Progress in Organic Coatings 68 (2010) 259–264

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Mercapto functional azole compounds as organic corrosion inhibitors in a polyester-melamine coating

M. Mahdavian*, S. Ashhari

Department of Surface Coatings & Corrosion, Institute for Color Science and Technology, P.O. Box 16765-654, Tehran, Iran

ARTICLE INFO

Article history:
Received 6 March 2010
Received in revised form 3 April 2010
Accepted 12 April 2010

Keywords:
Neutral inhibition
Mild steel
EIS
Organic coatings
Corrosion protection

ABSTRACT

The corrosion inhibition of two mercapto functional azole compounds including 2-mercaptobenzimidazole (MBI) and 2-mercaptobenzoxazole (MBO) for mild steel in 1 M NaCl solution was studied by electrochemical impedance spectroscopy (EIS), then their impact on the protective performance of a polyester-melamine coating was evaluated using salt spray. EIS results revealed a higher corrosion inhibitive activity of MBI compared to that of MBO. Corrosion products were examined by SEM-EDX and FTIR. The results showed modification of the corrosion products in the presence of MBI and MBO. The salt spray results revealed an improved corrosion protection of the coatings formulated with MBI and MBO. There was almost no impact of MBI and MBO on adhesion strength and glass transition temperature of the coatings, meaning that their impact on the corrosion protection performance of the formulated coating could only be attributed to their effect on the corrosion products.

1. Introduction

Organic corrosion inhibitors and more extensively active inorganic anticorrosion pigments are used to formulate corrosion resistant coatings. Zinc phosphate [1,2] and its large family with modified anionic and cationic parts [3,4] could be used as active anticorrosion pigments for formulation of anticorrosion organic primers.

On the other hand, organic compounds like azoles [5–7], thioglycolate esters, mercaptocarboxylic acids [8], phenols, organic amines, organic sulfides, organic phosphates [9] disodium oleamide sulfosuccinate, lignosulfonic acid-doped polyaniline [10] could be used as organic corrosion inhibitors in organic coatings.

Organic corrosion inhibitors allow for the creation of optimal performing thin films and high gloss corrosion resistant coatings [11], which is connected to their dissolution in the binder system. In contrast with organic corrosion inhibitors, anticorrosion pigments depending on their fineness of dispersion usually are applied at a higher thickness and depending on the difference of refractive index of pigments and binder systems, they usually decrease the gloss of the formulated coatings.

The main functionality of corrosion inhibitors and active anticorrosion pigments in formulated coating is dissolution of active content in the water diffused into the coating. Then, the dissolved species could interact with the metal surface to adsorb, precipitate or make a complex layer on it. Depending on the type and extent of interaction of the inhibitors with metal surface they could be categorized from poor to excellent corrosion inhibitors. However, there are some other ideas about their performance in organic coatings. As an instance, Thorn et al. [11] summarized the effect of organic corrosion inhibitors in organic coatings as follows: (1) enhance the barrier properties of the coating, (2) function as anodic passivators, (3) improve the adhesion of coatings, (4) aid in surface wetting, and (5) increase the performance at defect sites in the film.

Corrosion resistant coatings are supposed to protect metal in corrosive environments, which could be simulated in laboratories using salt spray (5% NaCl). Preparation of extracts from anticorrosion pigments [12,13] and corrosion inhibitors [14,15] in NaCl solution is a common method to evaluate their anticorrosion performances prior to their application in organic coatings.

This paper intends to study the interaction of mercapto functional azole compounds with mild steel surface in 1 M NaCl solution using different electrochemical and non-electrochemical techniques and to compare their influence as corrosion inhibitor in polyester-melamine coating system.

2. Experimental

2.1. Material preparation

A laboratory grade NaCl was used to prepare 1 M NaCl solution. Two mercapto functional azole compounds including

* Corresponding author. Tel.: +98 21 22969771; fax: +98 21 22947537.
E-mail address: mahdavian-m@icrc.ac.ir (M. Mahdavian).

0300-9440/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.porgcoat.2010.04.002

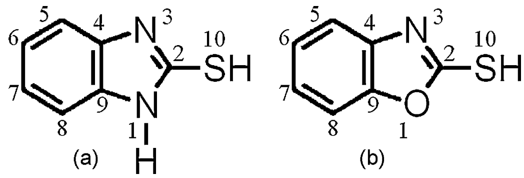

Fig. 1. The chemical structures of MBI (a) and MBO (b).

2-mercaptobenzimidazole (MBI) and 2-mercaptobenzoxazole (MBO) were obtained from Merck and used without further purification. The chemical structures of these compounds are shown in Fig. 1. The test solutions were prepared at 1 mM of the mercapto functional azole compounds.

Mild steel panels with a composition presented in Table 1 were polished using emery paper 800 and then degreased and cleaned using acetone.

Polyester (Uralac SN805) and melamine-formaldehyde (Uramex MF821 B) were obtained from DSM Company. A dispersion of zinc phosphate (5%, v/v), talc (5%, v/v) and titanium dioxide (10%, v/v) was prepared in polyester (PE) component using high speed disk disperser; then, the dispersion was milled to obtain 15 μm fineness. The mill base was mixed with melamine-formaldehyde (MF) with the ratio of 30:70 of MF to PE. In order to evaluate the corrosion inhibition of MBI and MBO, 0.01 moles of the compounds were added to 100 g coating material. The coating with no azole compound was considered as blank coating. The coatings were applied using 60 μm bar coater on mild steel panels. All coatings were cured at 140 °C for 20 min. The samples with a dry film thickness of 35 ± 2 μm were used for salt spray and pull-off tensile strength measurements.

2.2. Studies on bare metal

2.2.1. Electrochemical studies

An area of 1 cm^2 of each sample was exposed to the electrolytes while other areas of the plate were sealed with a beeswax–colophony mixture. EIS measurements were carried out using IVIUM COMPACTSTAT after 24 h immersion in test solutions at 25 ± 1 °C. EIS was implemented at open circuit potential within frequency range of 10^{-2} to 10^{+4} Hz with 10 mV perturbation. Reference electrode and counter electrode were silver–silver chloride and graphite, respectively. Throughout the electrochemical tests, a 1 M NaCl solution with no inhibitor was taken into consideration as blank solution.

2.2.2. Non-electrochemical studies

Corrosion products on mild steel specimens in the presence and absence of MBI and MBO were characterized using FTIR and SEM-EDX. The condition of the specimens and instruments were as follows.

2.2.2.1. FTIR. The spectroscopy of the corrosion products formed on the surface of the samples was examined using diffuse reflectance FTIR (PerkinElmer Spectrum One) at the range of 4000–450 cm^{-1}. The transmittance FTIR of the corrosion products released to the electrolytes was recorded by the same instrument using KBr disc method at the same range of the wavenumber.

Table 1
The composition of steel panels.

Elements	wt%
C	0.190
Si	0.288
Mn	1.390
Cr	0.026
Mo	0.018
Co	0.388
Cu	0.297
Nb	0.334

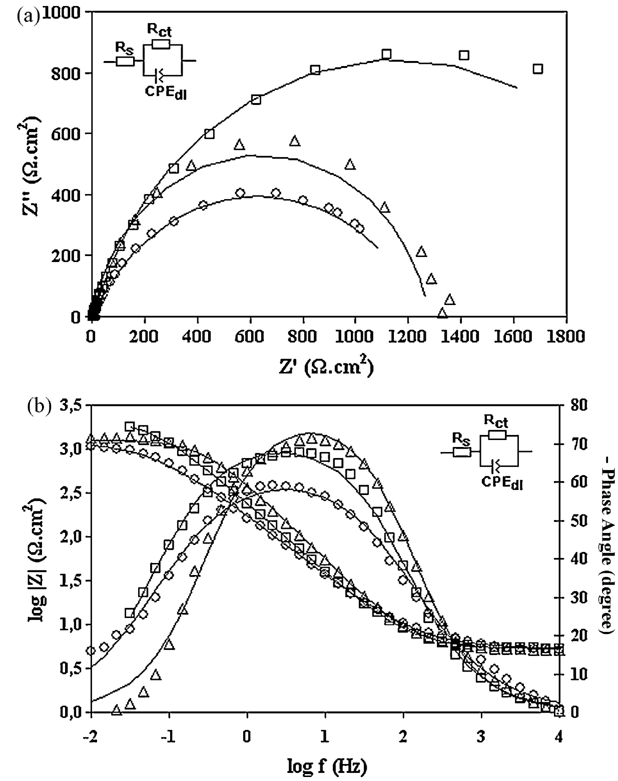

Fig. 2. Nyquist (a) and Bode (b) diagrams of mild steel in 1 M NaCl solution containing 1 mM of MBI (□), MBO (△) along with blank (○) solution. The curve fittings with the provided equivalent circuit are shown by corresponding solid lines.

2.2.2.2. SEM-EDX. The surface of the specimens after 24 h exposure to the 1 M NaCl solution containing MBI or MBO were analyzed using SEM/EDX (Philips XL30).

2.3. Studies on coated metal

Differential scanning calorimetry (DSC) was examined on the cured coatings using PerkinElmer Pyris 6 from −40 to +140 °C at scan rate 10 °C/min. Then, the coated samples were scribed and exposed to salt spray (5% NaCl) for 240 h. Salt spray test was performed according to ASTM B 117. The edges and back of all panels were protected using a beeswax–colophony mixture. Blisters, rust and disbonding were evaluated on coated metal after exposure to salt fog; then, pull-off tensile strength was examined using Defelsko Positest on an area with a 2-cm diameter.

3. Results and discussion

3.1. Studies on bare metal

3.1.1.1. Electrochemical measurements

The EIS diagrams obtained in the presence and absence of MBI and MBO in 1 M NaCl are illustrated in Fig. 2.

Absolute impedance at low frequencies could approximate DC current polarization resistance when corrosion process is under activation control. The recorded EIS spectra in Fig. 2 show one depressed capacitive loop for each measurement; meaning that there is no detectable protective coating on the samples and the corrosion process is under activation control. The use of MBI in