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Chromate leaching from inhibited primers
Part I. Characterisation of leaching

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Abstract

Leaching and characterisation studies have been undertaken on two chromate-inhibited epoxy polyamide primers. Leaching was carried out in 5% (w/v) NaCl solutions at different pH values (1, 3, 5 and 7) and the amount of Cr released into solution was monitored over time. Cr release was initially high, but as the immersion time increased the leaching from the primers slowed. Prior to and after immersion, the primers were characterised by a number of techniques including electron microprobe analysis, X-ray microdiffraction, Raman spectroscopy, and positron annihilation lifetime spectroscopy. The unexposed primers were found to contain the inorganic phases $SrCrO_4$, $BaSO_4$ and TiO_2 (anatase or rutile). Upon immersion, water uptake by the primers was observed, together with a decrease in the amount of $SrCrO_4$ in the primers. These studies provide insights into the mechanism of chromate leaching from inhibited primers.

Keywords: Coatings; Primers; Chromate; Leaching; Corrosion

1. Introduction

Chromate-inhibited primers are used extensively throughout industry as a component in corrosion protection systems for a range of metals. In general, the corrosion protection system consists of (i) a conversion or anodised coating, (ii) an inhibited primer and (iii) a topcoat [1–3]. The conversion coating is most commonly a chromate conversion coating (CCC), while anodising is done in either chromic acid, phosphoric acid or boric/sulphuric acid anodising baths. Typical primers consist of a chromate pigment (such as $BaCrO_4$ or $SrCrO_4$) in an epoxy polyamide matrix, together with other compounds such as fillers, UV absorbers and colouring agents [4–7]. The chromate pigments $BaCrO_4$ and $SrCrO_4$ are selected for their favourable physical properties, namely their low but finite solubility, their saturated solutions having a pH in the range 7–9.5, their efficient inhibition against corrosion for a range of metals, and compatibility with the polymer matrix [5]. Finally, the topcoat is composed of a robust polymer layer, which protects against environmental erosion and mechanical abrasion [8].

The protection system therefore provides a barrier to the ingress of moisture and corrodents, but also contains a reservoir of inhibitor in the form of chromate that is available to heal defects in the coating [2,6,9,10]. Chromate inhibits corrosion by leaching from the protection system, migrating through condensed moisture on the surface and reacting with actively corroding sites, thereby resulting in passivation [4,6]. The mechanism of corrosion protection by chromate is an active area of research, with a particular emphasis on the suppression of pitting [11–17]. Chromate is known to act as both a cathodic and anodic inhibitor, thus reducing the overall electrochemical activity of the corroding surface. The details of how chromate passivates the surface at the site of a defect, however, are less well understood [17]. Very little chromate is required to deactivate corrosion reactions at the surface of aluminium alloys. Studies have revealed that as little as 10^{-5} M $CrO_4{}^{2-}$ can inhibit oxygen reduction reactions on aluminium alloy 2024-T3 [11]. Pride et al. [12] have demonstrated that 2.5×10^{-5} M $CrO_4{}^{2-}$ causes a significant decrease in metastable pit formation. Reduction in stable pit initiation has been observed with as little

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as 10^{-4} M chromate on unpassivated panels of AA2024-T3 [13].

In recent years, there has been a renewed effort to characterise and understand chromate protection systems. For conversion coatings, many studies have been undertaken on polished surfaces of AA2024-T3 and have provided insight into the mechanism of deposition. Xia and McCreery [18] have clarified the role of ferricyanide as an accelerator, while other studies have identified the slower rate of reaction of the conversion coating with intermetallic particles that occurs both on AA2024-T3 [19–24] and AA7075-T6 [25]. To date, however, there appear to be only four papers in the literature that deal with the commercial deposition process (alkaline clean, Cr(VI)/HF/HNO_3 deoxidiser and ferricyanide-accelerated conversion coating bath) as applied to AA2024-T3 [26–29] and used here.

While chromate has been shown to leach from conversion coatings [30,31], the majority of the chromate released for the purposes of protecting the surface comes from the primer [32]. Leaching of chromate from the primer is a complex phenomenon and, in the context of a defect in the coating system, will involve a number of steps. These include (i) transport of water into the defect and across the damaged edge of the primer, (ii) transport of water into the primer to the inhibitor particles, (iii) dissolution of the inhibitor particles, and (iv) transport of the inhibitor through the primer to the defect site. In comparison with the numerous studies on conversion coatings, the physicochemical characterisation of the primer has received little attention. The majority of studies have focussed on investigating the ingress of water into the primer using electrochemical methods [4,33,34]. For example, Fedrizzi et al. [4] found that the coating capacitance changed with the uptake of water. Using the Brasher–Kingsbury equation [35], they were able to ascertain the volume fraction of water in a phosphate-containing primer. Furthermore, they found that the uptake of water did not follow Fick's second law in the case of $SrCrO_4$, due to the strong water–$SrCrO_4$ interaction. Carbonini et al. [34] found that coating capacitance curves exhibited several distinct regions, which they attributed to water uptake, $SrCrO_4$ dissolution, and blocking of pores within the primer by re-precipitation of $SrCrO_4$.

Apart from electrochemical studies, the only other techniques that have been used extensively in the characterisation of chromate-inhibited primers are the positron-based techniques of positron annihilation lifetime spectroscopy (PALS) and Doppler broadening energy spectroscopy (DBES). Both PALS and DBES probe the free volume or voids within a material. These properties are important to inhibited primers, particularly with regard to their barrier properties and to the mechanism of inhibitor release. Madani et al. [36] have used PALS to examine water uptake in epoxy systems incorporating a selection of corrosion inhibitors. The same authors have studied voids at the interface between a $SrCrO_4$ inhibitor phase and an epoxy matrix using PALS [37]. Cao et al. [38] have examined primer/topcoat systems on AA2024-T3 using DBES, although they obtained information about the topcoat only.

In this paper, the leaching of $SrCrO_4$ from two chromate-inhibited primers is reported and is characterised using a variety of analytical techniques. Leaching was carried out using immersion experiments in static solutions at ambient temperature and over a range of pH values (1, 3, 5 and 7). These pH values were chosen to reflect the pH range that might occur in defects in the paint system such as in pits in the underlying metal [39,40]. The release of chromate into solution was monitored for up to 73 days by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Prior to and after immersion, the primers were characterised by electron microprobe analysis, X-ray microdiffraction, Raman spectroscopy, and positron annihilation lifetime spectroscopy (PALS). In a companion paper (Part II [41]), the leaching data obtained in this work is converted into leaching rates and a quantitative model for the leaching of chromate from these primer systems is described.

2. Experimental

2.1. Alloy

The metal substrate was aluminium alloy 2024-T3, containing 4.31 wt.% Cu, 1.5 wt.% Mg, 0.6 wt.% Mn, 0.08 wt.% Si and 0.17 wt.% Fe, as determined by ICP-AES.

2.2. Sample preparation

According to the conditions described in Table 1, 12.7 × 7.6 cm panels of AA2024-T3 were wiped with acetone and processed through alkaline cleaning, deoxidising and conversion coating steps. A silicated alkaline cleaner (Gibson Process 204B), chromate-based deoxidiser (Henkel, Parker + Amchem #7) and chromate conversion coating (Henkel, Alodine 1200) were used. Processing was carried out in a 60 L process line (CSIRO, Clayton, Australia) and deionised water was used for all solution preparation and rinsing. The panels were then primed with either PRC Desoto PR143 chromate-inhibited primer (BAE Systems, Salisbury, Australia) or an Anzol chromate-inhibited primer (DSTO Aeronautical and Maritime Research Laboratories, Maribynong, Australia). Both of these primers are qualified under Mil-P-23377 specification. Panels primed with the Anzol primer were painted on one side only, the other side coated with Stop-Off Lacquer, and results adjusted accordingly. Coating thicknesses were determined using an eddy current technique (Fischer Instrumentation Ltd Isoscope MP3 eddy current meter). Calibration was done using 11.3 and 48.4 μm calibration foils

Table 1
Process conditions used to prepare coatings on AA2024-T3 panels

Process	Time (s)	Temperature (°C)
Acetone wipe	–	–
Alkaline clean	300	60
Rinse 1	120	15
Deoxidiser	300	21
Static rinse 1	30	21
Rinse 2	120	15
Conversion coating	120	21
Static rinse 2	30	21
Rinse 3	120	15
Dry	<24 h	21