AN IMPROVEMENT TO THE ANTICORROSIVE PROPERTIES OF EPOXY POWDER COATING BY ZINC PHOSPHATE AND ZINC ALUMINUM PHOSPHATE PIGMENTS

Alireza Ghanbari and Mohammad Reza Mohammadzadeh Attar*

Polymer Engineering and Color Technology Department, Amirkabir University of Technology, Tehran, Iran

ABSTRACT

Epoxy powder coatings containing zinc aluminum phosphate (ZAP) and zinc phosphate (ZP), which are the 2nd and 1st generation of phosphate-based pigments respectively, were applied to the surface of mild steel sheets. The anticorrosive performances of the coated samples were studied using electrochemical impedance spectroscopy (EIS). Cathodic disbonding resistance and the adhesion performance of the two coating systems were measured by cathodic delamination and pull-off test respectively. The charge transfer resistance and double layer capacitance obtained from EIS revealed the greater anticorrosive performance of the coating modified by zinc aluminum phosphate compared to the one treated with zinc phosphate. While an electrolyte diffuses in the organic coating, phosphate pigments dissolve and make a passive layer on the surface of mild steel. Due to the more solubility of ZAP in comparison with ZP, the cathodic desbonding resistance and adhesion of the epoxy powder coating containing ZAP were greater than those of ZP-loaded powder coating. The results show that the anticorrosive performance of the epoxy powder coating containing ZAP is better than that of the epoxy powder coating modified with ZP.

Keywords: Phosphate Pigment, Powder Coating, EIS, Cathodic Disbanding, Pull-off Test

INTRODUCTION

Epoxy powder coatings have been widely used to protect metal substrates from corrosion [1,2]. Different kinds of organic and inorganic pigments have been used to improve the anticorrosion performance of epoxy powder coatings. Chromates due to their excellent anticorrosion performances have been widely used to improve the protection behavior of the epoxy coatings. However, chromates are toxic and carcinogenic [3,4]. Environmental regulations have become stricter in recent years. Attempts have been carried out to use environmentally friendly alternatives. Zinc phosphate is one of these alternatives. New modifications are performed and new generations of ZP have been produced [3-5].The anticorrosive performance of zinc phosphate and zinc aluminum phosphate (the first and second generation of phosphate-based pigments respectively) in epoxy powder coatings was studied using electrochemical impedance spectroscopy (EIS). It is well known that the inhibitive performance of various anticorrosive compounds could be successfully investigated by EIS. EIS offers a

powerful method to examine the corrosion phenomenon of the metallic substrates by providing qualitative and quantitative data [6-8]. One of the most important requirements of protective coatings is resistance against cathodic disbondment. The combination of cathodic protection and organic coatings is used in order to ensure the long-term protection of steel structures continuously exposed to an electrolyte [8]. As a result, the anticorrosive performance and cathodic disbonding resistance of organic coatings are two vital parameters for a variety of organic coating systems [9]. The disbonding is referred to the loss of bond at the edge of holidays in the coating due to the high-pH environment beneath the film as a net result of cathodic reaction [10,11]. In this study, an attempt is made to improve the adhesion properties as well as the anticorrosion resistance of an epoxy powder coating on the surface of mild steel. ZAP and ZP were used to improve the anticorrosion performance as well as coating resistance against cathodic delamination. Furthermore, the role of pigment type on the adhesion of the epoxy powder coating was investigated using pull-off test.

EXPERIMENTAL

Preparation of Epoxy Powder Coatings

Epoxy powder coatings were prepared using ZP and ZPA pigments according to Table 1.

Table 1: The formulation of epoxy powder coating used in this work

Component	w/w%
Epoxy Resin (Bisphenol A), EEW=750	72.4
Hardener (Dicyandiamid)	3.9
Degasing Agent	0.49
Flow Agent	1.21
Wax	7
Pigment (ZP or ZAP)	15

The compounds listed in Table 1 were blended in an extruder and then grinded to make a fine powder. The ZP and ZAP pigments were supplied by Heubach Co. Epoxy powder coatings were applied to the ST 37 steel samples. Samples were cured at 180 °C for 20 min. The dry film thickness (DFT) of the coatings was about 30±5 μm.

Characterization

The anticorrosion performance of the epoxy powder coatings was studied by electrochemical impedance spectroscopy (EIS). To this end, an area of 1 cm^2 of each sample was exposed to 3.5 wt% NaCl solution up to 63 days. The test was carried out at open circuit potential (OCP) within a frequency range of 10 mHz to 10 kHz (with the perturbation of ±10 mV). FRA software was used to analyze the information obtained from EIS measurement. EIS was carried out in a three-electrode electrochemical cell including reference electrode (saturated Ag/AgCl), auxiliary electrode (Pt), and working electrode. In order to evaluate the cathodic disbonding of coated substrates, an artificial hole with a diameter of 1 mm was drilled at the center of each sample. The test was carried at the cathodic potential of -1.38 V vs. Ag/AgCl using a magnesium sacrificial anode. A pull-off test method was employed according to ASTM D 4541-02; studs with a diameter of 25.4 mm were fixed to the surface of the coated panels with a cyanoacrylate adhesive. The fixture was pulled at 5 mm.min^{-1} using an Instron machine (the universal testing instrument) until the powder coating material was detached from the substrate. For each test, four replicate samples were employed, with the average value cited.

RESULTS AND DISCUSSION

Two different coating systems studied herein are presented in Table 2.

The anticorrosion performances of the epoxy powder coatings, modified with ZP and ZPA pigments, were studied by EIS. The Nyquist plots of the samples are shown in Figure 1.

Table 2: Different coatings studied herein

Pigment of epoxy powder coating	Substrate	Abbreviation
ZP	Bare mild steel	ZP_b
ZAP	Bare mild steel	ZAP_b
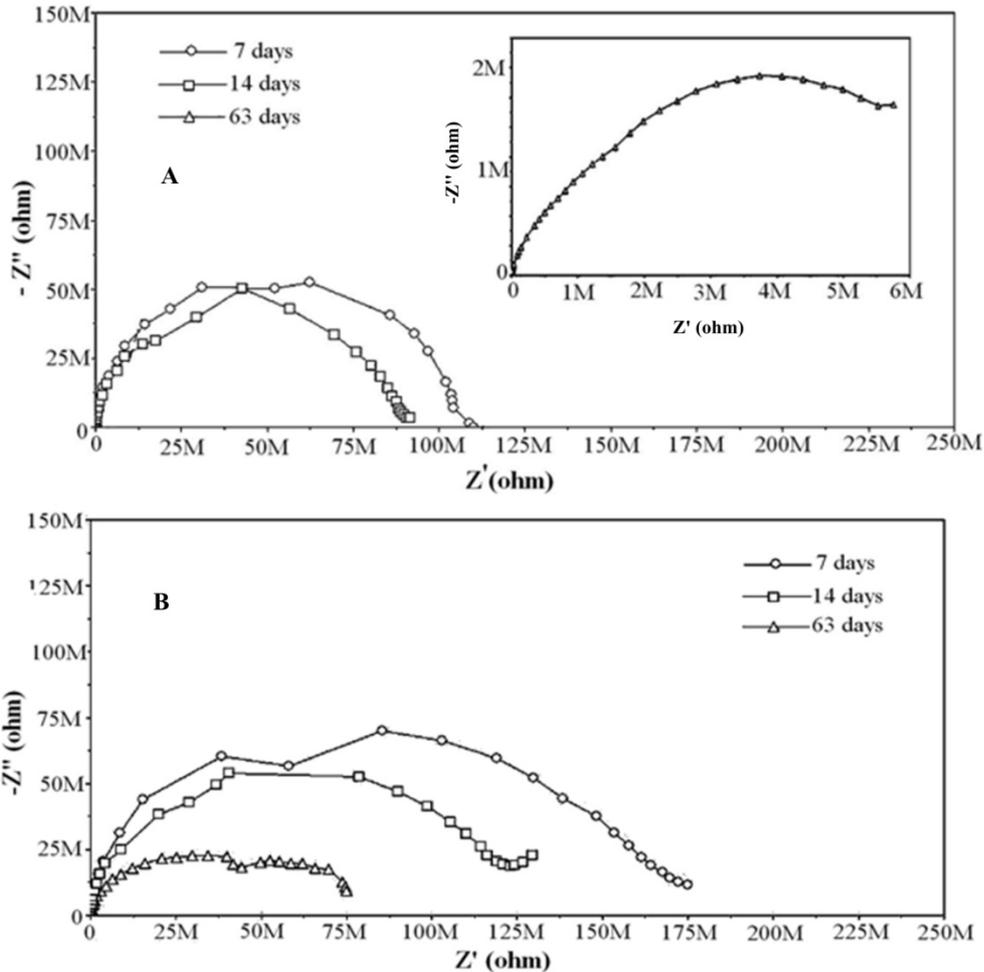
Figure 1: Typical Nyquist diagrams of ZP_b (A) and ZAP_b (B) during different immersion times in a 3.5 wt.% NaCl solution

Using electrical model shown in Figure 2, the Nyquist plots were fitted by AUTOLAB FRA software (Table 3) [6].

In Figure 2, R_s and R_{ct} represent electrolyte resistance and charge transfer resistance respectively; C_{dl} stands for double layer capacitance and R_c is coating resistance.

The values of coating resistance (R_c) is signify-cantly decreased after 63-day exposure time. Moreover, R_{ct} and C_{dl} are observed after 63 days of sample immersion. This observation can clearly show the electrolyte diffusion to the coating/metal interface.
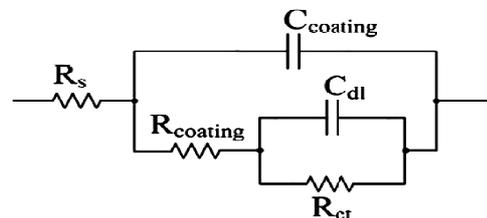
Figure 2: Equivalent electrical model of the coated mild steel

The order of R_c and R_{ct} of the samples is ZAP_b > ZP_b, while the order of C_{dl} of the samples (after 63 days) is ZP_b > ZAP_b.

Table 3: Characteristic parameters evaluated from the impedance diagram for coating systems

	Immersion time (Days)	$R_{coating}$ (Mohm.cm^2)	R_{ct} (Mohm.cm^2)	$C_{dl} \times 10^8$ (F.cm^{-2})
ZAP$_b$	7	163.9	-	-
	14	122.3	-	-
	63	33.9	42.4	5.82
ZP$_b$	7	107	-	-
	14	90.9	-	-
	63	1.98	12.53	10.05

The results show that the anticorrosive performance of ZAP-modified samples is greater than that of ZP-treated samples. When ZP and ZAP pigments are exposed to aqueous solutions, the Zn^{2+} and phosphate ions will be extracted from pigments in the coating matrix (Equation 1) [5].

$$Zn_3\left(PO_4\right)_2 \rightleftarrows 3Zn^{2+} + 2PO_4^{-3} \qquad (1)$$

Furthermore, when electrolyte reaches coating/metal interface, the following electro-chemical reactions happen [4].

$$Fe \rightleftarrows Fe^{2+} + 2e^- \qquad (2)$$

$$2H_2O + 2O_2 + 4e^- \rightleftarrows 4OH^- \qquad (3)$$

The corrosion products of steel substrate (Fe^{2+} and OH^-) react with Zn^{2+} and PO_4^{3-} ions and following reactions happen [8,9].

$$Zn^{2+} + 2OH^- \rightleftarrows Zn\left(OH\right)_2 \downarrow \qquad (4)$$

$$3Fe^{2+} + 2PO_4^{3-} \rightleftarrows Fe_3\left(PO_4\right)_2 \downarrow \qquad (5)$$
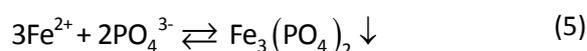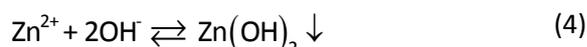
As a result, the reaction of corrosion products and pigment extracts produces insoluble species, namely $Zn(OH)_2$ and $Fe_3(PO_4)_2$, and reduces the corrosion of substrate according to the two following mechanisms:

1. Pore plugging of organic coating and decreasing the diffusion of corrosive species to the metal surface;

2. the passivation of steel substrate due to the formation of a passive layer on the metal surface and hindering the access of aggressive species to the metal surface.

By considering the mentioned mechanisms, the solubility of the phosphate pigments is the most important parameter in determining the anticorrosive performance of phosphate pigments.

The solubility of ZP and ZAP are completely different. The results obtained from the ICP-OES analysis of ZP and ZAP pigments in a 3.5 wt.% NaCl solution are shown in Table 4 [5].

Table 4 shows the higher solubility of zinc and phosphate ions of ZAP compared to ZP; also, the results show the better anticorrosion performance of ZAP-loaded coating compared to the sample containing ZP. It is quite clear that pore plugging and the formation of a passive layer is more probable in the coating containing ZAP compared to the one modified by ZP because of the more solubility of ZAP. This indicates that the permeation of the corrosive electrolyte into the coating containing ZPA is considerably lower compared to the coating containing ZP.

The passive layer and pore plugging can hinder corrosive electrolyte permeation into the surface of metal. This can be responsible for the increase in mild steel corrosion resistance against a 3.5 wt% NaCl solution. Therefore, the film formation at metal/coating interface containing ZAP is more effective than the one created in the coating reinforced with ZP.

Table 4: The result of ICP-OES analysis of the pigment extracts in a 3.5 wt.% NaCl solution

		ZP extract	ZAP extract
Solubility [mg/l]	**[Zn]**	7.81	39.02
	[P]	1.32	16.21

This can be understood from the higher value of R_{ct} of the ZAP-loaded sample. The decrease in R_{ct} of ZP-loaded sample is greater than that of the ZAP-loaded coating. This is because of the higher diffusion of corrosive electrolyte into the surface of metal when it is coated by the epoxy coating containing ZP.

The results of pull-off adhesion test and dis-bonded area after 5 days immersion in a 3.5 wt.% NaCl solution are presented in Table 5.

As it can be seen in Table 5, pigment type varies the adhesion of coating to the steel substrate. Pigment dissolution increases the surface polarity of the steel (Figure 3). Therefore, the adhesion strength of the coating to the metal surface can be enhanced.

Table 5: Results of pull-off adhesion test and disbonded area after 5 days immersion in a 3.5 wt.% NaCl solution for different coating systems

	ZP_b	ZAP_b
Pressure (psi)	2800	3100
Disbonded Area (mm^2)	615	200
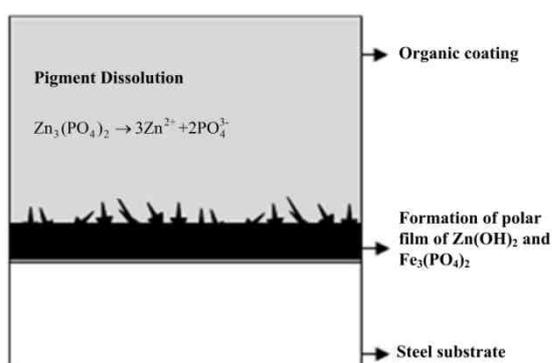
Figure 3: Precipitation of the phosphate pigment and the increment of surface polarity

On the other hand, the passive film of pigment extract, i.e. $Fe_3(PO_4)_2$ and $Zn(OH)_2$, formed on the metal surface is polar and increases the coating/interface adhesion. Coating with stronger adhesion bonds can significantly decrease the corrosion product creation as well as corrosion products spread beneath the coating [5]. An increment in adhesion can increase the cathodic disbandment resistance of the coating systems (Table 5).

CONCLUSIONS

The effect of ZP and ZAP in the epoxy powder coating on the bare mild steel substrate was assessed. Based on the results obtained, the following conclusions can be drawn:

- The anticorrosive performance of ZAP in the epoxy powder coating was greater in comparison with ZP. The EIS results showed that the resistance parameters of epoxy powder coatings containing ZAP were greater than those of the samples containing ZP. The solubility of zinc and phosphorus ions is higher in ZAP than ZP, causing a marked drop in the charge transfer resistances of ZP.

- Due to more solubility of the ZAP pigments, the adhesion of epoxy powder coating containing ZAP is better than the ZP-loaded coating.

- The cathodic disbondment resistance of the coating systems studied in this work follows the sequence of $ZAP_b > ZP_b$. This could be attributed to the difference in the solubility of pigments and the difference in the polarity of the substrates, which leads to the formation of a protective layer and an increase in adhesion strength.

REFERENCES

[1] Andersen P. J., Johansen V., "Particle Packing and Concrete Properties,"

American Ceramic Society, **1995**, *12*, 111-146.

[2] Heikal M., Diadamony H. E., and. Morsy M. S., "Limestone-filled Pozzolanic Cement*," Cem. & Concr. Res*., **2000**, *30*, 1827-1834.

[3] Bonavetti V., Donza H., Menendez G., Cabera O., and Irassar E. F., "Limestone Filler Cement in Low W/C Concrete: A Rational Use of Energy*," Cem. & Concr. Res*., **2003**, *33*, 865-871.

[4] Pera J., Husson S., and Guilhot B., "Influence of Finely Ground Limestone on Cement Hydration," *Cem. & Concr. Comp.* **1999***, 21*, 99-105*.*

[5] Svermova L., Sonebi M., and Bartos P. J. M., "Influence of Mix Proportions on Rheology of Cement Grouts Containing Limestone Powder," *Cem. & Concr. Comp*., **2003**, *25*, 737-749.

[6] Saout G. L., Le´colier E., Rivereau A., and Zanni H., "Chemical Structure of Cement Aged at Normal and Elevated Temperatures and Pressures Part I. Class G Oilwell Cement," *Cem. & Concr. Res*., **2006**, *36*, 71-78.

[7] Hodne H., Saasen A., O'Hagan A. B., and Wick S. O., "Effects of Time and Shear Energy on the Rheological Behavior of oil Well Cement Slurries," *Cem. & Concr. Res.*, **2000***, 30*, 1759-1766.

[8] Niu Q., Feng N., Yang J., and Zheng X., "Effect of Superfine Slag Powder on Cement Properties," *Cem. & Concr. Res*., **2002**, *32*, 615-621.

[9] Glasnovi A. and Hraste M., "The Grinding Equation in the Investigation of the Coarse Dispersing System of Cement," *Cem. & Concr. Res.,* **1982**, *12*, 415-424.

[10] Agawa K., Uchikawa H., Takemoto K. and Yasui I. V., "The Mechanism of the Hydration in the System C_3S Pozzolans," *Cem. & Concr. Res*., **1980**, *8*, 683-696.

[11] Davraz M. and Gunduz L., "Engineering Properties of Amorphous Silica as a New Natural Pozzolan for Use in Concrete", *Cem. & Concr. Res*., **2005**, *35*, 1251-1261.