Characterization of inhibitor storage and release from commercial primers

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ABSTRACT

Commercial primers are applied on aluminum alloys that are used in aerospace applications to prevent corrosion attack from aggressive environments. These primers contain inhibitors that help combat corrosion. During field operations, these primers store and release inhibitors to protect the underlying alloy. The goal of this study is to characterize storage and release behaviors of these commercial primers to better understand the rate and mechanism by which inhibitors are released. Three commercial primers were investigated in this study; 1) Akzo Nobel 10P20-13 High Solid Primer that contains strontium chromate ($SrCrO_4$), 2) Deft 02GN084 (Pr-based), and 3) Hentzen 16708TEP ($BaSO_4$-based). The primers were coated on a Teflon tape, then stripped off and broken to small pieces. Pieces of the primer coating were immersed into solutions of different Cl^- concentration, temperature, time, and pH. The solutions were then filtered and characterized by inductively coupled plasma mass spectroscopy (ICP-MS) to analyze the solution chemistry. Results showed that $SrCrO_4$ primer release behavior follows power law kinetics. Solubility limits played an important role in dictating the release kinetics of the chromate primer when accumulation of Cr ion occurs.The effect of pH and temperature can alter this solubility limit. Chloride seems to promote release of chromate because of greater ionic strength. The Pr-rich primer released a large amount of Ca^{2+} upon exposure and release kinetics were not time-dependent thereafter. The Ba-rich primer did not release soluble constituents to any significant extent.

1. Introduction

Aluminum alloys are susceptible to localized corrosion, which can degrade structural integrity and reliability in aerospace structures. This type of corrosion is difficult to detect because of its small extent of attack. Nonetheless, a small amount of corrosion damage can trigger other failure modes such as fatigue cracking and lead to significant failures. Therefore, aircraft components are coated with highly protective multi-layered coating systems, particularly in areas where regular inspections are difficult or impossible. Aluminum alloy surfaces are typically subjected to some surface pretreatment prior to painting. One of the most effective methods is an application of a chromate conversion coating [1,2]. Conversion coatings promote adhesion and reinforce the natural passivity of aluminum alloys, thus preventing corrosion attack. However, the most important layer for corrosion protection is the primer, which provides a reservoir of soluble inhibitor [3]. These corrosion inhibitors reinforce the passivity imparted by the conversion coating and strengthen the natural passivity of aluminum alloys. Lastly, the outermost layer is one or more top coats that provide barrier protection and give a desired appearance.

Corrosion inhibiting pigments are added to primer coatings during the coating formulation process. These pigments usually contain sparingly soluble salts that release inhibiting ions when subjected to aqueous or humid conditions. Strontium chromate, $SrCrO_4$, is widely used due to its effectiveness as a corrosion inhibitor. Chromates inhibit by stifling oxygen reduction due blocking action associated with reductive adsorption of Cr species on the alloy surface. Although it is a powerful corrosion inhibitor, it is a highly toxic and it is considered an environmental hazard. As a result, there is a desire to replace it in commercial and military primer formulations [4,5]. Benign chromate alternatives are preferable to chromate systems [6].

When coating systems are exposed to atmospheric conditions, a primer absorbs moisture, which dissolves some of the $SrCrO_4$ primer, releasing the chromate inhibitor [7]. Soluble CrO_4^{2-} interacts with the underlying aluminum surface at active sites to stifle the oxygen reduction reaction. This inhibition process is powerful and acts even if the coating system experiences some amount of mechanical damage or degradation. As a result, chromate coating systems are said to be "self-healing" [8]. The leachability of chromate from primer is an essential characteristic of commercial chromate primer systems [4,9].

The leach rate of chromate from primers has been characterized to a certain extent, but some aspects of this behavior remain unreported

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[7,10–12]. Xia et al. studied the release of hexavalent chromium from a chromate conversion coating using ultraviolet-visible spectroscopy and found that leaching kinetics depends on pH, ionic strength and ratio of chromate conversion coating surface area to solution volume [13]. Posek and Thierry studied the release rate of chromate from an epoxy resin. They found that the release rate exhibited a logarithmic time dependence [14]. Scholes et al. found that the release rate of chromate from a primer with polyamide cured epoxy was greatest around 600 $\mu g/cm^2$ at a pH of 1, but the release rate at other pH values was around 200 $\mu g/cm^2$ [7]. Furman et al. claimed that the release rate followed a time dependence of $t^{0.25}$; somewhat slower than the standard Fickian, $t^{0.5}$ behavior [12]. The effect of temperature on leaching has not been widely reported.

Primer leaching behavior was the focus of this study. Whether non-chromate primers are less protective than chromate primers because of leaching rate or because of the protective mechanism of the non-chromate primer is a question that has not been thoroughly explored. The goal of this study is to characterize leaching kinetics of commercial chromate and non-chromate primers at different pH values, temperatures, and ionic strength and understand the limiting factors that dictate leaching kinetics.

2. Experimental procedures

To characterize leaching behavior, strips of primer with a constant with fixed thicknesses and areas were exposed to aqueous solutions whose temperature, pH, Cl^- concentration, and exposure time were varied. To mimic primers in real field environments, moisture saturated condition was simulated by immersing primer in solution. Over time, the primer samples released inhibitors into solution. Three primers were investigated in this study. All of them complied with MIL-PRF-23377. The primers used in this experiment were 1) Akzo Nobel 10P20-13 High Solid Primer, 2) Deft 02GN084, and 3) Hentzen 16708TEP. Only Akzo Nobel 10P20-13 primer contained strontium chromate. Deft 02GN084 is a Pr-based primer while Hentzen 16708TEP used $BaSO_4$ as a main corrosion inhibitor. Components were mixed in a ratio of 3:1 according to manufacturer standards. The induction time was approximately 30 min before application of the primer coating was applied to a Teflon-covered glass slide.

Glass slides with 25.2×75.6 mm dimensions were covered with high density Teflon tape from Taegaseal™. With a syringe, 1 mL of primer containing epoxy was spread onto the Teflon tape. A fixed volume was applied to ensure a consistent amount of pigment in each primer sample. The primers were air dried for 2 h before being cured at 65 °C for 24 h. After the cure, the glass slide and the Teflon tape were removed from the dried primer sample. Each strip of dried primer was then broken into areas of ~0.5 cm^2. Pieces were placed into 15 mL vials for exposure to solution. Five milliliters of the desired solution was added to each vial. The total exposed surface area of the primer was 38.2 cm^2 (exposed surface area was twice the top surface of the area of the glass slide). The surface area of the edge of the primer samples was ignored because it was insignificant compared to the sample faces. Each primer sample was exposed to a fixed 5 mL volume of solution. Exposure times were 4 h, 12 h, 1 day, 3 days, 5 days, 7 days, 15 days, and 30 days. The temperatures were 25, 35, or 60 °C. The temperature of 35 °C is that of widely used accelerated test ASTM B117. The pH levels were 3.5, 5.5, or 10. The pH adjustments were made using concentrated HCl and NaOH. It is important to note that pH 5.5 was the pH value of 0.1 M NaCl stock solution. This pH range exhibits real pH value in working environments because corrosion reactions can cause a change pH value in the real environments. After exposure, the solutions were filtered using *Fisher Brand* filter papers with medium porosity and P5 qualitative rating. Each condition was performed in triplicate.

To make samples for EIS measurements, AA 7075-T6 coupon was cut to 25.2×75.6 mm in dimension to match the size of the glass slide. After the coupon was rinsed with acetone, with a syringe, 1 mL of primer was spread on the 7075-T6 coupon. Samples were then cured at 65 °C for 24 h. The thickness of the primers was approximately 200 μm, but thickness was not uniform, especially on the edges. The exposed area were in the middle.

Solution chemistries were measured to track inhibitor release from the primer samples. Solution chemistry was measured using inductively coupled plasma − mass spectroscopy (ICP-MS). This technique uses Argon plasma to ionize elements in a sample solution. Ionized atoms then enter into a mass spectrometer for identification and quantification. ICP-MS is capable of part per billion elemental sensitivity, but does not differentiate between oxidation states. Additionally, elements with similar masses result in overlapping peaks in the mass spectrum and organic matter such as carbon, hydrogen, oxygen, and nitrogen cannot be detected. ICP-MS was carried out using a *Perkin Elmer SciEX ELAN 600* and solutions were diluted 100X before analysis. Data for each exposure condition were collected three times to ensure measurement reproducibility. Semi-quantitative measurements were collected initially to ensure that all elements leached from primers were analyzed. A full quantification with a five-point calibration curve was then performed with known concentrations of Sr, Cr, Ca, and Ba, which were the primary inhibiting species found by the initial semi-quantitative data collection.

Energy dispersive X-ray spectroscopy (EDS) on primer samples before and after immersion in 0.1 M NaCl solution was performed using *FEI/Phillips XL-30* environmental scanning electron microscope (ESEM). The beam energy was 15 kV with a 12 mm working distance to maximize counts per second. The elemental analysis was completed with *EDAX*® Analysis Software. The density of pigments was calculated by transforming EDS maps into a grey scale image. A threshold was established and all pixels with grey scale intensity greater than the threshold were counted as pixels representing pigment particles. The number of pixels associated with pigment particles was summed and reported as a measure of pigment particle density in the sample. The same threshold was applied to all images to standardize the analysis routine.

3. Results

3.1. Inhibitor release from Hentzen 16708TEP and Deft 02GN084

Hentzen 1670TEP did not release soluble constituents to a significant extent. Barium sulfate is present in the Hentzen formulation and it was detected only in minute concentrations. Fig. 1 shows the amount of Ba^{2+} released as a function of time. The amount released is plotted as $\mu g/cm^2$ of exposed primer coating and as total concentration in moles per liter. No significant trend in the amount of Ba^{2+} released was observed. Evidence of aluminum alloy corrosion inhibition by Ba^{2+} was not found in the literature, so it is unknown if Ba^{2+} concentrations like these are protective, nor is it certain that these concentration levels
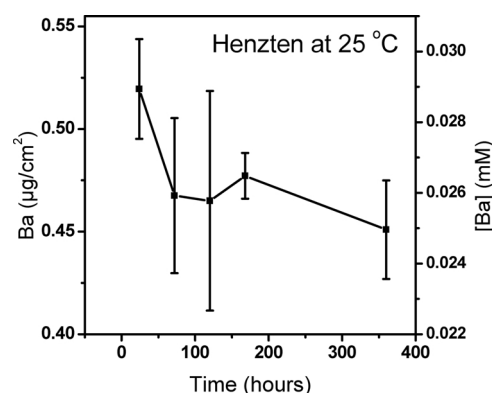

Fig. 1. Barium concentration per exposed area vs time from Hentzen 16708TEP primer.