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Non-substrate EIS monitoring of organic coatings with embedded electrodes

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ABSTRACT

Electrochemical impedance spectroscopy provides a quantitative evaluation of the protection afforded by coatings on metals. Two constraints are that the coating is under immersion and that the substrate acts as the working electrode with the counter and reference electrodes located in the electrolyte. The use of embedded electrodes placed between a topcoat and primer can relax these constraints and make EIS monitoring more applicable to coatings in the field. A two-electrode, non-substrate configuration involves two embedded electrodes on a coated panel acting as the working and counter/reference electrodes. This configuration has been used to characterize the interlayer between a topcoat and primer under the assumption that the current passed through the interlayer. Simulated results have been presented where current passage for a non-substrate configuration was through the metal substrate. The results associated with a urethane topcoat/epoxy primer system and an alkyd topcoat/alkyd primer system are presented to demonstrate the feasibility of monitoring the substrate where the substrate is not an electrode. The degradations of the coatings were induced using the ac–dc–ac accelerated test where the immersed coatings were subjected to cycles that involved a dc cathodic potential condition that promoted the cathodic reactions at the metal/coating interface.

1. Introduction

Metallic structures are subjected to corrosion that bear a large economic cost and safety concerns to society [1]. The prevalent method for mitigating corrosion is organic coatings that isolate the metal substrate from the environment and reduce the transport of species from the environment to the metal surface [1]. Coating formulations are developed for specific substrates exposed to given environments where the design lifetime is years for undamaged coating systems. Coatings can degrade in the field with periodic performance monitoring in the field providing information to discern whether a coating is performing as designed or is in need of replacement. Premature degradation of coatings in the field can arise due to defects introduced while the coating is being applied under conditions not consistent with the manufacturer's specification. Defects in the coating can also arise due to mechanical impacts that expose the metal surface to the environment.

Visual inspection is still the relied upon method for coating performance in the field and provides a qualitative characterization that is weighted by the inspectors experience. Visual inspection is limited to failures that are on the coating surface while corrosion beneath delaminated and blistered coatings that originate at the metal/coating interface may go undetected. Conventional acceleration methods such as salt spray (ASTM B117), Prohesion® and Prohesion®/QUV (ASTM G85) that induce coating failure also rely on visual evaluation with qualitative results used for ranking coating performance [2,3].

Electrochemical impedance spectroscopy (EIS) and electrochemical noise method (ENM) have become applicable experiments in the evaluation of the corrosion protection provided by coatings on metal substrates [2,4–14]. These electrochemical methods provide a quantitative characterization of the corrosion protection properties of coatings unlike the traditional visual based methods. The development of affordable potentiostats coupled with user-friendly software has increased application of EIS and ENM for coating evaluation. The conventional EIS experimental setup for coated metals includes a section of the coating being exposed to a liquid electrolyte contained in a cell attached to the coating surface. A three-probe electrochemical configuration is used with a counter electrode and reference electrode located in the electrolyte and the metal substrate as the working electrode. A two-probe configuration without a separate reference electrode would include the counter acting as a pseudo reference electrode. These configurations are convenient for laboratory bench top experiments but provide a hindrance for field application.

Electrodes embedded in coatings have been used for monitoring coating performance [15–23] and can provide a field applicable configuration for EIS measurement. Embedded electrodes are located between the topcoat and primer of two-layer coating systems with the electrodes electrically connected by an insulated wire through the topcoat. Embedded electrodes have been used to monitor water uptake in the two layers of a topcoat/primer sys-

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tem simultaneously [16,17]. The degradation of coating systems exposed to thermal cycling and ac–dc–ac accelerated test conditions has been monitored in situ with embedded electrodes [18,19]. EIS data acquired using embedded electrodes have been analyzed with equivalent circuits to identify the layers of bulk topcoat, bulk primer, topcoat–primer interlayer, and the region of coating/metal adhesion that were associated with a two-layered coating [20]. Embedded electrodes have also been used to acquire ENM data associated with the coating failure and corrosion process associated with coated aluminum alloy 2024-T3 panels [15,21]. In these applications, the electrochemical experiments have been performed in a conventional setup where an electrolyte is placed on the coating surface.

Embedded electrodes provide a unique feature where the presence of an immersing electrolyte is not a necessity to conduct the electrochemical measurement. Applications have been reported by Allahar et al. where coating systems with embedded electrodes have been monitored in situ under accelerated test conditions of QUV/Prohesion [22] and Prohesion [23]. In these applications EIS measurements were made using configurations that included the substrate as the working electrode and a non-substrate configuration where two embedded electrodes conducted the two-electrode EIS measurement. The passage of current between the electrodes was shown to be non-inclusive of the substrate during the early part of the exposure following which the passage included the substrate. The non-substrate configuration was used by Miszczyk and Schauer to determine the effect of moisture on the interlayer adhesion between the topcoat and primer [24]. In this non-substrate EIS measurement, the passage of current was demonstrated to be through the primer/topcoat interlayer such that the inter-adhesion properties of this interlayer were determined. Finite-element simulation of the current distribution between two embedded electrodes in a coated substrate have been reported by Nogueira et al. that demonstrated that the electric current route between the electrodes was through the primer and the conductive metal substrate instead of along the interlayer between the topcoat and primer [25].

Characterizing the corrosion protection performance of a coating system requires that the coating/metal interface be monitored. Applications with embedded electrodes for in situ monitoring using two-electrode EIS or reverse ENM configurations require electrical connection to the metal substrate. A non-substrate configuration would be field applicable, as it would relax the constraint of the substrate acting as the working electrode, which requires a direct electrical connection to the substrate in the vicinity of the sensor. The experimental result of Miszczyk and Schauer [18] demonstrated that a non-substrate configuration was associated with the topcoat/primer interlayer performance while the simulations of Nogueira et al. [25] demonstrated that a similar configuration would be associated with the metal/coating interface.

Experimental results are presented for two coating systems equipped with embedded electrodes which demonstrated both possibilities. The degradation of the coating systems was promoted using the ac–dc–ac accelerated test method. This is an aggressive method that includes the application of a cathodic potential that promotes cathodic reactions promoting failure and reducing lifetime [4–8] in much shorter times as compared with conventional accelerated test methods. The results indicated that an EIS experiment conducted between two embedded electrodes could be used for monitoring the degradation of specific coating systems.

2. Experiment

The EIS experiments were conducted on two industrial coating systems obtained from Kumkang Chemical Company, Korea. One coating system consisted of an epoxy primer and a polyurethane topcoat and the second consisted of an alkyd primer and an alkyd topcoat. These systems would be referred to as the urethane and alkyd systems, respectively. Both coating systems were coated on standard steel panels, which had been polished by 200 grit sandpaper and 800 grit sandpaper sequentially. Each of the coated panels had platinum electrodes embedded between the primer and the topcoat. Platinum leaves as thin as 130 nm were obtained from Wrights of Lymm Ltd., Manchester, England and used as the electrode material. A schematic diagram of two electrodes embedded between the topcoat and the primer separated by 6 cm on a 3 inch by 5 inch panel is shown in Fig. 1. Platinum leaves supported by tissue paper were cut into the designed shape. The surface area of the electrode was 5.28 cm^2, made by removing four 0.8 cm square sections from a 2.8 cm square such that the width of any remaining section was 0.4 cm.

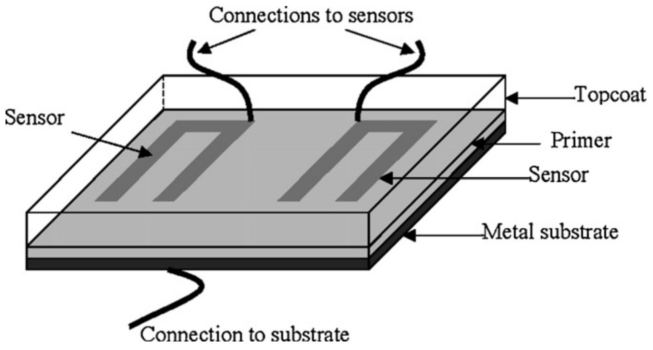

Fig. 1. Schematic diagram of embedded electrodes placed between a topcoat and a primer.

A thin layer of epoxy resin composed of D.E.R. 331 epoxy resin/Ancamide 2353/methyl ethyl ketone = 5/3/5 (by weight), was applied onto the cured primer surface where the electrode was to be placed. The platinum electrode placed on this epoxy resin adhered to the primer after 10 min of solvent flash off. The supporting tissue paper was then removed and a paper tissue was used to remove any excess epoxy resin on the surface of the coating and electrode. A copper core electrical conducting wire was soldered onto the embedded electrode in a location as shown in Fig. 1 after the adhesive epoxy was fully cured. The wire/electrode joint was sealed with an epoxy resin composed of D.E.R. 331 epoxy resin/Ancamide 2353 = 5/3 by weight. This seal harden at room temperature in 1 day after which the topcoat was applied with the electrode embedded between the topcoat and primer. The approximate neat dry film thickness of the primer and the total coating system were approximately 50 μm and 100 μm, respectively, with a standard deviation of about 5 μm.

The ac–dc–ac method was used to promote degradation of the coating systems. It is a cyclic method that involves a testing step, a cathodic potential step, and a rest step [4–8,19] all carried out with the coating being immersed in electrolyte. The electrolyte used in the experiments was 3.5 wt.% NaCl solution.

The test step included electrochemical monitoring of the coating by EIS at the open circuit potential. The cathodic potential step involved the application of a negative direct current (dc) potential relative to the open circuit potential between the embedded electrode and the substrate for a given time. After the cathodic step, the coating was allowed to recover to the open circuit potential and reach a steady state during the rest step. The electrochemical monitoring would then begin the next cycle. Each cycle took a day with the testing step having approximately 1 h, the cathodic potential step various time periods and the rest step between 16 h and 23 h in duration. The cathodic potential steps used in the ac–dc–ac method were −2 V for 1 h (days 0–18), −4 V for 4 h (days 19–40), −4 V for 8 h (days 41–80). A step of −8 V for 8 h (days 81–90) was used for the alkyd system.