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Corrosion protection of carbon steel by solvent free epoxy coating containing hydrotalcites intercalated with different organic corrosion inhibitors

Nguyen Thuy Duong[a,b], To Thi Xuan Hang[a], Arnaud Nicolay[b], Yoann Paint[c], Marie-Georges Olivier[b,c,*]

[a] Institute for Tropical Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoï, Vietnam
[b] Université de Mons (UMONS), Faculty of Engineering, Materials Science Department, 20 Place du Parc, Mons, Belgium
[c] Materia Nova Research Center, Parc Initialis, Avenue Copernic, Mons, Belgium

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ABSTRACT

Hydrotalcites intercalated with two different corrosion inhibitors: 2-benzothiazolythio-succinic acid (BTSA) and benzoate (BZ) were prepared by coprecipitation method and incorporated (1.5 wt.%) in solvent free epoxy coatings. The obtained hydrotalcites were characterized using infrared spectroscopy, X-ray diffraction, scanning electron microscopy and zeta potential measurements. The solid suspensions in epoxy resin were characterized by rheology and Turbiscan. The corrosion protection performance of the epoxy coating containing hydrotalcites applied on carbon steel was evaluated by electrochemical impedance spectroscopy, salt spray test and adhesion measurement. It was shown that the BTSA and BZ were intercalated in hydrotalcite and their loading was about 22 wt.% and 27 wt.%, respectively. The presence of BZ modified hydrotalcite (HT-BZ) improved significantly the corrosion protection of solvent free epoxy coating. Corrosion protection performance of epoxy coating containing HT-BZ was higher than that of epoxy coating containing BTSA modified hydrotalcite (HT-BTSA). The corrosion protection performance of coatings appears to depend on the dispersion degree of hydrotalcite particles in the epoxy matrix and the solubility of organic inhibitor in the electrolyte.

1. Introduction

Organic coatings are widely used for corrosion protection of metals. Due to the environmental problems related to the use of volatile organic solvents, many researches focus on the implementation of solvent free organic coatings. Organic acids are used as corrosion inhibitors in industry for corrosion protection of copper, steel, aluminum alloys. These organic compounds have several molecular bonds containing nitrogen, sulphur and oxygen atoms through which they can be adsorbed on the metal surface [1–4]. Benzoic acid and its substituted compounds are widely used as corrosion inhibitors and their inhibition efficiencies depend on the nature of the substituent and the substrates [5–7]. Benzoate compounds are studied as corrosion inhibitors for steel, zinc, copper, copper alloys, aluminum and aluminum alloys. The influence of benzoate concentration, pH, and dissolved oxygen on the corrosion of iron was previously investigated. The inhibition effect of benzoate is based on the blocking of anodic surface sites by the inhibitor molecule [8–13].

Dicarboxylic acids like adipic, succinic acids have been studied as corrosion inhibitors in combination with Zn salts for carbon steel in NaCl solution and a high inhibition efficiency was achieved. It was shown that a protective film is formed on the metal surface consisting of a complex between Fe^{2+} cations and carboxylic acid and a precipitate of zinc hydroxyde $Zn(OH)_2$, [14,15]. Corrosion inhibitors based on succinic acid derivates are used in organic coatings such as 2-benzothiazolyl-succinic acid and amine salt of 2-benzothiazolyl-succinic acid [16].

Hydrotalcites have been used as conversion coatings for aluminum alloys and galvanized steel [17–21]. Protection performance and adhesion of organic coatings were improved with the presence of hydrotalcite layers.

Hydrotalcites due to their lamellar structure and their global positive charge can be used to trap anionic inhibitors and to avoid undesirable interactions between inhibitor and matrixes dur-

* Corresponding author at: Université de Mons (UMONS), Faculty of Engineering, Materials Science Department, 20 Place du Parc, Mons, Belgium.
E-mail address: marjorie.olivier@umons.ac.be (M.-G. Olivier).

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ing the crosslinking reactions. By using hydrotalcites as inhibitor nanoreservoirs, the release of inhibitor species can also be triggered by exchange with the chloride anions contained in the aggressive electrolyte. Recently, hydrotalcites are studied as nanocontainers of corrosion inhibitor in organic coatings and sol-gel coatings for corrosion protection of aluminum alloys [22–30]. Hydrotalcites intercalated with different inorganic and organic anions like divanadate, vanadate, molybdate, aminobenzoate, benzoate, benzotriazolate, ethyl xanthate and oxalate were prepared before assessment of their corrosion protection. The coatings doped with hydrotalcites intercalated with divanadate offer a self-healing effect and show higher corrosion protection performance than that of chromate-based systems [25,31]. Organo-modified hydrotalcites improved barrier properties of the coating. However, the water uptake process causes blistering of the film [26]. HTs can provide effective inhibition against filiform corrosion propagation on AA2024-T3 alloy coated by organic coatings [27,28]. The addition of HTs to sol–gel films improved the corrosion resistance of coated AA2024-T3 alloy evaluated by salt spray test [29].

Evaluation of protection performance of coatings containing hydrotalcite intercalated with benzotriazolate, ethyl xanthate and oxalate for corrosion protection of aluminum alloys highlighted the inhibition efficiency to be depending on the structure of the organic anion, increasing in the following sequence: ethyl xanthate < oxalate < benzotriazolate [28].

Hydrotalcites containing 2-mercaptobenzothiazolate and quinaldate were synthesized and incorporated in organic coatings for corrosion protection of AA2024 aluminum alloy. It was shown that inhibitive anions can be released from hydrotalcite and the coatings containing modified hydrotalcites have self-healing properties [32].

Organic coatings containing molybdate intercalated hydrotalcite and HT-MoO_4^{2-}/ZnO were also investigated on magnesium alloys. The results indicated that the MoO_4^{2-} anion may be released from hydrotalcite in NaCl solution by exchange reaction with chloride, whereas ZnO particles can attract negatively charged anions, leading to the formation of a reinforced layer on the surface of the magnesium alloy [33].

Even if many surveys are related to corrosion protection of aluminum alloys, few studies concern the assessment of the efficiency of hydrotalcites intercalated with corrosion inhibitors for the protection of carbon steel. Nevertheless, protection performance of alkyd coating containing hydrotalcite intercalated with vanadate was reported and compared with coatings containing ion exchange silica and $ZnCrO_4$. It was shown that the inhibitive efficiency of hydrotalcite intercalated with vanadate was lower than that of $ZnCrO_4$ [34].

Anticorrosion efficiency of benzoate intercalated Zn–Al hydrotalcite used as inhibitive species for carbon steel was previously studied. The results indicated that the benzoate anions release from hydrotalcite and are replaced by aggressive chloride anion adsorbed on the hydrotalcite. In a 3.5 wt.% NaCl solution, the direct addition of HT-benzoate decreases significantly the corrosion rate of carbon steel [35]. To date, no study has considered the corrosion protection obtained by addition of HT-benzoate in an organic coating applied on carbon steel.

In our previous works, hydrotalcites modified by 2-benzothiazolythio-succinic acid inhibitor (HT-BTSA) were synthesized, incorporated in a solvent based epoxy coating and applied on carbon steel [36–38]. The obtained results proved that HT-BTSA improved corrosion protection, adhesion and resistance to cathodic disbonding of solvent based epoxy coatings.

In this work, hydrotalcites intercalated with two different corrosion inhibitors: 2-benzothiazolythio-succinic acid and benzoate were prepared and incorporated in solvent free epoxy coatings applied on carbon steel. The effect of the modification of hydrotalcites by corrosion inhibitor on dispersion and stability of charged epoxy resin was studied and the protection performance of coatings was investigated.

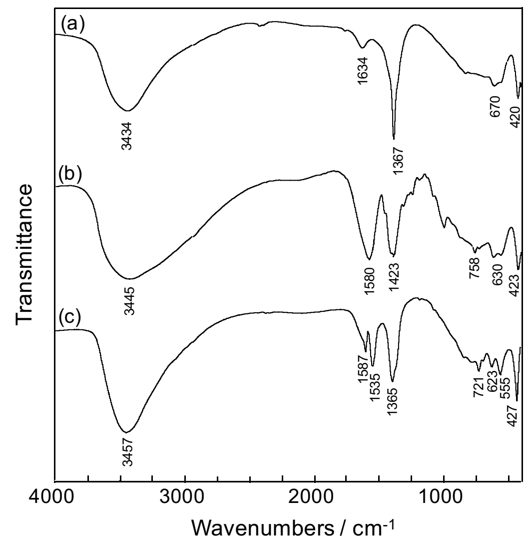

Fig. 1. FT-IR spectra of (a) hydrotalcite (HT); (b) hydrotalcite intercalated with 2-benzothiazolylthio-succinic acid (HT-BTSA) and (c) hydrotalcite intercalated with benzoate (HT-BZ).

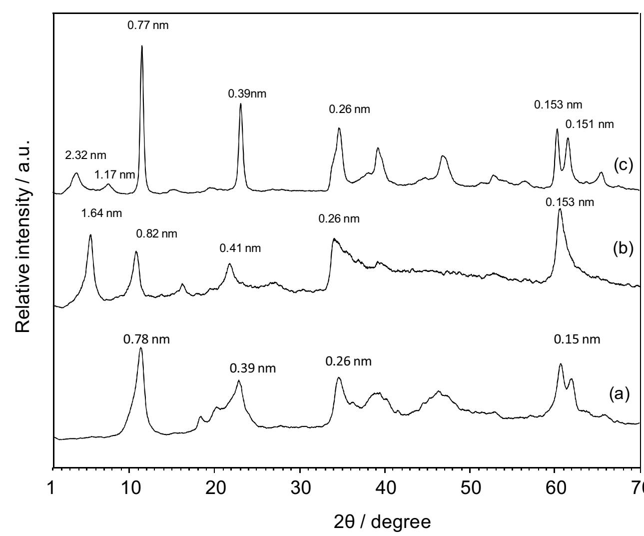

Fig. 2. XRD patterns of (a) HT; (b) HT-BTSA and (c) HT-BZ.

2. Experimental

2.1. Materials

Sodium hydroxide, zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$) were purchased from Sigma Aldrich. 2-benzothiazolylthio-succinic acid (BTSA) was obtained from Ciba Company and sodium benzoate (BZ) was purchased from VWR.

For the coatings, carbon steel sheets (150 mm × 10mm × 2 mm) were used as substrates. Sheets were polished with abrasive papers from grade 80 to 600 and cleaned with ethanol.