

Corrosion Inhibition of Automotive Aluminum Alloys in Water-Ethylene Glycol Solutions

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ABSTRACT

Commercially available vapor phase corrosion inhibitors were evaluated to determine their corrosion inhibition for aluminum alloys in a water-ethylene glycol (C₂H₆O₂) mixture. When the temperature exceeds 80°C, ethylene glycol can decompose into organic acids. The resulting acid environments cause severe corrosion of aluminum alloys. Electrochemical and constant immersion tests were carried out to study the effects of several inhibitors. The corrosion behavior was studied at multiple temperatures. Corrosion inhibitor VCI-A at 2.5% dosage showed excellent corrosion protection. It maintained a steady, low corrosion rate during long term exposure by neutralizing pH and forming a hydrophobic film. VCI-B inhibitor, also showed the ability to reduce the corrosion rate of aluminum in ethylene glycol solutions. However, due to its high pH chemistry, the effective dosage should be maintained at 2.5% to avoid any potential increase in pH that can promote localized corrosion or under-deposit corrosion attacks. The results of this investigation demonstrated that both inhibitors can lower the corrosion rate in water-ethylene glycol solutions by neutralizing pH and forming stable films.

Keywords: Cyclic polarization, electrochemical Impedance spectroscopy, vapor phase corrosion inhibitors, pitting corrosion, polarization resistance, ethylene glycol, elevated temperature.

INTRODUCTION

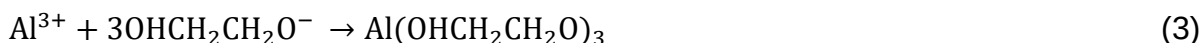
The efforts to lower automotive component weight to make cars more fuel efficient has increased the demand for aluminum alloys. In these applications, substantial amounts of heat are generated due to engine combustion, making it necessary to cool the engine systems. Metals in an engine application will rely on coolant to transfer heat. Corrosion behavior is another consideration for metals. Aluminum alloys, similar to the metals they are replacing, are sensitive to corrosion, especially in an aqueous alkaline environment. The breakdown of the protective surface film of aluminum oxide when exposed to hydroxyl ions (OH^-) makes it more susceptible to corrosion. Ethylene glycol (EG) is a chemical compound that has an alcohol with two $-\text{OH}$ groups. [1] One of the main uses for ethylene glycol is in the automotive industry as an antifreeze and coolant because it has a much lower freezing point than water. Ethylene glycol ($\text{C}_2\text{H}_4(\text{OH})_2$) in the car's cooling system neutralizes temperature by removing and circulating heat. The temperature of the engine coolant can reach between 160°C to 200°C . EG decomposes at high temperatures into organic acids (glycolic, formic, acetic, and oxalic acids) which creates a corrosive environment for metals and can cause severe pitting corrosion at high temperatures. [2,3]

There was research on the corrosion behavior of different metals like carbon steel, 2024 Al-alloy, 3036 Al-alloy, 6063 Al-alloy, and magnesium alloys [4-8] in EG solutions. The presence of impurities often found in ethylene glycol/water mixtures, such as ferric, copper, and chloride ions, can further exacerbate corrosion. At room temperature, the metals in EG had good corrosion resistance, but, when subjected to cyclic heating and cooling this led to thermal shocking [9], which was detrimental for the metals. Moreover, in applications like solar collector systems and cooling systems, there are different types of metals that are galvanically coupled together in cooling systems which create another corrosion problem for these systems [10]. This galvanic coupling is more dangerous for aluminum, which is more electrochemically active in comparison to some other metals. In addition to this, impurities and other metal ions exacerbate corrosion problems in Al alloys [11]. Chloride ions can settle at the disrupted film locations and lead to pitting corrosion by setting up micro galvanic cells [12]. Another case, regarding aluminum alloys solar collector systems that were connected to copper piping and steel water pumps, then exposed to chlorine contaminants and metal ions (Cu^{2+} and Fe^{3+}), resulted in severe corrosion. The combination of the corrosive environment and poor combination of materials lead to rapid system failure by galvanic corrosion [13, 14]. Even at room temperature, 6063 Al alloys tested in different concentrations of Ethylene Glycol and in NaCl solutions faced severe critical pitting corrosion due to the presence of chlorides [15]. These examples illustrate some of the complications for aluminum alloys that can result from uninhibited EG. The addition of corrosion inhibitors to the ethylene glycol/water mixtures can help in mitigating this problem and improve the life of the components [16].

Vapor Corrosion Inhibitors (VCI) along with the water-ethylene glycol mixture is an effective approach to preventing corrosion of aluminum alloys. Much research has been done in the development of appropriate corrosion inhibitors [17-22] to protect aluminum alloys in different

environments. Corrosion inhibitors can be used to counter the decomposition of ethylene glycol into organic acids at elevated temperatures. There are two steps involved in the inhibition of metallic corrosion by VCI molecules, the first step is vaporization of these VCI molecules into the environment, and the second step is dissolution of these molecules into pre-adsorbed moisture film that enhances the hydrophobic character of the moisture film on the metal. The VCI protects the metal by neutralizing acidity or by forming the protective film over the surface of the metal, isolating it from the environment, and neutralizing the corrosive agents and maintaining the pH of the environment. Therefore, the pH of the solution is maintained in the range of passivation to control the corrosion of Al alloys. In this investigation, two commercially available corrosion inhibitors (VCI-A and VCI-B) with an amino carboxylate acid-base were examined.

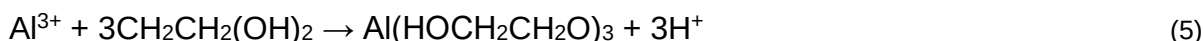
The corrosion mechanism of aluminum alloys in ethylene glycol can be described by the anodic dissolution of aluminum and the cathodic reduction of the environment. At the anode, hydroxide ions are used by the oxidation of aluminum to form an aluminum oxide that consists of Al_2O_3 , $\text{AlO}(\text{OH})$, and $\text{Al}(\text{OH})_3$ as seen in the equation (2). This oxide film can enhance the corrosion resistance of the aluminum alloy. Yet, dissolved oxygen in the solution will diffuse to the surface of the aluminum alloy and become reduced to hydroxide ions at the cathode. In the ethylene glycol environment, there is an additional layer of $\text{Al}(\text{OHCH}_2\text{CH}_2\text{O})_3$ formed on the surface of the aluminum, as shown in equation (3), which can improve the corrosion resistance.



Glycols can actually increase the threat of corrosion for some metal systems. Glycols produce organic acids as they degrade, especially when heated. If left in solution, these acids will lower the pH to initiate corrosion of aluminum alloys. In the absence of oxygen, the increasing corrosion potential of the aluminum electrode when exposed to the contaminated solution indicates that aluminum is also experiencing oxidation, and a layer of film is being formed on the metal surface. The cathodic reaction is dominated by the reduction of ethylene glycol:



Therefore, the pH drop promotes corrosion of aluminum by ethylene glycol:



This film formed is more stable and offers excellent corrosion resistance at room temperature. But at high temperatures, ethylene glycol starts to degrade into organic acids bringing the pH of the solution from 8 to 2.0-2.5. Aluminum alloys generally show good passivity in the pH between ~4 to 9, but a decrease in pH, due to the formation of organic acids, degrades the passive aluminum oxide film (Al_2O_3) into soluble AlO_2 . The interaction of these acids with the surface of aluminum leads to localized corrosion.

EXPERIMENTAL PROCEDURE

The corrosion behavior of UNS A96061-T6 were investigated using cyclic polarization, electrochemical Impedance Spectroscopy (EIS), and constant immersion in boiling solution (per ASTM G123 test setup) of 50% EG solutions with addition of 2.5% and 5.0% of two commercially corrosion inhibitors: VCI-A and VCI-B (amino carboxylate acid-based). All electrochemical tests were conducted at room temperature (23°C), 60 and 90 °C. The logic of selecting these temperature ranges is due to the fact that glycols decompose and produce organic acids at elevated temperatures, especially when heated above 80 °C. Cyclic Polarization tests were conducted in 50% EG solution with inhibitors addition at room temperature and elevated temperatures. Electrochemical Impedance Spectroscopy (EIS) is a well-established quantitative method for the accelerated evaluation of the corrosion inhibitors performance. Electrochemical impedance spectroscopy (EIS) with the input frequency over 100 kHz to 1.0 mHz in different solutions and in different temperatures. The Bode plots are plotted to compare the corrosion behavior in each solution. To verify the corrosion protection effectiveness of these corrosion inhibitors, the constant immersion in boiling solution (~104°C or 219 °F) in the 500ml Erlenmeyer flasks (similar to ASTM G123 test setup to minimize solution evaporation during the test) for 240 hours. The surface of samples was examined every 48 hours under optical microscope and scanning electron microscope and corrosion rate was measured base on weight changes.

RESULTS AND DISCUSSIONS

Electrochemical polarization behavior of UNS A96061-T6 Aluminum alloy in different concentrations of corrosion inhibitor at different temperatures was conducted and a comparison of polarization behavior at 90°C is shown in Figure 1. Results indicated that both VCI-A and VCI-B are anodic corrosion inhibitors capable of lowering the corrosion rate and expanding the passivation range for aluminum in service condition at elevated temperatures. The corrosion rate based on the cyclic polarization test results were as follows: for the control (50% EG solution): 0.44 $\mu\text{A}/\text{cm}^2$ (0.20 mpy); with 2.5% VCI-A: 0.06 $\mu\text{A}/\text{cm}^2$ (0.025 mpy); and when a 5.0% VCI-A was added to solution, the corrosion rate decreased to 0.055 $\mu\text{A}/\text{cm}^2$ (0.023 mpy). For 2.5% VCI-B: 0.07 $\mu\text{A}/\text{cm}^2$ (0.03 mpy); and when a 5.0% VCI-B was added to solution, the corrosion rate increased to 0.174 $\mu\text{A}/\text{cm}^2$ (0.075 mpy). These results are very promising. The pH of the solution however, has an important role on the stability of the protective oxide. VCI-A has a moderate pH range of 8.2-8.5, therefore, it is a safer inhibitor for aluminum alloys.