The Effect of Corrosion Inhibitors on the Corrosion Fatigue of Aircraft Aluminum Alloys

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ABSTRACT

Corrosion fatigue is an area of concern for the United States Air Force (USAF) and other Department of Defense organizations. Often the USAF corrosion prevention systems include chromate containing coatings, typically in the form of chromate conversion coatings and primers. Chromate has been used successfully for many years on USAF aircraft to prevent corrosion damage. However the environmental and personnel risks associated with chromate coatings have caused the USAF to pursue non-chromate containing corrosion prevention coatings[1]. To fully quantify chromate replacement coatings an understanding of the effects that chromate has on corrosion fatigue must be fully documented and understood. Some researchers have shown that high levels of inhibitors (chromate; molybdate) added to full immersion corrosion fatigue tests on 7xxx series aluminum alloys slow the fatigue crack growth rate substantially [2-5]. The limitation of this research was that the amount of inhibitor present in the environment was not related to leach rates of chromate from polymeric coatings.

The majority of USAF aircraft are protected from corrosion by polymer coatings loaded with corrosion inhibitors; for these inhibitors to slow fatigue crack propagation the corrosion inhibitors must become mobile from hydration of the polymer coating matrix. Based on this mechanism of corrosion inhibitor release, the examination of atmospheric corrosion fatigue becomes important to help understand how inhibitors work in real world situations with hydrated salt layers rather than fully immersed solutions.

Work has been completed by SAFE Inc., at the USAF Academy's Center for Aircraft Structural Life Extension (CAStLE) examining the ability of corrosion inhibitors leached from coatings to protect against corrosion fatigue damage. Based on a literature review of inhibitor leach rates and leaching tests, three test protocols were designed using a single edge notch (SEN) fatigue sample to mimic the geometries present in aircraft. These test methodologies include a bulk solution test (500 mL), which would represent areas in an aircraft where large amounts of fluid accumulate, an occluded geometry test cell (0.1 mL) to mimic areas like lap-joints and other small spaces that can collect electrolyte, and a

thin film test method using a relative humidity controlled salt layer that would simulate the boldly exposed surface. Once this baseline database using the SEN samples has been produced, the three test geometries will be transitioned to the examination of the effect of chromate and other inhibitors on the pit-to-crack transition.

Key words: chromate, corrosion fatigue, AA7075-T651, environmentally induced cracking, fatigue inhibition, molybdate

INTRODUCTION

As the United States Air Force (USAF) and Department of Defense (DoD) extend the life of current assets corrosion damage becomes a larger concern for aging fleets. At the same time the DoD has moved to phase out the use of chromates as a corrosion inhibitor due to the environmental and personnel risks[1]. Chromates are used in a variety of corrosion prevention coatings including conversion coatings and primers. Corrosion damage is of concern to the aircraft sustainment community for many different structural integrity reasons; including the fact that corrosion damage may act as a stress raiser and initiate fatigue cracks. While it has been documented that high levels of chromate added to a bulk solution can inhibit fatigue crack propagation, it has not been shown that chromate leaching from a coating can do the same[2-5]. However, if chromate does provide protection that slows corrosion fatigue crack propagation the removal of chromate from coating systems would mean that undocumented protection is lost. At the same time, chromate is considered the benchmark for all other corrosion inhibitors to meet so having a comparison point for chromate free inhibitors would also be beneficial.

Most of the prior corrosion fatigue work with aluminum alloys was completed using inhibitors added to a bulk NaCl solution or deliquesced onto the surface of a sample rather than the migration of inhibitors from polymer matrix coatings[2-5]. When polymeric coatings were applied the environment selected for testing was not representative of service raising questions about the applicability of the results[6]. The inhibitors used for most of these fatigue studies were high solubility inhibitors, rather than low solubility inhibitor which are typically used in coatings [2-5]. These differences may be of importance as the leaching of inhibitors is purposely controlled in organic coatings in order to make the life of coating acceptable[7-10]. That said, this inhibitor leaching would be the source of any inhibitor that could affect fatigue crack propagation. All of these effects on inhibitor leaching from polymer coatings, makes understanding the leaching rate of known coatings and inhibitors critical to designing appropriate fatigue test criteria. An understanding of the chromate leach rate from coatings and how chloride concentration, pH and other factors could change the amount of chromate present in a solution was needed. To answer these questions a literature review of chromate leaching rates and inhibitor pigment solubility effects was completed. Leaching studies using prototype polymer films were also completed for comparison to the published leaching rates. Using the researched leaching rates, this work proposes to determine the effect of the corrosion inhibitors chromate and molybdate in amounts that could be leached from at a coating on fatigue crack growth rates.

Leaching Effects

For current commercial coatings the loading amounts of inhibitors can vary, but are designed such that the coating is not depleted of inhibitor during a maintenance cycle, typically 6 to 8 years [7-10]. Organic coatings with inhibitors are generally understood to readily absorb water or other liquid environments through inherent defects in the coating resulting in interconnected pores which allows inhibitor pigments within the coating to dissolve and dissociate in electrolyte within the coating itself[7-10]. Typically pigments with low water solubility are selected for use in coatings so that (a) osmotic pressure-induced blisters are avoided, and (b) the inhibitor remains in the coating over long times rather than rapidly dissolving out when first in contact with corrosive environments [7,8]. Because of the low solubility of the inhibitors

used in coatings, only low concentrations of inhibitors would be expected to leach into the surrounding solution, limiting the overall amount of inhibitor available in the crack tip. For the previously completed bulk solution corrosion fatigue testing (sample fully immersed), Na_2CrO_4 (solubility in water: 87.6 g/100mL) and Na_2MoO_4 (65.0g/100mL) were used as inhibitors; these salts have a much higher water solubility than coating pigments ($SrCrO_4$: 0.096g/100mL, $CaMoO_4$: 0.0011g/100mL)[7,8,11]. Table 1 gives the properties desired for inhibitor pigments for loading into a polymer coating [7,8].

For the bulk solution fatigue testing previously completed, Na_2CrO_4 and Na_2MoO_4 were typically used, which are salts with much higher water solubility than typical in an inhibitor pigment loaded into a coating[2-4,7,8]. Table 2 shows the solubility of the typical coating pigments, $SrCrO_4$ and $CaMoO_4$, in water compared to those of Na_2CrO_4 and Na_2MoO_4. It should be noted that all other physical properties of Na_2CrO_4 and Na_2MoO_4 are within the acceptable limits for coating use other than solubility [7]. The physical properties of strontium chromate and calcium molybdate fall within the acceptable ranges for all pigment parameters [7]. The high water solubility can cause blistering of the polymer and cause the inhibitor to leach from the polymer too quickly which also make them undesirable for use in coatings[7,8].

Table 1: Property requirements of inhibitor pigments [7].

Inhibitor Pigment Parameter	Desired Value
Solubility in Water	< 2g/100mL
pH of Saturated Solution	7-9.5
Specific Gravity	1.5-5
Particle Size Distribution	2-6 µm
Solubility in Organic Medium	Practically Insoluble
Vapor Pressure at 20 C	<1/10,000 mmHg
Melting Point	>100 C

Table 2: Solubility in water for typical chromate and molybdate pigments compared to Na_2CrO_4 and Na_2MoO_4 [11].It should be noted sodium chromate is within acceptable ranges for all of the other parameters in Table I.

Inhibitor Pigment	Solubility in Water
$SrCrO_4$	0.096 g/100mL
Na_2CrO_4	87.6 g/100mL
$CaMoO_4$	0.0011 g/100mL
Na_2MoO_4	65.0 g/100mL

In the published data on the leaching of the four commercial epoxy primers found in the literature studied varied by about 16 times between the high and low leaching coatings[7,9,12-14]. The loading amount of chromate for all of the coatings can vary, and the coating properties can also greatly affect the leaching rates[7,8]. More research is needed into how the polymer matrix and leaching electrolyte change the leaching rates.

From the published data, there is no significant difference in leaching rates with the variation of low chloride content in the leaching solution, (0.1 M or less NaCl), however higher chloride content (0.85 M) makes a large difference, nearly doubling the amount of CrO_4^{2-} leached from the coating[7,9,13]. This result suggests there could be a threshold of chloride content over which the chloride is detrimental to the polymer matrix allowing for more inhibitor release. Because the baseline leaching rates for the commercial primers are different it is difficult say what the overall effect of chloride has, but some

publications state that chloride content affects leaching because chloride can be detrimental to the polymer matrix[7,8].

In another leaching study, adjustments to pH did not cause large changes in the amount of chromate leached[13]. There is some suggestion that more acidic environments cause more leaching, but the change in the amount of chromate leached is about the same as the scatter with NaCl concentration changes, which is less than the leaching amount changes between epoxy primer formulations leaving the effect unclear[13].

EXPERIMENTAL PROCEDURE

To determine the effect chromate has on corrosion fatigue damage in DoD relevant materials a single edge notch (SEN) specimen was used for all fatigue testing, shown in Figure 1. The samples were made from a peak-aged, legacy age-hardenable Al-Zn-Mg-Cu aluminum alloy and temper (7075-T651). The sample was loaded into a computer-controlled servohydraulic test frame and tested using a direct current potential drop (dcPD) system. The fatigue test was a constant ΔK=6 MPa√m test with a stress ratio (R) of 0.65. The loading frequency was varied from 0.02 to 20 Hz in a 0.06M NaCl environment.
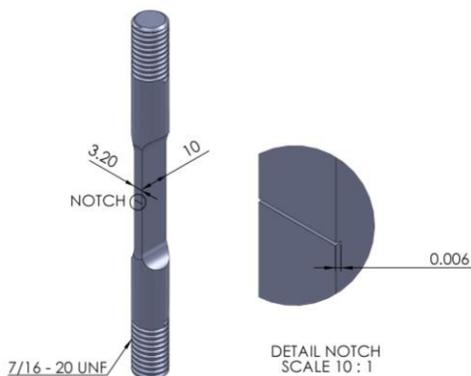
Figure 1: Single edge notch (SEN) specimens were made of 7xxx series aluminum alloy. All dimensions in millimeters.

To allow for the examine leaching effects of inhibitors, four research coatings containing different loading amounts of $SrCrO_4$ (either 12 or 17 weight percent) and epoxy bases were developed by Luna Innovations [(1)]. These films were designed such that their leaching rates should allow for comparison to published leaching studies on Department of Defense approved coating systems without the variability of commercial coatings. Leaching studies were completed by exposing the free-standing films in 100 mL of DI water for 2 and 4 days. The surface area in contact with water for each film was 29 cm^2. The leached liquid samples were then examined using UV-Vis Spectroscopy using 0.001299 M and 0.00033 M CrO_4^{2-} standards serially diluted from a 1000 ppm CrO_4^{2-} (0.0065 M) purchased standard solution (K_2CrO_4 was used for the standards) to determine the amount of CrO_4^{2-} present.
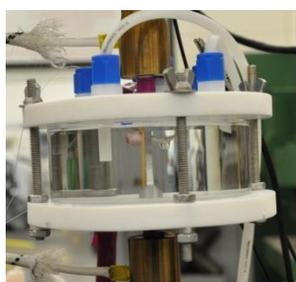
The results of the leaching from the $SrCrO_4$ films appear in Table 3 in terms of mg CrO_4^{2-}/cm^2 of coating. Table 3 also gives the leaching data converted into mol/L of CrO_4^{2-} to allow comparison with published results. Based on the leaching results, Film 1 was selected for fatigue crack growth testing given the high leaching amount and relatively high remaining CrO_4^{2-} remaining in the film, both desired for fatigue testing. Based on the original inhibitor loading amounts Film 3 had already leached the majority of the inhibitor making it undesirable for long immersion fatigue tests.

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[1] Luna Innovations, 706 Forest St, Charlottesville, VA 22903

Figure 2 shows the SEN sample and three different test configurations. Expected chromate concentrations were calculated for each configuration using the leaching rates from Table 3. The Bulk Testing label refers to a standard test cell filled with 500 mL of solution with a SEN sample primed on all four sides (Coating Surface Area: 7.92 cm^2). The Restricted Volume refers to a very small cell containing approximately 0.1 mL of solution covering a 2 cm high portion of the flat on the SEN sample (Coating Surface Area: 5.28 cm^2) which seeks to mimic areas such as lap joints and other occluded regions of aircraft. The Coating Surface Area to Volume ratio for the reduced volume cell was determined using aircraft components at USAFA. Thin Film refers to salt deliquesced to form a 100 μm thickness film (8x10^{-5} L) onto the four flat surfaces of the SEN sample (Coating Surface Area: 7.92 cm^2). The Thin Film environment is used to mimic how atmospheric corrosion is understood to occur on aircraft structure rather than a large pool of liquid around the sample. Table 4 shows the expected leaching concentrations of CrO_4^{2-} based on the film leaching results (Table 3) for the different testing geometries used in the program.

Table 3: Leaching results for SrCrO$_4$ primer films with 29 cm^2 surface area leached into 100 mL DI water. Original leaching data obtained by UV-Vis Spectroscopy.

Film Number	Concentration (mg/cm^2) 2 Days	Concentration (mM) 2 Days	Concentration (mg/cm^2) 4 Days	Concentration (mM) 4 Days
1	0.310	0.4	0.414	0.6
2	0.241	0.3	0.310	0.4
3	0.483	0.7	0.552	0.8
4	0.310	0.4	0.379	0.5

| Bulk Solution Test Cell (500 mL) | Reduced Volume Test Cell (0.1 mL) | Atmospheric (Thin Film) Exposure[3] |

Figure 2: Sample Volumes used for Concentration Calculations

The leach rates from the model films were compared to that expected from published CrO_4^{-2} leaching rates [7,9,12,13]. To make the comparison, the published leaching data were converted to molarity using the geometries and volumes of the Luna film leaching experiments and the testing geometries reviewed above to confirm the leach amounts were reasonable.

Table 4: Expected leaching results for $SrCrO_4$ primer films converted to the test three geometries. All concentrations are in terms of mol/L (M) CrO_4^{2-}. Original leaching data obtained by UV-Vis spectroscopy.

*above the $SrCrO_4$ solubility limit of 0.0047 M CrO_4^{2-} [11]

Film Number	Expected Concentration (M) Bulk Solution (500mL) 4 Days	Expected Concentration (M) Restricted Volume (0.1 mL) 4 Days	Expected Concentration (M) Thin Film (0.08 mL) 4 Days
1	3.21×10^{-5}	0.021*	0.201*
2	2.41×10^{-5}	0.016*	0.151*
3	4.28×10^{-5}	0.029*	0.268*
4	2.95×10^{-5}	0.020*	0.184*

To examine similar inhibition effects with a possible chromate replacement inhibitor, calcium molybdate ($CaMoO_4$), the University of Southern Mississippi (USM) developed and completed leaching studies on three $CaMoO_4$ containing primers [2]. Each primer had a different loading amount of MoO_4^{2-} (20.8%, 28.7%, 36.9% weight percent). USM coated and scribed AA 7075 panels (Surface Area: 6.45 cm^2) prior to completing leaching experiments in 100 mL DI water. The leaching results appear in Table 5 along with the concentrations expected for the three test conditions. Table 5 shows that the higher the loading amount of MoO_4^{2-}, the lower the leaching amount. This result is highly unexpected, and the mechanism behind this result is currently not understood. USM originally hypothesized the solubility limit between the $CaMoO_4$ and solution might have been exceeded, but that is not the case as the leaching values are always below the solubility limit of 0.05mM and no solids were noted in solution [11]. Also, as the inductively coupled plasma mass spectrometry (ICP-MS) is capable of detecting 1 part per billion, mismeasurement of the calcium molybdate in solution is also unlikely. The explanation for these results remains to be determined.

Table 5 : Leaching results for the $CaMoO_4$ coatings developed by USM [2]. Original leaching data produced by inductively coupled plasma mass spectrometry (ICP-MS).

*above solubility $CaMoO_4$ limit of 0.055mM [11]

Loading Amount	Leaching Concentration (100mL) 4 Days	Expected Concentration (M) Bulk Solution (500mL) 4 Days	Expected Concentration (M) Restricted Volume (0.1 mL) 4 Days	Expected Concentration (M) Thin Film (0.08 mL) 4 Days
20.8% MolyWhite	1.8×10^{-6}	4.3×10^{-7}	2.9×10^{-4}*	0.003*
28.7% MolyWhite	4.1×10^{-7}	1.0×10^{-7}	6.7×10^{-5}*	6.0×10^{-4}*
36.9% MolyWhite	4.7×10^{-7}	1.1×10^{-7}	7.7×10^{-5}	7.0×10^{-4}*

Based on the leaching rates researched, a test plan was developed to move forward with the test matrix in Table 6 for all corrosion fatigue inhibition testing. This testing would determine the effect of

the corrosion inhibitors chromate and molybdate in amounts that could be leached from at a coating on fatigue crack growth rates. Another theory to be tested was the low solubility inhibitors could inhibit fatigue crack propagation by forming solids within the crack and causing crack closure much like traditional corrosion product.

**Table 6: Test matrix to determine the effect of chromate and molybdate in leached concentrations.**

| Inhibitor	Inhibitor Form	Environment	Amount (concentration in solution or wt % in coating)
Na_2CrO_4 /Na_2MoO_4	Salt	Bulk Solution NaCl	<0.5/0.002mM
$SrCrO_4$ /$CaMoO_4$	Salt	Bulk Solution NaCl	<0.5/0.002mM
$SrCrO_4$ /$CaMoO_4$	Salt	Bulk Solution NaCl	>4.7/0.05mM
$SrCrO_4$ /$CaMoO_4$	Primer	Reduced Volume NaCl (< 0.1 mL)	17%/20.8%
$SrCrO_4$ /$CaMoO_4$	Primer	Atmospheric NaCl	17%/20.8%
$SrCrO_4$ /$CaMoO_4$	Primer	Bulk Solution NaCl	17%/20.8%

RESULTS AND DISCUSSION

Testing was completed using inhibitor pigments that would be found in commercial molybdate coatings, calcium molybdate ($CaMoO_4$). All testing was completed at a constant ΔK=6 MPa√m, R=0.65 in a bulk (500 mL) 0.06 M NaCl solution. The results for this test are shown in Figure 3 [3,4]. The starting concentration of $CaMoO_4$ was 0.002 mM (yellow star) which is below the solubility limit, the concentration was then increased to 0.01 mM $CaMoO_4$ (orange star), for these concentrations the solubility limit would be expected to have been exceeded in the crack, as the inhibition concentration within the crack is expected to be higher than in the bulk solution. The crack growth rates for the two concentrations of $CaMoO_4$ are in line with the pure 0.06 M NaCl showing no inhibition with the low concentrations of calcium molybdate added to a bulk solution and no inhibition due to crack closure. All other data in Figure 3 are from other published work [3,4]. The lack of inhibition is likely due to the low concentration of the inhibitor not allowing for enough solids to forms to allow for crack closure to occur or for ionic inhibition.

Testing has also been completed to validate the methodology for holding the relative humidity constant for the atmospheric salt tests. The test procedure requires the deposition of salt on the surface of the sample; the salt layer is allowed to dry and then is rehydrated and held at a constant relative humidity. Precise control of the chamber relative humidity is needed to ensure the concentration of salt on the surface of the sample remains constant during the test. Baseline testing has been completed using glycerin baths from ASTM [(3)] D5032, in these tests the relative humidity is held constant (98%) without the application of the salt layer [14]. Figure 4 shows the results of these baseline tests, which are in line with the full immersion crack growth rates [3-4]. The high relative humidity was selected for initial testing as the concentration of NaCl is expected to be approximately 0.06 M, the relationship with $CaMoO_4$ has not yet been determined[15].

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[3] ASTM International (ASTM), 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959
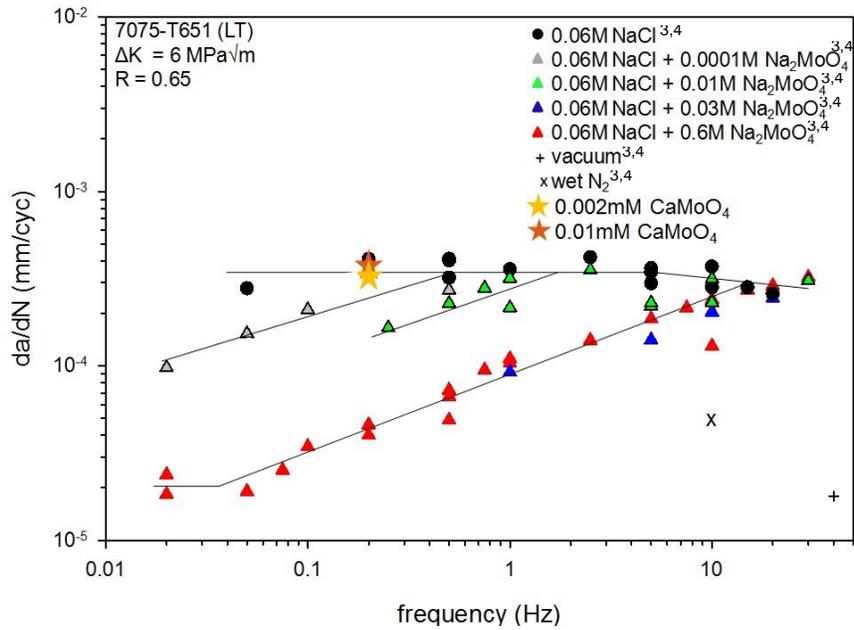
Figure 3: Measured crack growth rate curves compared from coating relevant calcium molybdate to published data for bare specimens in a fully immersed bulk solution [3,4].
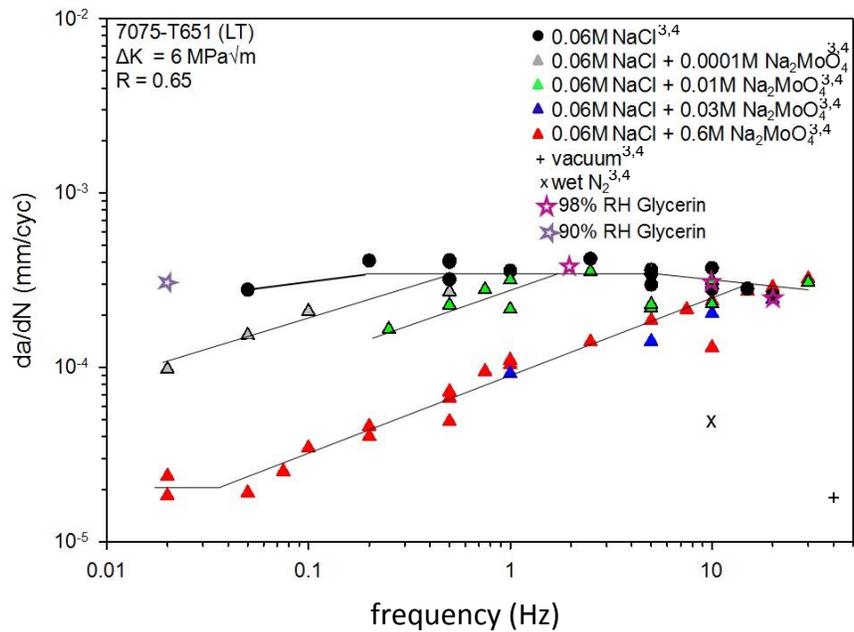
Figure 4: Measured crack growth rates for samples held at 98% relative humidity as compared to full immersion testing and the corrosion fatigue inhibitor sodium molybdate [3,4].

CONCLUSIONS

Low solubility corrosion inhibition pigments ($CaMoO_4$) have not shown the ability to reduced fatigue crack growth rates in bulk 0.06 M NaCl solutions whether through passive film formation or crack closure. The effect of chromate on small scale fatigue damage can be characterized for the different primer types. The analysis of surface area-to-volume for leaching suggests that a thin salt film may be

more applicable than full immersion testing for aircraft applications, particularly lap joints. New coating designs that might apply high levels of inhibitors at areas of damage also should be explored.

ACKNOWLEDGEMENTS

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