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# CHARACTERIZATION STUDIES OF AQUEOUS IMMERSION SOLUTIONS OF NOVEL ENVIRONMENTALLY FRIENDLY ORGANOMETALLIC CORROSION INHIBITORS USED TO CURE ALUMINUM 2024, 6061, AND 7075 ALLOYS SUBSTRATES IN CORROSIVE MEDIA

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## ABSTRACT

In this investigation, aqueous immersion solutions of novel environmentally friendly corrosion inhibitors that are used to inhibit corrosion of Aluminum 2024, 6061 and 7075 substrate surfaces in corrosive media are characterized since immersion solutions are indicators of the extent of corrosion, which can even be observed visually in a qualitative manner. In addition to visual observations revealing the extent of corrosion qualitatively, the pH and oxidation-reduction potential of the immersion solutions were measured with respective probes prior to and after the immersions and relevant conclusion made extensively to propose the chemical mechanisms with regards to the inhibitors used for corrosion inhibition of aluminum alloys.

Inhibitors used were previously synthesized by the author as replacements for carcinogenic hexavalent chromium inhibitors. Syntheses and characterization studies of the novel environmentally friendly corrosion inhibitors, the results of weight-loss tests performed to obtain the inhibition efficiencies of these inhibitors and characterization studies of the substrate surfaces immersed in aqueous inhibitor solutions by means of different surface techniques such as FT-IR, X-Ray, SEM, XPS and digital imaging were reported in author's various work elsewhere in the literature.

**KEYWORDS:** Carcinogenic, Characterization, Conversion Coating, Immersion, Probe, Substrate

## INTRODUCTION

The mobility of aqueous Cr6+ within biological systems and its reactivity with biochemical oxidation mediators make it highly toxic, carcinogenic and generally regarded as a very hazardous soil and groundwater pollutant [1-6]. Dermatitis and skin cancer have been reported among workers merely handling components protected by a chromate film [7]. Many reviews in the literature point out to toxicity of chromates associating Cr6+ with lung cancer. Although there is no general agreement on the details for the Cr6+ induced damage to DNA resulting in cancers, it is clear that Cr6+ is highly water soluble and it passes through cell membranes, and highly reactive intermediates such as Cr5+ stabilized by alpha hydroxyl carboxylates and Cr4+ are genotoxic and react either directly or through free radical intermediates to damage DNA [8-13]. The International Agency for Research on Cancer (IARC) has determined that Cr(VI) is carcinogenic to humans. The World Health Organization (WHO) has determined that Cr(VI) is a human carcinogen [14]. The Department of Health and Human Services (DHHS) has determined that certain Cr(VI) compounds (calcium chromate, chromium trioxide, lead chromate, strontium chromate, and zinc chromate) are known human carcinogens [15]. Finally, the EPA has classified Cr(VI) as a Group A, known human carcinogen by the inhalation route of exposure [16-21].

However, despite their negative aspects, to date, no replacements exist in the market for carcinogenic chromates with the same efficiency for a range of aluminum alloys and steel, neither as pigment nor as a metal pretreatment [22-23].

Given the toxicity and carcinogenicity of chromates, the purpose is not only to synthesize and characterize efficient corrosion inhibitors for certain alloys of certain metals to be applied in different environments, but also to find environmentally friendly corrosion inhibitors for successful chromate replacements. In this regard, the standard for an environmentally friendly inhibitor is considered as having acceptable or no toxicity compared to chromate inhibitors.

Studying the reasons underlying the success of chromate inhibitors seemed to be the first reasonable approach one might take before formulating chromate replacements, e.g., synergistic combinations of oxyanion analogues of chromates with those of hydroxyacids and metal cations that are known for their corrosion inhibiting efficiencies having the general formula of (M)x(hydroxyacid)y(M'aOb)z, which constituted the first phase of this research by the author [24].

Syntheses and chacaterization work was followed up with the weight-loss tests to obtain the inhibition efficiencies of respective inhibitors, while in this study, aqueous immersion solutions of novel environmentally friendly corrosion inhibitors that are used to inhibit corrosion of aluminum alloy substrate surfaces in corrosive media are characterized.

Three aluminum alloys were chosen for the corrosion inhibition tests in aqueous environments that are Aluminum 2024, 6061, and 7075 alloys due to their common use in industry and, specifically, in aircrafts.

## CHARACTERIZATION OF IMMERSION SOLUTIONS

Immersion solutions are indicators of the extent of corrosion, which can even be observed visually in a qualitative manner.

In addition to visual observations revealing the extent of corrosion qualitatively, the pH and oxidation-reduction potential of the immersion solutions were measured with respective probes prior to and after the immersions and relevant conclusion made extensively to propose the chemical mechanisms with regards to the inhibitors used for corrosion inhibition of aluminum alloys.

Two readings were taken per sample, one before immersion and another after completion of immersion.

Inhibitors used were previously synthesized by the author as replacements for carcinogenic hexavalent chromium inhibitors.

Syntheses and characterization studies of the novel environmentally friendly corrosion inhibitors, the results of weight-loss tests performed to obtain the inhibition efficiencies of these inhibitors and characterization studies of the substrate surfaces immersed in aqueous inhibitor solutions by means of different surface techniques such as FT-IR, X-Ray, SEM, XPS and digital imaging were reported in author's various work elsewhere in the literature.

### ORP Measurements

ORP is proportional to the concentration of oxidizers or reducers in a solution, and their activity or strength. It provides an indication of the solution's ability to oxidize or reduce another material. The addition of an oxidizer will raise the ORP value, while the addition of a reducer will lower the ORP value. The ORP values of immersion solutions were measured to determine whether the redox capable inhibitor compounds had gone thorugh redox reactions or not. Dissolved oxygen may be reduced by the metal substrate and leading to lowering of the ORP value but comparison to the control solution should negate this effect.

Immersion solutions of gluconate salts and their molybdenum esters revealed decreasing ORP values; while immersion solutions of vanadium esters and boron esters in general had increasing ORP values with the initial ORP values ranging between 300 mV to 750 mV and the final ORP values ranging from 350 mV to 650 mV.
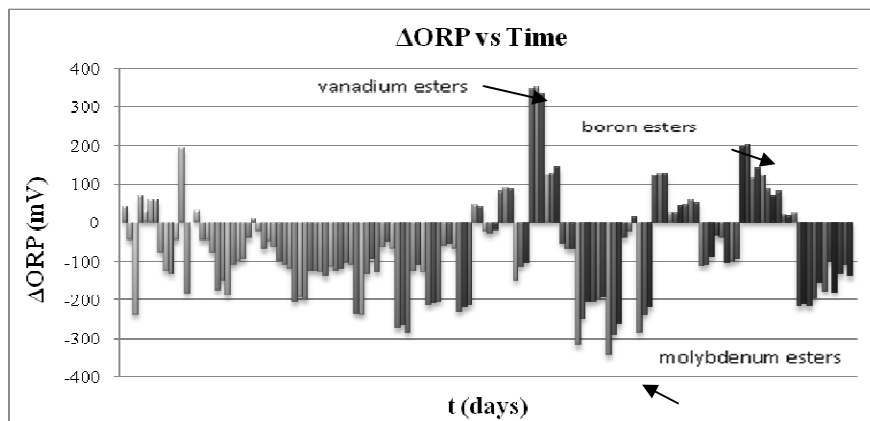
**Figure 1**: ΔORP vs. Time Graph of Immersion Solutions of Various Inhibitors during Immersions

ΔORP graphs indicated that ORP values lowered by an average of roughly 100 mV with molybdenum esters, potassium benzilate, and aluminum lactate having the highest decreases. Potassium benzilate vanadate and calcium gluconate borate esters had the highest increase in ORP values. Vanadate esters had the lowest initial ORP values as well.
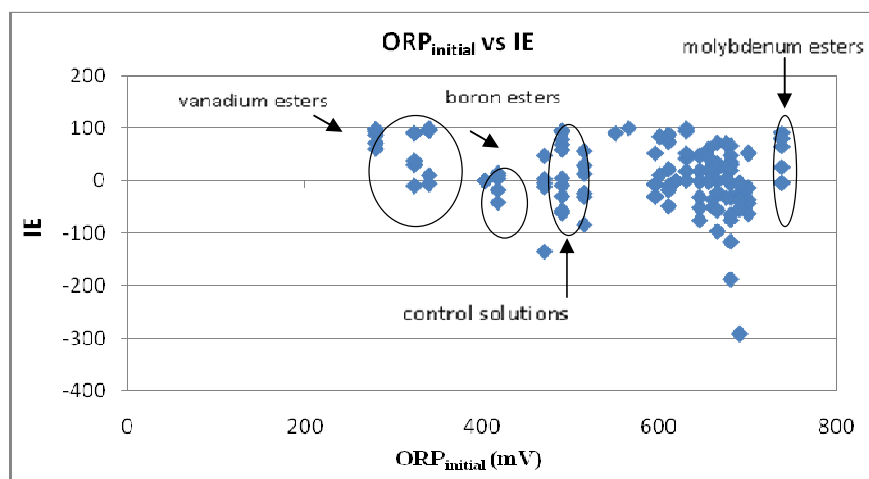


**Figure 2: Initial ORP Values vs. Inhibition Efficiency Graph of Immersion Solutions of Various Inhibitors**

ORP is proportional to the concentration of oxidizers or reducers in a solution. It increases with the addition of an oxidizer and the decreases with the the addition of a reducer. Initial and final ORP values of immersion solutions of vanadium esters in particular were opposite to what was predicted. Only the ORP values of immersion solutions of vanadium esters were lower than the controls. Boron esters had slightly higher ORP values than control solutions, while all the other immersion solutions had significantly higher initial ORP values than control solutions. Molybdenum esters had the highest ORP values. Very high initial ORP values implied the preservation of +6 oxidation state of molybdenum in the hydroxy-acid formulation (+6 oxidation state as in the reactant $MoO_3$ and as in molybdates) corresponding to a strong oxidizing ability, which led to high initial ORP values. Reduction potential of hexavalent molybdenum to molybdenum oxides such as $MoO_2$ in near neutral basic solutions is reported as -0.780 V [25-31], thus resulting in the preservation of +6 oxidation state of molybdenum against a mild reducing agent such as gluconate.

However, against a very strong reducing agent as aluminum metal, hexavalent molybdenum is likely to reduce to pentavalent state in molybdenum oxide explaining the black depositions on the substrate surfaces. The half-reaction potential of Al to $Al(OH)_3$ is reported to be -2.300 V in basic solutions and as -1.676 V in acidic conditions [25-31].

As for the boron esters, the fact that the initial ORP values were almost equal to the ORP values of control solutions indicated the inertness of boron esters in terms of redox potentials. In other words boron was already complexed in its +3 oxidation state and was inert towards any oxidation and reduction reaction. The highly negative reduction potentials of trivalent boron to elemental boron support this conclusion [25-31].

In the case of vanadium esters significantly lower initial ORP values implied the addition of a reducer rather than an oxidizer. The oxidation state of vanadium in $V_2O_5$, which was used as a precursor to gluconate vanadate esters, is +5. However reacting with gluconate salts, which are known to be mild reducing agents, vanadium seemed to be reduced to its lower oxidation states, which is likely considering the reduction potentials of vanadium. In neutral to basic conditions reduction potential of $VO_4^{3-}$ to $V_2O_3$ is reported to be 1.366 V [25-31].

In conclusion, vanadium atoms already were in lower oxidation states initially in the form of vanadium esters, which were then transformed into insoluble vanadium oxides on the substrate surfaces with increasing local pH values without involvement of any oxidation-reduction process, which explains the small changes in ORP values for vanadate esters. That small change that is positive and 100 mV in average between the $ORP_{final}$ and $ORP_{initial}$ values of vanadium esters was likely due to the migration of reducing agents that are lower oxidation state vanadiums, from the solution phase to the substrate surface in the form of deposition of vanadium oxides.

ΔORP/ORPinitial vs IE graph below indicates that in average ORP values were roughly decreased about a quarter for the tested compounds.



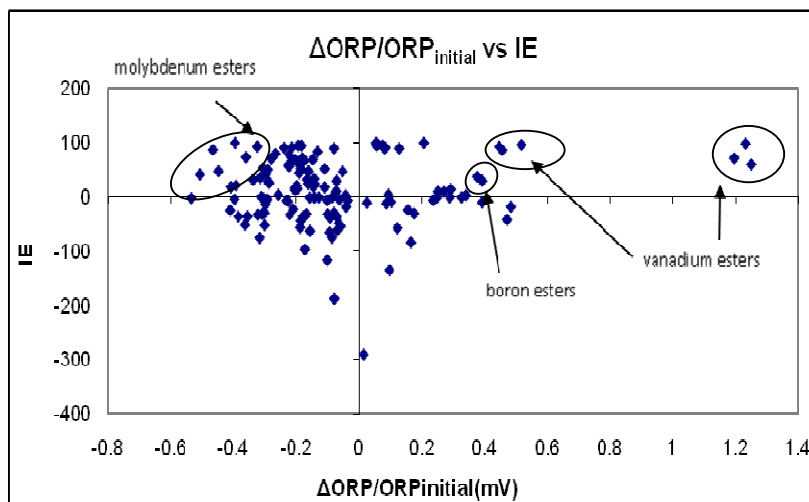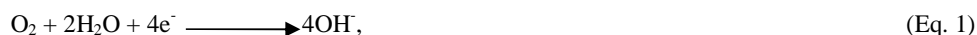**Figure 3: ΔORP/ORP$_{initial}$ Ratios vs. Inhibition Efficiency Graph of Immersion Solutions of Various Inhibitors**

**pH Measurements**

Due to the anodic reaction of corrosion process, that is,

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-, \hspace{3cm} \text{(Eq. 1)}$$

an increase in pH is expected in corroding systems. Accordingly the pH of the immersion solutions of good inhibitors increased only slightly, while large increases were observed for compounds with no positive effect to corrosion inhibition. Some inhibitors were organic acids initially, thus resulting in low initial pH values around 2.

ΔpH values of immersion solutions were within ~ -0.1 and 2.9, with ineffective inhibitors such as gluconate salts and their borate esters having ΔpH values around 2 along with control solutions and solutions of second immersions.

Highly efficient inhibitors such as chromium(III) acetate, zinc gluconate, and vanadate esters of calcium gluconate, zinc gluconate and potassium benzilate had decreased pH values after immersions. Thus, changes in pH were in agreement with inhibition efficiency and ORP measurements.
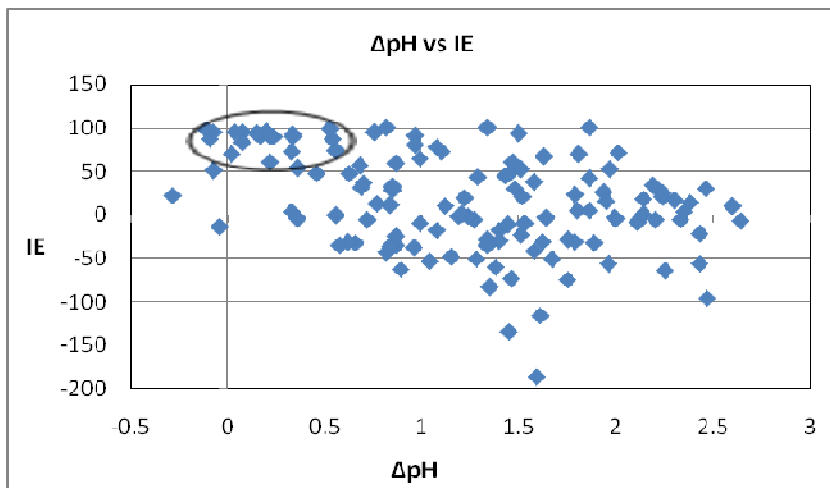


**Figure 4: ΔpH vs. Inhibition Efficiency Graph of Immersion Solutions of Various Inhibitors**

When ΔpH values were plotted versus inhibition efficiencies, it was observed that inhibitors with high inhibition efficiency values had negligible changes in pH opposed to inhibitors with low inhibition efficiencies.

## CONCLUSIONS

Immersion solution studies revealed that formation of trivalent vanadium oxide coatings might not have been due to a redox reaction but rather due to an ion-exchange mechanism between $Al^{3+}$ and $V^{3+}$ cations in the protective aluminum oxide layer leading to the repair and repassivation of the substrate surface resulting in a uniform clear protective coating, while coating of molybdic oxides were formed as a result of a redox reaction between the molybdenum esters of hydroxy-acid salts and the aluminum substrate leading to the formation of a non-uniform albeit protective, rough coating.

Based on characterization studies oxidation-reduction potential and pH measurements of immersion solutions before and after completion of immersions; it was concluded that hydroxy-acid salts, gluconates in particular, slightly damaged the naturally protective aluminum oxide film on the substrate surface by forming complexes with aluminum cations leading to their dissolution. This effect has been minimized when hydroxy-acid salts were complexed with metal oxyanions. Instead, these complexes reacted with aluminum surface to deposit lower oxidation state oxides and hydroxides of the metal oxyanions.

## ACKNOWLEDGMENTS

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