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ORIGINAL PAPER

EIS and ENM as tools to evaluate inhibitive performance of second generation of phosphate-based anticorrosion pigments

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Abstract The anticorrosion performance of zinc aluminum phosphate pigment was evaluated using electrochemical impedance spectroscopy, the electrochemical noise method and DC polarization. The results of the electrochemical tests revealed the superiority of zinc aluminum phosphate in comparison with zinc phosphate in terms of inhibitive characteristics. The trend and magnitude of resistances and current density plus the appearance of the impedance spectra and the power spectral density of the current noise indicated deposition of a layer on the surface of samples exposed to ZPA extract. SEM/EDX analysis confirmed the precipitation.

Keywords Anticorrosion pigment · Electrochemical impedance spectroscopy · Electrochemical noise method · Surface analysis

1 Introduction

Increasing concerns about the toxicity of chromates are a driving force for switchover to chrome-free pigments. Numerous efforts have been made to find reliable alternatives with the same level of performance as is provided by chromates [1–8]. One of the most common replacements is zinc phosphate (ZP) pigment which has been extensively used; however, various researches have reported that ZP is not as effective as chromate-based pigments [5, 9, 10]. Therefore, modification is crucial to meet growing demands for highly effective non-toxic anticorrosive pigments. The inhibiting properties of zinc phosphate may be improved through different methods. Of them, modification of the anionic part as well as the cationic constituent has been proven to be efficient [10–14]. Because of the increased solubility and higher phosphate content, second generation phosphate-based anticorrosion pigments reveal superior performance compared to ZP [12, 13, 15–17].

Through taking advantage of EIS and ENM as two electrochemical techniques widely used in corrosion studies, the inhibitive performance of various anticorrosive compounds was investigated. EIS has become a routine tool for practical corrosion prediction. The technique provides qualitative and quantitative data and offers a powerful method to examine the corrosion phenomenon of the metallic substrates [18–22]. ENM is traced back to stochastic pulses occurring in the corrosion potential or galvanic current of a freely corroding cell. It is a non-intrusive technique giving both kinetic and mechanistic information [23–27].

The objective of the present work is to study performance of zinc aluminum phosphate (ZPA) representing the second generation of phosphate-based anticorrosion pigments with the use of EIS and ENM. In order to provide further assessment on the effectiveness of the modification approach, DC polarization as well as surface analysis (SEM/EDX) were also utilized.

2 Experimental

2.1 Materials

Steel specimens with the composition shown in Table 1 were used. They were polished to achieve a surface roughness of 3–5 µm (peak to valley), followed by

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Table 1 Composition of steel panels

Elements	Fe	C	Si	Mn	P	S	Cr	Mo	Co	Cu	Nb
% wt	97.7	0.19	0.415	1.39	<0.0050	<0.0050	0.026	0.018	0.0559	0.0429	0.0481

Table 2 The result of ICP-OES analysis

Pigments	Solubility (mg l^{-1})	
	[Zn]	[P]
Zinc phosphate (ZP)	7.89	1.46
Zinc aluminum phosphate (ZPA)	38.96	16

degreasing with acetone. To seal the edges and back sides of the steel panels, they were covered with a beeswax-colophony mixture, leaving an area of 1 cm^2 unmasked.

The commercial grade anticorrosion pigments used in this study were zinc phosphate and zinc aluminum phosphate, which are known under the trade marks ZP and ZPA, respectively, according to datasheets published by the supplier (Heubach Ltd.). In order to prepare extracts, 2 g of each pigment was stirred in 1 L 3.5% w/w NaCl aqueous solution for 24 h then filtered as mentioned elsewhere [28]. The concentration of the species dissolved in the pigment extracts was measured by inductively coupled plasma-optical emission spectrometry (Varian Vista Pro ICP-OES). The result of the analysis is presented in Table 2.

2.2 Methods

EIS measurements were carried out at open circuit potential (OCP) within the frequency domain 10,000–0.01 Hz using a perturbation amplitude of 10 mV. Polarization curves were provided at a scan rate of 1 mV s^{-1}. The steel panel as the working electrode, platinum counter electrode and Ag/AgCl reference electrode were connected to the terminals of an Autolab instrument model PGSTAT12. Data analysis for EIS and linear polarization (LP) was made using FRA and GPES software, respectively.

Electrochemical potential and current noise were simultaneously measured in a freely corroding system employing two nominally identical working electrodes and an Ag/AgCl reference electrode which were connected with the ECN port of an Autolab model PGSTAT12. The noise data were recorded for 1,024 s at a sampling rate of 1 s. The data were statistically analyzed after removing the DC trend using the moving average removal (MAR) method.

The morphology and chemical composition of the layer precipitated on the surface after 24 h of immersion in the pigment extracts were studied using a SEM/EDX model Philips XL30.

3 Results and discussion

The results of ICP-OES analysis summarized in Table 2 clearly show an increase in solubility of ZPA in comparison with ZP. This means that the modified ZP is able to release higher concentrations of Zn and phosphate ions functioning as inhibiting species for the steel.

EIS data as Bode diagrams of steel samples after 1, 4 and 24 h of immersion in 3.5% NaCl solutions containing ZP and ZPA extracts are depicted in Fig. 1. All the plots revealed one time constant except for ZPA after 24 h exposure characterized by two relaxation times. Figure 2 shows two different equivalent circuits proposed to model the spectra, where R_s represents the solution resistance, R_{ct}

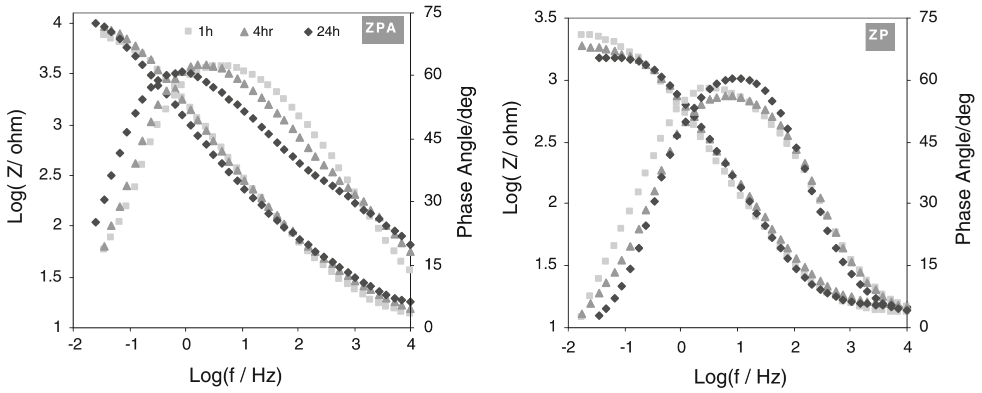

Fig. 1 Bode diagrams for steel panels after 1, 4 and 24 h immersion in ZP and ZPA extracts

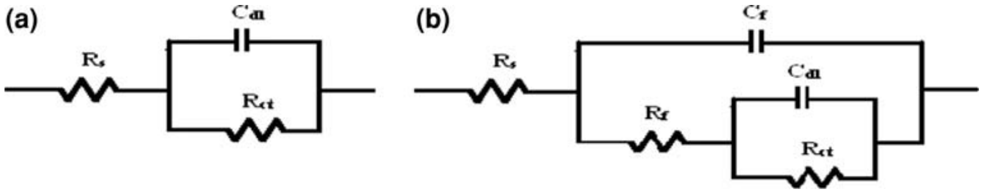

Fig. 2 Equivalent circuit to model the EIS spectra obtained from samples immersed in **a** ZP extract for all exposure and ZPA extract after 1 and 4 h and **b** ZPA extract after 24 h

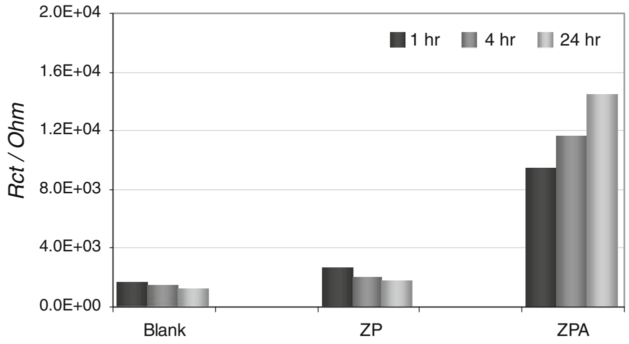

Fig. 3 Influence of ZP and ZPA presence on charge transfer resistance (R_{ct})

the charge transfer resistance, C_{dl} the double layer capacitance, R_f the precipitated layer resistance and C_f the precipitated layer capacitance.

The phase angle (θ) at high frequencies is one of the useful elements which is extracted from EIS data. It is able to facilitate evaluation of the behavior of the system under study when the frequency is high. The tendency of AC current to pass through the resistor in the circuit leads to a drop in the phase angle. Hence, the system exhibiting higher resistance can be characterized by higher phase angle [29]. Accordingly, phase angle values (θ) of 4.32 and 19.82 at 10 kHz for the samples exposed to ZP and ZPA extracts, respectively, may reflect enhanced inhibitive characteristics of ZPA. This is supported by the results of ICP-OES where ZPA appears to release more corrosion inhibiting species.

The influence of the presence of ZP and ZPA on the charge transfer resistance (R_{ct}) is shown in Fig. 3. A superior inhibitive performance is deduced from the significant difference between R_{ct} values of modified pigment

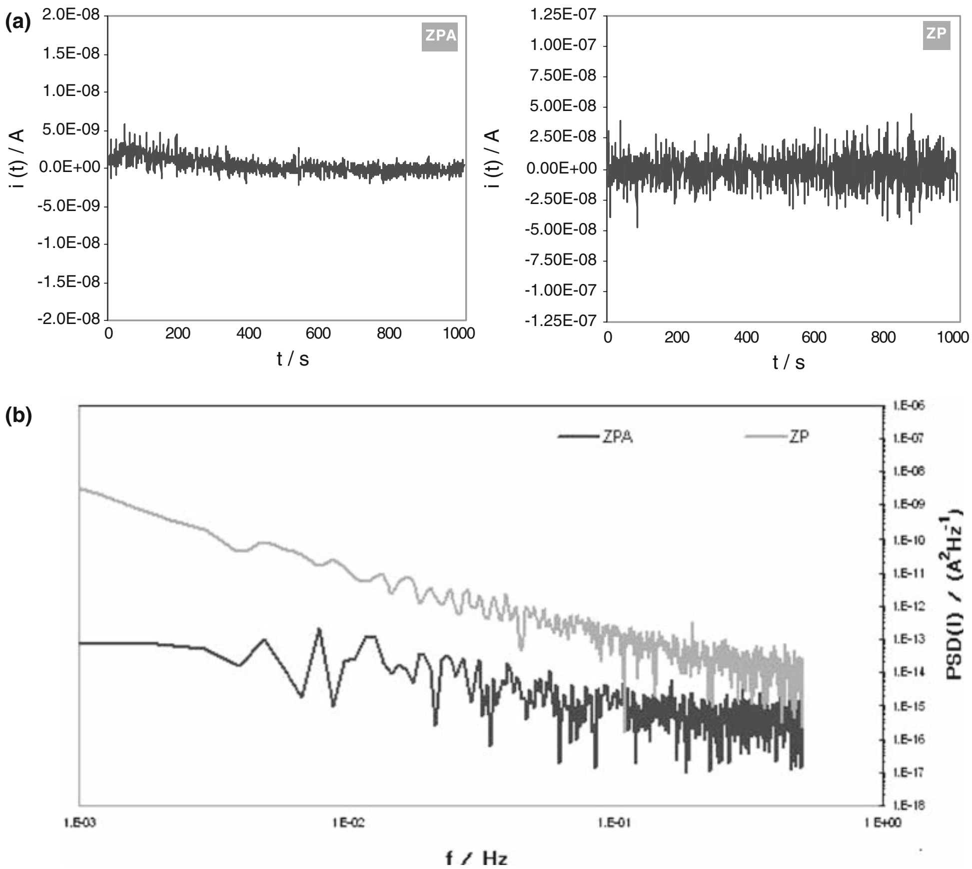

Fig. 4 Time records of electrochemical current noise associated with steel panels after 24-h immersion in ZPA and ZP extract (**a**) and the corresponding PSD(I) plots (**b**)

in comparison with those of ZP. Moreover, an ascending trend is met in terms of charge transfer resistance in the presence of ZPA as time elapses. Precipitation of a protective layer on the steel may be responsible for this trend.

The time records of electrochemical current noise and the corresponding PSD plots associated with the steel specimens after 24 h immersion in the test solutions are presented in Fig. 4a, b, respectively. The samples exposed to ZP extract generated current fluctuations with higher amplitude compared to those dipped in ZPA extract. The slope of the PSD(I) plot for ZP is higher than that for ZPA. A drop in the noise level, as well as the appearance of an approximately frequency-independence in the current noise spectral analysis indicates lower electrochemical activity reflecting an improvement in the corrosion inhibition [30, 31].

The noise resistance (R_n) obtained through dividing the standard deviation of potential by the standard deviation of current (σ_V/σ_I) is a measure of inhibitive performance [23, 32]. Figure 5 displays the variation of R_n for the samples immersed in the solutions as a time function. Interestingly, a good trend correlation between R_{ct} and R_n values is observed. In the presence of ZPA, a significant increase in both R_{ct} and R_n parameters demonstrates excellent corrosion protection. The increasing trend of charge transfer and noise resistance within exposure to ZPA extract suggests that the surface is gradually covered by a protective layer.

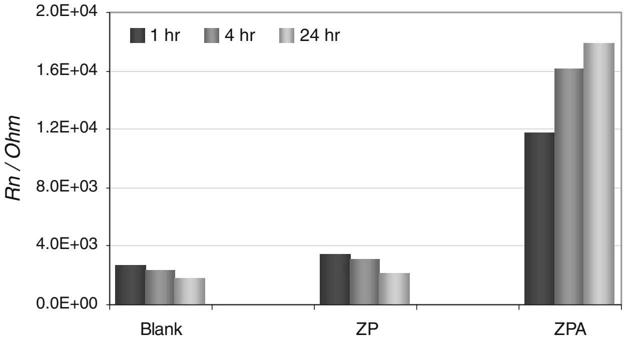

Fig. 5 Noise resistance (R_n) evolution in presence of ZP and ZPA

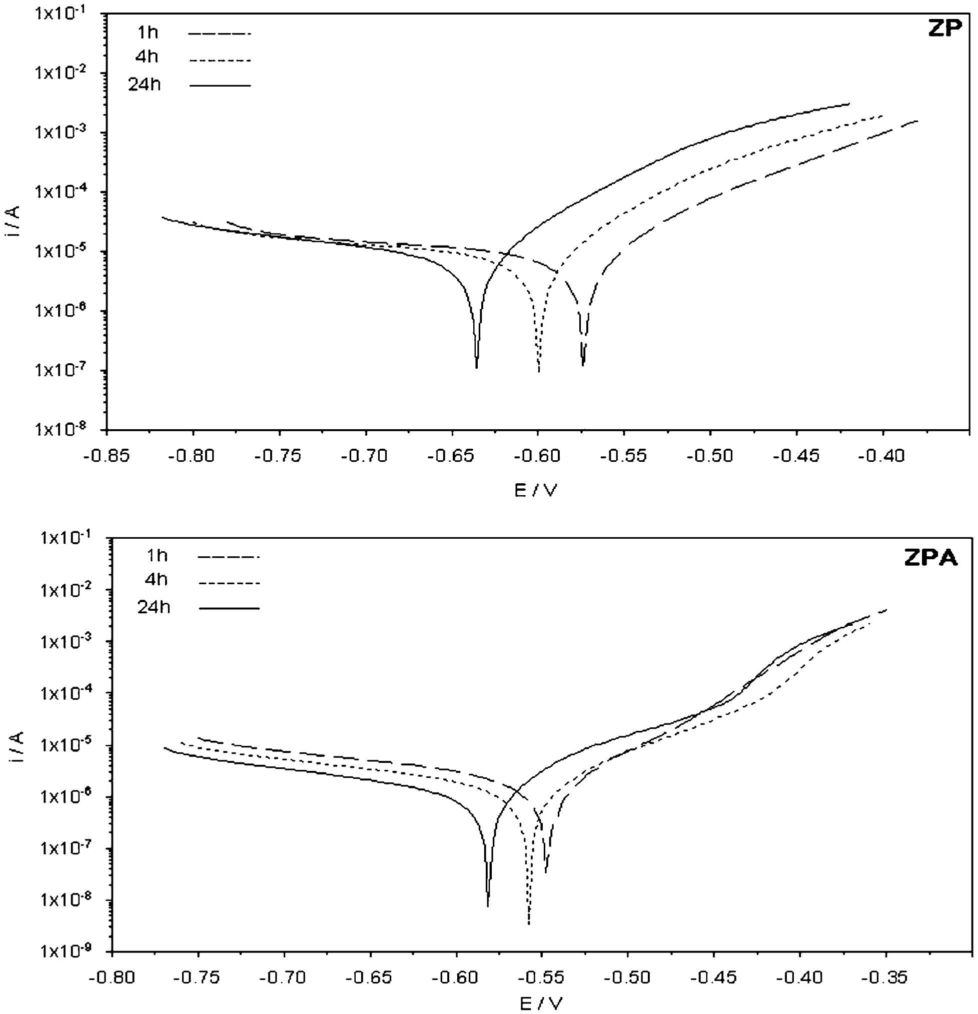

Fig. 6 Time dependent polarization curves of the samples exposed to ZP and ZPA extracts

Figure 6 shows polarization curves plotted for the samples exposed to ZPA and ZP extracts. ZPA has a noticeable effect on both cathodic and anodic branches. Deposition of a layer on the surface may be responsible for cathodic and also anodic polarization, supported by current density values which are exhibited in Fig. 7. Based on the comparative data in Fig. 7, introducing ZPA to 3.5% NaCl solution leads to a progressive decline in values of current density while a reverse trend is encountered in the presence of ZP. Thus corrosion inhibition is enhanced in the presence of modified pigment with exposure time. Since the rate of introducing the inhibitor to the metal surface under stagnant conditions is primarily dependent upon diffusion, which is a slow process [33], the continuous improvement in anticorrosion performance may be attributed to a precipitated film which grows with time. The deposition is able to restrict access of aggressive species to the metal surface.

Figure 8 shows the surface morphology of samples immersed in ZPA and ZP extracts after 24 h. The images confirm speculation relating to film formation. In other words, deposition occurs on the panel surface exposed to 3.5% NaCl solution containing ZPA extract while no layer is detected in the case of ZP. The composition of the precipitated film detected by EDX was mainly Fe (90.59%), Zn (2.99%), P (3.34%) and Al (0.54%).

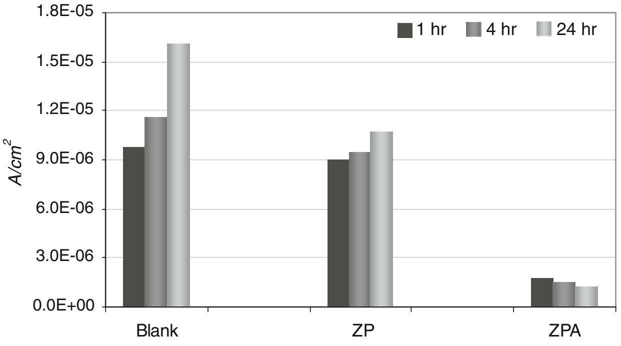

Fig. 7 Current density variations in the presence of ZP and ZPA

4 Conclusion

Investigation of the inhibitive behavior of ZPA representing second generation phosphate-based anticorrosion pigments by means of electrochemical techniques along with surface analysis led to the following conclusions:

- Phase angle (θ) at 10 kHz as a measure of corrosion prevention exhibited a notable effect of ZP modification.
- The trend and magnitude of R_{ct} and R_n as well as current density values and the appearance of impedance spectra and PSD(I) suggest that surfaces exposed to ZPA are covered gradually by a protective layer. This was supported by the results of SEM/EDX.
- A good trend correlation was demonstrated by comparing the values of R_n obtained by the noise data analysis and those of R_{ct} provided through EIS data analysis.
- The superior anticorrosion performance of ZPA, releasing much more inhibiting species in accordance with ICP-OES results, revealed the effectiveness of ZP modification.

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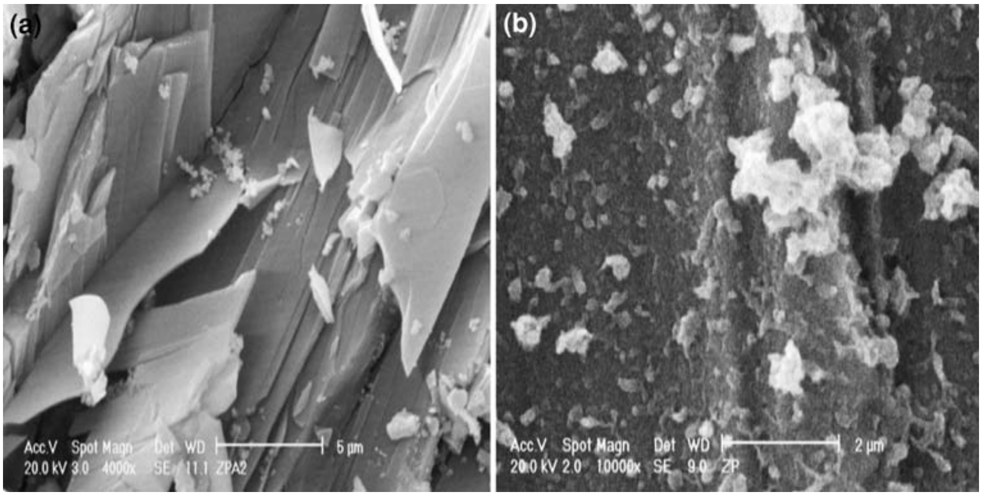
Fig. 8 SEM image of the sample surface immersed in **a** ZPA and **b** ZP extract after 24 h



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