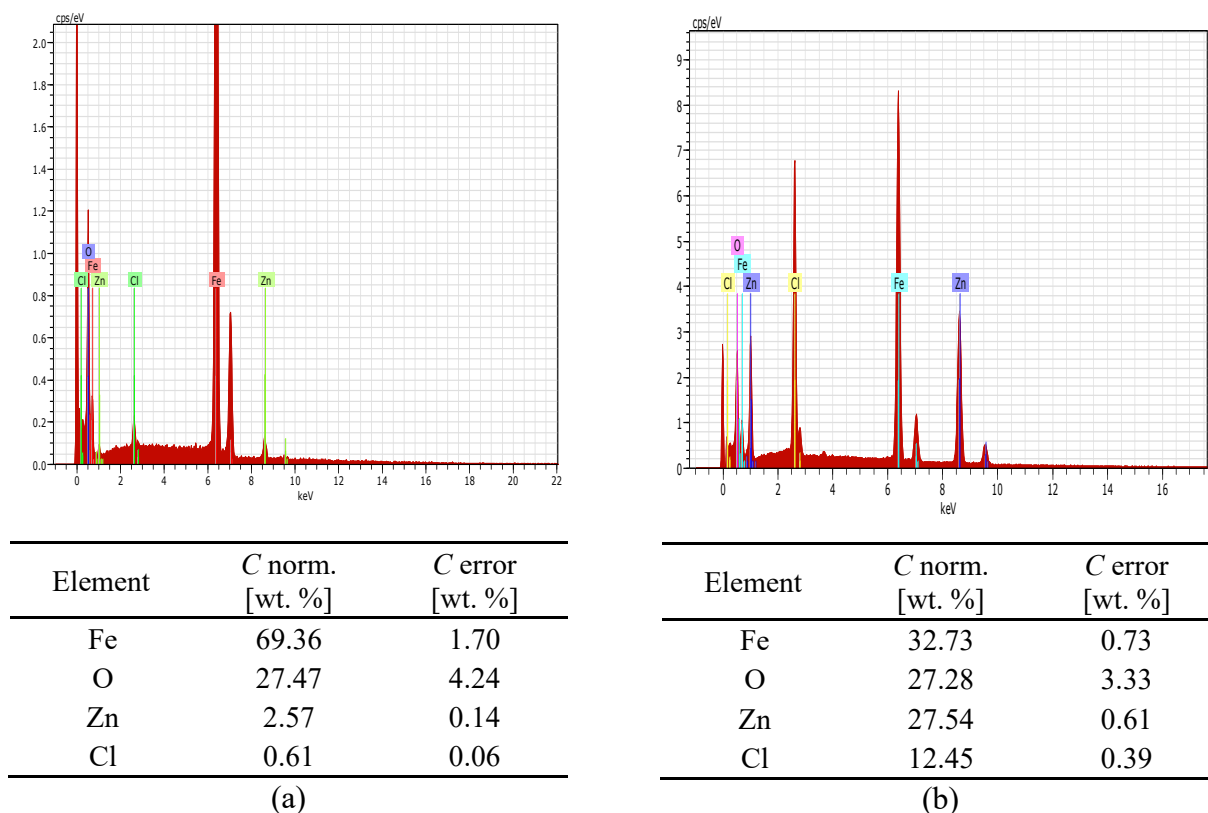


Fig. 9 Energy-dispersive X-ray analysis results of the organic coating containing zinc at PVC: (a) (PVC = 35 %), (b) (PVC = 45 %)

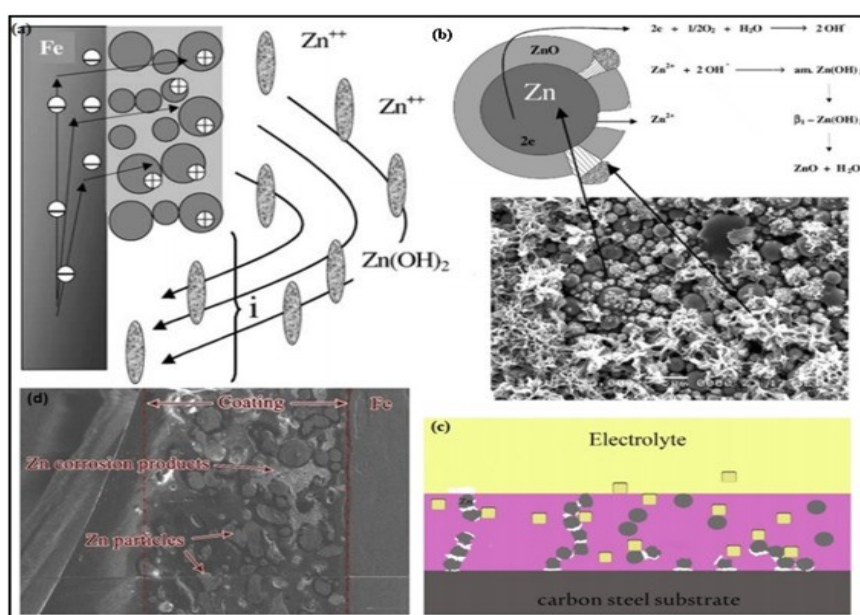


Fig. 10 Cathodic protection of metal by zinc pigments [25]

The electrochemical process that prevents air and moisture from penetrating the substrate below is changed into the barrier effect as the conductivity of coating is reduced. The electrical contact between the spherical zinc particles and the steel substrate deteriorates quickly, which reduces the coating's ability in its role of a sacrifice. In order to ensure a continuous electrical conductivity by creating a particle-to-particle-to-substrate electrical contact and the resultant percolation channel, substantial concentrations of zinc (often higher than 85 wt. %) are then needed. A stable inorganic film is formed by the pore-filling action of zinc salts like zinc carbonates, zinc sulphate, and zinc hydroxide, which causes the dependence on particle size and zinc content.

Conclusions

The research work with a complete of tests on epoxy-based zinc rich coatings with different PVC of zinc (0–45 %) can be summarized by saying that the corrosion protection efficiency of coatings is achieved best if zinc is present at the optimal concentration. Anticorrosion properties depend on the protection mechanism of coatings like barrier, sacrificial, inhibitor and cathodic protection. The work performed herein has given detailed understanding on different corrosion protection based on the composition of coatings. Coatings with zinc PVC low 0–10 % have the binder in excessive amount, which gives the protection only by acting as a barrier between the surface and environment with blocking of the contact, which then protects the metal from getting corroded. An increase of zinc PVC in the coating makes a closely packed layer of zinc pigment in the film acting as a barrier along with binder. Advantage of higher concentration of zinc is that it provides an additional corrosion protection because zinc is more reactive than iron, zinc gets corroded and protects iron by giving the cathodic protection. At same time, zinc corrosion products (ZnO) fill pores of any indentation occurred in the film and acting as inhibitor for further corrosion propagation. This combined mechanism of corrosion protection offers excellent advantage to zinc. On the basis of the corrosion tests performed and the related studies on morphology of sections and surfaces of the films by using SEM it has been found that the most efficient concentration of zinc dust lies in a range of PVC = 35 % to PVC = 45 %.

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