



The effect of mixture of mercaptobenzimidazole and zinc phosphate on the corrosion protection of epoxy/polyamide coating



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ARTICLE INFO

Article history:

Received 11 February 2015

Received in revised form 1 April 2015

Accepted 27 April 2015

Available online 20 May 2015

Keywords:

Epoxy coating

Protective performance

Anticorrosion pigment

Corrosion inhibitor

Mild steel

ABSTRACT

The protective performance of solvent-borne epoxy/polyamide coatings formulated with zinc phosphate anticorrosion pigment was improved through the addition of 2-mercaptobenzimidazole as an organic corrosion inhibitor. In addition to determining the optimum percentage of mercaptobenzimidazole, the electrochemical impedance spectroscopy data could show the influence of inhibitor concentration on the epoxy behavior within 35 days of immersion in 3.5 wt% NaCl solution. The improved corrosion protection and adhesion strength in the presence of the pigment and inhibitor were connected to the deposition of a protective layer at the coating/substrate interface which might limit active zones for electrochemical reactions. The precipitation was confirmed using electrochemical impedance spectroscopy, polarization curves and SEM/EDX surface analysis.

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1. Introduction

One of the effective approaches to achieve a reliable and long-term corrosion protection is to use inorganic pigments with the capability of releasing corrosion inhibiting species [1–4]. Although chromate pigments offer good corrosion inhibition, their use has been restricted due to hazardous effect on the environment and human health [5,6]. The zinc phosphate pigment as conventional alternative for the toxic compounds has reported to reveal poor corrosion inhibitive performance due to its low solubility [7]. Thus, various enhancement approaches have been proposed which led to developing second and third generations of phosphate-based anticorrosion pigments [8–11]. Through taking advantage of surface analysis and electrochemical methods in both solution and coating phases, the previous works indicated the superior anticorrosion function of zinc aluminum phosphate (ZPA) and zinc aluminum polyphosphate (ZAPP) compared to zinc phosphate [8,12]. Moreover, the use of some organic corrosion inhibitors such as azoles [13–15], thioglycolate esters, mercaptocarboxylic acids [16], phenols, organic amines, organic sulfides and organic phosphate in protective coatings formulation [17] has been reported in the literature. The organic corrosion inhibitors allow for the creation

of optimal performing thin films and high gloss corrosion resistant coatings [18], probably due to their dissolution in the binder system. The main functionality of corrosion inhibitors and electrochemically active anticorrosion pigments in a coating formulation is the dissolution of active content in the permeated water. The released inhibiting species could then interact with the metal surface to adsorb, precipitate or make complex layer on it [19]. Accordingly, the type and extent of the interactions may allow categorizing the compounds from poor to excellent corrosion inhibitors [19]. According to Thorn et al. [18], organic corrosion inhibitors can enhance the coating barrier properties and function as anodic passivators. Moreover, they are able to improve the film adhesion strength and to aid in surface wetting. Mahdavian et al. [19,20] reported the effectiveness of some azole compounds as organic corrosion inhibitor in polyester–melamine and epoxy coatings. The EIS and salt spray results showed an enhancement in protective performance of polyester–melamine coatings in the presence of 2-mercaptobenzimidazole and 2-mercaptobenzoxazole, which could be connected to their effect on the crystalline structure of the rust as confirmed by SEM and FTIR [19]. Moreover, the azole compounds were shown to increase the cathodic disbonding resistance of epoxy coatings through two dominant mechanisms: (1) charge transfer resistance increment and diminished cathodic reaction rate because of the inhibitors adsorption on the surface and (2) increase of glass transition temperature which led to reduced permeability of the films toward water and oxygen [20].

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Although there are several papers on using either organic inhibitors or anticorrosion pigments in the coating formulation, the effect of their combination on the protective performance of polymeric coatings has been rarely studied in the literature. This paper intends to compare the corrosion resistance of mild steels covered by solvent-borne epoxy including a mixture of mercaptobenzimidazole (MBI) and zinc phosphate (ZP) with that of mild steels coated with epoxy films incorporating either solely the inhibitor or pigment in 3.5 wt% NaCl solution. Further assessment on the effectiveness of the combination was facilitated using surface analysis as well as electrochemical measurements in the solution phase.

2. Experimental

2.1. Materials

The composition of mild steel panels with the dimension of 9 cm × 9 cm × 0.1 cm is presented in Table 1.

The solvent-based coatings were prepared using a bisphenol A epoxy resin G277071X75 (75% in xylene) and a polyamide curing agent (80% in xylene), purchased from Saman Chemical Co. The epoxy value and density of the epoxy resin was 0.14–0.16 Eq. per 100 g and 1.08 g/cm³, respectively. The epoxy resin and polyamide curing agent were mixed with the ratio of 70:30.

The zinc phosphate (ZP) anticorrosion pigment was supplied by Heubach Ltd Co. According to the supplier, the oil absorption, density and average particle size of the pigment were 20 g/100 g, 3.7 g/cm³ and 2–3.5 μm, respectively. A laboratory grade sodium chloride was used to prepare 3.5 wt% NaCl solution as the corrosive electrolyte. The chemical structure of organic corrosion inhibitor used in this research is presented in Fig. 1. The mercaptobenzimidazole (MBI) inhibitor in analytical grade was supplied by Merck and used without further purification.

After addition of 2 g of ZP to 1 L 3.5 wt% NaCl solution and stirring for 24 h, the mixture was filtered to prepare the pigment extract. To obtain the solution containing mixture of the corrosion inhibitor and pigment, 1 mM MBI was added to the ZP extract before filtration and further stirred for 2 h. The pH values of the prepared solutions are presented in Table 2.

Prior to coating application, the steel samples were acid pickled using hydrochloric acid (20 wt%) for 10 min. The plates were immediately rinsed by distilled water and blow-dried with compressed air, followed by acetone degreasing.

The epoxy coatings were formulated with ZP anticorrosion pigment and different concentrations of MBI corrosion inhibitor. Since the epoxy coating with 36.5% of zinc phosphate was shown to exhibit superior corrosion resistance [8], all formulations in this study were prepared at the optimum pigment volume concentration with addition of 0.25, 0.5, 1.0 and 1.5 wt% MBI. Moreover, a ZP pigmented epoxy coating with no inhibitor was used as reference. A mixture of the epoxy resin, anticorrosion pigment, leveling agent (BYK-306), defoamer (EFKA-2025), wetting and dispersing agent (EFKA-5044) was prepared using a high speed disk disperser. The dispersion was then pearl-milled for 3 h to obtain an average fineness lower than 15 μm. After addition of the polyamide resin containing MBI to the epoxy resin dispersion, the mixture was applied on the substrates using a quadrangular film applicator. The dry coating thickness was 30 ± 5 μm after the curing process at 80 °C for 40 min [21].

Table 1
The composition of mild steel panels.

Element	Fe	C	Si	Mn	S	P	Cr	Mo	Co	Cu	Nb
wt%	Balance	0.19	0.415	1.39	<0.005	<0.005	0.026	0.018	0.0559	0.0429	0.0481

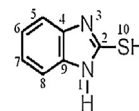


Fig. 1. Chemical structure of mercaptobenzimidazole corrosion inhibitor.

Table 2
pH values of the test solutions.

Sample	3.5 wt% NaCl solution containing			
	No additive	ZP	1 mM MBI	ZP + 1 mM MBI
pH	6.57	6.42	6.36	6.2

2.2. Methods

The EIS and polarization measurements were performed using a three-electrode cell including the specimen with an exposure area of about 1.0 cm² as working electrode, a platinum counter electrode and a Ag/AgCl reference electrode which was connected to the terminals of an Autolab model PGSTAT302N. After 24 h of immersion in the test solutions, polarization curves were obtained at a scan rate of 1 mV/s from –200 mV to +200 mV of OCP. The data was obtained from the curves using NOVA 1.8 software. The corrosion behavior of coated substrates was assessed using EIS which was carried out at open circuit potential (OCP) within the frequency domain 10 kHz to 10 mHz using a sine wave of 10 mV amplitude peak to peak. The impedance spectra were provided after 7 and 35 days of immersion in 3.5 wt% NaCl solution at 25 °C without de-aeration. The EIS data was analyzed using Zsimpwin software.

To perform visual inspection on the coated samples, some photos were taken using a digital camera after 35 days of immersion. To analyze the surface of bare metals after 24 h of exposure to the different solutions, a scanning electron microscope/energy dispersive X-ray analysis (SEM/EDX model VEGA//TESCAN-LMU) was employed.

The adhesion of ZP pigmented epoxy coatings with different concentrations of MBI corrosion inhibitor was measured by a PosiTest digital Pull-Off adhesion tester (DeFelsko Corp.). To perform the experiment, the dollies affixed by a 2-part Araldit™ Epoxy adhesive were pulled away from the coated plates. The maximum force for lifting the dolly was considered as a measure of the adhesion strength between the coating and substrate. The adhesion loss was measured after 35 days of immersion in 3.5 wt% NaCl solution.

The tests all were carried out using three replicates to ensure repeatability.

3. Result and discussion

The polarization curves of the bare metals exposed to the different solutions after 24 h are shown in Fig. 2.

Some parameters including current density (i_{corr}), corrosion potential (E_{corr}), anodic tafel slope (β_a) and cathodic tafel slope (β_c) which were obtained from the polarization curves are presented in Table 3. The corrosion inhibition efficiency (η) values were calculated according to Eq. (1).

$$\eta = (1 - i/i_0) \times 100 \quad (1)$$

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