

AQUEOUS CORROSION INHIBITION STUDIES OF ALUMINUM 2024, 6061, AND 7075 ALLOYS BY OXYANION ESTERS OF α -HYDROXY ACIDS AND THEIR SALTS

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ABSTRACT

In this investigation, corrosion inhibition of certain aluminum alloys in aqueous solutions has been tested primarily via weight-loss tests for their direct corrosion inhibition efficiencies and also for their conversion coating formation abilities. Effects of variables such as inhibitor concentrations, immersion periods, and cationic constituents on the individual and synergistic inhibition efficiencies as well as on their conversion coating formation capacities have been studied. Inhibition efficiency data were recorded using statistics. Some of the studied inhibitors were noted for their very high inhibition efficiencies and a few for their unusual conversion coating formation capabilities. Using the data available in literature and the experimental data obtained in this study, aqueous corrosion inhibition mechanisms of aluminum alloys by oxyanion esters of α -hydroxy acids and their salts are suggested.

KEYWORDS: Conversion Coating, Immersion, Inhibition Efficiency, Substrate, Weight-Loss

INTRODUCTION

The mobility of aqueous Cr^{6+} 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 Cr^{6+} with lung cancer. Although there is no general agreement on the details for the Cr^{6+} induced damage to DNA resulting in cancers, it is clear that Cr^{6+} is highly water soluble and it passes through cell membranes, and highly reactive intermediates such as Cr^{5+} stabilized by alpha hydroxyl carboxylates and Cr^{4+} 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 $(M)_x(\text{hydroxyacid})_y(M'aOb)_z$, which constituted the first phase of this research by the author [24]. Syntheses and characterization work was followed up with the weight-loss tests to obtain the inhibition efficiencies of respective inhibitors.

In this study, corrosion inhibition of certain aluminum alloys in aqueous solutions has been tested primarily via weight-loss tests for their direct corrosion inhibition efficiencies and also for their conversion coating formation abilities. 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.

Effects of variables such as inhibitor concentrations, immersion periods, and cationic constituents on the individual and synergistic inhibition efficiencies as well as on their conversion coating formation capacities have been studied. Inhibition efficiency data were recorded using statistics. Some of the studied inhibitors were noted for their very high inhibition efficiencies and a few for their unusual conversion coating formation capabilities. Using the data available in literature and the experimental data obtained in this study, aqueous corrosion inhibition mechanisms of mild steel by oxanion esters of α -hydroxy acids and their salts are suggested.

WEIGHT-LOSS TEST METHOD

The weight-loss method was used extensively throughout this study to assess inhibition efficiencies of corrosion inhibitors. Using metal coupons to assess inhibition efficiencies is the oldest and simplest method in monitoring of corrosion [25]. Coupons are described as small pieces of metal, usually of rectangular shape, which are inserted in the process stream and removed after a period of time that is greater than 24 hours [26-27]. The most common and basic use of coupons is to determine average corrosion rate over the period of exposure [28]. This is accomplished by weighing the degraded coupon before and after immersions followed by its exposure to various acidic solutions to remove corrosion deposits on the substrate surface. The difference between the initial and final weights of the coupon, that is the weight loss, is compared to the control. The control coupon is the substrate of the same metal alloy exposed to the same environment with no inhibitor present. At least two and preferably more specimens should be exposed for each condition [29]. The reasons why the weight-loss method has been chosen to assess inhibition efficiencies were first, tested inhibitors are all water soluble and second it is easy to obtain accelerated corrosion conditions, and third small amounts of inhibitors are sufficient for testing.

Weight-loss tests were performed based on the following parameters; type of the substrate, type of inhibitor, inhibitor amount in the immersion solution in ppm (part per million), chloride ion concentration in immersion solution in M, and immersion period. The type of the substrate is of crucial importance since the alloying elements in the substrate have different corrosion resistivities and might also react differently with the tested inhibitors. For instance, Aluminum 2024 alloy has high amounts of copper and Aluminum 7075 alloy has high amounts of zinc, which is why both alloys have lower corrosion resistivities than Aluminum 6061 alloy. An inhibitor concentration of 200 ppm was determined to be optimal for a system of 100 ml solution. Also, a 7 day immersion period was found to be the best immersion period. Instead of the chloride concentration of 60 ppm commonly used in the weight-loss tests of mild steel coupons, a concentration of 0.5 M was used for the aluminum. The high 0.5 M chloride concentration is closer to seawater values as is required to achieve measurable weight losses. Seawater chloride concentration is given as 19000 mg/L or ppm [27] by USGS (United States Geological Survey) for Pacific Ocean of California, which is close to 0.325 M in molarity terms or 3.5% by weight. The reason why 0.5 M salt concentration or 5% salt percentage by weight has been chosen as the concentration instead of 0.35 M was to match the traditional 5% salt concentration of salt fog chambers so that the

inhibition efficiencies of the same inhibitors in aqueous solutions and in sol-gel coatings could be compared.

Preparation of Coupons/Weight-Loss Apparatus

For the preparation of coupons, mild steel and aluminum alloy metal sheets were cut in dimensions of 1x1 inch. A hole is drilled at the corner of the coupon so that the coupon could be hanged in solution via a durable polymeric material such as a fishing-line that does not corrode.

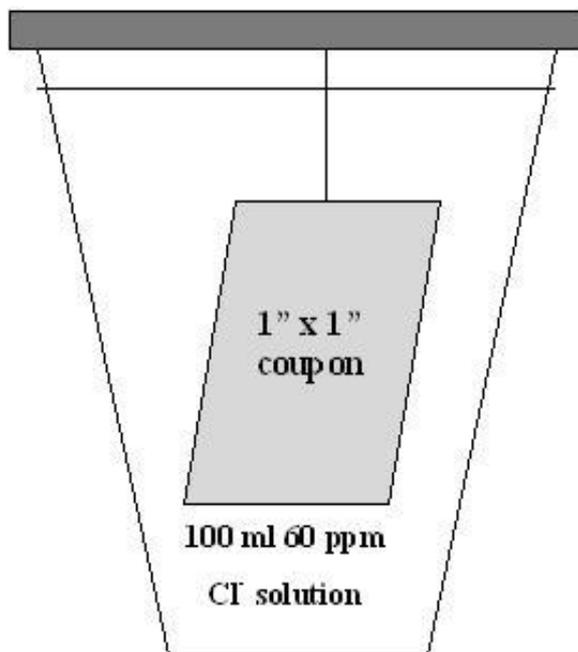


Figure 1: Weight-Loss Apparatus

The standard methods for “Preparing Specimens for Weight-Loss Tests” developed by the ASTM (American Society for Testing and Materials) [25-26] were followed with no alteration. Before immersion, aluminum coupons were degreased first by dipping in hexane followed by dipping in methanol. Afterwards, the coupons were placed in aerated Oakite-164 alkaline cleaner solution at 150 °F for 10 minutes. The Oakite bath was prepared in the same manner used for degreasing of mild steel coupons by dissolving 60 g of Oakite detergent in 1000 ml of water at 180 °F. Next the coupons were treated with a pickling solution composed of Henkel Surface Technologies brand acid-based Deoxalume 2310 (70% water, and 20% concentrated nitric acid, and 10% Deoxalume). The Deoxalume is composed of 10-30% sulfuric acid, 10-30% ferric sulfate, 1-10% ammonium bifluoride. Coupons were dipped into the pickling solution for 6.5 minutes. After the immersions were completed, coupons were dipped into concentrated nitric acid for 5 minutes followed by drying and weighing.

Immersion periods of 3, 7 and 14 day periods were chosen since periods less than 24 hours are not enough for the system to come into an equilibrium [30], while a period of more than 14 days was too long to test many samples, that are needed for comparison purposes. Given the condition of accelerated corrosion, a period of 7 days has been determined to be the optimum period of immersion. After completion of immersion tests, coupons were exposed to an acidic solution described by ASTM to remove corrosion products for accurate weight-loss results. In case of specimens of aluminum and aluminum alloys, direct use of concentrated HNO_3 is inscribed by ASTM to remove corrosion deposits for periods of 1 to 5 min at 20°C to 25°C. It is indicated by ASTM that longer times may be required in certain instances; however such instances did not occur in this study meaning all specimens were cleaned of corrosion deposits thoroughly after 10 minutes of exposure.

Inhibition Efficiency Calculations

Inhibition efficiencies were calculated based on the comparison of weight loss values of inhibitor treated coupons and those of controls with the following formula;

$$IE = 100[1-(W_2/W_1)]\% \quad (\text{Eq. 1})$$

where

- W_1 = corrosion rate in the absence of inhibitor
- W_2 = corrosion rate in the presence of inhibitor
- W_1 & $W_2 = (W_{\text{final}} - W_{\text{initial}}) / W_{\text{initial}}$

The concentration of the inhibitors and the immersion periods were varied to obtain any possible trends of inhibition efficiencies, however inhibitor concentration of 200 ppm in 100 ml distilled water and a period of 7 days were chosen as the standard conditions after many trials as explained earlier.

Inhibition efficiency values calculated by means of the above formula were inserted into a t-distribution function formula to obtain statistically significant results. T-distribution is used rather than Z-distribution due to the low number of samples according to following formula [31];

$$IE = \mu \pm t \frac{\sigma}{\sqrt{n}} \quad (\text{Eq. 2})$$

where t is equal to the critical t-distribution value for 90% confidence limit with usually two degrees of freedom based on n , which is the number of samples. Often, only one sample has been put into test at the beginning to determine the presence of any kind of inhibition. When corrosion inhibition was observed, three more samples of the same inhibitor have been put into test, thus resulting in $n = 3$ and degrees of freedom, that is $(n-1)$, equaling to 2. Critical t-distribution value for 90% confidence limit with two degrees of freedom is reported as 2.920 [32].

Formulas for the mean (μ) value and standard deviation (σ) are as follows;

$$\mu = \frac{1}{n} \sum_{i=1}^n x_i = \frac{1}{n} (x_1 + \dots + x_n) \quad (\text{Eq. 3})$$

$$\sigma = \sqrt{\frac{1}{n} \sum_{i=1}^n (x_i - \bar{x})^2} \quad (\text{Eq. 4})$$

The results found with inhibition efficiency formula were calculated to be statistically significant by hypothesis testing. For the inhibition efficiency values to be significant, the difference between the mean inhibition efficiency value and that of control must be bigger than the following [33];

$$\mu - \mu_{\text{standard}} > t (\sigma/\sqrt{n}) \quad (\text{Eq. 5})$$

Since there is no inhibition efficiency for control solutions, $\mu_{\text{standard}} = 0$, thus the equation is simplified to the following;

$$\mu > t (\sigma/\sqrt{n}) \quad (\text{Eq. 6})$$

Insertion of critical value for t-distribution, standard deviation, and number of sample values into the above equation lead to the conclusion that mean inhibition efficiency values even for inhibitors with slight inhibition properties were statistically significant.

Weight Loss Test Results

Gluconate Salts

Only zinc and chromium gluconates were effective for inhibiting corrosion of aluminum alloys as seen Fig. 2. Therefore, it can be concluded that the metal ions were the main corrosion preventing constituents. This conclusion is supported by the acceleration of corrosion by sodium gluconate.

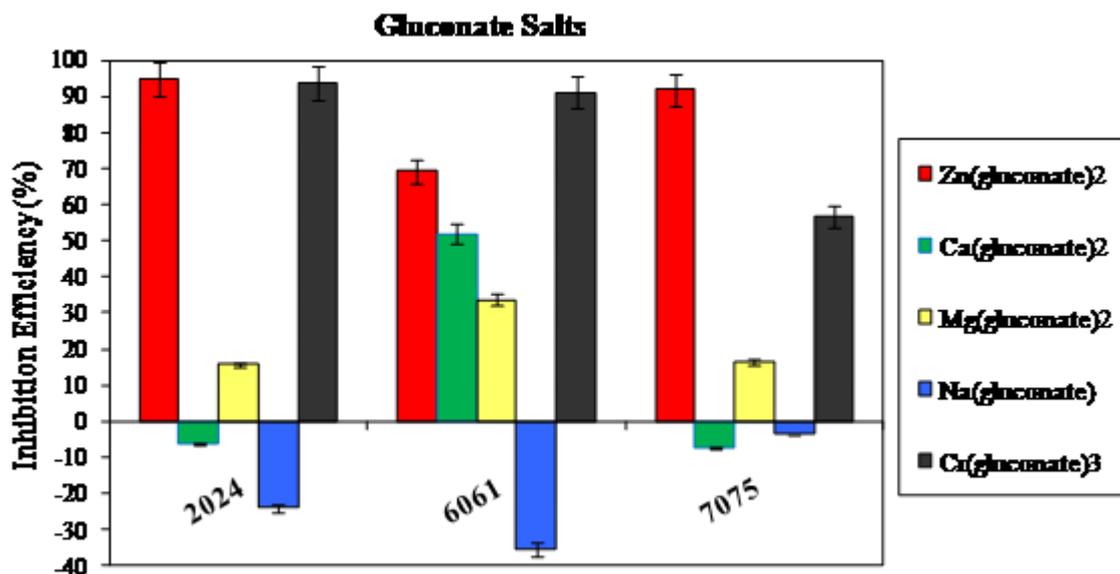


Figure 2: Inhibition Efficiency Graph of Gluconate Salts of 200 ppm

Group III Gluconates and D-Glucose

Results for the inhibitors in this category are quite different from those observed with mild steel corrosion. $\text{Al}(\text{gluconate})_2\text{OH}$, for example, did not have effect on corrosion inhibition except for 7075 alloy. However, $\text{B}(\text{gluconate})_2\text{OH}$, and $\text{B}(\text{glucose})$ and their precursors, boric acid and D-glucose, had better inhibition efficiencies than those of $\text{Al}(\text{gluconate})_2\text{OH}$ and gluconate salts of Mg, Ca, and Na.

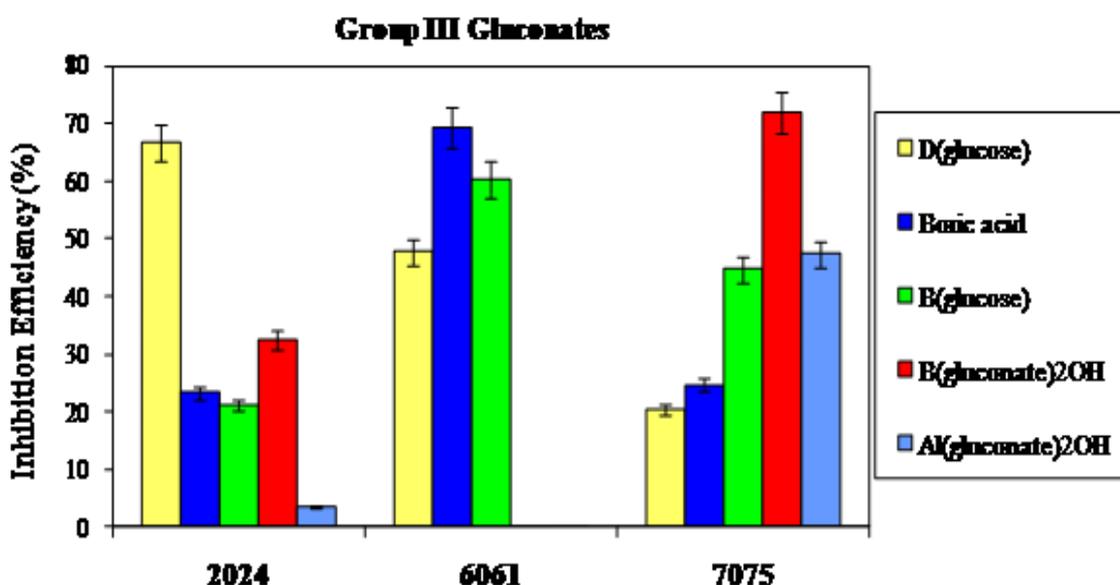


Figure 3: Inhibition Efficiency Graph of $\text{M}^+(\text{X}^{-1})_{n-1}\text{OH}$ Type Gluconates

Application of Other $\text{M}^+(\text{X}^{-1})_{n-1}\text{OH}$ and $\text{M}^+(\text{X}^{-1})_n$ Type Compounds

Compounds similar to gluconate salts were tested and the results are shown in Figure 4.

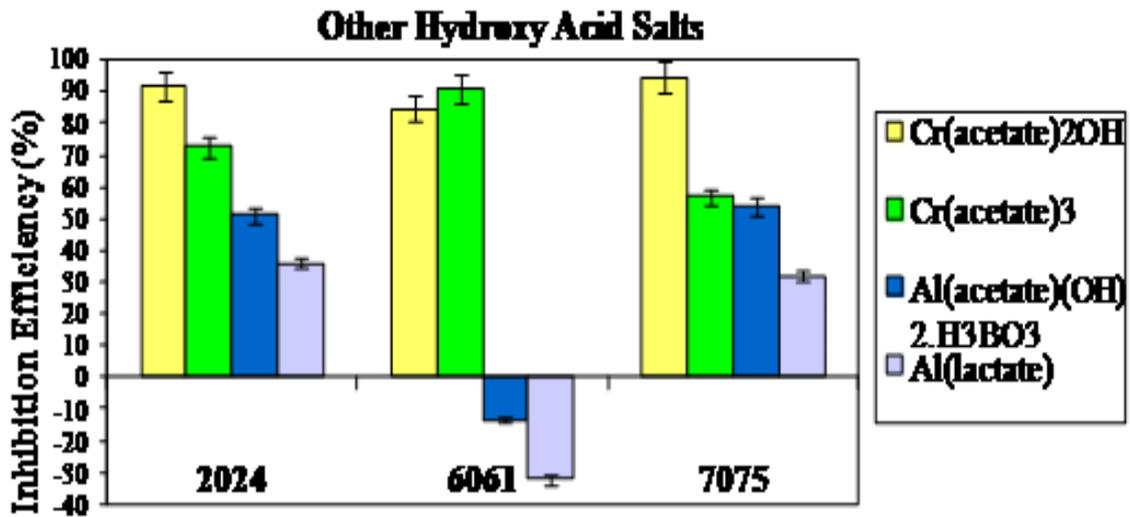


Figure 4: Inhibition Efficiency Graph of $M^{+n}(X^{-1})_{n-1}OH$ and $M^{+n}(X^{-1})_n$ Type Salts of Other Carboxylic Acids Other than Gluconates

Among the tested salts, $Cr(acetate)_3$ and $Cr(acetate)_2OH$ performed very well and were similar to $Cr(gluconate)_3$. Aluminum salts inhibited corrosion for 2024 and 7075 alloys, while they accelerated corrosion in the case of 6061 alloy. The reason that $Al(acetate)(OH)_2.H_3BO_3$ performed slightly better than $Al(lactate)$ could be due to presence of boric acid, which also inhibited corrosion when tested separately. Overall, when gluconate and other carboxylic acid salts of metal cations such as Cr^{+3} , Al^{+3} are compared; acetate and lactate salts seemed to perform better than gluconate.

Molybdenum Esters of Gluconate Salts

In contrast to what was observed with gluconate salts, the inhibition efficiencies of molybdenum esters of gluconates were almost perfect for 2024 alloy and also very high for 6061 and 7075 alloys as shown in Figure 5. This observation indicated that the molybdenum constituent inhibited corrosion since earlier results already revealed that gluconates had a slightly negative effect on corrosion inhibition.

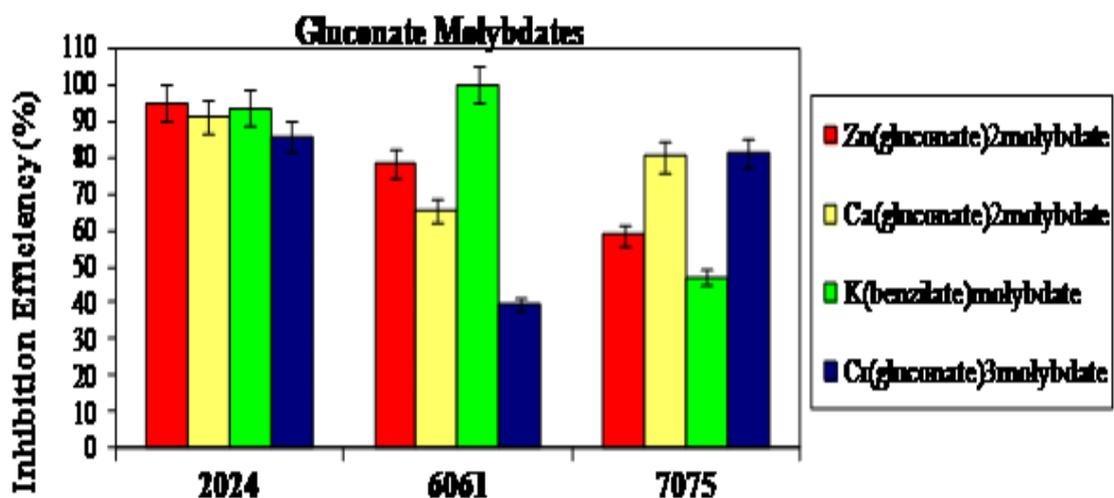


Figure 5: Inhibition Efficiency Graph of Molybdenum Esters of Gluconates and Benzilates

Vanadium Esters of Gluconate Salts

The vanadium esters of gluconates inhibited corrosion even better than the molybdenum esters as shown in Figure 6. Surface characterization indicated that vanadium esters and molybdenum esters inhibited corrosion by forming insoluble oxides and hydroxides on the substrate surface, thus assisting repassivation.

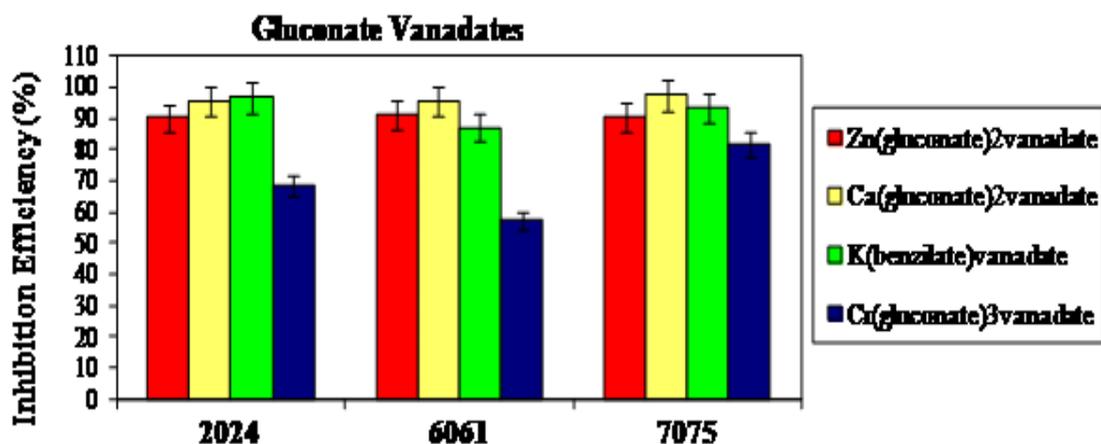


Figure 6: Inhibition Efficiency Graph of Vanadium Esters of Gluconates and Benzilates

Boron Esters of Gluconate Salts and Derivatives

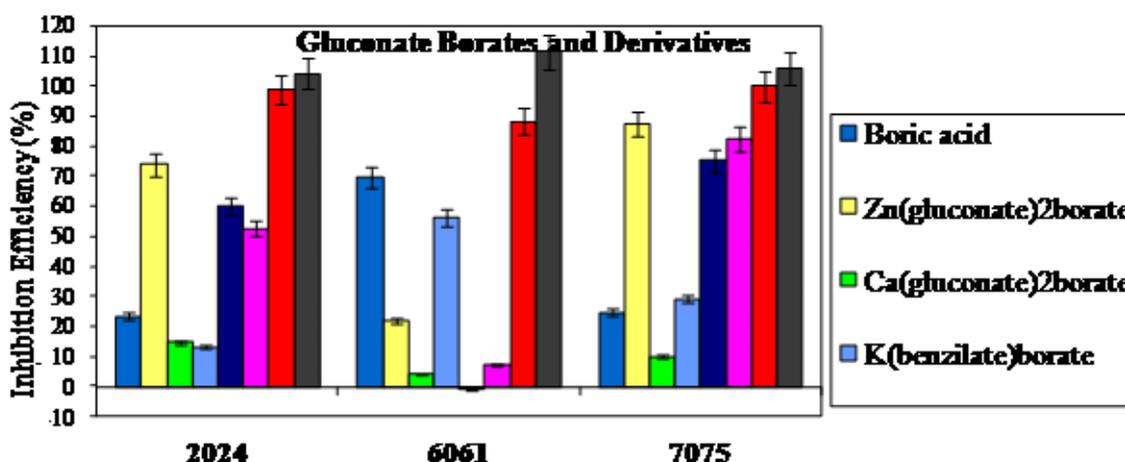


Figure 7: Inhibition Efficiency Graph of Boron Esters of Gluconates and Benzilates and Their Derivatives

Boron esters of gluconate salts inhibited corrosion to varying extent depending on the cationic constituent as seen from the results in Figure 7. When compared to the parent gluconate salts, the boron esters have almost identical inhibition efficiencies. Thus, the boron constituent did not seem to inhibit corrosion unlike the molybdenum and vanadium esters of gluconates. Neutral to slightly negative effect of borates on corrosion of aluminum is reported in the literature [28].

The perfect inhibition efficiencies of chromium borates are also noteworthy. Separation of a very fine fraction of chromium borate with a sieve of 25 μm resulted in better inhibition efficiencies. This could be due to forming a better suspension in water and higher surface area. Inhibition efficiencies were even higher than 100% in some tests, which indicated deposition on the substrate surface. Amorphous chromium borate could lead to the formation of chromium oxides and hydroxides at sufficiently high local pH values that passivates surface while boron constituent might act as a facilitator in this process or more likely it could be a part of the passive layer as in the case of traditional chromium phosphate conversion coatings [29]. X-ray powder diffraction of the samples however revealed that the synthesized CrBO_3 was amorphous (The product was also found to be insoluble when tested both with Atomic Absorption Spectrometer and Colorimeter).

Zinc Carboxylates

Unlike what was observed for mild steel all three tested zinc carboxylates revealed very good results as seen in

Figure 8. Zinc tartrate was the best reagent with %100 inhibition efficiency for all three aluminum alloys.

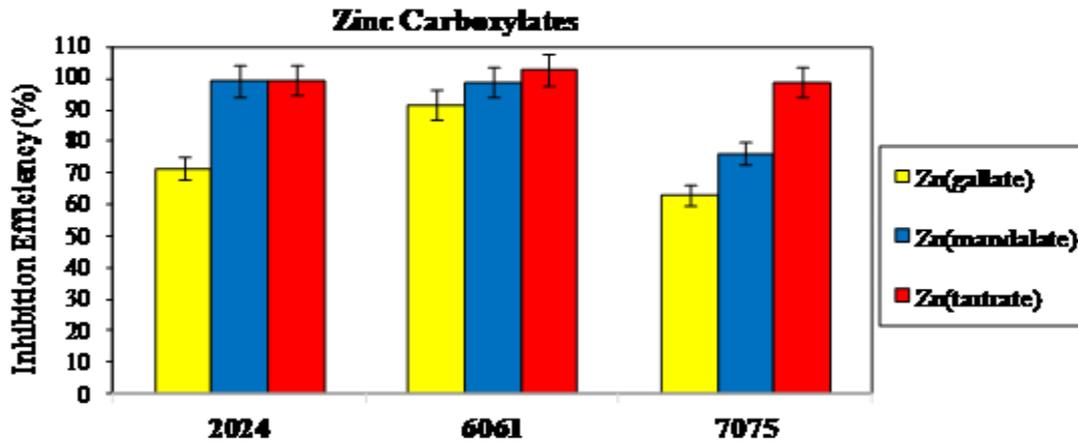


Figure 8: Inhibition Efficiency Graph of Zinc Carboxylates

Chromium Carboxylates

Cr(III) carboxylates also inhibited the corrosion of aluminum alloys extremely well even at concentrations as low as 25 ppm for poorly soluble chromium butyrate and chromium propionate salts as seen below in Figures 9 and 10. Chromium octanoate and chromium caproate salts could not be tested due to their total insolubility in water. The results confirmed the effect of solubility on the inhibition efficiency with the highest soluble Cr(III) carboxylate among tested carboxylates having the highest inhibition efficiency and vice versa.

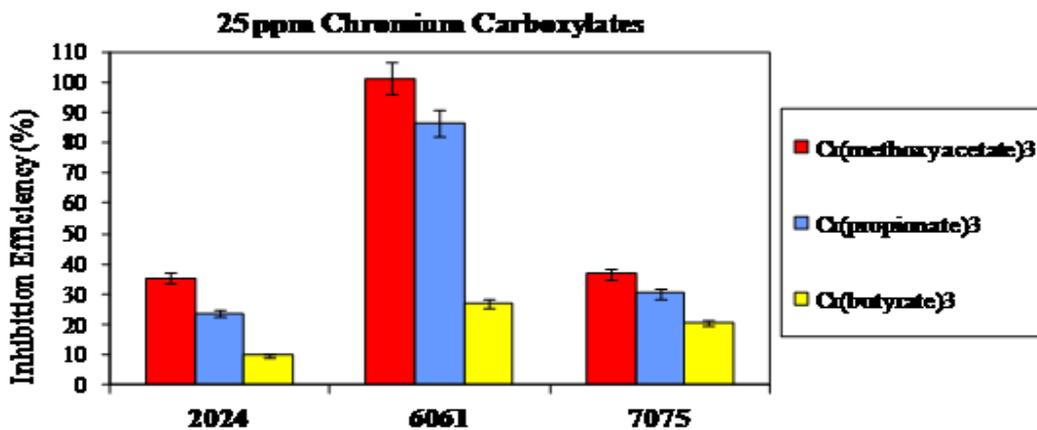


Figure 9: Inhibition Efficiency Graph of 25 ppm Chromium Carboxylates

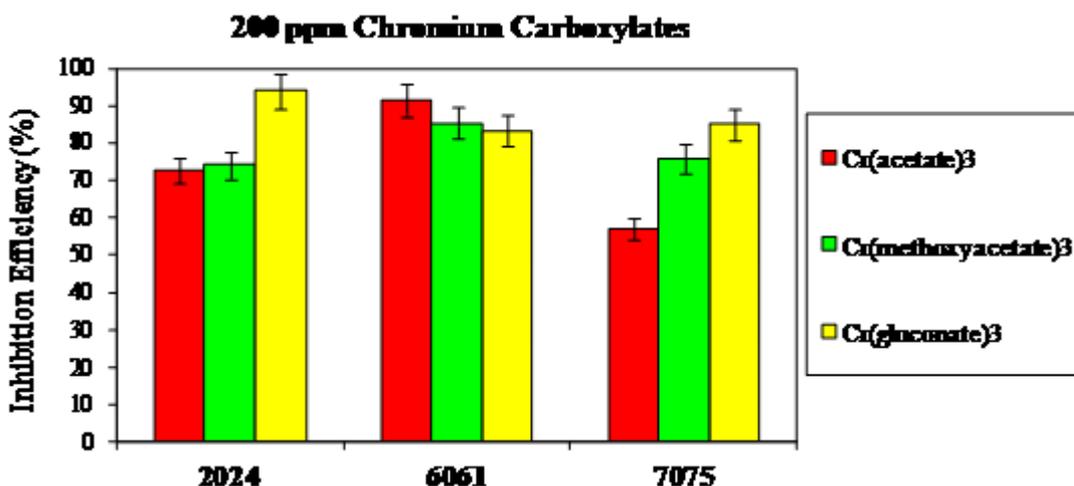


Figure 10: Inhibition Efficiency Graph of 200 ppm Chromium Carboxylates

Various Cr (III) Compounds

In addition to the organic acid salts and their oxyanion esters, several Cr(III) and Zn(II) salts were synthesized and tested for corrosion inhibition activity as well. Many chromium(III) salts tested under this category showed considerable inhibitive activity. CrOOH synthesized via hydrolysis of chromium borate was the most efficient, while nanoparticulate Cr(OH)₃ was the least. In the case of Al 2024 corrosion, commercial grade CrOOH and Cr(OH)₃ synthesized using different reagents than the nanoparticulate Cr(OH)₃ synthesis had also very little inhibition efficiencies.

DISCUSSIONS

Effect of Concentration on Inhibition Efficiency

Varying concentrations from 25 ppm up to 50 ppm resulted in a general trend of increase in inhibition efficiencies with the exception of the molybdenum esters of gluconates. Inhibition efficiencies slightly varied between the 50 ppm and 200 ppm values depending on the type of inhibitor and type of substrate. Inhibitors used to treat 6061 alloy had slightly decreasing inhibition efficiencies when concentrations were increased from 50 ppm to 200 ppm. In contrast, inhibitors that were used to treat 2024 and 7075 substrates had slightly increasing inhibition efficiencies. For concentrations of 200 ppm up to 500 ppm the inhibition efficiencies seemed to decrease in general with the largest decreases observed for the inhibitors used to treat the 6061 alloy. These results suggested that the optimum inhibitor concentration for a 100 ml solution system should be between 50 and 200 ppm; closer to 200 ppm for 2024 and 7075 alloys and closer to 50 ppm for 6061 alloy. As a reason for the discrepancy regarding 6061 alloy, inhibitor amounts over 50 ppm are more than sufficient in most cases, which only increases the conductivity of the solution leading to lower inhibition efficiencies. The amount of 25 ppm was also included in the testing, since compounds as chromium borate chromium oxy-hydroxide were only very slightly soluble.

Effect of Cationic Constituent on Inhibition Efficiency

Zinc cations inhibited aluminum corrosion very well and trivalent chromium cations inhibited aluminum corrosion even better.

Effect of Zn Cations

All formulations with zinc cations inhibited aluminum corrosion considerably, with zinc tartrate, zinc mandelate, zinc gluconate vanadate, and zinc gluconate better than zinc gluconate borate, zinc gallate, and zinc gluconate molybdate. Please refer to Figure 11 for inhibition efficiencies of the inhibitors with zinc constituent.

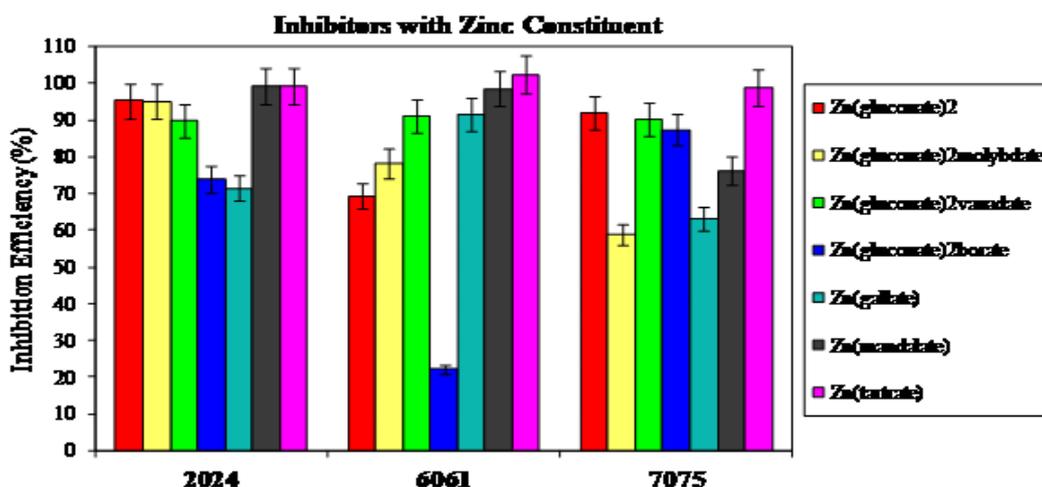


Figure 11: Inhibition Efficiency Graph of Various Compounds with Zinc as the Cationic Constituent

Effect of Cr Cations

As shown in Figure 13, chromium gluconate vanadate was the most efficient inhibitor among the formulations with trivalent chromium cations. On the other hand, chromium gluconate borate had negligible or negative inhibition efficiencies in the case of aluminum 6061 alloy. These results correspond with the inhibition efficiency results of other boron esters of gluconate and benzilate salts. The solubilities of chromium (III) carboxylates also seemed to affect the inhibition efficiencies. When inhibition efficiencies of chromium acetate, chromium propionate, chromium butyrate were compared, the least soluble chromium butyrate yielded the least inhibition efficiency and the most soluble chromium acetate resulted in the highest inhibition efficiency as shown in Figure 14.

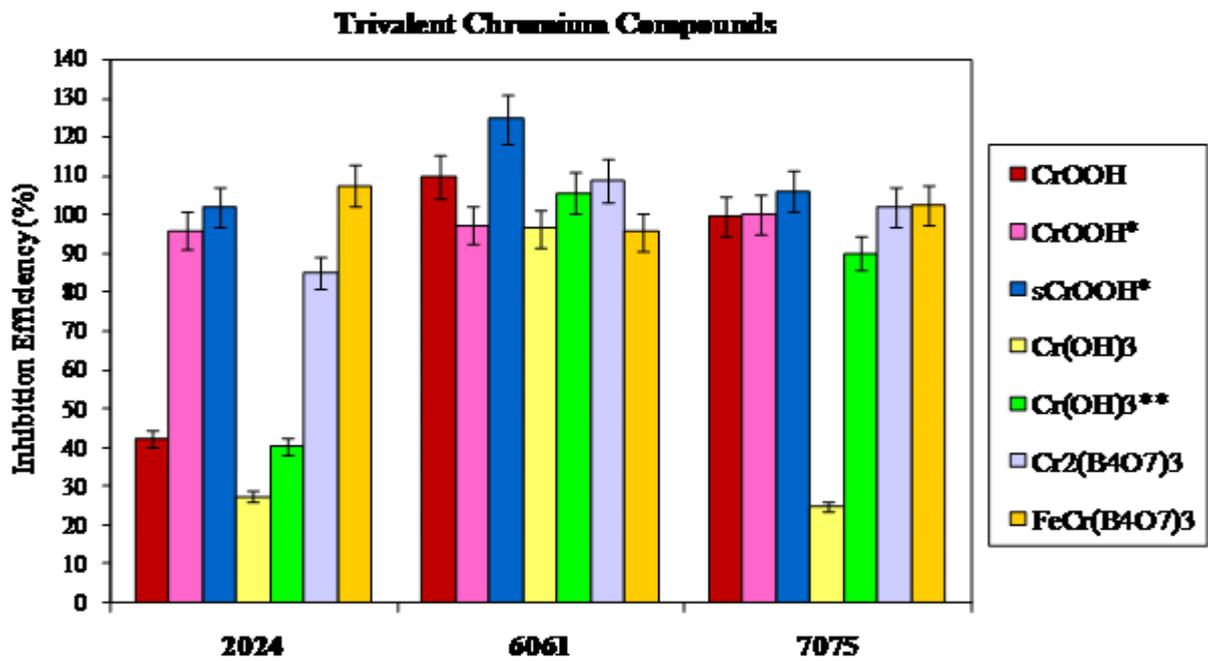


Figure 12: Inhibition Efficiency Graph of Various Trivalent Chromium Compounds *synthesized CrOOH, **nanoparticulate Cr(OH)₃

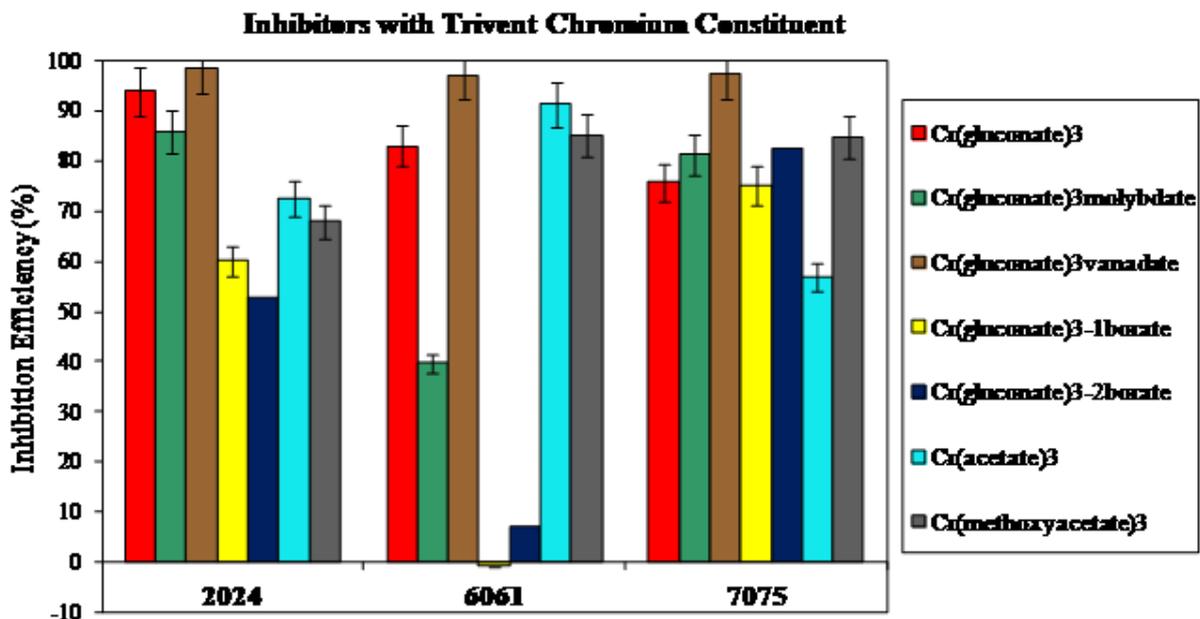


Figure 13: Inhibition Efficiency Graph of Various Compounds with Trivalent Chromium as the Cationic Constituent

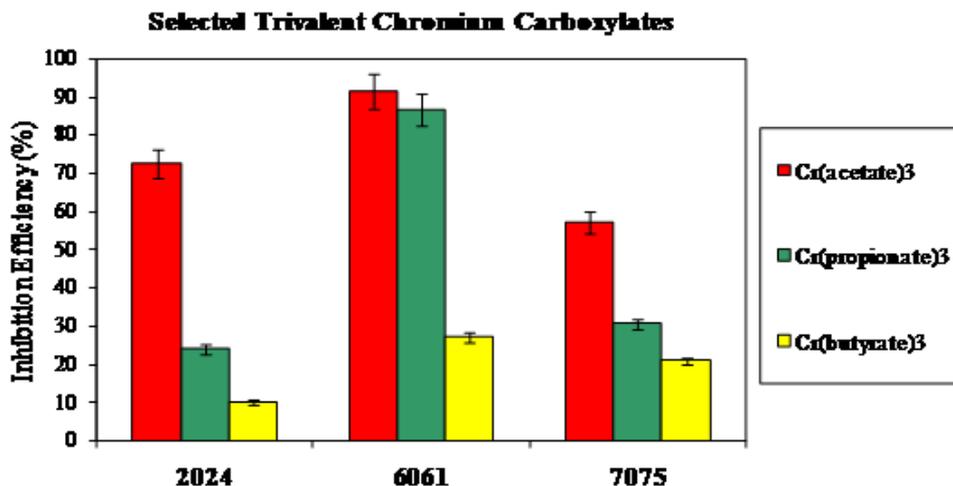


Figure 14: Inhibition Efficiency Graph of Trivalent Chromium Carboxylates with Different Water Solubilities Effect of Ca, K and Other Cations

Magnesium and calcium cations had positive effects on Al 6061 corrosion due to their cathodic inhibitive activity. This was deduced from the comparison of inhibition efficiencies of calcium and magnesium gluconates with that of sodium gluconate.

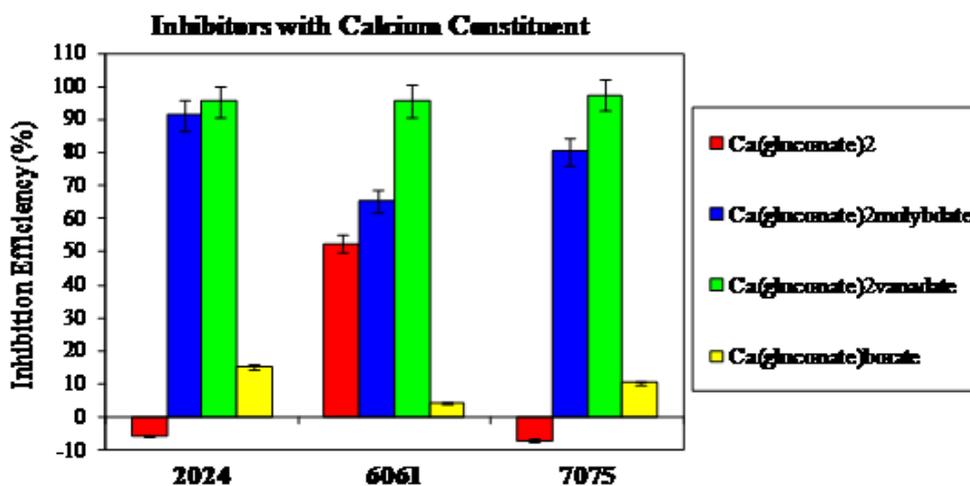


Figure 15: Inhibition Efficiency Graph of Various Compounds with Calcium as the Cationic Constituent

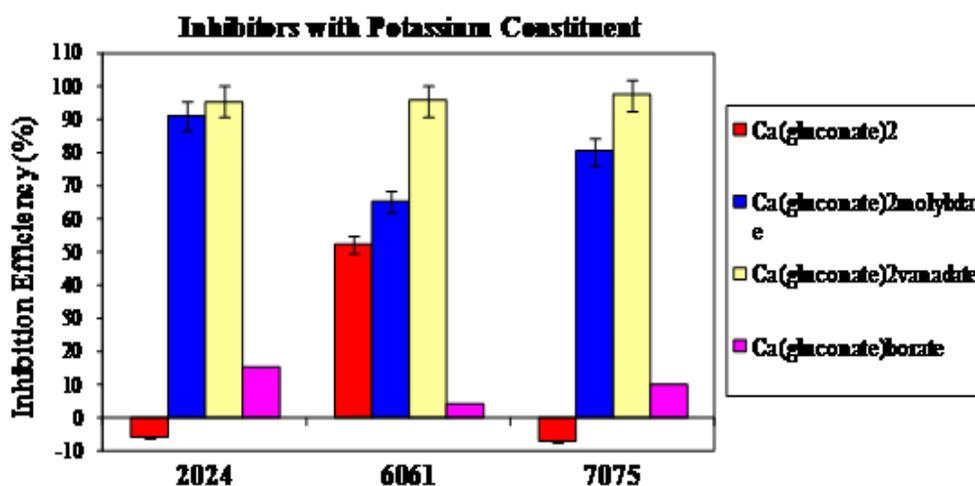


Figure 16: Inhibition Efficiency Graph of Various Compounds with Potassium as the Cationic Constituent

It can be deduced from the results that the anionic constituent had the major impact on inhibition efficiency values with vanadates, molybdates, and borates showing pronounced inhibition efficiencies. Other than directly being involved in corrosion reactions, cations also determine the solubilities of reactants due to the common ion or foreign ion effect. For instance, it has been reported that the addition of 1000 ppm of Fe^{2+} had a slight positive effect on the corrosion rate for Al 7075 alloy in the presence of 0.1 M NaCl solution [34]. However due to very small amounts of reactants, the foreign ion effect could not be observed in the weight-loss tests of this study.

Conversion Coating Formation Studies

In addition to weight-loss tests to measure the direct inhibition efficiencies of inhibitors for aluminum corrosion in aqueous solutions, inhibitors were also tested for conversion coating formations on substrate surfaces and if present these conversion layers were examined and characterized by means of a variety of techniques.

Via Regular Weight-Loss Tests

Coupons those already immersed in the solutions of inhibitors were immersed in salt water for a second period of time to observe any corrosion inhibition due to a possibly formed conversion coating.

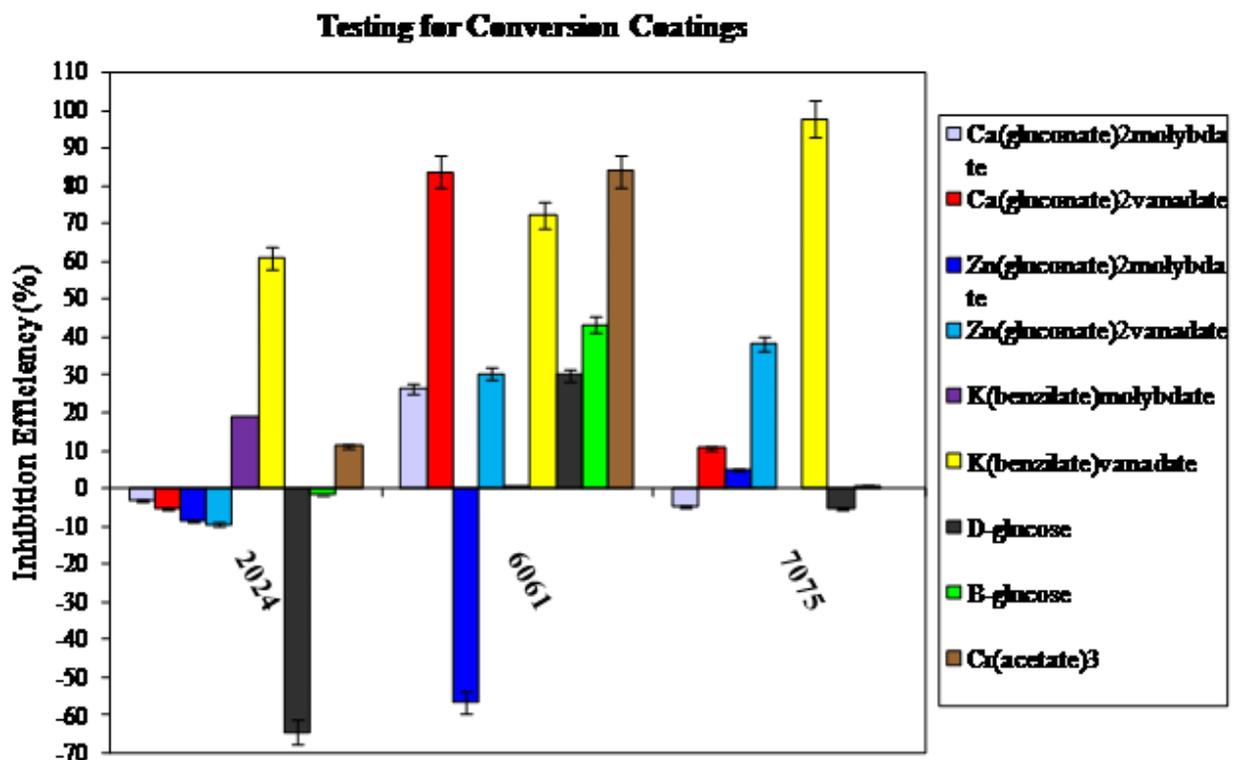


Figure 17: Inhibition Efficiency Graph of Various Compounds for an Additional 7 days for Testing Conversion Coating Formation

The results revealed a few successful candidates for conversion coating formation on aluminum substrates as shown in Fig. 17 such as potassium benzilate vanadate, chromium acetate, zinc gluconate vanadate, calcium gluconate vanadate in the order of decreasing inhibition efficiencies. The fact that potassium benzilate vanadate performed better than zinc gluconate vanadate suggested that the cathodic inhibitive activity of zinc cations was no longer effective during second immersion period. Alternatively, the benzilates may have been incorporated into a protective layer on substrate surface during first immersion period resulting in a stable protective layer. The lower benzilate solubility could lead to sufficient stability for prevention of corrosion during second immersion period. Regardless, the vanadate constituent

seemed to be the major contributor to the passivation of the substrate surface. Chromium acetate also held up well during second immersion period suggesting the formation of a passive chromium oxide-hydroxide layer on the substrate surface. Other inhibitors with positive inhibition efficiencies during second immersion period were calcium gluconate molybdate, D-glucose, and B-glucose in the case of Al 6061 alloy.

Via Measurements of Gained Weight

In addition to inhibition efficiency calculations based on weight-loss values, changes in weights of the coupons after the immersions but before cleaning with acid solution were measured to provide evidence of a deposition on the surface. A weight increase after completion of the immersions but before cleaning with concentrated nitric acid solution may be due to two types of depositions; first a conversion coating formation due to inhibitor compounds, second a deposition layer of corrosion products.

Comparing weights of coupons before and after the cleaning with concentrated nitric acid solution revealed whether a stable protective coating was present on the substrate surface or not, assuming that a stable protective coating is not dissolved when treated with concentrated nitric acid for 5 minutes. Results are shown in Table 1, in which the inhibitors that formed protective depositions on the substrate surface are underlined, while the ones that had depositions of corrosion products or a mixed deposition of both corrosion products and inhibitor originated compounds are written in italic letters.

Table 1: Weight Increases of Metal Substrates Due to Immersions in Inhibitor Solutions

Substrate	Inhibitor	W _{before} (g)	W _{after} (g)	W ₂ -W ₁ (g)	%Wt Increase*	IE**
2024 Al	<u>K(benzilate)molybdate</u>	5.0867	5.1041	0.0174	0.34207	93.08
2024 Al	<u>Zn(gluconate)₂vanadate</u>	5.0907	5.0905	-0.0002	-0.003929	90.06
2024 Al	<i>Cr(prop)₃</i>	5.0375	5.0375	0	0	23.87
2024 Al	<i>Cr(butyrate)₃</i>	5.1161	5.143	0.0269	0.52579	9.95
2024 Al	<u>Syn. CrO(OH)</u>	5.0701	5.0748	0.0047	0.0927	95.87
2024 Al	Al(gluconate) ₂ OH	5.0918	5.098	0.0062	0.12176	3.59
2024 Al	Ca(gluconate) ₂ borate	5.0791	5.0936	0.0145	0.28548	14.82
6061 Al	<u>K(benzilate)molybdate</u>	4.6652	4.6688	0.0036	0.07717	100
6061 Al	<u>Zn(gluconate)₂vanadate</u>	4.6522	4.6521	-0.0001	-0.00215	91.03
6061 Al	<u>Cr(propionate)₃</u>	4.6917	4.6928	0.0011	0.02345	86.62
6061 Al	<i>Cr(butyrate)₃</i>	4.6539	4.6613	0.0074	0.15901	26.99
6061 Al	<u>Syn. CrO(OH)</u>	4.6893	4.6948	0.0055	0.11729	97.38
6061 Al	Al(gluconate) ₂ OH	4.6833	4.6899	0.0066	0.14093	-4.67
6061 Al	Ca(gluconate) ₂ borate	4.6501	4.6634	0.0133	0.28602	3.83
7075 Al	<i>K(benzilate)molybdate</i>	6.3211	6.3386	0.0175	0.27685	47.14
7075 Al	<u>Zn(gluconate)vanadate</u>	6.297	6.2979	0.0009	0.01429	90.53
7075 Al	<i>Cr(prop)₃</i>	6.3318	6.3386	0.0068	0.10739	30.43
7075 Al	<i>Cr(butyrate)₃</i>	6.3093	6.3225	0.0132	0.20921	20.76
7075 Al	<u>Syn. CrO(OH)</u>	6.2987	6.3086	0.0099	0.15718	100
7075 Al	<i>Al(gluconate)₂OH</i>	6.2635	6.2685	0.005	0.07983	47.49
7075 Al	Ca(gluconate) ₂ borate	6.2649	6.2664	0.0015	0.02394	10.07

* (before cleaning), ** (after cleaning)

CONCLUSIONS

Molybdenum and vanadium esters together with formulations consisting of zinc and trivalent chromium cations were most efficient inhibitors for aluminum corrosion. With sodium gluconate revealing slightly negative inhibition efficiencies, the complexing property of gluconate this time aided the dissolution of protective aluminum oxide coating on the surface.

Other gluconate salts such as magnesium gluconate and calcium gluconate inhibited corrosion around 10% unlike sodium gluconate while zinc gluconate effectively inhibited corrosion indicating the sole effect of cationic constituent. Magnesium, calcium, and zinc cations are known for their cathodic inhibitive activity due to forming insoluble hydroxides with zinc cations being the most inhibitive ones. Trivalent chromium was also considered to inhibit corrosion through a similar mechanism in which it forms insoluble chromium hydroxides and oxides.

Both molybdenum and vanadium esters of hydroxy-acid salts effectively inhibited corrosion of aluminum alloys with potassium benzilate vanadate inhibiting the corrosion very effectively even during a second immersion period, without a supply of inhibitor. There was much evidence for the formation of protective coatings originating from the molybdenum and vanadium esters.

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.

Weight-loss tests of the inhibitors for corrosion of aluminum alloys revealed quite different results than those for mild steel in author's previous studies reported in the literature elsewhere. For instance hydroxy-acid salts performed poorly with the exception of zinc gluconate, which was attributed to the cathodic inhibitive activity of zinc cation. Another example was the metal oxyanion esters of hydroxy-acids; molybdate and vanadate esters of hydroxy-acids performed well but borate esters that performed well in the case of mild steel performed poorly for aluminum alloys.

Trivalent chromium compounds performed very well in the case of aluminum alloys. Several inhibitors that were not initially tested for mild steel corrosion were also tested for aluminum corrosion; among them were zinc and trivalent chromium carboxylates, which all performed very well in aqueous solutions provided that the inhibitor is water soluble. Hydroxy-acid esters of molybdates and vanadates seemed to form protective coatings consisting of their lower oxidation state oxides and hydroxides. Vanadate esters and benzilate vanadate ester in particular seemed to perform more lasting protective coatings than others.

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.

Trivalent chromium compounds performed very well, possibly via a similar inhibition mechanism of hexavalent chromium forming insoluble oxides and hydroxides of trivalent chromium, only this time there was no hexavalent chromium present in the media.

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