



Application of the electrochemical noise to investigate the corrosion resistance of an epoxy zinc-rich coating loaded with lamellar aluminum and micaceous iron oxide particles



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ARTICLE INFO

Article history:

Received 27 February 2013

Accepted 24 July 2013

Available online 1 August 2013

Keywords:

A. Zinc

B. EIS

C. Cathodic protection

C. Paint coating

ABSTRACT

The effects of partial replacement of zinc particles by micaceous iron oxide (MIO) and lamellar Al particles on the corrosion protection properties of an epoxy zinc rich coating were studied. Electrochemical noise (ECN), electrochemical impedance spectroscopy (EIS) and salt spray were utilized in order to investigate the cathodic protection properties of the coatings. Results showed that partial replacement of zinc dust particles by barrier MIO and Al particles caused corrosion protection properties enhancement of the zinc rich coating without reducing its sacrificial properties. The MIO loaded coating showed better corrosion protection properties compared with Al loaded one.

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1. Introduction

Epoxy coatings have been widely used in order to protect metals against corrosion in corrosive environments. Many different types of anticorrosive pigments including zinc phosphates [1], zinc chromates, nanoparticles [2,3] and additives [4] have been utilized in order to enhance the protective properties of an organic coating. Metallic particles have been widely used in the organic/inorganic coatings to protect metal bodies in corrosive marine and industrial environments even when there is a slight mechanical damage to the coating [5–9]. The ratio of pigment volume concentration (PVC) to the critical pigment volume concentration (CPVC) in common organic paints is <1. However, the corrosion protection ability of the zinc-rich coating does not come from barrier properties. The zinc dust presented in the coating provides cathodic protection. To this end, the ratio of PVC/CPVC should be >1. In fact, the zinc particles sacrificial action occurs when there is a continuous contact between the metal particles. Zinc-rich coatings provide good sacrificial protection during earlier stages of its service life. However, zinc oxides/hydroxides will be produced at the later stages, causing metal particles contacts reduction. In fact, corrosion products of zinc can fill the coating porosities and therefore reduce its cathodic

protection duration [10–18]. In this case, the coating shows more barrier properties instead of cathodic protection against corrosive electrolyte. The sacrificial protection of a zinc-rich paint depends on many factors mainly zinc content and the morphology of the particles [13]. Recent findings show that smaller and lamellar particles give better results than larger and spherical particles. In recent years, attempts have been carried out to produce zinc-rich paints with enhanced corrosion protection properties. Schaefer and Miszczyk [6] studied the cathodic protection properties of a zinc rich coating by the replacement of a small part of micro-size zinc dust by nanoparticulate zinc. They showed that exchanging a small part of zinc microparticles by nanoparticulate zinc could improve the electrochemical action of the coating. Arianpouya et al. [19] studied the synergistic effect of nanozinc/nanoclay additives on the corrosion performance of zinc-rich coating. They found that both nano-zinc and nano-clay particles increase the corrosion resistance of the zinc-rich coating by enhancing its barrier properties. Jagtap et al. [20] found that addition of small amount of zinc oxide to the zinc-rich coating improved its barrier properties and therefore corrosion resistance. Zhang et al. [21] studied the zinc rich coating protective properties in the presence of modified silicon-based vehicle and lamellar Zn (Al) pigments. They found that zinc rich coating protective properties were enhanced in the presence of the pigments. Gergely et al. [22] studied the corrosion protection properties of the zinc-rich coatings loaded with nano-size alumina supported polypyrrole. They found that nano-size alumina

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provided moderate galvanic function with enhanced electrolytic barrier properties. Kakaei et al. [23] investigated the effects of partial replacement of zinc particles by micaceous iron oxide (MIO) on the corrosion protection behavior of an inorganic zinc rich coating. They showed that MIO particles reduced cathodic protection duration but increased the barrier properties of the zinc rich coating. The corrosion protection properties of the inorganic zinc rich coating were enhanced in the presence of barrier MIO particles. The effects particle size and shape on the zinc particles protective properties were studied. Kalendova [13] and Jagtap et al. [24] have found that corrosion protection properties of the zinc-rich coating can be enhanced by reducing zinc particle size. Moreover, the lamellar particles resulted in better cathodic protection against corrosive electrolyte compared with lamellar one. Hare and Kurnas [25] studied the effect of pigment/binder ratio on the corrosion performance of zinc-rich coatings. Park et al. [26] investigated the zinc particles surface modification on their sacrificial properties. They showed that surface modification of the zinc particles is an effective way to increase the sacrificial properties of the zinc-rich coating at intermediate concentrations of zinc particles by reducing their chemical reactivity. In this way, the rate of oxidation of zinc particles can be significantly reduced. As a result, the zinc rich coating loaded with surface modified particles showed longer service life compared with the coating loaded with unmodified particles.

The aim of this work is studying the effects of partial replacement of zinc particles by micaceous iron oxide (MIO) and lamellar Al particles on the corrosion protection properties of an epoxy based zinc-rich coating. Two different aims have been followed by replacement of zinc particles by MIO and Al pigments in the zinc-rich paint. These are (1) reducing zinc content in the zinc-rich coating formulation and (2) enhancing the coating service life. The aluminum particles are thermodynamically active and tend to react with oxygen and water. As a result, the surface of pigment usually includes an aluminum oxide/hydroxide layer. The oxide/hydroxide layer causes a decrease in aluminum particles sacrificial properties. However, the oxide layer seems to be sensitive against alkaline condition. The oxide layer will be removed from the surface of particles after exposure to alkaline pHs. This can lead to an increase in particles activity of reaction with oxygen and water [27–29]. Unlike Al, MIO is an inert pigment without electrochemical activity [27]. Because of its lamellar shape, it is known as a barrier pigment. It has been attempted to investigate the corrosion protection properties of zinc-rich paint in the presence of MIO particles.

The aim of this work is to investigate the effects of partial replacement of zinc particles by micaceous iron oxide (MIO) and lamellar Al particles on the corrosion protection properties of an epoxy based zinc-rich coating. Different techniques including electrochemical noise (ECN), electrochemical impedances spectroscopy (EIS) and salt spray test are used in order to investigate the zinc-rich paints corrosion protection properties. Measuring the OCP values in 3.5 wt% NaCl solution at different immersion times, the sacrificial protection of the coatings are studied. SEM was used to reveal coatings morphology before and after exposure to salt spray test.

2. Experimental

2.1. Materials and samples preparation

Epoxy zinc-rich coatings were prepared using an epoxy resin of Epiran-01 (obtained from Khozestan petrochemical (Iran)). The solid content and density of the epoxy resin were 75% and 1.099 g/cm³, respectively. Different types of pigments including zinc, alu-

minum and micaceous iron oxide (MIO) were used in the zinc rich coating formulation. The zinc particles were prepared from Iran Zinc Powder Co. The average particle size, oil absorption and density of the zinc dust used in this study were 5 μm, 6.7 g 100 g⁻¹ pigment, 6.95 g cm⁻³, respectively. The aluminum pigment (with lamellar shape) used in this study was an aluminum paste (supplied by Hempel Co.) with average size, density and oil absorption of 10 μm, 1.40 g cm⁻³ and 21 g 100 g⁻¹ pigment respectively. The MIO was supplied by MIOX SG Co. The density and average size of the pigment were 4.8 g cm⁻³ and 18 μm, respectively.

Four types zinc-rich coatings were prepared using Zn, Al and MIO pigments at different pigment volume concentrations (PVCs). The critical pigment volume concentration (CPVC) values were calculated according to following equation:

$$C = \frac{1}{1 + \left(\frac{O \times D}{93.2}\right)} \quad (1)$$

where C, O and D are critical pigment volume concentration (CPVC), oil absorption and density of the pigment respectively. The results obtained are given in Table 1.

Additives including leveling agent (BYK-306, 1 wt%), defoamer (Efka-2025, 0.5 wt%) and rheological modifier (Aerosil 200, 0.5 wt%) were added to the coatings formulations. The mixtures were then mixed for 20 min under mechanical mixing (1000 rpm). Finally, a stoichiometric value of polyamide curing agent (having solid content of 50%) was added to the coating formulations. The coatings prepared were then applied on the steel panels. The St-37 type (0.04 wt% Al, 0.05 wt% S, 0.05 wt% P, 0.32 wt% Mn, 0.34 wt% Si, 0.19 wt% C and 99.01 wt% Fe) steel panels were prepared from Foolad Mobarakeh Co. The steel panels were sand blasted to Sa2 1/2 before the paint application. The steel substrates were then degreased by acetone followed by drying in an oven at 40 °C. The epoxy zinc-rich coatings were then applied on the cleaned steel substrates at wet film thickness of 120 μm using a film applicator. The coated samples were kept at room temperature for 15 days. The dry film thickness of 60 μm was measured on the cured samples after 15 days.

2.2. Methods

2.2.1. OCP measurements

The open circuit potential (OCP) values of the zinc-rich paints were measured in 3.5 wt% NaCl solution at different immersion times. The OCP values were measured using an HIOKI type voltmeter with respect to an Ag/AgCl reference electrode at different immersion times. The test was carried out on three replicates to ensure the measurement repeatability.

2.2.2. Salt spray test

The salt spray test was carried out in a salt spray cabin S85 V400 (made by Pars Horm Co.) according to ASTM B117. The test was done on 3.5 cm × 3.5 cm area of the samples having the same coating thickness (60 μm). The rest of the coating surface was masked by a waterproof mixture of 3:1 of beeswax-colophony. The test was carried out on three replicates to ensure the measurement repeatability.

Table 1
The zinc rich coatings formulations.

Sample	Parameter	PVC	PVC/CPVC
	Pigment mixture		
Mixture 1	70 wt% Zn	59.36	1.05
Mixture 2	60 wt% Zn + 10 wt% MIO	59.93	1.08
Mixture 3	60 wt% Zn + 10 wt% Al	60.36	1.06
Mixture 4	60 wt% Zn + 5 wt% MIO + 5 wt% Al	61.04	1.14

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