Progress in Organic Coatings 76 (2013) 1674–1682

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Comparisons of clear coating degradation in NaCl solution and pure water

Qixin Zhou, Yechun Wang*

Mechanical Engineering, North Dakota State University, NDSU Dept. 2490, P.O. Box 6050, Fargo, ND 58108, USA

ARTICLE INFO

Article history:
Received 4 February 2013
Received in revised form 10 July 2013
Accepted 26 July 2013
Available online 22 August 2013

Keywords:
Coating degradation
Water uptake
NaCl solution
Pure water
Electrochemical impedance spectroscopy

ABSTRACT

Organic coating's degradation behavior is essential to its corrosion protective function and has been widely studied. A main function of anti-corrosive organic coatings is acting as barriers to water uptake and ion diffusion. It is of great fundamental importance to study the influence of different working fluids on the degradation of organic coatings. In this study, a 3.5 wt% NaCl solution and the pure water are adopted as the working fluids based on their distinct properties. The commercially available polyurethane and epoxy based clear coatings are chosen for evaluation. The coating degradation is monitored by electrochemical impedance spectroscopy (EIS) measurement. Equivalent circuit models are employed to interpret the EIS spectra. The time evolution of coating resistance, capacitance, and water volume fraction of the coating is analyzed. Besides the fact that the coating's barrier property is deteriorated by the percolating of both NaCl solution and pure water, we also discover that pure water leads to faster coating degradation, demonstrated by a more substantial decrease in coating resistance, a more prominent increase in coating capacitance, and a greater saturated water volume fraction.

1. Introduction

The primary function of organic coatings is to protect metallic objects and structures against corrosion. Organic coatings can provide barrier functions between the substrate and the environment in order to resist the transportation of water, oxygen, ions and other aggressive species to the coating metal interface [1–3]. The continuous migration of aggressive species will lead to coating delamination and underfilm corrosion, and eventually cause the loss of corrosion protective function of organic coatings. Along with the coating degradation, the water uptake process is important since water is the medium for the diffusion of oxygen and ions, and it can also nucleate delamination [4–6]. Therefore, the performance of organic coatings which can reduce the water invasion will greatly influence their protection efficiency to metallic substrates [3,7,8].

Various studies have investigated the degradation behavior of organic coatings. Electrolytes like NaCl solution are most often adopted for corrosion studies, e.g. Refs. [9–14]. In addition to NaCl solutions, the influence of pure water (e.g. deionized or distilled water) on the corrosion of metallic materials has been investigated [15–18]. Frequently, pure water was used in gravimetric methods to study water diffusion in free-standing films, e.g. Refs. [19–21]. Taylor and Moongkhamklang investigated the initial water entry into epoxy coatings using distilled water and NaCl solutions as working fluids [22]. Their usage of distilled water had validated the autofluorescence properties of epoxy coatings, which served as a foundation for the employment of fluorescence microscopy in their study. They observed a higher density of fluorescence sites on coatings exposed to distilled water than samples exposed to electrolyte solutions. However, this study only provided information for initial water entry and did not focus on the time-dependent degradation behavior of the coatings. An FTIR/ATR method was employed to investigate the non-Fickian sorption and desorption of pure water and electrolyte solution into epoxy coatings [23]. Water diffusion coefficients were obtained in that study but the long-term coating degradation was discounted. Different from existing works, this study focuses on the influence of working fluids on the long-term deterioration of coatings in terms of its corrosion protective functions, or barrier properties, as a result of coating degradation and water uptake. It is the first time that the influence of pure water as working fluid was compared with that of NaCl solution for the afore-mentioned purpose and scope.

It is of great fundamental importance to study the influence of different working fluid on the degradation of organic coatings. The coating degradation could be influenced by water uptake and ion diffusion determined by both the working fluid and the coating barrier properties. For example, study has shown that the cathodic delamination rate of a polyester coating on mild steel was greatly influenced by the diffusion of anions; as a result, the delamination

* Corresponding author. Tel.: +1 701 231 6732; fax: +1 701 231 8913.
E-mail address: yechun.wang@ndsu.edu (Y. Wang).

0300-9440/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.porgcoat.2013.07.018

rate in KCl solution is higher than that in KBr solution [4]. Once the aggressive species, like water, oxygen, and ions, have percolated through organic coatings to the coating-metal interface, degradation is considered to take place. Cathodic electrochemical reaction then takes place by consuming water and oxygen. Meanwhile, the metal substrate is corroded as a result of anodic reaction. Also, the coating will delaminate from the substrate and small "pockets" which contain corrosion products will be generated in the coating-metal interface [4,24]. Due to the oxygen involved in the cathodic reaction, the corrosion process can be influenced by the concentration of dissolved oxygen which percolates to the coating-metal interface [7,8,25,26]. As a result, the oxygen concentration in the working fluid may be one of the important influencing factors for the corrosion process. The concentration of dissolved oxygen in pure water is higher than that in NaCl solutions under same conditions. For example, pure water contains 9.1 mg/L dissolved oxygen at 20 °C under 101.1 kPa, while sea water with a salinity of 35 has 7.2 mg/L dissolved oxygen under the same condition [27]. Hence it is compelling to evaluate the coating degradation by using pure water as the working fluid in which the oxygen concentration is different from that in NaCl solutions.

The aim of this study is to improve the understanding of barrier properties of organic coatings by differentiating the influences of pure water and NaCl solution on the degradation and water uptake behavior of coatings. This paper will first compare the influence of the two different working fluids on coating degradation as characterized in line by electrochemical impedance spectroscopy (EIS) measurements. The EIS method has been found to be the major, standard, and adequate investigation tool to evaluate organic coatings. It has been employed in our previous study on coating degradation in flowing fluids including pure water [28]. The EIS spectra will then be interpreted by suitable equivalent circuit models. We then present the time evolution of coating resistance, capacitance, and the water volume fraction of the coatings. The time dependent behaviors of the afore-mentioned properties of the coatings immersed in pure water will then be discussed by comparing with those for coatings in NaCl solution.

2. Materials and methods

2.1. Coatings and sample preparation

The commercially available polyurethane and epoxy based clear coatings were chosen for evaluation. These coatings have been widely used as base coat in marine coatings [29–33]. We purposefully chose different coatings, or, similar coatings with different curing agents and/or processing methods, to increase the diversity of the coating samples and to generalize our conclusions. A polyurethane coating, denoted as P, was composed of 67.4 wt% acrylic polyol (Joncryl 906, BASF), 15.0 wt% polyisocyanates (DESMODURN 3200, Bayer Material Science), 17.0 wt% tertiary butyl acetate (TBA, ASHLAND), and 0.6 wt% dibutyltin dilaurate (DBTD, Sigma–Aldrich), in addition to one drop of polyether modified polydimethylsiloxane (BYK-300, Chemie). Coating P was formulated by mixing all components well before application. The epoxy resin, EPON 828, was crosslinked with three different amine curing agents with different AHEW numbers to generate three types of epoxy/amine coatings. The epoxy coating, denoted as E1, was formulated by base component, 63.5 wt% epoxy resin (EPON Resin 828, Miller-Stephenson), 30.3 wt% modified mannich based curing agent (EPI-CURE Curing agent 3251, AHEW 350–390, Resolution Performance Products), and 6.2 wt% xylene. Another epoxy coating, denoted as E2, was composed of 73.3 wt% epoxy resin (EPON Resin 828, Miller-Stephenson) as the base component, 20.3 wt% cycloaliphatic amine (Amicure PACM, AHEW 54.2, Air Products) as the epoxy curing agent, and 6.4 wt% xylene. The third epoxy coating, denoted as E3, was composed of EPON Resin 828 (Hexion Specialty Chemicals) as the base component, and EPIKURE 3164 as curing agent (AHEW 256, Hexion Specialty Chemicals). The weight ratio of curing agent to EPON Resin 828 is 1.36. All four coatings that we used were clear coatings with no pigments, so their barrier property against water uptake is provided by the polymer network only; in this way, the ingress behavior of water into these coatings may be comparable.

Q-panel standard steel panels (S-36 from Q-Panel Lab Products) were used as the metal substrate. Before painting, the panels were pretreated by abrasion with 320 and 600 grit sand paper, and then cleaned with acetone and hexane. The coatings of P, E1, and E2 were applied by the draw-down method and cured at 80 °C for 0.5 h. The epoxy coating E3 was applied by air spraying and cured at room temperature for 24 h. All the coating samples were allowed to completely dry for several days at the room temperature before testing. The coating thickness was measured at several locations of different coating surfaces using an Elcometer 415 coating thickness gauge. The average coating thickness of P, E1, E2, and E3 before immersion were 50.6 ± 3.2 μm, 65.5 ± 6.1 μm, 68.4 ± 6.4 μm, and 31.9 ± 1.3 μm, respectively.

Table 1
Property for 3.5 wt% NaCl solution and pure water.

Working fluid	pH	Conductivity
3.5 wt% NaCl	6.70 ± 0.1	57.5 ± 0.1 ms/cm
Pure water	7.58 ± 0.2	167.5 ± 14.3 μs/cm

2.2. Stationary immersion and EIS test

The working fluids adopted in this paper for coatings immersion were pure water and 3.5 wt% NaCl solution. The 3.5 wt% NaCl solution was prepared using the same pure water. The pH and conductivity value of the pure water and 3.5 wt% NaCl solution was measured as shown in Table 1. The fluid samples for pH and conductivity tests were open to the air at the room temperature, which was under the same condition as the immersion test. The pH and conductivity values were observed to be constant for blank solutions (without coating immersion), when the property of working fluids was monitored during the experiment. The conductivity value for the pure water employed in this study was measured about 167.5 μs/cm, which is larger than the reported value for highly purified water such as deionized or distilled water [15,34,35], but it is still smaller than that of the 3.5 wt% NaCl solution by orders of magnitude. In the current work, we are not interested in studying the coating degradation in highly purified water, since its properties, especially the ion concentration is almost impossible to maintain during coating immersion due to the exposure to the coating sample and the air.

The traditional three-electrode EIS setup was employed for evaluating coating degradation as shown in Fig. 1. An O-ring glass cell was attached to the coating surface with a glass tube clamp. The testing area of each coating sample is 7.07 cm^2. A cardboard was placed on the rear side of the panel to insulate the substrate from the clamp. The glass cell was filled with working fluids: pure water or 3.5 wt% NaCl solution. Three samples of each coating system were tested for pure water or NaCl solution immersion. The electrochemical cell was composed of a platinum counter electrode, a saturated calomel reference electrode, and the metal substrate as the working electrode. EIS measurements were performed using the Reference 600 Potentiostat by Gamry Instruments. The scanning frequency range was from 10^{-2} to 10^5 Hz with 10 points per