

The Effect of Flow Rate on Corrosion Currents from Various Aircraft Primers

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ABSTRACT

The functional life of paint in DoD is defined by the barrier properties and protective corrosion inhibiting capacity of the coating system. The time till corrosion initiation of an underlying substrate can thus be defined in general terms as 1) the time for an external environment to reach the coating/substrate interface through coating porosity, coating cracking, or mechanical damage and 2) inhibitor exhaustion/depletion. In other words, once a coating system has been breached, protection is afforded by the availability of inhibitors at the defect site. In this work, the parameters that influence inhibitor exhaustion will be examined. The onset of corrosion at a defect is a function of inhibitor release rate, the ratio of inhibitor to aggressive ions, and consumption of inhibitor in the vicinity of the defect. In this paper, the effect artificial inhibitor consumption on corrosion rate through the use of a flowing cell and a Multi-electrode Array probe will specifically be explored. The effect of flow rate on corrosion current will be shown for three different military primer systems. Steady state inhibitor concentrations at each flow rate will be used to explain the individual effects of flow and chromate content on corrosion current.

Key words: Inhibitor exhaustion, Multi-electrode Array, coating

INTRODUCTION

Once a coating system has been breached, protection is afforded by the availability of inhibitors at the defect site. The onset of subsequent corrosion, therefore, is a function of inhibitor release rate, the ratio of inhibitor to aggressive ions, and consumption of inhibitor in the vicinity of the defect. The parameters affecting each of these processes must be understood in order to appropriately model the onset of corrosion for either a first principles or an empirical approach. The influence of coating properties and environmental conditions on inhibitor exhaustion is discussed below.

Inhibitor release rate is potentially the single largest factor governing corrosion protection at a defect ¹. It is a complex of function of diffusion through a coating and inhibitor solubility, and inhibitor interactions include matrix binding forces and dissolution kinetics ^{2,3}. Numerous authors have shown that leach rate is a complex function that has a strong Fickian diffusion term as well as an additional term resulting in non-Fickian behavior. The later affect has been attributed to dissolution kinetics within the polymer matrix for systems with high release rates and good solubility in corrosive electrolytes ^{2,4-6}. Tabor

further described a complex diffusion functionality involving transport of environment into and diffusion of inhibitors out of the coating ⁷. His model demonstrates the complex dependence between coating properties, solubility, and inhibitor/coating interactions.

It has been documented that coating barrier properties have a strong influence on corrosion. In work by Petry ⁸, coating impedance and inhibitor leach rate from a coating defect reveals that for systems with topcoats that have high barrier properties, low chromate leach rates and high corrosion rates are observed. Comparison of primer systems with similar chromate loading but differing impedance similarly reveals that high barrier properties result in low leach rates ⁹. These barrier properties are further affected by pH and chloride which have been shown to increase inhibitor release rates by lowering barrier properties and increasing diffusivity through the coating ^{9–11}. For an atmospheric exposure, therefore, the ability of an inhibitor to protect a defect is dependent on wetting and the presence of enough moisture to permeate the coating system (i.e. environments with higher average RH and high salt loads). It is also reasonable to assume that if coating system barrier properties change due to aging processes corrosion initiation may be affected similarly ^{9,12}.

Regardless of alloy substrate or type of inhibiting ions, inhibitor effectiveness is a strong function of the rate of inhibitor release and the total amount in solution ^{1,3,13,14}. The critical ratio is a function of inhibitor strength ¹³. The amount of inhibitor ions in solution is a strong function of solubility in solution. While chromate ions are fairly stable over a wide pH range, solubility of meta-vanadate, zinc, and praseodymium compounds are a strong function of pH ^{1,14–18}. Therefore, environmental exposure will affect solubility and the protectiveness of inhibitors in different ways.

Consumption of inhibitors within an electrolyte solution complicates the processes since concentrations can drop below their critical levels for substrate protection. The largest driving force for consumption of inhibiting ions under stagnant conditions is corrosion processes. Delamination and blistering of a coating on steel and aluminum is often associated with electrochemical reactions. For aluminum, corrosive blister formation in coatings is accompanied by the appearance of cathodic blisters in the same vicinity ¹¹. Nguyen, Pommershin, and Bi argue that for coated steel, cathodic reaction kinetics under the delamination site result is the transfer of Na^+ ions along the interface leading to increased delamination rates or blister growth ^{19–21}. In both cases, the driving force for delamination and blister formation and increased corrosion is the anodic reaction rate. Therefore, it can be reasoned that the role of inhibitors to slow corrosion will also reduce delamination and blistering. Depletion of inhibitors in an electrolyte is linked with substrate oxidation ^{2,4,11,22}. For example, the highest depletion rates have been observed for higher chloride content or exposure of less corrosion resistant alloys. Inhibitor consumption will result in sustained release of the inhibitors from a coating system to maintain critical levels in the electrolyte which eventually results in a more rapid inhibitor exhaustion and subsequent uncontrolled corrosion. Consequently, to afford protection, inhibitor concentration must remain above the critical concentration long enough for a protective layer to form.

For corrosion protection to be maintained, therefore, relatively high leach rates must be maintained ¹. The primary role of many inhibitors is to reduce cathodic current density by the formation of a protective film. In the case of chromate, $\text{Cr}^{+3}/\text{Cr}^{+6}$ complexes are formed on various metals ^{2,10,23–25}. Prosek indicated that once film adsorption onto cathodic sites was complete, the depletion rate of Cr^{+6} from solution significantly slowed ²².

While significant work has been done to characterize the mechanisms of coating failures and inhibition, no work has been done to address mechanisms of inhibitor exhaustion. It is clear from field experience and laboratory exposures that inhibition exhaustion does occur and corrosion can be observed within a coating defect. In this paper, the effect artificial inhibitor consumption on corrosion rate through the use of a flowing cell and a Multi-electrode Array probe is specifically explored. The effect of flow rate on corrosion current will be shown for three different military primer systems. Steady state inhibitor concentrations at each flow rate will be used to explain the individual effects of flow and chromate

content on corrosion current. The end goal is to provide a framework from which tests to study inhibitor exhaustion can be realized.

EXPERIMENTAL PROCEDURE

In this section, we describe the flowing test cell and the construction of the Multi-electrode Array (MEA) probe. Further, details of the test solutions, primers evaluated and exposure conditions are outlined.

Cell Design and Fabrication

A small volume cell used in this work is shown in Figure 1. The cell is equipped for mounting the MEA probe and for performing electrochemical measurements as needed. A platinum wire counter electrode is pressed into a groove within the cell exposure volume. A well for a reference electrode is machined into the body of the cell. The reference well is in electrochemical contact with the cell exposure volume through a frit mounted in a machined lug-in tube.

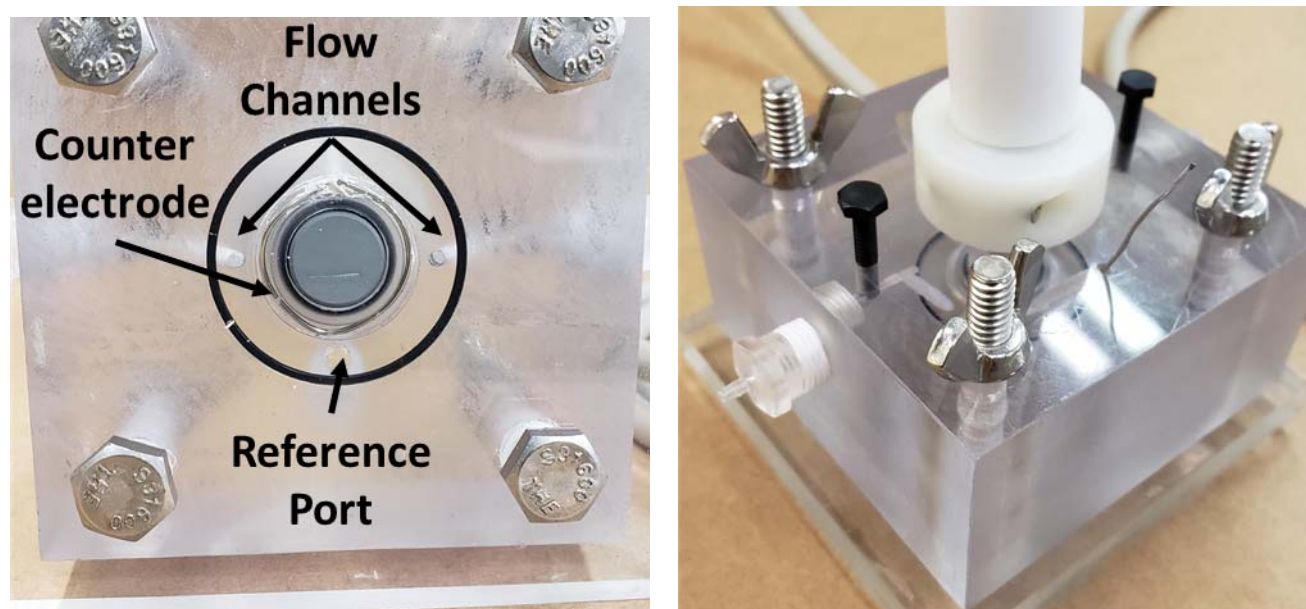


Figure 1: (a) Image of the small volume test cell from the bottom. (b) Image of the small volume test cell with the MEA probe inserted.

A 2 in x 2 in (5.08 cm x 5.08 cm) coated sample is mounted to the bottom of the cell using a threaded mounting plate and is sealed against the cell body with an o-ring. The exposed diameter of the substrate is 3 cm yielding an exposed area of 7.07cm². The machined height of the exposure cell is 0.75mm. This is within the range of electrolyte layer thicknesses under atmospheric conditions. The volume of the cell in the region of the sample is therefore ~ 0.530 mL (S/V ~13.34cm⁻¹). Two 0.0625" (0.159 cm) flow channels are machined into the cell to accommodate fluid flow. The in and out channels are equipped with threaded rods. These rods are used to isolate the sample region within the cell in order to perform testing under stagnant conditions. Therefore, the effective volume of the cell under stagnant conditions is greater than 0.530 mL and measured to be ~ 1.2 mL (S/V = 5.89).

A peristaltic pump is used for fluid flow. The highest flow rate achieved within the cell was 7.2 mL/min at a pump rate of 400 rpm. Thus, there will be an exchange of fluid in the immediate exposure area of the cell (0.53 mL) of up 13.58 times per minute at the highest flow rate.

MEA Design and Fabrication

For this work, a linear 20 wire MEA was fabricated (**Figure 2**). Each wire is 250 μ m AA7075 T-0 (UNS A97075) coated with polyimide to prevent shorting and minimize crevice corrosion down the length of

the wire. The wires are mounted close packed in an epoxy matrix. Each wire is soldered to an individual connector of a ribbon cable and subsequently potted to ensure stability at the connections. The cell was designed to accept the probe as shown in Figure 1b. An o-ring seal within the cell prevents leakage of cell fluid through the MEA port. Currents from all 20 channels of the MEA were acquired as a function of time. For each time, all anodic currents were added and a plot of “Total Anodic Current (A)” is plotted vs. time.



Figure 2: Photographic image of the MEA probe: (a) end view showing the 20 AA7075 wires and (b) a side view showing the mounting assembly.

Materials and Solution

Samples of UNS A97075 were coated with one of three primers: Cr-P = PPG 02Y040A[†], Pr-P = PPG 44GN948[†], or nCr-P2 = Hentzen 16708[‡]. After painting, samples were subsequently cut into 2 in x 2 in (5.08 cm x 5.08 cm) pieces for use in the flow cell. Control tests employing no coating primer were undertaken by sealing the cell directly on the polymer backplate. All testing was performed in 0.6 M NaCl at neutral pH. A subset of experiments was performed with the addition of saturated additions of CrO_4^{2-} as SrCrO_4 and in some cases pH was adjusted to pH = 3. All solutions were mixed using 18 M Ω DI water.

Exposure Conditions

Samples were exposed under various flow conditions. For a rapid assessment of the effect of inhibition as a function of flow rate, testing was performed under non-steady state flow rates in rising flow rate tests. Solution was initially pumped into the test cell at a high rate. Once it was clear no bubbles were present (less than five minutes was required), the pump was stopped and the cell sample volume was isolated by tightening the isolation screws. This stagnant condition was maintained for one hour to allow for corrosion inhibition to initiate on the MEA probe. Subsequently, the flow rate was stepped from roughly 0.096 mL/min to 7.2 mL/min by adjusting the pump rate to 6 rpm, 10 rpm, 20 rpm, 40 rpm, 80 rpm, 200 rpm, and 400 rpm. Each pump rate condition was held for 1 hour prior to the initiation of the next step. The average and standard deviation of the “Total Anodic Current” was calculated over the entire hour at each flow rate step and recorded. Note that solution volume was measured during each flow regime to calculate the flow rate. This was necessary as it was found that for a given pump rate, flow rate would change slightly as a function of the aging tubing.

Subsequent testing of chromated primers was performed under single flow rate conditions for up to seven days. In these tests, samples were pretreated under stagnant conditions to allow for inhibition of the MEA prior to introducing flow. In one set of experiments, samples were preconditioned for two hours followed by the introduction of solution flow for two hours and were then returned to stagnant

[†] Trade Name

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