Progress in Organic Coatings 101 (2016) 225–232

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Inhibition of the corrosion of iron heritage objects after treatment with long-chain monocarboxylic acids in ethanolic solutions

Elbeshary A.A. Mohammed, Michel De Keersmaecker, Annemie Adriaens*

Department of Analytical Chemistry, Ghent University, Krijgslaan 281-S12, 9000 Ghent, Belgium

ARTICLE INFO

Article history:
Received 8 December 2015
Received in revised form 21 June 2016
Accepted 19 July 2016
Available online 30 August 2016

Keywords:
Iron corrosion
Heritage objects conservation
Corrosion inhibitions
Carboxylic acids
Coating

ABSTRACT

Ethanolic solutions of long-chain carboxylic acids with the general formula $CH_3(CH_2)_{n-2}COOH$ ($12 \leq n \leq 16$; HC_{12}, HC_{14}, and HC_{16}) are used to coat iron heritage objects. Prior to treatment, the iron surface is passivated electrochemically in a borate buffer solution to obtain a ferrihydrite film that simulates the natural oxide layer on real artefacts. The coatings are characterized by Fourier transform infrared spectroscopy. The corrosion inhibition properties are examined by using linear sweep voltammetry and electrochemical impedance spectroscopy in a corrosive solution to simulate the corrosive environment in museums with uncontrolled conditions. The results showed that these carboxylic acids form a protective barrier and inhibit iron metal corrosion and that HC_{14} has the highest inhibition efficiency.

1. Introduction

Iron is present in many cultural heritage objects that suffer degradation through atmospheric corrosion in open museums and uncontrolled environmental conditions. Corrosion can be avoided or delayed by protective coatings [1,2]; however, coatings for protecting metallic cultural heritage objects from corrosion must meet a number of requirements [2–4]. The coating should have no or very little effect on the surface appearance; it should be as reversible as possible so it can be removed to return the object to its original state; it should not modify the material of the original artefact; it must have long-term efficiency because heritage artefacts are intended to be preserved for as long as possible; and finally, it should be easy to maintain. These considerations impose important limitations on the selection of corrosion inhibition coatings.

Effective protective coatings that fulfil these requirements include sodium salts of saturated linear carboxylic acids of the general formula $CH_3(CH_2)_{n-2}COONa$ (NaC_n). The degree of inhibition of those coatings depends on the length of the carbon chain and the carboxylate concentration; longer chains at higher concentrations result in higher effectiveness [5]. However, the solubility of the sodium monocarboxylates decreases with increasing chain length [3]. Studies of carboxylate coatings for iron artefacts [6–10] have shown that the decanoate anion ($n = 10$) in water is the best inhibitor, because it demonstrates a good balance of efficiency, solubility, and ease of application.

In this paper, we study longer chain monocarboxylic acids with chain lengths of $12 \leq n \leq 16$, written as HC_{12}, HC_{14}, and HC_{16} in ethanol to avoid the problem of the low aqueous solubility of long sodium monocarboxylate molecules. To simulate the natural corrosion of real iron artefacts, the iron surface was passivated electrochemically in a borate buffer solution to obtain an oxide film [11,12]. The iron samples were immersed in an ethanolic solution of an acid for 24 h and dried in air overnight.

The coatings were characterized by Fourier transform infrared spectroscopy (FT-IR) by identifying the functional groups of the expected compound. The corrosion rate of the coated samples were evaluated using linear sweep voltammetry (LSV) by determining the corrosion current density (I_{corr}) and the corrosion potential (E_{corr}). Electrochemical impedance spectroscopy (EIS) was used to evaluate the coating quality and measure the resistance to moisture penetration. In addition, a salt spray test was used to assess the durability of the coating.

2. Experimental

2.1. Chemicals

Ethanolic 50 mM solutions were prepared by dissolving dodecanoic acid HC_{12} (1.1420 g, 98%, Sigma-Aldrich, USA), tetradecanoic

* Corresponding author.
E-mail addresses: elbeshary.ahmed@ugent.be (E.A.A. Mohammed), michel.dekeersmaecker@ugent.be (M. De Keersmaecker), annemie.adriaens@ugent.be (A. Adriaens).

http://dx.doi.org/10.1016/j.porgcoat.2016.07.011
0300-9440/

acid HC_{14} (1.2822 g, food grade, Sigma-Aldrich, USA) and hexadecanoic acid HC_{16} (1.4224 g, food grade, Sigma-Aldrich, USA) in ethanol (100 mL).

The corrosive medium used in the electrochemical experiments was ASTM D1384-87 solution, consisting of 1.04 mM Na_2SO_4 (Merck, Germany), 1.64 mM $NaHCO_3$ (Merck), 2.82 mM NaCl (assay 100%, Prolabo, Belgium), referred to hereafter as ASTM solution (pH = 8.3).The borate buffer solution (pH 8.4) used for electrochemical passivation of the iron coupons was made by mixing 150 mM H_3BO_3 (purity 99%, Acros Organics, Belgium) and 37.5 mM $Na_2B_4O_7{\cdot}10H_2O$ (reagent ACS, Acros Organics).

Iron coupons were made from iron sheet (99.5%, Advent Research Material Ltd., UK) and were 2 mm thick and 12.6 mm in diameter.

2.2. Preparation of the iron coupons

The iron samples were prepared by washing and degreasing them with kitchen detergent (Dreft, P&G, Belgium), and then rinsing them thoroughly with water. The samples were sonicated in acetone for 10 min. Afterwards, they were polished with 600 grit silicon carbide, followed by a 1200 grit polishing paper by using a damp abrasive disc (Met II, Buehler, USA) to remove visible surface defects and to expose a fresh metal surface. After each polishing step, the surface was rinsed with Milli-Q water, and then sonicated in acetone for 3 min.

2.3. Iron sample treatment

2.3.1. Iron passivation

Real iron artefacts are naturally oxidized and already have an oxide layer. The samples were artificially oxidized to obtain an oxide layer that simulated the natural corrosion of real artefacts. The iron samples were potentiostatically passivated in the borate buffer solution at 400 mV (vs SCE) for 1 h. The current density measured during the passivation process was plotted against time on a logarithmic scale (Fig. 1). The slope of the curve from 10 s to 1 h was −1. This confirmed that a dense passive oxide film was formed that consisted of iron oxide/hydroxide (ferrihydrite)[12].

2.3.2. Coating of the samples

After passivation, the samples were rinsed with demineralized water followed by absolute ethanol, and then immersed in the ethanolic carboxylic acid solution for 24 h. The samples were removed and dried overnight.

2.4. Fourier transform infrared spectroscopy

FT-IR spectra were recorded in the range of 4400–600 nm with an FT-IR spectrometer (Spectrum 1000, Perkin-Elmer, USA) equipped with a horizontal attenuated total reflection cell (Pike MIRacle, PIKE Technologies, USA). Spectra were measured on two different coupons at five different points on each coated coupon. No differences were observed among the spectra.

2.5. Electrochemical experiments

2.5.1. Linear sweep voltammetry

Potentiodynamic polarization measurements were performed in a three-electrode electrochemical cell containing the ASTM solution and connected to a potentiostat (Autolab PG-STAT 20, Metrohm, Switzerland). A platinum mesh counter electrode and Ag/AgCl reference electrode were used. The potentiodynamic polarization curves were recorded in an aerated ASTM solution at 25 °C and this in a potential window of −1 to +1 V with a scan rate of 0.003 V s^{-1}. All potentials are given relative to the reference.

2.5.2. Electrochemical impedance spectroscopy

EIS measurements were performed in a three-electrode electrochemical cell containing the ASTM solution and connected to the potentiostat equipped with a frequency response unit (FRA module, Eco Chemie B.V., Utrecht, Netherlands). A graphite counter electrode and an Ag/AgCl reference electrode were used. Impedance spectra were measured in an aerated ASTM solution at 25 °C at the open circuit potential in the frequency range of 100 kHz–0.1 Hz. The frequency was distributed logarithmically across 120 points and an amplitude of 0.01 V.

2.6. Salt spray test

The salt spray test was done with a salt spray chamber (SC1000, Weiss Technik, Belgium), following the ASTM B117 standard and employing a 5% sodium chloride solution at 35 °C. Prior to exposure, the edges of the samples were covered with a nail polish. The samples were removed from the salt spray chamber after 24 h. Then, they were rinsed with Milli-Q water, and dried in air. The samples were imaged, before and after exposure, using SMZ800 Nikon optical microscope coupled with a Nikon Digital System (DS Fi1) at 2× magnification.

3. Results and discussion

3.1. Coating characterization

3.1.1. Fourier transform infrared spectroscopy

FT-IR spectroscopy was used to identify the coating by comparing its spectra with that of the corresponding acid powder. Fig. 2 shows the spectrum of the HC_{14} coating and that of the HC_{14} powder. The transmittance for the coating was much higher than that for the acid powder. This may be attributed to the small amount of the acid on the coated sample (thin film) compared with the reference acid powder [13,14]. The spectra of the coating and the reference acid contained characteristic CH_2 vibrations (four symmetric/asymmetric C—H stretching peaks around 2900 cm^{-1}). Both spectra contained the most characteristic peak of the long-chain carboxylic acids at 1698 cm^{-1}, which corresponded to the C=O stretching, and the peak was strong in the HC_{14} powder [15]. The remaining peaks in the fingerprint region were the same for the acid powder and the coating, indicating that the acid did not form iron carboxylate and that the acid was physisorbed on the passivated surface of the iron. Literature data show that fatty acids can be chemisorbed or physisorbed on the iron surface depending on the nature of the substrate [16,17]. Sophie et al. studied the adsorption mechanism of stearic acid (HC_{18}) on Fe_2O_3 and FeOOH at 50 °C. For Fe_2O_3, most of the acid molecules were chemisorbed, forming an iron carboxylate. The opposite was true for FeOOH, where most of the acid molecules were physisorbed and few molecules reacted with the iron. In our work, surface analysis of the oxide layer formed on the iron surface during the passivation step indicated that FeOOH formed [12]; therefore, the acid was physisorbed on the iron surface and did not react chemically with FeOOH to form iron carboxylate as shown by the FT-IR results [16,17].

The physisorption between the sample and coating may make the coating easy to remove. However, it can be used in a museum where the environment is controlled, and hence, the corrosive environment is low, or it can be used as a temporary. Also, as the coating is not colored, it does not affect the appearance of the object, and complies with the visual requirements for protective coatings for iron heritage objects.