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Corrosion Inhibition of Aluminium Alloy by Chemical Inhibitors: An Overview.

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Abstract

Aluminium is a widely used metal in every sphere of human endeavour. Hence, its corrosion comes as no amazement. Globally, studies are being conducted to suppress this unwanted action of corrosion. Chemical inhibitors are the focus but besides chemical inhibitors, plant extracts could as well be used to inhibit the mechanism of corrosion. Polymeric inhibitors fall under this category. It is believed that these chemical inhibitors should be employed in industrial purposes. They will save millions and produce little to no toxic emission. From findings, the various techniques employed in investigation of corrosion inhibition are weight loss (the fundamental and most common method), electrochemical impedance spectroscopic (EIS) measurements and potentiodynamic polarization.

Keywords: Corrosion, inhibitors, aluminium, environment, organic

1.0 Introduction

Aluminium is one of the most widely used metals in the world today. Aluminium occupies about 8% of the earth's crust, is the third most common element on earth's crust after oxygen and silicon which also makes it the most abundant metal in the world [1]. Aluminium because of its good characteristics and its versatility is the world's most used metal after steel [2]. Its uses are quite widespread ranging from aircraft design, building construction, and consumer products such as AC units, refrigerators and food processing utensils as well. Aluminium alloys are also frequently used in deep-sea labour where lightweight components and great mechanical attributes are requested [3]. This paper summarizes the inhibitory actions of various chemical inhibitors on Aluminium.

It is a buoyant, corrosion-resistant metal that has a sound attraction to oxygen. It is because of these properties that it is widely preferred in the design and construction of aircrafts, buildings and domestic applications [4]. Aluminium has splendid formability, high mechanical and electrical conductivity, light weight (density of 2.7 g/cm³) and high reflectivity. It is one of the cheapest when compared to other metals of similar properties and is so copious that it is almost double the abundance of iron [1]. It is third in abundance to silicon and oxygen. It has a material appearance alternating from silvery tone to approximate gray, which depends on the texture of the surface. Aluminium does not dissolve in alkanols although it can be aqueous. It has a considerable yield strength for the pure metals and the alloys and when compared to steel, it is 33% dense and stiff [5].



Aluminium is also a good conductor of heat and electricity and is also non-ferromagnetic; this makes aluminium very important in electrical applications. Aluminium has a property of retaining its strength at low temperatures making it a desirable material in cryogenic operations. Aluminium is also non-pyrophoric, which is an important characteristic when handling inflammable materials [6]. Although Aluminium has a sound attraction to oxygen, it is still highly resistant to most vicinities and a great assemblage of chemical substances. This is because of the unreactive and prophylactic characteristics of the aluminium oxide films which are formed on the surface of the metal. In almost all situations, the aluminium corrosion rate declines swiftly with passage of time. In only rare cases such as sodium hydroxide, is the rate of corrosion similar to the normal (Aluminium Federation). Oxide films deplete in a surrounding where the pH levels are either below 4 or above 8.5 and this will frequently lead to a rise in aluminium corrosion rate although this is also determined by the ions that can be found in that specific surrounding. However, in effervescent surroundings, the metal is quickly coated with a saturated oxide film. This oxide film is virtually inert and serves to curb more oxidation. The tenacity of the film relies almost solely on the temperature, surroundings and alloy elements. The oxide films formed at ambient temperature estimate to about 2.5nm of tenacity on pure aluminium. Exposing to temperature above 400 degrees produces films that have above 25nm which is up to 10 times the ambient temperature. If the oxide film is annihilated even by a scratch then a new oxide is created instantly from the uncovered metal [5].

Metal corrosion repression by the inhibitive organic compounds is a component of their ability to absorb on a base metal surface creating obstruction layers against corrosive species in the media. The shielding strength of organic inhibitors is a function of plenteous factors, examples are the quality of the metal surface, the attributes of dilapidating media and the chemical composition of the inhibitor. These factors make it urgent for unbiased selection. Aluminium is also a recyclable metal. By recyclable we mean that it can be used over and over again and the good thing with aluminium is that recycled aluminium is comparable to virgin aluminium, meaning there is no deterioration in the characteristics of aluminium when recycling it. This characteristic greatly saves energy costs as the production of recycled aluminium scraps is 5% of the energy when producing virgin aluminium. Currently 60% of aluminium is recyclable after being used and improvements on that percentage are being made [4].

2.0 Corrosion Types and Corrosion Inhibitors

Corrosion is a process where the metal deteriorates. Corrosion is a natural process and in the presence of a moist atmosphere, chemically active metals get corroded. Aluminium doesn't corrode in many environments but environment in which the pH limit destroys the thin oxide layer of aluminium. Below are the following common corrosion situations encountered:

- i. Uniform attack: the even degradation of a metal over a large area with respect to time. This is the most common form of corrosion and can be inhibited by chemical inhibitors
- ii. Galvanic corrosion: the corrosion that occurs when two dissimilar metals are in contact with one another. When they are together the more active metal acts as the anode and the more noble metal acts as the cathode, and in corrosion the anode is the metal that deteriorates, this form of corrosion can be avoided by good design. [7].

- iii. Crevice corrosion: in aluminium, crevice corrosion does not really have much effect due to the oxide layer protecting aluminium [8].
- iv. Pitting Corrosion: the type of localized corrosion that happens on oxide layer surfaces that aren't completely protected from corrosion. In an event that any part of the thin oxide layer is damaged at a certain point in the metal, that point of the damage becomes the anode as it is more reactive than the parts that are protected by the metal film. The area of the anode to the cathode determines how rapidly the exposed part of the aluminum would corrode [7].
- v. Intergranular corrosion: the type of corrosion that happens on a path along the grain boundaries. This can happen as a result of heat that distorts the structure of the boundaries and this forms precipitates which cause the corrosion. This can be curbed by heating and quenching the material [9].

The utilization of corrosion inhibitors is one of the most effective and practical methods of preventing and stopping corrosion in all kinds of media. An efficacious inhibitor must also send water from the metallic region, converse with the anodic or cathodic vicinities of reaction to deter the oxidation as well as decrease the corrosion reactions, and inhibit movement of corrosion-active strains and water across the metallic surroundings [10-13].

Corrosion inhibitors are diminutive components that when included in minute proportions to a surrounding, decreases the corrosion rate of the metal left unprotected in that vicinity. They are widely categorized into two sections namely: those that expatiate on the makeup of a protective oxide film through an oxidizing phenomenon and those that prevent corrosion by exclusively absorbing on the metallic region and creating a barrier that inhibits access of corrosive mediums to the metallic vicinity [14-17]. There are many kinds of inhibitors deployed when it comes to aluminium and all of the alloys associated with it. Some are organic and others are inorganic. Examples include: Conductive polymers such as Polypyrrole, Polythiophene, Polyaniline and Polyindole [18-20]. Others are polymer 17 and also the use of honey [21]. Other organic inhibitors are inhibitors such as plants and organic coatings [22]. Some inorganic inhibitors for aluminium include Strontium chromate, chrome phosphate, zinc chromate and also 8-hydroxyquinoline [19, 23-24].

2.1 Review of Literature

Corrosion is the destructive result of reaction between a metal or an alloy and the immediate environment [25-28]. The inhibiting effects of several chemical compounds, both organic and inorganic, on the corrosion of pure aluminium and its alloys have been investigated at large because of the tremendous technological importance of these materials [29]. From aliphatic amines to hydrazine compounds [30-32] to ethoxylated fatty acids [33] as well as lanthanide salts [34], addition of these chemical substances and more decrease the corrosion rate of Al and its alloys in various solutions.

[34] investigated the corrosion behaviour of an AA5083 alloy and galvanized steel samples in 3.5% NaCl solution and reported that local corrosion takes place in the areas around the intermetallic compound of Al₆- (Mn, Fe, Cr). The characteristics of the overlying process of corrosion in each case determine the inhibition mechanism followed when lanthanide salts (Cerium) is added to the NaCl environment. Thus, the corrosion of the AA5083 alloy is first inhibited by the precipitation of cerium ions on the intermetallics acting as permanent cathodes.

For the latter, lead particles were detected on the surface. These particles do not act as permanent cathodes.

[35] conducted corrosion inhibition studies of pure Aluminium (Al), (Al + 6%Si) and (Al + 6%Cu) alloys in 1.0 M hydrochloric acid corrosive environment with sodium dodecyl benzene sulphonate ($C_{18}H_{29}NaO_3S$) acting as inhibitor. The techniques used were electrochemical impedance spectroscopic (EIS) measurements, potentiodynamic polarization and weight loss within temperature range of 50-140 °F. Their results showed that the anionic surfactant inhibited the corrosion rate of the metals acting as a cathodic inhibitor. Complete inhibition is observed around its critical micelle concentration (CMC). The efficiency of inhibition for the three Al samples increased in the following order: Al > (Al+ 6% Cu) > (Al+ 6% Si) [35].

According to [36], the resistance of aluminium against corrosion in solutions with lower hydrochloric acid concentrations could be attributed to rapidly formed surface oxides. The chloride ions present produced wide-ranging localized attacks. These ions are belligerent and they prevented formation of the passive film fast-tracking the process of anodic dissolution. The pitting corrosion of aluminium is as a result of the movement of chloride ions through the oxide film, or due to the chemisorbed chloride ions onto the oxide surface where they act as reaction partners, assisting dissolution through the formation of oxide-chloride complexes. An increase in concentration of the corrosive environment resulted in a rise in the dissolution rate of aluminium [36]. The results obtained indicated that Tween 20 and 81 are more effective inhibitors of the corrosion action of the pure metal as compared to hexadecylpyridinium bromide (HDPB). Under the CMC, the inhibition of used surfactants is negligible. Higher inhibition efficiencies were observed as the concentration of Tween 20 reached values closer to the CMC.

The AA6xxx series aluminium alloys (or the Al-Mg-Si alloys) are extremely heat-treatable wrought alloys that have impressive strength to match with high conductivity, both electrical and thermal [37-39]. A study has been carried out on the corrosion inhibitive qualities of cerium dibutylphosphate [$Ce(dbp)_3$] on AA2024-T3 aluminium alloy in sodium chloride aqueous solutions, conversely, $Ce(dbp)_3$ has proven to be a good corrosion inhibitive agent for the protection of high-strength aluminium alloys in aqueous chloride environment [13].

2.2 Polymeric Chemical Inhibitors

Polymers can be used as corrosion inhibitors for various metals. For instance, polyaniline has attracted considerable attention due to its good environmental stability and its numerous potential applications. Some applications, however, have been limited as a result of the poor processability of the polymer [40]. Results from [25] showed that monomeric surfactants (MC_{12}), (MC_{10}) and (MC_6) as well as their analogues polymeric surfactants constrain the corrosion of pure aluminium in a 0.5 M HCl environment. Measurement of the weight loss was the technique employed. The inhibitory action of these polymeric surfactants is because of their adsorption leading to development of barrier film on the metal surface which then separates the metal from direct interaction with the corrosive solution. The inhibition efficiency of $PC_{11}R$ was also proved to be greater than that of PC_{12} polymer. This was as a result of the elimination of the terminal - SO_3H groups present in PC_{12} while the terminal - CH_3 chains in $PC_{11}R$ steadies its inhibition efficiency.

2.3 Examples of organic chemical inhibitors

Some examples of organic inhibitors are: 4-(benzo [d]thiazol-2-ylthio) phthalonitrile (BTThio) and tetrakis[(benzo[d]thiazol-2-yl-thio) phthalocyaninato] gallium (III) chloride (ClGaBTThioPc). These inhibitors were tested for their corrosion inhibitive properties on aluminium [41]. The corrosion inhibitive behaviours of these inhibitors were monitored using computational and electrochemical techniques. Results reveal predominant cathodic character by the inhibitors for the corrosion inhibition of aluminium and its alloys. Potentiodynamic polarization measurements show a remarkable spike in the inhibition efficiency values, for BTThio results show an increase from 46.9 to 70.8% and 59.7-81.0% for ClGaBTThioPc within the concentration range of 2 to 10 μM . SEM measurements give us an understanding that these organic inhibitors offer protection of the metal surface from acid attack and energy dispersive X-ray (EDX) measurements show that the most probable way by which the inhibitors protect the metal surface would be by shielding it from the corrosion attacks of Cl^- from the acid [41].

Corrosion inhibition of another alloy of aluminium widely used in the aerospace industry for the reason of its optimal weight to strength ratio, aluminium alloy 2024, was investigated in [24]. The alloy is very prone to localized corrosion as a result of the segregation of the intermetallic particles within its grain boundaries. Localized pitting corrosion starts at the position of the most prominent intermetallic inclusions occupying approximately 3% of the alloy's geometric surface [24]. Several organic compounds were tested as possible inhibitors for this alloy of aluminium. The methods employed were EIS, X-ray photoelectron spectroscopy, scanning electron microscopy equipped with energy dispersive spectroscopy and de-polarization. Results revealed that the three most effective were salicylaldehyde ($\text{C}_6\text{H}_4\text{CH}=\text{NOH}-2\text{-OH}$), quinaldic acid ($\text{C}_{10}\text{H}_7\text{NO}_2$) and 8-hydroxyquinoline ($\text{C}_9\text{H}_7\text{NO}$). They decrease the rate of the anodic reaction [24].

3.0 Extracts from Various Technological Methods

Table 1 portrays the remarks of some authors who investigated the corrosion inhibition of aluminium and aluminium alloys.

Table 1: Some authors' remarks and physical data on investigation of corrosion inhibition of Al and its alloys using water soluble polymers [25]

Author	Metal type	Inhibitor	Corrosion medium	Method of investigation	General remarks
Ogurtsov <i>et al.</i> [42]	Aluminium alloy	Doped and undoped polyaniline (PANI)	0.1 M HCl and 3.5% NaCl solutions	Electrochemical impedance spectroscopy (EIS)	<ul style="list-style-type: none"> * Polyaniline can provide corrosion protection of Al alloy in both NaCl and dilute HCl solutions * The degree of the corrosion protection of the Al alloy by the undoped PANI is higher than that of the doped PANI * Based on the obtained corrosion currents, it is possible to believe that the thickness of the surface of protective aluminium oxide layer plays a key role in the inhibiting effect
Muller <i>et al.</i> [43]	Aluminium	High molecular weight of styrenemaleic acid copolymers	Mixture of water and butyl glycol V/V 9:2 at pH=10	AAS by measuring soluble Al(III) acrylate in solution and volumetric measurement of hydrogen	<ul style="list-style-type: none"> * The inhibition efficiency is measured by volumetric measurement of the hydrogen produced by the corrosion * The lower is the acid number of copolymers, the lower is the volume of hydrogen
Abdallah <i>et al.</i> [44]	Aluminium	Polyamide	Oxalic acid	Potentiostatic and –dynamic anodic polarization techniques	<ul style="list-style-type: none"> * The inhibition efficiency increases with increasing polyamide concentration until a critical value and then decreases * The inhibitive behaviour of the polymer is due to adsorption of the polyamide compounds on the metal surface and formation of insoluble complexes. * The adsorption process was found to obey Temkin adsorption isotherm

Muller <i>et al.</i> [45]	Aluminium	Low and high molecular weight Polyacrylic acids (PAAC)	Water and Butyl glycol V/V 9:2 at pH = 10	Atomic adsorption spectroscopy (AAS) by measuring soluble Al acrylate in solution	<ul style="list-style-type: none"> * In the concentration range from 0.3-0.5 wt% of PAAC, low molecular weight PAAC has markedly inhibition effect than high molecular weight. * In case of the concentration range 0.05-0.1 wt%, low molecular weight PAAC has no effect where the high molecular weight of PAAC has an inhibition effect
Umoren <i>et al.</i> [46]	Aluminium	Polyvinyl pyrrolidone (PVP) and polyacrylamide (PA)	HCl	Weight loss, hydrogen evolution and thermometric techniques	<ul style="list-style-type: none"> * The inhibition efficiency increased with increasing inhibitor concentrations but decreased with increasing temperature * The inhibitor efficiency of PVP is higher than PA which may be due to the differences in their molecular structures * The inhibitors (PVP and PA) obey Freundlich, Temkin and Flory-Huggins adsorption isotherms. * Results obtained from the kinetic and thermodynamic parameters indicate spontaneous and physical adsorption of the inhibitors.

4.0 Conclusion

This study has shown that various corrosion chemical inhibitors and techniques are applied in carrying out research work to mitigate corrosion of aluminium and its alloys. The corrosive behaviour of aluminium-magnesium alloy and galvanized steel were observed in NaCl solutions. Cerium in form of lanthanide salts, appeared as dispersed islands due to precipitation on the cathodes. Corrosion inhibition investigations conducted for pure aluminium shows that sodium dodecyl benzene sulphonate acted as the inhibitor. This review has explained the concept of corrosion inhibitory action in one of the most popular materials in the world, Aluminium. It has highlighted multiple various past reports on this subject. The recyclable metal although possessing certain natural resistance to the corroding process needs certain additives to be able to withstand the environments in which it is placed in. Polymers have been meticulously discussed. Polymers like styrenemaleic acid polymers were investigated using volumetric analysis.

Polyaniline, one of the most frequently used polymers, was also identified as an effective inhibitor.

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