

The Influence of Pigment Volume Concentration (PVC) on Corrosion Behaviour of Zinc-Rich Epoxy Coatings

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Abstract

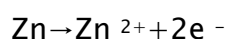
In this work, the effect of the ratio of the pigment volume concentration (PVC) to the critical pigment volume concentration (CPVC), denoted here after by Λ , on the corrosion behaviour of the zinc-rich epoxy coatings has been investigated. Paints based on epoxy resin and polyamide hardener were prepared at different Λ values (0.80, 0.90, 0.96, 1.05, 1.14 and 1.23) and applied on degreased and sandblasted mild steel sheets at 60 microns dry film thickness. In order to investigate the corrosion behaviour of the zinc-rich epoxy coatings, the painted mild steel electrodes were studied during exposure to 5%NaCl solution for up to 90 days and electrochemical impedance spectroscopy test (EIS) has been taken after 7 and 90 days exposure. In parallel, continuous salt spray test in accordance with ASTM B117 has been done for 2000 hours. The results showed that, corrosion resistance can be affected greatly by the PVC/CPVC ratio and conclusions offered each of the techniques used are quite similar. It has been proved that coatings with PVC=59% or $\Lambda=1.14$ have better corrosion resistance in comparison with other ratios.

Keywords: Corrosion protection, zinc-rich paints, Electrochemical Impedance Spectroscopy.

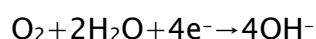
Introduction

Zinc-rich primers (ZRP) are one of the most effective coatings which have been successfully used as anti-corrosion primers since the 1930s in order to protect steel from corrosion [1]. They are widely used in various aggressive environments such as offshore, industrial, etc. because of their unique

property of protecting the metal even when there is a slight mechanical damage to the coating. In these coatings at the beginning of immersion, zinc particles provide a cathodic protection of the steel substrate [1,2]. Then, as time passed, a long term protection develops due to the formation of zinc corrosion products, which reinforce the barrier effect of the paint by blocking the pores of the coating[1,3]. The anodic process corresponding to zinc dissolution takes place on zinc particles inside the polymeric film through the overall reaction:



The cathodic process which corresponds to oxygen reduction is often considered to take place at the surface of the steel substrate according to the below reaction⁴.



There are many different factors such as pigment volume concentration (PVC), shape and size of the zinc dust which are effective on physical properties and corrosion resistance of the solvent-based ZRPs [3,4]. In common liquid ZRP, zinc is usually introduced as spherical pigments with a mean diameter ranging from 5 to 10 micrometre.

One of the most important parameters whose variations have a significant effect on the characteristics of coatings is the ratio of the pigment volume concentration (PVC) to the critical pigment volume concentration (CPVC). In early studies of the effect of PVC on coating performance properties, corrosion resistance was evaluated by the traditional salt-spray testing method in accordance with ASTM B 117-85. However, the relevance of this approach to the testing of paints for their corrosion resistance properties are very limited (because it does not offer any information about the corrosion process which takes place in the metallic substrate surface) and has been widely criticized. Since physicochemical changes in the characteristics of primers are very significant as the Λ parameter changes, different techniques have been proposed to be able to perform its optimal determination [5]. Over the last decade, considerable progress has been made in the attempts to apply electrochemical methods or techniques to evaluate the corrosion resistance properties of organic coatings when applied to metallic substrates

[6,7]. A wide frequency scan ac impedance study, often referred to as electrochemical impedance spectroscopy (EIS), seems to be especially appropriate.

At PVC below the CPVC, a dry coating film is a continuous coating, a composite consisting of pigment particles randomly embedded in a continuously connected matrix of polymer. Above the CPVC, there are void structures in the film due to insufficient polymer, but the pigment particles can still be thought of as being continuously connected. The polymer is still continuously connected globally, but voids will cause the polymer to lose local connectivity, and thus the sharp drop-off in mechanical properties of the coating just above the CPVC. A new phase, air, is now present in the film and its properties drastically affect those of the film, especially with regard to density, mechanical, thermal, transport properties and optical properties. Above CPVC there is not enough resin to cover the pigment surface and an important amount of the polymer is absorbed in the pigment [8]. It is well known that to process a conventional paint with good barrier protection, the ratio of pigment volume concentration (PVC) to critical pigment volume concentration (CPVC) shall be < 1 . Higher value of this ratio is known to influence the mechanical and permeability characteristics of the coating. However, while formulating a ZRP, formulator keeps this ratio > 1 because the sacrificial action of zinc commences only when there is continuous contact between metal particles, i.e. percolation path [9,10]. The main aim of the present work was to study the effect of varying the PVC/CPVC ratio on the corrosion behaviour of the zinc-rich epoxy coatings.

EXPERIMENTAL

Paints

Two component (2k) paints based on epoxy resin were prepared with high speed disperser at different Λ values. Type I epoxy resin based on bisphenol A and an aliphatic polyamide resin was added in component B of the formulation as a hardener. The pigment used in the study was spherical zinc dust (metallic Zn content = 96%) with a mean diameter ranging from 4 to $6\mu\text{m}$. A mixture of n-butanol with O-Xylene, M-Xylene and P-Xylene were used as

solvent. Characteristics of the different mixtures that were formulated are shown in Table 1.

The Λ values used in this work were obtained by the procedures developed by Bierwagen [11,12]. Using this methodology, CPVC values are calculated from pigment properties according to the following relationship:

$$CPVC = \left[\frac{\phi}{\sum_{i=1}^P x_i(1+U_i^a)} \right] \quad (1)$$

where ϕ is the densest random packing factor for dry paint; i the increments of particle size 1, 2,..., m ; P the number of pigments in the paint; x_i the volume fraction of pigment containing particles of size i and U_i^a the volume of oil absorbed in pigment of particle size i . The values of PVC and Λ can be calculated according to the following relationships:

$$PVC = \frac{\text{volume(pigment)}}{\text{volume(dry coating)}} \quad (2)$$

$$\Lambda = \frac{PVC}{CPVC} \quad (3)$$

Table.1.Specifications of studied samples

Sample	Solid in Weight (%)	Solid in Volume (%)	PVC (%)	Λ
ZRP 1	70	57.4	42.3	0.80
ZRP 2	78	66.3	48.2	0.90
ZRP 3	80	68.2	51.6	0.96
ZRP 4	82	70.6	55.3	1.05
ZRP 5	84	72.1	59	1.14
ZRP 6	88	77.6	65	1.23

Substrates

Sandblasted cold-rolled low-carbon steel standardized test panels were used in order to ensure uniform substrate surfaces for testing purposes. All test panels were properly degreased with xylene and dried under IR lamp for 20 min prior to paint application, and paints were deposited by means of an automatic spray gun on to the substrate. The systems were allowed to cure under ambient air conditions for 6 days prior to testing. Dry film thickness

(DFT) of ZRP was measured using Elcometer 422 and the thicknesses were maintained within the $60 \pm 5 \mu\text{m}$ range. The edges and the rear side of the panels were coated with an epoxy coating to avoid corrosion of the unprotected part of the panels.

Testing Methods and Equipment

The electrochemical cells, shown in Fig.1, were obtained by sticking a glass cylinder on the sample sheet and filling it with the test solution. The exposed surface area was 2cm^2 . The coated samples exposed to 5% NaCl (by weight) in distilled water for periods up to 90 days. A carbon sheet counter electrode and a saturated calomel reference electrode (SCE) were used. Electrochemical impedance spectroscopy measurements were carried out using a frequency response analyser (AG&G 1025) and a potentiostat (AG&G 263A). The impedance measurements in all cases were carried out over a frequency range of 10 mHz up to 100kHz and the impedance spectra were analyzed using PowerSine software.

The equivalent circuit model, shown in Fig.2, was employed to analyse the EIS spectra. The circuit consists of a working electrode (metal substrate), a reference electrode, electrolyte resistance R_{Ω} , pore resistance R_{pore} , coating capacitance C_c , polarization resistance R_p and double layer capacitance C_{dl} . Fitting the EIS data to the circuit determined the values of its passive elements. The tolerance of the evaluated data was usually below 0.1% [5].

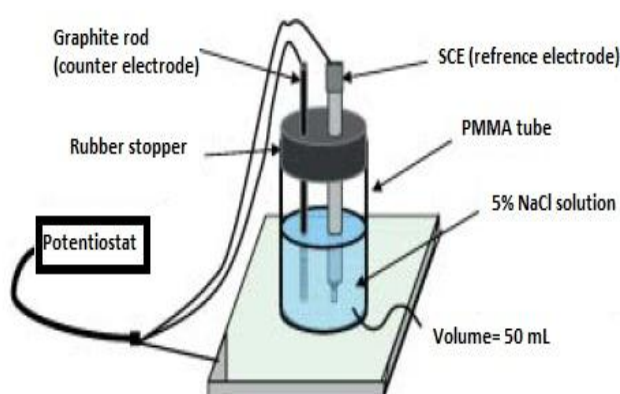


Fig.1. Schematic of test cell and experimental set up

Finally the accelerated salt fog test was performed in accordance with ASTM B 117 during different periods of time (up to 2000 hr) on the painted steel samples for comparing their results with the electrochemical ones. After these periods, samples were evaluated for blistering and rusting.

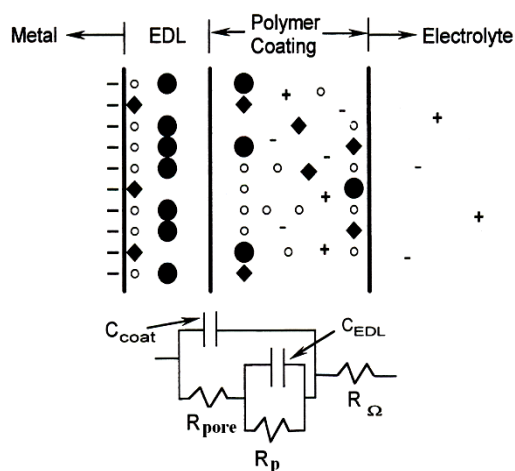


Fig.2. Equivalent circuit used to modelise EIS results.

SEM observations were made using a Vega©Tescan microscope. Test samples were coated with Au-Pd previous to the SEM analyse. SEM data were used to characterize freshly prepared ZRP samples and the morphology and heterogeneities of corrosion products formed after different exposure times in 5% NaCl solution.

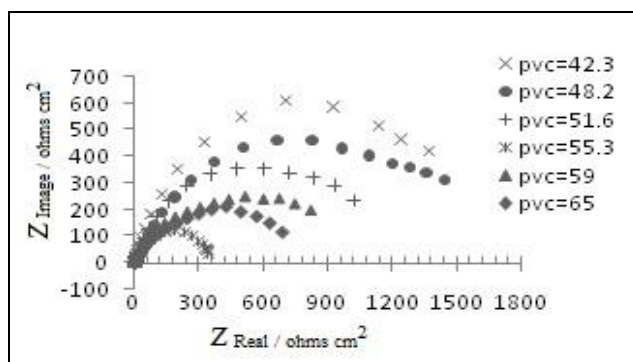
RESULTS AND DISCUSSION

The anticorrosive protection of organic coatings depends on a large number of factors: type of binder, type and size of pigmentation particles, film permeability, and so on. However, one of the most important parameters for final film characteristics is without a doubt the Λ =PVC/CPVC ratio. In ZRPs the anticorrosive properties are based on two mechanisms. First, the inhibitive pigments in the primer are able to modify the interfacial environment at the metal surface beneath the coating, so that the surface is passivated or electrochemically ennobled in some way. Second, the corrosion products blocked the pores of the coating and enhanced the barrier effects of the film and a long term protection will be initiated [5].

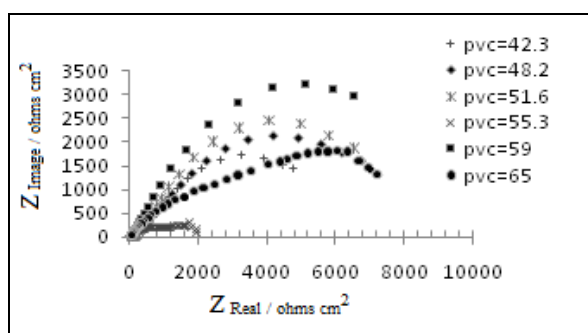
Electrochemical Impedance Spectroscopy (EIS) was a good technique to characterize the electrical properties of organic coatings and any change may come over during exposure to corrosive environments. Depending on the amount PVC and exposure time, there are different shapes of Nyquist diagrams.

At Nyquist diagrams, high and middle range of frequency exhibit the characteristics of coating; however, at low frequencies, the impedance behaviour is related to diffusion and corrosion phenomena. The value of coating resistance has direct relationship with the semi-circle diameter of the Nyquist plot (R_p) which can be calculated with PowerSine software. Whenever the arc at the high frequencies can be related to the insulating properties of the coating, the length of its chord enables the estimation of the resistance of both binder and corrosion products [13]. Figure 3 represents the Nyquist plot for the impedance of specimens tested after 7 and 90 days immersion in 5% NaCl solution.

According to the Nyquist diagram in Fig.3(a), after 7 days immersion, samples with lower PVC values exhibit better corrosion behaviour. At high PVC, the pigment addition can reduce cross-linking density and create some voids in the coating; therefore, the resistance of coating (R_{pore}) is low and water can penetrate into the film. After immersion, by penetrating the water through the film, the zinc pigments are gradually activated and the galvanic protection mechanism initiated. In this stage, the second mechanism of protection is not still active. After a certain amount of time, the chord length pertaining to the high frequency loop observed in Nyquist diagrams tends to increase according to the exposure time in electrolyte. This effect can be related to the formation and accumulation of insoluble corrosion products within the coating, whereas small amounts of pigment particles sustain the electrical contact among them as well as with the steel substrate. the corrosion products of the zinc sealed the pores which are existed in the coating and act like a strong barrier against the corrosive agents; so, as can be seen at Fig.3(b), after a long term exposure (90 days), the coating with PVC=59% has the highest polarization resistance (R_p) and exhibit better anti-corrosion characteristics rather than other specimens.



(a)



(b)

Figure.3. Nyquist plot of the samples immersion in 5% NaCl solution, (a) after 7 days, (b) after 90 days

Continuous salt spray (fog) testing in line with ASTM B 117–85 was performed for 2000 hr to support the electrochemical investigations. Results corresponding to degree of rusting on painted steel surfaces are shown in Table 2.

Table.2.Evaluation of the salt-spray chamber performance

Sample	PVC (%)	Blistering (Hour)	10% Red rust (Hour)
ZRP 1	42.3	100	550
ZRP 2	48.2	100	450
ZRP 3	51.6	100	300
ZRP 4	55.3	–	400
ZRP 5	59	–	1200
ZRP 6	65	–	975

According to visual observations during testing, particularly in the nearest zone to scribe, the sample with PVC=59% had the best corrosion resistance among other samples that exhibit quite similar results with electrochemical studies.

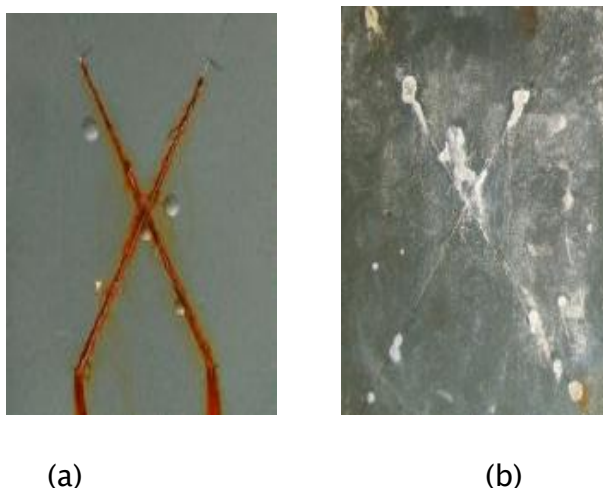


Fig.4. Salt spray test results after 600 hours exposure. (a) PVC=51.6% (b) PVC=59%.

Fig.4 clearly illustrated the formation of white rust, i.e. corrosion products of zinc on sample with PVC=59%. As described in previously, corrosion products of zinc do not dissolve easily in corrosive environment; hence, provide additional barrier protection to the substrate.

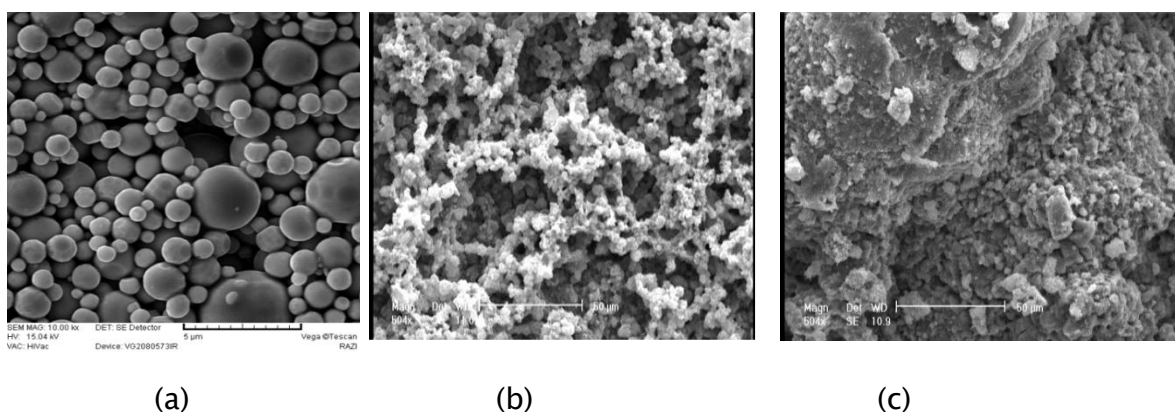


Fig.5. Top view SEM micrographs of ZRP. (a) Before exposure. (b) After 7 days exposure, and (c) After 90 days exposure to 5% NaCl solution.

SEM micrographs reveal an increasing amount of zinc corrosion products as immersion time increases from 7 days to 90 days. Fig.5 displays SEM

micrographs corresponding to ZRP with PVC=59% at different immersion time in 5%NaCl solution.

As can be seen in this figures, before exposure, there is electrical contact among zinc particles as well as with the steel substrate; there are also some voids in the coating which are created due to insufficient binder to cover all the pigments.

By permeating the water through the voids existing in the coating, the zinc particles will be activated and the galvanic reaction will be initiated; consequently, the corrosion products of the zinc particle will be formed which can be seen in the images after 7 days exposure. After a long-time exposure (90 days), an impermeable and compact barrier with higher thickness is formed by insoluble zinc corrosion products cover the whole particles and gradually blocked all of the voids and pores of the coating.

CONCLUSIONS

The corrosion behaviour of different zinc-rich paints based on epoxy resin and prepared at different Λ values (0.80, 0.90, 0.96, 1.05, 1.14, and 1.23) were studied by SEM analysis, electrochemical and accelerated tests. Anticorrosion performance of zinc-rich coatings is affected greatly by PVC/CPVC ratio. Electrochemical impedance spectroscopy test allowed separating each type of protection mechanisms: initial stage of cathodic protection and a stage of barrier type layer afterwards. It has been concluded that in short time, coatings with lower Λ values exhibited good corrosion protection performance which mainly comes from barrier protection mechanism coming mainly from the epoxy resin but in long-time exposure, ZRPs with $\Lambda=1.14$ exhibited the best corrosion characteristics due to galvanic protection and barrier effect of corrosion products. Accelerated test was performed for comparing their results with the electrochemical ones and the results were quite similar.

ACKNOWLEDGEMENTS

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