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The effects of zinc aluminum phosphate (ZPA) and zinc aluminum polyphosphate (ZAPP) mixtures on corrosion inhibition performance of epoxy/polyamide coating

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ABSTRACT

The epoxy/polyamide coating was loaded with different pigment mixtures of the zinc phosphate (ZP), zinc aluminum phosphate (ZPA) and zinc aluminum polyphosphate (ZAPP) pigments. The electrochemical impedance spectroscopy (EIS) and salt spray test were used to investigate corrosion inhibition performance of the coatings. The adhesion strengths of the coatings were measured by a pull-off test. Results revealed lower coating pull-off strength loss when the ZPA and ZAPP pigments were used. A significant decrease in number of blisters together with low pull-off strength loss and best corrosion inhibition properties were observed when the mixture of 80:20 of ZAPP:ZPA was used.

1. Introduction

Utilizing organic coatings serve as a key method to protect metal structures against corrosion. Attempts have been made to improve the corrosion inhibition of the coatings using different types of pigments i.e. nano material, metal oxides and layer silicates in recent years [1–4]. Using inorganic pigments with capability of releasing corrosion inhibiting substances (like chromates) is one way to achieve a reliable performance [5–8]. In spite of having good corrosion inhibition properties, the use of chromate pigments has been restricted due to its negative effects on the environment and toxicity. Among several non-toxic anticorrosive pigments developed so far, the zinc phosphate types are the most widely employed as an alternative. These pigments can slightly dissolve in water followed by precipitation of a passive oxide film on the metal surface. This passive film can block the active zones on the metal surface and reduce the rate of electrochemical process [9–12]. The conventional zinc phosphate pigment, due to its low solubility in water, has poor corrosion inhibitive performance. Therefore, several physical and chemical modifications have been performed on this pigment to improve its solubility as well as its corrosion inhibition. This has led to introducing second and third generations of these pigments [13–16]. In previous works, it was shown that zinc aluminum phosphate (ZPA) and zinc aluminum polyphosphate (ZAPP) represent better corrosion inhibition performances in comparison with conventional zinc phosphate and zinc chromate pigments due to their higher solubility in water [13]. It was also indicated that ZAPP has better corrosion inhibition properties than ZPA [17]. The electrochemical impedance spectroscopy (EIS) is a powerful non-destructive method to evaluate the corrosion inhibition performance of the organic coatings. The quantitative and qualitative data obtained from EIS can assess the coating system against corrosion process. By taking advantage of EIS technique, inhibitive characteristics of the anticorrosive pigments can be examined [18–23].

The present work intends to evaluate the effect of ZP and mixture of ZAPP and ZPA pigments in the epoxy/polyamide coating when the corrosion inhibition and adhesion properties are considered.

2. Experimental

2.1. Materials

The st-37 type steel panels (10 cm × 7 cm × 0.15 cm) were prepared from FooladMobarake Co. The elemental composition of the steel is presented in Table 1.

A G27 7071X75 (base on bisphenol A) type epoxy resin together with a polyamide curing agent (supplied by Saman Co.) were used to produce the epoxy coatings. Different types of pigments including ZP, ZPA and ZAPP were prepared from Heubach Ltd Co. The pigments technical information is presented in Table 2. The CPVC values were calculated for each of the pigments (the results

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Table 1
The elemental composition of the steel panels.

Elements	Fe	C	Si	Mn	P	S	Al
Wt%	99.01	0.19	0.34	0.32	0.05	0.05	0.04

are given in Table 2) using Eq. (1) [24]:

$$\mathrm{CPVC} = \frac{1}{1 + (\mathrm{O.A.} \times \rho/93.5)} \tag{1}$$

where O.A. and ρ represent oil absorption and pigment density respectively.

2.2. Sample preparation and coating application

The oxide/hydroxide, mill scale and other kinds of contamination were removed from the steel substrates before paint application. To this end, an acid pickling procedure was carried out on the steel samples using hydrochloric acid (20 wt%) for 10 min. Then samples were washed by distilled water followed by degreasing using acetone. Finally, samples were kept in a desiccator.

The epoxy coatings were prepared using different mixtures of ZAPP and ZPA pigments. To this end, the weight mixtures of 100:0, 80:20, 60:40, 40:60, 20:80 and 0:100 of ZAPP:ZPA pigments were added to the epoxy resin formulation. All formulations were prepared at constant lambda (pigment volume concentration (PVC)/critical pigment volume concentration (CPVC)) of 0.6. In addition to these coating formulations, the epoxy coatings without any pigment and loaded with ZP (PVC = 36.5%) were prepared as reference samples. The mixture of resin and particles were then mixed by a pearl-mill mixer until the average particle size up to 10 μm was achieved. The leveling agent (BYK-306), defoamer (Efka-2025) and dispersing agent (DispersBYK 110) were utilized to control the film application properties and the pigment dispersion stability. The composites were then mixed with a stoichiometric value of a polyamide curing agent (70:30). At the end, the final coatings were applied on the cleaned steel panels using a film applicator. The dry film thickness of 20 ± 2 μm was obtained after the coating curing process at 120 °C for 30 min.

2.3. Characterization

The corrosion inhibition performance of the coatings was studied by the salt spray and electrochemical impedance spectroscopy (EIS) analyses. The salt spray test was carried out on $3 \times 3\ \mathrm{cm}^2$ areas of the samples in a salt spray cabin S85 V400 (made by Pars Horm Co.) according to ASTM B117. The NaCl 5% w/w solution was directly sprayed to the samples for 240 h.

The corrosion resistance of the coated samples was also studied by an AUTOLAB PGSTAT12 type EIS. The perturbation and frequency range of the measurement was ±10 mV and 10 kHz–10 mHz respectively. The electrochemical system which was used included platinum electrode (auxiliary electrode), KCl (3 N) Ag/AgCl electrode (reference electrode) and metal sheet (working electrode). The experiment was carried out on $9\ \mathrm{cm}^2$ area after 7 and 35 days immersion times. A frequency response analysis (FRA) program was utilized in order to analyze the results obtained from the Nyquist and Bode plots. A Posi test digital pull-off adhesion tester (DeFelsko Corp) was used to determine the epoxy coating adhesion strength before (dry pull-off) and after 35 days immersion (wet pull-off) times in NaCl 3.5% w/w. The coatings morphology changes were studied by an optical microscope (Leica DMRX) and a digital camera after 35 days immersion in NaCl 3.5% w/w solution.

3. Result and discussion

3.1. Corrosion inhibition properties investigation

The electrochemical performance of the coatings was studied by an EIS technique. The Nyquist and Bode plots of the samples are displayed in Figs. 1 and 2. As can be seen in these figures, most of Nyquist plots composed of two time constant semicircle revealing the corrosive electrolyte permeation into the coating/metal interface.

Figs. 1 and 2 show a capacitive behavior at high frequency and a resistive behavior at low frequency regions. In the capacitive behavior the high resistant coating impede current to path through the coating resistance. Unlike capacitive behavior, in the resistive behavior, the low resistant coatings afford current to path through conductive pathways [25]. For the all coatings, the EIS response reveals a capacitive behavior at frequency region from 10 kHz to 10 Hz after 7 days immersion. The capacitive behavior observed at high frequencies, which is related to the first time constant, represents barrier properties of the coating [26,27]. The break frequency values (f_b) of the samples were measured from Figs. 1 and 2 and the results obtained are displayed in Fig. 3.

As can be clearly seen in Fig. 3, the f_b increased after 35 days immersion compared to 7 days immersion. This observation reveals that the capacitive region was considerably shifted to higher frequencies. It can be seen that the increase in f_b, revealing the shift in capacitive region to higher frequencies, of the blank sample and ZP loaded coating were higher than other samples. This observation obviously declares a significant reduction in the barrier properties of these two coatings after 35 days immersion. Despite blank and ZP sample, the f_b values of the coating reinforced with 80:20 ZAPP/ZPA did not change significantly which confirms better barrier properties of this coating.

One of the factors which can affect the corrosion inhibition performance of the coatings is the solubility of the pigments. The solubility data for ZP, ZPA and ZAPP pigments are summarized in Table 3 [28,29].

As can be seen in Table 3, the modified pigments including ZPA and ZAPP have higher solubility than ZP one. Moreover, the solubility of Zn ions of ZAPP is significantly higher than ZPA. Another difference of these two pigments is the higher aluminum content of ZAPP (11–13%) compared with ZPA (4–5.5%). The ZPA and ZAPP are active pigments with corrosion inhibitive behavior. In previous works, it was shown that ZAPP and ZPA could release

Table 2
Technical data for the employed pigments.

Pigment	Trademark	Zinc (%)	Phosphorus		Aluminum (%)	Density (g/cm^3)	Oil absorption (g/100 g)	CPVC (%)	Average particle size (μm)
			As P_2O_5 (%)	As PO_4 (%)					
Zinc orthophosphate hydrate	Zinc phosphate ZP10	50.5–52	–	47–49	–	3.7	20	55.8	2–3.5
Zinc aluminum polyphosphate	HEUCOPHOS ZAPP	28–31	46–49	–	11–13	3.1	35	46.3	2–3.5
Zinc aluminum phosphate	HEUCOPHOS ZPA	38.5–40.5	–	53–56	4–5.5	3.1	40	43	2–3.5