A study of performance of corrosion prevention compounds on AA2024-T3 with electrochemical impedance spectroscopy

F. Gui, R.G. Kelly *

*Center for Electrochemical Science and Engineering, Department of Materials Science and Engineering,
University of Virginia, Charlottesville, VA 22904, USA*

Abstract

The performance of corrosion prevention compounds (CPC) on AA2024-T3 was assessed with electrochemical impedance spectroscopy (EIS). The good correlation between the protection performance of CPC and both the interfacial impedance and double layer capacitance allowed two assessment criteria to be defined; as found for AA7075-T6, excellent protection was exhibited by CPC-coated surfaces with interfacial impedances above $0.1\,\mathrm{M\Omega\,cm^2}$ or double layer capacitances below $7.6 \times 10^{-8}\,\mathrm{F/cm^2}$. A correlation between double layer capacitance (C_{dl}) and corroded area was also obtained. This latter correlation offers an alternative to evaluation of CPC performance via the corroded area calculated from C_{dl}. In addition, a prediction method was demonstrated based on impedance parameters that showed the feasibility of using data from 30 days to predict the performance of CPC after 180 days exposure. It was found that the CPC failure can be greatly accelerated without changing the relative ranking among the CPC used by introducing intentional scratches on CPC-coated specimens. In particular, the minimum time needed to rank various CPC was reduced to 8 days for scratched specimens from several months for unscratched ones.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Corrosion prevention compounds; Interfacial impedance; Double layer capacitance; Corroded area determination

1. Introduction

Corrosion prevention compounds (CPC) are materials that can both prevent new corrosion sites from forming as well as suppress corrosion that has initiated. They are widely used on aircraft as a relatively inexpensive way of protecting against corrosion at compromised areas of the coating systems and in occluded regions [1]. CPC are often classified according to their ability to displace water and the appearance of the film after application (e.g., water-displacing; hard film, waxy). Although CPC have been widely used for decades, no generally accepted test methodology exists for assessing or screening CPC performance for aerospace applications. Specifications have generally focused on easily measured physical and chemical properties, including compatibility with other materials and safety.

Various salt spray tests have long been used for assessing organic coatings, but there is persistent dissatisfaction with the correlation between such tests and the performance in more benign field applications [2,3]. More recently, sensitive electrochemical methods have been shown to allow coating system performance to be assessed in environments that mimic service or in actual service itself. Thus, instead of attempting to greatly accelerate the damage and thereby risk altering the damage mode responsible, a more sensitive measurement of the degradation allows less aggressive, but more relevant, solutions to be used.

Because of its non-invasive nature and its ability to discriminate coating performance, electrochemical impedance spectroscopy (EIS) has been widely used as a non-destructive technique to study organic coatings on metals to gain complementary information to that obtained by traditional methods for characterizing the behavior of organic coatings in corrosion environments [4–8]. In studies of epoxy-coated steel and an epoxy-coated magnesium alloy, Scully and Hens-

---

* Corresponding author. Tel.: +1 434 982 5783; fax: +1 434 982 5799.
E-mail address: rgk6y@virginia.edu (R.G. Kelly).

ley found a correlation between the magnitude of the low frequency impedance and long-term coating deterioration [9,10]. In other work, Hack and Scully [11] used EIS to quantify the defect area of organic-coated steels in seawater via the breakpoint frequency method. Other applications of EIS to the study of organic coating include the monitoring of water uptake under cyclic wet–dry condition with coating capacitance [12] and its use on the study of corrosion behavior of internally coated metal containers [13]. In addition, EIS also has been used to assess long-term exposure behavior of coatings on steel immersed in seawater. The relative performance ranking after 2 years exposure was paralleled by determined by EIS, although it seems that EIS alone is not adequate for evaluating blistering of organic coatings where the blisters develop between the coating layers [14].

The present study demonstrates the level of protection provided by CPC for aluminum alloys and the ability of parameters derived from EIS measurements to both assess and predict CPC performance on these aerospace materials. In the present context, assessment quantifies protection, whereas prediction describes the ability to use short-term measurements to forecast long-term performance. A method described predicts the long-term performance of CPC using parameters extracted from short-term test data. Comparisons are made between the impedance behavior of CPC and that of typical organic coatings, demonstrating that not all impedance analyses that provide insight for organic coatings are applicable to CPC.

2. Experimental

2.1. Specimen preparation

The specimens used in this work were cut to 7.62 cm × 7.62 cm (3 in. × 3 in.) from an aluminum alloy (AA) 2024-T3 sheet with a thickness of 0.229 cm (0.090 in.) and composition of (wt%): Cu 3.8–4.9, Mg 1.2–1.8, Mn 0.3–0.9, Ti ≤ 0.15, Zn ≤ 0.3, Fe ≤ 0.5, Si ≤ 0.5, Ni ≤ 0.1, and (Fe + Ni) ≤ 0.5. Each specimen was cleaned by sequentially degreasing in an ultrasonic bath with acetone for 5 min and methanol for another 5 min, rinsing in high-purity water, and finally drying in air. A flat electrochemical cell was used for impedance measurements. The area of the specimen in contact with the O-ring used to seal the cell was taped with 63.5 μm thick polyester tape to avoid damage to the CPC film. The total exposed area was 13.1 cm^2. Four commercial CPCs were studied in this work: Amlguard (LHB Industries, St. Louis, MO), Dinitrol® AV30, Dinitrol® AV8 (DINO-LAB, Hässleholm, Sweden), and LPS3 (LPS Laboratories Inc., Tucker, GA). These CPC cover the range of US military specifications (MIL-C-85054) as well as Boeing materials specifications (BMS3-23 and BMS3-29). The film types of CPC chosen here include three that form hard, dry films (Amlguard, AV8 and AV30) and one that forms a waxy film (LPS3). All were applied by spraying. After application of

the CPC, all specimens were allowed to dry overnight before exposure to the solution. The thickness for dry CPC films was between 15 and 20 μm. In some cases, local penetration of the dried CPC was made with a knife to create X-shaped scratches on the surface in order to test damaged surfaces.

2.2. Exposure methods

The lap joint simulation solution (LJSS) was used as the exposure solution with composition as follows [15]: 20 mM NaCl, 4 mM NaHCO$_3$, 4 mM NaNO$_2$, 2 mM NaF, adjusted to pH 9. This solution has been shown to mimic that found in isolated occluded regions that are widespread on aircraft. Constant and alternate immersion exposures were both investigated. Alternate immersion involved cycles of immersion in the LJSS for 12 h followed by drying in the air for 12 h.

2.3. Electrochemical impedance spectroscopy

EIS spectra were generated as a function of exposure time. Each spectrum was obtained after monitoring of the open circuit potential (OCP) for 1 h. Spectra were generated after 2 and 5 days and then once a week thereafter. Later, the test time interval increased with increasing exposure time. The spectra for scratched AA2024-T3 under constant immersion was generated every day then stopped after 2 weeks of immersion. The EIS measurements were performed using a Solatron SI 1260 impedance/gain-phase analyzer in combination with a Solatron 1287 electrochemical interface. The frequency range used was 100 kHz to 10 mHz, and the voltage amplitude was 7 mV rms. For samples exposed to alternate immersion, EIS was performed at the end of the wet portion of the cycle.

Interfacial impedance was used to characterize the resistance of CPC film to corrosion. It was obtained by subtracting the resistance of the solution from the impedance magnitude measured at the lowest tested frequency (10 mHz). Polarization resistance (R_p) and double layer capacitance (C_{dl}) values were obtained by fitting the impedance spectra to equivalent circuit models with ZView® (Scribner Associates, Southern Pines, NC). The equivalent circuit models used were generally of the form shown by Beaunier et al. [16] and Mansfeld et al. [17], although in some cases, a Warburg element was added to improve the fit. The electrochemical parameters, such as polarization resistance and double layer capacitance, were extracted from the fitted data. The fitting quality was controlled by the fitting error. Generally, the fitting was considered as good when the fitting error for each parameter was less than 10%, and such good fits were generally easily achieved. Note that the polarization resistance is always the same or less than the interfacial impedance as defined, with the difference being due to impedance related to mass transport processes. The percentage of corroded area was calculated from digital images of the scratched specimens using the image processing software package AnalySIS® (Soft Imaging System, Lakewood, CO).