

# *INTRODUCTION*

## **1.1- Definition of Corrosion**

Corrosion is defined in different ways but the usual interpretation of the term is an attack on a metallic material by reaction with its environment. The concept of corrosion can also be used in a broader sense, where this includes attack on non metallic material.

## **1.2-Importance of Corrosion Studies**

The importance of corrosion studies is two folds. The first is economic, including the reduction of material losses resulting from the wasting away or sudden failure of piping, tanks, metal components of machines, ships, hulls, marine, structures...etc. The second conservation, applied primarily to metal resources, the world's supply of which is limited, and the wastage of which includes corresponding losses of energy and water resources accompanying the production and fabrication of metal structures.

## **1.3-Basic Causes Necessary for Corrosion**

### **1.3.1- Condition necessary for corrosion**

For the purpose of this manual, electrochemical corrosion is the most important classification of corrosion. Four conditions must exist before electrochemical corrosion can proceed :

- 1-There must be cathode.
- 2-There must be anode (something that corrodes).
- 3-There must be continuous conductive liquid path (electrolyte, usually condensate and salt or other contamination).

4-there must be a conductor to carry the flow of electron from the anode to the cathode. This conductor is usually in the form of metal-to-metal contact such as in bolted or riveted joints.

The elimination of any one of the four conditions will stop corrosion.

### **1.3.2- Environmental factors**

At normal atmospheric temperatures the moisture in the air is enough to start corrosive action. Oxygen is essential for corrosion to occur in water at ambient temperatures. Other factors that affected the tendency of a metal to corrode are:

- 1- Acidity or alkalinity of the conductive media (PH factor).
- 2- Stability of the corrosion products.
- 3- Biological organism (particular anaerobic bacteria).
- 4- Variation in composition of the corrosive medium.
- 5- Temperature.

### **1.3.3- Effect of material selection**

One of the fundamental factors in corrosion is the nature of the material . Material are usually selected primarily for structural efficiency, and corrosion resistance is often a secondary consideration in design.

### **1.3.4- Water intrusion**

Water intrusion is the principal cause of corrosion problems encountered in the field use of equipment . Water can enter an enclosure by free entry, capillary action, or condensation . With these three modes of water entry acting and with subsequent confinement of water, it is almost certain that any enclosure will be susceptible to water intrusion.

The corrosion problem at KSC is complex. The presence of salts and acid on metal surface greatly increase the electrical conductivity of any moisture present and accelerates corrosion. Moisture tends to collect on direct particles.

#### **1.4 – Classification of Corrosion**

Corrosion has been classified in different ways .The more preferred classification is based on mechanisms, which falls in two type;

**1-Chemical corrosion:** in which the metal is converted into its oxide when the metal is exposed to a reactive gas or non-conducting liquids.

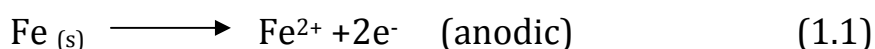
**2-Electrochemical:** : The formation of hydrous oxide film occurs when the metal is immersed in a conducting liquid containing dissolved reactive substance. The reaction is considered to take place at the metal-solution interface, due to the heterogeneity on the metal surface, which creates local anodic and cathodic sites on the metal.

#### **1.5- Electrochemical Theory of Corrosion**

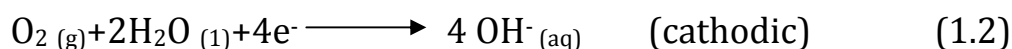
Electrochemistry is a branch of chemistry dealing with relation ships between electricity and chemical reaction .it involves oxidation and reduction (redox) reactions. Corrosion is an example of a type of electrochemical reaction since a substance- oxidizing agent- oxidizes a metal in its environment . In the natural environment, oxgen gas is a good oxidizing agent. Most metal have lower reduction potential than  $O_2$  , therefor they are easily oxidized in the presence of oxygen .metals such as gold , silver and platinum are not so easily oxidized and are some time referred to as noble metals. The reason

for the lack of oxidation in these noble metals are varied and some time complex.

One of the most familiar corrosion process of the oxidation of iron (rusting). Iron metal is spontaneously oxidized in the presence of  $O_2$  and an aqueous electrolyte solution. Physical strains (scratches, dents, bends ,ect..) present on the iron are more easily oxidized than other areas. This directly relates to physics, i.e, the way electric field are generated at the surface of the metal . Stronger field are generated at the physically strained parts of the metal. The result is that regions are anodic (oxidation occurs) and simultaneously different areas are cathodic which a reduction reaction occurs.



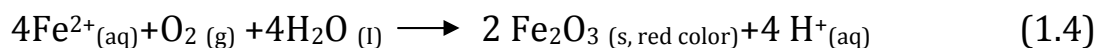
The electrons that are released flow through the iron metal to the cathodic region where they react with oxygen:



these two half reactions together give the over all reaction :



Common experience with this process (e.g., car fenders) tends to show that  $Fe^{2+}$  is eventually oxidized further to  $Fe^{3+}$ , in the compound iron (III) oxide (rust):



In the experimental setup, this last reaction does not occur. The  $Fe^{2+}_{(aq)}$  reacts with  $[Fe(CN)_6]^{-}$ , which is a blue color . The gel you use contains phenolphthalein, an indicator that is pink in basic solution. Since reduction of  $O_2$  results in a basic solution , one will observe a pink color at the cathodic region .Thus, phenolphthalein and  $[Fe(CN)_6]^{3-}$  are used to show cathodic and anodic region .

Further complication arise if we have a system where two different metal in contact with another metal. When this situation is encountered, electric field is set up due to the difference in the reduction potential of the two metals. This field is stronger than any effect caused by physical strain. Thus, one metal will act entirely as the anode, while the other's becomes the cathode one can use standard reduction potentials to determine which metal will act as the anode \cathode.

When considering a bimetallic system, the metal with the more positive reduction potential will be reduced (cathode) and the metal with the more negative reduction potential will be oxidized (anode). For example, if copper and zinc were connected electrically and immersed in an electrolyte solution, we might expect that the copper would be the cathode and the zinc the anode, based on their relative reduction potentials.

## **1.6- Type of Corrosion**

### **a. General corrosion**

Called uniform corrosion, defined as the uniform loss of metal from the entire exposed surface of the metal.

**b. Galvanic corrosion.** Galvanic corrosion occurs when two different metal or coating which are joined together in the presence of an electrolyte . Each metal has a potential different from any other metal when placed in an electrolyte.

**c. Concentration-cell corrosion.** This form of corrosion is sometimes referred to as “crevice corrosion,” “gasket corrosion,” and “deposit corrosion” because it commonly occurs in localized areas where small volumes of stagnant solution exist. At least five types of

concentration cells exist; the most common are the “oxygen” and “metal ion” cells.

**d. Pitting corrosion.** is a randomly occurring, highly localized form of attack on a metal surface, Steel and galvanized steel pipes and storage tanks are susceptible to pitting corrosion and tuberculation by many potable waters. Various grades of stainless steel are susceptible to pitting corrosion when exposed to saline environments.

**e. Intergranular corrosion.** Corrosion occurs at the grain boundaries of an alloy. The cathodic grains of Stainless steel the 2000 and 7000 series aluminum alloys. Welding , stress relief annealing, improper heat treating, or overheating in service generally establish the microscopic; that make a material susceptible to inter granular

**f. Fretting corrosion** :when two or more parts rub against each other these rubbing removing the corrosion products and exposed metal to electrolyte.

**g. Selective leaching or Demetalification.** Removal of one of the alloying elements in an alloys by an electrolyte; typical examples the removal of zinc in chloride waters from brass.

**h. Erosion corrosion.** Erosion is the removal of metal by the movement of fluids against the surface on the metal.

## **1.7 –Methods of Corrosion Protection**

### **1.7.1-Application of protective coatings**

Metallic structures can be protected from corrosion in many ways. A common method involves the application of protective coatings made from paints, plastics or films of noble metals on the structure itself (e.g., the coating on tin cans). These coatings form an impervious barrier between the metal and the oxidant but are only

effective when the coating completely covers the structure. Flaws in the coating have been found to produce accelerated corrosion of the metal.

### **1.7.2- Polarize or shift the potential of the metal**

Another method of reducing corrosion is to polarized or shift the potential of the metal enabling it to act as a cathode (rather than an anode) in an electrochemical cell . One example is the galvanizing of steel with a coating of zinc. The iron and zinc then function as the electrodes of a cell. Zinc is the more readily oxidized metal of the pair and functions as the anode and corrodes, while the iron functions as the cathode. The zinc is used up and protection is effective as long as some zinc remains. Sacrificial anodes work on the same principal but use an external electrode made from a readily oxidized metal; this form of protection is commonly used on buried pipelines.

### **1.7.3 . Cathodic protection**

Cathodic protection is an electrical method using an impressed direct current to flow from auxiliary anodes, derived from an external power supply is a related form of protection which metal forced to be the cathode in electro chemical cell .

### **1.7.4. Material selection**

Material selection is summarized as follows:

**1-**Use corrosion resistant material including plastics and non metallic in severe environments.

**2-**Avoid dissimilar metal couples,

**3-**Avoid the use of back to back structural shapes .when The exterior use of unistrut can not be avoided as stainless steel in



addition .alternate especially in highly corrosive areas. Structural shapes shall be considered as C- or d- shaped channel

**4-**Aviod the use of alloys susceptible to stress corrosion

### **1.8. Corrosion Inhibitors**

To inhibit corrosion, small amounts of corrosion inhibitors can be added to water systems and process streams to reduce corrosion rates to acceptable values. In general, corrosion inhibitor incorporate themselves in to corrosion product films in such away as to increase the film capacity to prevent corrosion .The polar nature of some molecules promotes ,adsorption but the idea that corrosion inhibitor films act as barriers is erroneous. An inhibitor molecule usually is in constant motion, the rate of adsorption on to the surface is dependent on the nature of the molecule, as well as the concentration of the inhibitor in the fluid. The same is true for the process of adsorption . It is important inhibitor treatment to maintain a sufficient concentration of the molecule in the fluid so that the adsorption rate at least equals the desorption rate .this process is commonly referred to as passivation.

### **Types of Corrosion Inhibitors**

#### **a-Organic**

These materials are characterized by high molecular weight structures, in corporating nitrogen or phosphorous groups. They are usually highly polar molecules.

\*phosphate Ester

\*phosphonates

#### **b- Inorganic**

Salts of some metals and amphoteric elements act as corrosion inhibitors. Quite often these material have tenacious film –forming or passivation effects . in some instances, they react with the metal surface.

- Chromate Salts.
- Zinc Salts.
- Moly bdate compounds.
- Phosphates.
- Nitrite Salts.
- Silicate compounds.

### **1.9. Corrosion Inhibition.**

#### **1.9 .1. Corrosion inhibition in acid solutions**

Acid solution are widely used in industry where the most important fields of application are industrial acid cleaning and oil well acidizing because of general aggressivity of acid solution .

The selection of inhibitor mainly depends on the type of acid its concentration, temperature and velocity of flow ,the presence of dissolved organic and or inorganic substance and on the type of metallic material exposed to the action in acidic solution.

Most of well known acid inhibitor are organic compound containing nitrogen ,sulfate and oxygen<sup>(1-8)</sup> .

#### **1.9.2. Factor affecting inhibitor action in aggressive acid medium**

##### **1- Inter action of the inhibitor on the metal surface**

Physical a desorption and chemisorptions are the principle type of interaction between organic inhibitor and a metal surface

### **i- Physical adsorption**

It is the result of the electrostatic attractive forces between inhibiting ions or dipoles and the electricity charged surface of the metal. The charge of the metallic due to the electric field at the outer Helmholtz plan of the electric double layer existing at the metal \ solution interface the surface charge can be defined the potential of the metal  $E_{corr}$  vs. its zero potential charge (ZPC)( $E_q=0$ ) <sup>(9)</sup> when the difference  $E_{corr} - E_q=Q$  in negative charge cation a desorption is favored. When  $Q$  becomes positive the behavior is related not only to positively or negatively charged compound; but also to dipole whose orientation is determined by the value of the  $Q$  potential.

According to antropov (9) at equal value of  $Q$  of different metal similar behavior give in habiting species should be expected in the same environment.

In study the adsorption of ion at the metal \solution interface, it was first assumed that ion maintained their total charge during adsorption giving rise in electrostatic bond. Lorene <sup>(10-12)</sup> suggested that partial charge is present in the adsorption of ions; a certain amount of covalent bond in the adsorption process the partial charge concept studied by Shultz and kappitz <sup>(13)</sup> and others <sup>(14-16)</sup>. The term electrosorption valency was chosen because of its analogy with the electrode reaction valency which enters in to Faraday's laws well as the Nernst equation.

### **ii- Chemisorptions**

This process involves charge sharing or charge transfer from the inhibitor molecule to the metal surface in order to form co - ordinate type of bond the chemisorptions process take place more

slowly than electrostatic adsorption and with higher activation energy. It depends on the higher temperature.

Chemisorptions is specific for certain metals and is not completely reversible<sup>(17)</sup>. The bonding occurring with electron transfer

clearly depends on the nature of the metal and the nature of organic inhibitor. In fact; electron transfer is typical for transition metal having vacant, low energy electron orbitals.

the structure characteristics of the rest of the molecule influence the electron density on the hetero atom and as consequence; the strength of the chemisorptions bond. Regular the systematic changes in the molecular structure, as the introduction of substituents in various position on the aromatic and hetero cyclic compounds, may influence electron density and ability of compound to inhibit corrosion.

Relationship between electronic structure and efficiency of various classes of inhibitors has been deduced from quantum mechanical calculation<sup>(18-20)</sup> in this way, the order of the bond along the bond line, the index of free valence and the charge of atom in the free and adsorbed state has been calculated. Other structure parameter influencing the inhabiting efficiency may be mentioned. Thus, the projected molecular area<sup>(21)</sup> molecular weight<sup>(22)</sup> of various series or organic compound has been correlated with variation in inhibiting efficiencies.

#### **a- Interaction between adsorbed inhibitors**

When the coverage of the metal surface by adsorbed inhibitor species, lateral interaction between inhibitor molecules may arise influencing the inhibition efficiency. Attractive lateral interaction usually give rise to stronger adsorption and higher inhibition

efficiency . This effect has been show in the case of compound containing long hydrocarbon chain due to attractive Vander Waals forces in the presence of ions or molecules containing dipoles, repulsive interaction may occur, weakling the adsorption and diminishing the inhibition efficiency.

### **c- Interaction of the inhibitor with water molecules**

Due to adsorption process of an inhibitor , water molecules are being removed from the metal surface during the adsorption process of molecule .The interaction energy between molecule and water changes as it passes from the dissolved to adsorbed state. This change forms the important part of the free energy of adsorption. Increasing the size of the hydrocarbon portion of an organic molecule will increase the salvation energy of an inhibitor leading to decrease the solubility and increasing adorability <sup>(23)</sup> .

### **d- Relationship between inhibitor reactivity and efficiency**

The nature of the inhibitor initially present in acid solution may change with the time and / or the electrodes potential as a consequence of reduction reaction, or formation of surface products. The inhibition due to the reaction product is usually called secondary inhibition; where as primary inhibition may be higher or lower than secondary inhibition depending on the effectiveness of the reaction produce t <sup>(24)</sup>.

## **1.9.3- Theories of corrosion inhibition**

### **1.9.3.1- Adsorption theory**

Organic inhibitors which presumably are not cable of oxidizing or precipitant the metal ion must have the ability to adsorb and impede either cathodic or anodic or both the reaction. Organic

inhibitors inhibit corrosion by adsorption at metal\ solution interface. Most of the heterocyclic compounds containing nitrogen were believed to be cathodic inhibitors. But it has been shown by Hoar <sup>(25)</sup> that in some cases anodic inhibition is observed.

The mode of adsorption depends on:

- 1) The nature of the metal surface.
- 2) The chemical structure of the molecule.
- 3) The electrochemical potential at metal \solution interface.

The following are the different types of adsorption associated with organic inhibitors.

- 1) Electrostatic adsorption or electrosorption.
- 2) Chemisorptions and  $\pi$  orbital adsorption.

#### **1.9.3.2- Electrosorption**

In electrosorption the coulombic electrical forces which stretch out from the metal are much longer in range than the chemical forces which affect the molecules in chemisorptions.

#### **1.9.3.3- $\pi$ -Orbital adsorption**

In this type, the adsorption may result from  $\pi$ - orbital interaction with the metal. Organic compound with double and triple bond and this containing aromatic nucleus interact with metal by their  $\pi$  -bond orbitals.

#### **1.9.3.4 -Vander Waals adsorption**

The adsorbed molecules are held by weak Vander Waals forces and physically adsorbed molecules on solids forming multilayer, as the forces operating are weak Vander Waals type, the adsorbed

molecules may easily be removed or desorbed from the surface by lowering the bulk concentration of the adsorbate.

#### **1.9.3.5- Film theory**

In order to explain the inhibitive action of inhibitors in neutral and alkaline media, Evans<sup>(26)</sup>, attributed the inhibition to the formation of an insoluble film. In acid solution according to Hausler<sup>(27)</sup> and Putilova et al.<sup>(28)</sup> appreciably effective protection of metals by inhibitors is due to the formation of a layer of insoluble or slightly soluble corrosion product on the metal surface. The formation of insoluble or slightly soluble complex compound or the metal sulphide with compound like thioethers, thioalcohols and the formation of a protective film on the metal surface have been quoted as examples in support of the film theory.

#### **1.9.3.6- Adsorption isotherm**

List of some adsorption isotherms and their corresponding equations.

##### **1- The Henry Isotherm:**

The isotherm has the form:

$$\theta = KC \quad (1.5)$$

where K is the adsorption equilibrium constant, C is the concentration of the adsorbate in the bulk phase in moles per liter and  $\theta$  is the degree of surface coverage.

##### **2- The Freundlich Isotherm:**

The isotherm has the form:

$$\theta = KC^n \quad (1.6)$$

where K and C are defined as in Henry isotherm and n is a constant where  $0 < n < 1$ .

### 3- The Langmuir Isotherm:

The isotherm has the form:

$$\theta / 1 - \theta = KC \quad (1.7)$$

### 4- The Volmer Isotherm:

It has the form:

$$KC = \theta / 1 - \theta \exp (\theta / 1 - \theta) \quad (1.8)$$

where K, C and  $\theta$  are defined as above.

### 5- The Amagat Isotherm:

It has the form:

$$K C^n = \theta / 1 - \theta \exp (\theta / 1 - \theta) \quad (1.9)$$

which has the same form as the Volmer isotherm but the concentration is raised to the power n where  $0 < n < 1$ .

### 6- The Frumkin Isotherm:

The isotherm has the form:

$$KC = \theta / 1 - \theta \exp (-2 a \theta) \quad (1.10)$$

where a is a parameter characterizing the interaction between the adsorbed particles.

### 7- The Parsons Isotherm:

It has the form:

$$KC = \theta / 1 - \theta \exp \left[ \frac{2 - \theta}{(1 - \theta)^2} \right] - 2 \quad (1.11)$$

### 8- The Temkin Isotherm:

This Isotherm has the form:

$$\ln KC = a \theta \quad (1.12)$$

where all terms are defined as described above and  $\theta$  varies between  $0.1 < \theta < 0.9$ .



Note :

$a$  = interaction parameter.

$a > 0$ , Attraction.

$a < 0$ , Repulsion.

Interpretation of adsorption and performance of organic inhibitors can be evidenced by fitting the data to one of the adsorption isotherm

### **1.10- Techniques for Studying Corrosion**

#### **1.10.1-Chemical methods**

##### **1.10.1.1- Gravimetric**

The corrosion rate is evaluated by measuring the change in the weight of metal after exposing the metal specimen of known area to the particular environment for a specific period . This method yields the average rate and is accurate for measuring very low corrosion rate. Method of surface preparation and cleaning of corroded specimens are described by champion <sup>(29)</sup>.

##### **1.10.1.2- Gas -volumetric method**

In this method <sup>(30)</sup> a definite correlation between cathodic reaction rate and the anodic dissolution rate can be established.

##### **1.10.1.3- Solution analysis**

In this method <sup>(31)</sup> chemical or physical techniques are used to identify and estimate the concentration of ions of the metal under examination dissolving in the test environment.

### **1.10.2- Electrochemical methods**

#### **1.10.2.1- Tafel extrapolation method**

This method <sup>(32)</sup> is also described as Tafel plot method or Evan's diagram method or logarithmic polarization method. Actually the measurement of corrosion rate of the system involves the measurement of potential of the electrode for various applied current densities. A plot of E vs log (i) gives a Figure known as polarization diagram .The intercept of anodic and cathodic Tafel lines provides the corrosion current and Tafel slope give  $\beta_a$  , and  $\beta_c$  . In actual practice, polarization curves are obtained from galvanostatic or potentiodynamic method.

#### **1.10.2.2- Electrical resistance method**

An increase in the electrical resistance is a measure of corrosion<sup>(33)</sup> , a decrease in the cross section due to corrosion, increase the electrical resistance, the resistance of the exposed element is measured by Kelvin's bridge along with another element which is protected against corrosion . Instruments have been developed to measure these resistance ratios which are calibrated in mpy. The major advantage of this method is its ability to measure corrosion rate in the liquid and vapor phases and in aqueous and non- aqueous media. This method is used for continuous monitoring in chemical process industries.

#### **1.10.2.3- Polarization resistance method**

Stern and Geary <sup>(34)</sup> have shown that, there is a linear relationship between current and potential when  $\eta < 20$  mV and on measuring  $(d\eta/di)$   $\eta \rightarrow 0$  the corrosion current can be obtained from,

$$I_{\text{corr}} = \beta_a \beta_c / 2.3(\beta_a + \beta_c) \times [di/d\eta] \quad (1.13)$$

The above relationship is valid only for activation controlled reaction. Rajaagopalan and Rangarajan <sup>(35)</sup> have derived relationship with metal corrosion. The simultaneous determination of Tafel slopes and corrosion current at the corrosion potential have been suggested by many authors. Barnartt<sup>(36)</sup>, Reev and Bech Nielsen <sup>(37)</sup>, Oldham and Mansfeld <sup>(38)</sup>, Periasamy and Krishnaswamy <sup>(39)</sup> have made some improvements in this method. Mansfeld <sup>(40-41)</sup> has developed a computer programmer (CORFIT) for the quantitative determination of  $i_{\text{corr}}$  which requires simultaneous determination of both  $R_p$  and  $\beta$ . Various application and the developments of this technique have been reviewed by Lorenz and Mansfeld<sup>(42)</sup>.

#### 1.10.2.4- Coulostatic method

This method <sup>(43-44)</sup> is studied especially for the measurement of corrosion rates of metal in high resistant media. The polarization resistance ( $R_p$ ) is measured from the  $\eta$ - $t$  transient of the electrode on discharging a charged capacitor (C) through the cell. The electrode potential decay is

$$\eta_T = \eta_0 \exp (-t/c_{dl}R_p) \quad (1.14)$$

$\eta_t$  = over potential at any time "t"

$\eta_0$  = over potential immediately after charging the double layer. Of the electrode

$c_{dl}$  = differential capacity of the double layer.

The plot of  $\log \eta_t$  vs  $t$  is a straight line and the slope gives  $1/2.3 C_{dl}/R_p$  and the intercept is  $\eta_0$ .

### 1.10.2.5- Impedance measurements

Electrochemical impedance measurements is an appropriate method for corrosion studies, particularly for corrosion rate determinations <sup>(45)</sup> Mechanistic studies <sup>(46-48)</sup> passivation and passivity process <sup>(49-52)</sup> and for investigation in inhibited systems <sup>(53-58)</sup>. The theoretical analysis of Ac impedance measurements has been analyzed by Warburg <sup>(59)</sup> , to explain the frequency dispersion of the electrode –electrolyte interface and impedance in terms of mass transport (diffusion controlled )process.

Haruyama and Tsuru <sup>(60)</sup> and Mansfeld et al <sup>(61)</sup> have reviewed impedance method . A review of the application of these techniques in corrosion studies has been published by MacDonald et al. The use of Ac impedance technique in various cases has been reviewed by Gabrielli the schematic representation of the interface impedance .Solution resistance is represented by  $R_s$  , charge transfer resistance is given by  $R_{ct}$  or  $R_t$  and the double layer capacitance is represented by  $c_{dl}$  . Using Stern-Geary equation , $i_{corr}$  is obtained from  $R_t$  since.

$$I_{corr} = \beta_a \cdot \beta_c / 2.3 ( \beta_a + \beta_c ) . 1 / R_t . \quad (1.15)$$

### 1.10.2.6- Faradic distortion method <sup>(62)</sup>

On superimposing asinusoidal alternating voltage, i.e.  $E_m$  to the electrode at the corrosion potential, harmonic current components are produced due to the non-linear relationship

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between the current and the potential. Measurements of fundamental ( $i_1$ ), second harmonic ( $i_2$ ), and third harmonic ( $i_3$ ) current components are made for getting  $i_{\text{corr}}$  from the following relationships:

$$I_{\text{corr}} = i_1^2 / \sqrt{48 \cdot i_2 i_3} \quad (1.16)$$

$$1/b_a = 1/4.6 E_m [i_1/i_{\text{corr}} + 4i_2/i_1] \quad (1.17)$$

$$1/b_c = 1/4.6 E_m [i_1/i_{\text{corr}} + 4i_2/i_1] \quad (1.18)$$

The advantage of this method is that the measurement of corrosion current is possible at the corrosion potential without the use of anodic and cathodic Tafel slopes.

### **1.11 - Literature Survey on Corrosion of Aluminum and Aluminum-Silicon alloy and their Inhibition**

Aluminum is extensively used in various industrial operations and the study of its corrosion inhibition in pickling baths is of great importance. In the following a concise literature survey on corrosion inhibition of aluminum by some related organic and inorganic compounds in aqueous solutions medium is given in acidic medium and alkaline medium.

The effects of some organic compounds namely formamide, pyridine, gramine, dipyridyl, piperidine, benzoyl piperidine and dibenzyl disulphide on the corrosion of 2S aluminum in 1M sodium hydroxide and 1M hydrochloric acid have been investigated <sup>(63)</sup>. All the compounds are not effective as inhibitors by themselves in sodium hydroxide solution but their conjoint action with calcium enhances their inhibition efficiency to a great extent. In 1M hydrochloric acid their inhibition efficiency is high, contrary to its behavior in sodium hydroxide, does not possess any beneficial effect on the influence of these compounds. The polarization behavior of

aluminum in the acidic and the alkaline solutions in the presence of these compounds is discussed.

The inhibitive action of substituted anilines against the corrosion of B26S aluminum (Al-Cu alloy) in solutions of phosphoric acid has been studied <sup>(64)</sup>. At 0.5% inhibitor concentration in 0.033M acid the efficiency of the inhibitors increases in the order: O-chloroaniline < N-N-diethylaniline < p-anisidine < p-chloroaniline < m-chloroaniline < N-N-dimethylaniline < m-toluidine < methylaniline < m-anisidine < O-toluidine < o-anisidine < aniline < p-toluidine. At constant acid concentration the inhibitor efficiency increases with increase in the concentration of the inhibitor, whereas at constant inhibitor concentration the efficiency decreases with increase in the concentration of the acid. Very little correlation appears to exist between the  $pK_b$  values or the molecular weight of the inhibitor and the extent of inhibition. N-substituted alkyl anilines have less inhibitive properties than aniline. In the case of toluidine and anisidine the para-compounds appear to be more effective, whereas in the case of chloroaniline the meta-compound is more effective. Maximum inhibition is achieved in those cases where the pH of the inhibited solution lies in the range 3.55–5.75, but where the solution is required for use at low pH values, then meta- and parachloroaniline appear to be the most suitable inhibitors.

A set of aliphatic and aromatic aldehydes has been examined for their effectiveness in preventing the corrosion of aluminum (2S) in 1M NaOH solution and their influence on the anodic polarization behavior <sup>(65)</sup>. It has been found that the aromatic compounds are generally more effective as corrosion inhibitors than the aliphatic inhibitive nature of a solution.

The inhibition of corrosion of B26S aluminum (Al-4% Cu alloy) in solutions of sodium hydroxide has been studied by weight loss and galvanostatic methods<sup>(66)</sup>. At constant alkali concentration the inhibitor efficiency increases with increase in the concentration of the inhibitor (except hydroquinone), and at constant inhibitor concentration the efficiency decreases with increase in alkali concentration. At 2.0% inhibitor concentration in 0.1 M NaOH, the efficiency of the inhibitors increases in the order: p-hydroxydiphenyl (65.3%) < p-aminophenol < p-bromophenol < hydroquinone < p-chlorophenol < p-cresol < p-hydroxyacetophenone < p-nitrophenol < phenol (~ 100%). An increase in exposure period or temperature does not appear to have any marked effect on percentage inhibition which, in most of the cases, remains constant or shows a slight tendency to decrease. The average activation energy in inhibited NaOH in the temperature range 20–50°C is found to be 55 kJ/mole, which is almost the same as that in uninhibited alkali. Polarization data indicate that the inhibitors act as mixed inhibitors with greater effect on the anode reaction.

Inhibition and polarization properties of urea, thiourea (TU), acetyl thiourea (AcTu), phenyl thiourea (PhTu), o-tolyl thiourea (o-tol Tu), m-tolyl thiourea (m-tol Tu), p-tolyl thiourea (p-tol Tu), 1:3-diphenyl thiourea (di-phTu), 1:3-di-o-tolyl thiourea (di-o tol Tu), 1:3-di-m-tolyl thiourea (di-m-tol Tu) and 1 : 3-di-p-tolyl thiourea (di-p-tol Tu) have been studied in relation to the corrosion of aluminum (1060) in 20% nitric acid<sup>(67)</sup>. The polarization experiments were carried out using potentiostatic method. The inhibition efficiencies of the inhibitors were determined at (25-45)°C and it has been observed that the percentage inhibition efficiencies of the inhibitors

increase with increase in temperature., this is attributed to their action as cathodic depolarizers.. The potentiostatic anodic polarization curves in the presence of the inhibitors shift towards lower current density region as compared with the curve of the uninhibited solution.

The corrosion rates and potentials were measured at 30°C for aluminum in 0.1–0.5 M unstirred aerated sodium hydroxide solutions containing  $10^{-4}$ – $10^{-1}$  M  $\text{Na}_2\text{CrO}_4$ <sup>(68)</sup>. Galvanostatic anodic polarization measurements were carried out within the current density range  $10^{-6}$ – $10^{-1}$   $\text{Acm}^{-2}$ . At large dilutions the chromate ion markedly promoted the corrosion of aluminum: the promoting effect increases with concentration up to  $10^{-3}$  M. At higher concentrations the ion behaves as inhibitor, and the corrosion rate decreased sharply with concentration. The corrosion potentials and the polarization curves gave indications that the chromate ion accelerates both the cathodic and anodic reactions. Suggestions concerning their acceleration mechanisms are given, the passivation current increases with concentration up to  $10^{-3}$  M, and then decreases with further increase of concentration. The non-formation of the inhibiting film below  $10^{-3}$  M was explained on the basis that chromium oxide is formed through the disproportionation of an intermediate adsorbed species of valency less than six.

The inhibitive effect of Girard's T and P (G-T and G-P), oxalic, malonic and succinic acid hydrazides and acetophenone G-T, on the corrosion of aluminum in hydrochloric acid solutions was studied by thermometric and weight loss measurements <sup>(69)</sup>. Adsorption of these hydrazine derivatives leads to the formation of a monolayer of the adsorbate on the metal surface. The results indicated compounds



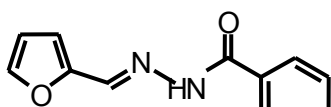
could be classified with the weakly adsorbed substances except acetophenone G-T is strongly adsorbed.

The inhibitive action of some  $\beta$ -diketo compounds on the corrosion of aluminum in 2M hydrochloric acid solution was studied using weight loss, hydrogen evolution and thermometric techniques<sup>(70)</sup>. The adsorb ability of inhibitors is dependant on the basicity of oxygen and nitrogen sites involved. The dissolution reaction of aluminum in hydrochloric acid solution is zero order in presence and absence of  $\beta$ -diketo compounds. The rate constant decreases as the inhibition efficiency increases. The activation energy of reaction increases with decreasing acid concentration and increasing inhibitor concentration. Values of the Arrhenius activation energies agree with those obtained for activation-controlled process.

The inhibition of the corrosion of aluminum in hydrochloric acid solution by some 4-(m-substituted phenylazo) pyrazoles has been studied by weight loss, thermometric and hydrogen evolution measurements<sup>(71)</sup>.

The inhibition efficiencies obtained from the different methods were concordant. Aluminum surface has through a one process. The order of decreased inhibition efficiency for the titled compounds was:  $-H > -CH_3 > -Cl > -OCH_3$ . It is evident that the electrophilic character of these substituents plays a determining role in imparting inhibition efficiency. Increase the positive charge on (acid form) of the inhibitor, which is adsorbed on the aluminum surface. The pK values were also determined and found to decrease in the same sequence as that of inhibition efficiency.

The inhibition efficiency of some furfural benzoyl hydrazones derivatives for the corrosion of aluminum in



hydrochloric acid solution has been investigated by polarization and weight loss methods <sup>(72)</sup>. The inhibitor used having the chemical formula:

where, R = -OCH<sub>3</sub> ( I ), -CH<sub>3</sub> ( II ), -H ( III ), -Cl ( IV ) and NO<sub>2</sub> ( V )

The compounds exhibit high corrosion inhibition efficiency as they adsorbed through two active centers; the heterocyclic oxygen and nitrogen of -NH group. The presence of conjugation in the furfural hydrazones part of the molecule makes the oxygen adsorption active center covered by the extensively delocalized electrons. The inhibition efficiency of the additives decreases in the order: I > II > III > IV > V. This order was explained on the basis of electron density on these molecules.

Corrosion rate of aluminum in 2M HCl solutions in absence and presence of N- (o-hydroxybenzylidene)-3-amino-1, 2,4-triazole, N- (o-hydroxy benzylidene)-5-amino-4-methyl isothiazole and N- (o-hydroxy benzylidene)-2-amino pyrazine was studied <sup>(73)</sup>. The inhibition efficiencies registered by the different methods have been found in good agreement. The inhibition effect depends on both the concentration and the character of the additives. The process occurs through physical adsorption. The degree of surface coverage ( $\theta$ ) of the adsorbed additives has been determined. The results obey the Langmuir adsorption isotherm. The effect of chemical constitution on the order of inhibition efficiency of the studied compounds was discussed.

The effect of (salicyl aldehyde) 2-hydroxy acetophenone ethylene di-imine (L1), phenyl hydrazine-2-hydroxy acetophenone (L2), N-isonicotinic amide salicylaldehyde imine (L3) and benzaldehyde-2-hydroxyazine (L4) on the dissolution of aluminum in 2M HCl was investigated using thermometric technique <sup>(74)</sup>. All the compounds act as inhibitors, and the order of inhibition was consistent with the basicity of oxygen and nitrogen sites involved and not the chain length. The order of inhibition efficiency was: L3 > L4 > L1 > L2.

The inhibitive effect of pyridine, aniline, 2-picoline, 3-picoline, 4-picoline and 2,4-lutidine on the corrosion behavior of aluminum alloys in 1% HCl solution was studied using weight loss and potentiostatic polarization techniques <sup>(75)</sup>. All the compounds are more effective for alloy compared to the other two alloys. An increase in temperature has negative effect on the inhibition efficiency. Polarization studies and steady state corrosion potential measurements reveal that the inhibitors retard the corrosion by predominantly acting on local cathodes although they are also partially effective on the anode.

The effect of urea, thiourea and some of its derivatives; namely phenylthiourea, o-tolylthiourea, m-tolylthiourea, p-tolylthiourea, 1,3-di-o-tolylthiourea, 1,3-di-m-tolylthiourea and 1,3-di-p-tolylthiourea on the corrosion of 1100 aluminum in 1% HCl solution was studied at different temperatures <sup>(76)</sup>. The inhibition efficiency of the inhibitors was found to increase with temperature increase from 25°C to 45°C. Better inhibition was given by all compounds after 48 hours immersion period the effectiveness of the compounds decreases,

The dissolution of aluminum in HCl and NaOH solutions in the presence of semicarbazide, thiosemicarbazide and sym-diphenylcarbazine as corrosion inhibitors has been studied using thermometric, weight loss and polarization methods<sup>(77)</sup>. The higher inhibition efficiency of aluminum in hydrochloric acid solution, The adsorptions of these compounds were found to obey Frumkin adsorption isotherm. Cathodic polarization measurements showed that these compounds are cathodic inhibitors and their adsorption in the double layer does not change the mechanism of the hydrogen evolution reaction. The results are analyzed in terms of both molecular and cationic adsorption.

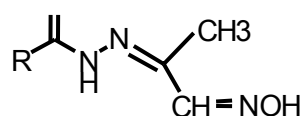
The inhibitive effect of some 4-arylhydrazone-2-pyrazoline-5-one derivatives on the dissolution of aluminum in 2M HCl has been investigated by weight loss, thermometric, hydrogen evolution and galvanostatic polarization techniques <sup>(78)</sup>. All the methods gave similar results. An increase in the concentration of the compound increases the inhibition efficiency leading to decrease in corrosion rate. The activation energy of the dissolution reaction increases as the inhibitor efficiency increased. The values of free energy of adsorption ( $\Delta G^{\circ}_{\text{ads.}}$ ) have been calculated and discussed. These compounds act as general type inhibitors adsorb on both anodic and cathodic sites. Electro capillary curves support the tendency of inhibitors to adsorb on the metallic surface.

Pyridine and some of its selected derivatives were studied as corrosion inhibitors for high purity aluminum in 2M HCl using D.C. polarization technique <sup>(79)</sup>. The studies were carried out in a wide range of concentration (from  $5 \times 10^{-5}$  to  $1 \times 10^{-3}$  M). The results revealed that pyridine derivatives are adsorbed on aluminum surface

according to the Freundlich isotherm. The obtained values of free energy of adsorption ( $\Delta G^\circ_{\text{ads.}}$ ) suggest that the adsorptive properties of the compounds under consideration is likely to be the physical type. The polarization curves showed that the compounds act as cathodic type inhibitors.

The effect of 1,10-phenanthroline (PHEN), bathophenanthroline (BPHEN), bathophenanthroline di-sulphonic di-sodium salt hydrate (BPHENS), 2,2'-bipyridyl (PIPY) and 2,4,6-tris (2-pyridyl)-1,3,5-tris (PYT) and their complexes with  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  ions on the corrosion of pure aluminum<sup>(80)</sup>. Measurements were carried out at cathodic, open circuit and potentials. The four inhibitors were found to be predominantly anodic type for pure aluminum and cathodic for its alloys.

The inhibition of the corrosion of aluminum in 2M HCl solutions by some bi-acetyl monooxime derivatives has been studied using weight loss, thermometric and galvanostatic techniques<sup>(81)</sup>. The inhibitors used were:



$\text{R} = \text{H}$  (I),  $-\text{CH}_2\text{CN}$  (II),  $-\text{CH}_2\text{CH}_3$  (III),  $-\text{CH}_2\text{CH}_2\text{CH}_3$  (IV) and  $-\text{CH}_2\text{CH}(\text{CH}_3)_2$  (V)

The three techniques gave concordant results. The inhibition efficiency of the additives increases in the order:  $\text{I} > \text{II} > \text{III} > \text{IV} > \text{V}$ . The inhibitors appear to function through general adsorption following the Langmuir adsorption isotherm. In the compounds studied, the N atom of  $-\text{NH}$  group, O atoms of both  $\text{C}=\text{O}$  and  $-\text{NOH}$  groups are the key atoms involved in the cathodic and anodic

chemisorptions, respectively. The cathodic adsorption depends on the effective electron density in N atom but the electron density on O atoms affects the anodic polarization. The cathodic polarization is more pronounced than the anodic polarization and can be interpreted on the basis that N atom is more basic than O atom. Steric hindrance due to increase in the number of bulky groups attached to C=O also play an effective part in determining the extent of adsorption and hence the order of inhibition of the inhibitors used. The steric hindrance increase in the order V > IV > III > II > I . On the other hand, the order of increasing inhibition efficiency is reversal to the order of increasing the steric hindrance.

The inhibitive effect of some hydrazine derivatives on the dissolution of aluminum in 2M HCl solution has been studied <sup>(82)</sup>. The volume of the hydrogen evolved was followed, as functions of the corresponding rates of dissolution were determined. The inhibition efficiencies of the hydrazine derivatives were evaluated as the percentage reduction in reaction rate. The obtained results were found to be in good agreement with those given by the thermometric and weight loss methods. Adsorption of the studied hydrazine derivatives occurs in one step as a monolayer of the adsorbate on the metal surface, with the exception of diformyl hydrazide. The results indicate the adsorption of hydrazine derivatives occurs through their carbonyl group. The inhibition efficiency of all inhibitors decreases in the following order: cyan acetyl hydrazide > cinnamyl hydrazide > tri-chloro acetyl hydrazide > Di-formyl hydrazide > salicyl hydrazide > iso butylryl hydrazide.

The results indicate that, all the inhibitors examined are adsorbed on the corroded surface of aluminum in one step except the diformyl

hydrazide is the only one among these compounds which contains two carbonyl groups where others contain only one carbonyl group. This behavior can be explained assuming that the hydrazines are adsorbed on the surface of aluminum through their carbonyl groups while their tails protrude into the solution. Adsorption through the carbonyl group on the aluminum metal surface would depend essentially on its charge density. The magnitude of the latter should depend on the substituted group accordingly, cyan acetyl hydrazide should exhibit the highest adsorption tendency and hence the largest corrosion inhibitive effect. In other hand, isobutyl hydrazide is the one with the lowest bonding power and hence the least corrosion inhibition property.

The inhibition of the corrosion of Al-Cu alloy in hydrochloric acid by some N-heterocyclic compounds has been studied in relation to the concentration of both acid and inhibitors<sup>(83)</sup>., the effect of temperature on the inhibition efficiencies has been studied. In general, at constant acid concentration, inhibition efficiency increases with increasing the inhibitor concentration and with rise in temperature. Except for the three picolines, the efficiency also increases with increase in acid concentration. The results indicated that, at an inhibitor concentration range from 0.05-1.0 M HCl the inhibition efficiency decreases in the following order:

acridine > pipridine > pyridine > 2-picoline > 3- picoline > 4-  
picoline.

The inhibitors appear to function through general adsorption following Langmuir adsorption isotherm. However galvanostatic polarization data suggest that in the case of all six inhibitors the

cathode is preferentially polarized under the influence of an external current (cathodic inhibitors).

Fouda et al. <sup>(84)</sup> investigated the inhibitive action of some oximes,  $\beta$ -diketones and hydrazides compounds on the corrosion of aluminum in 2M hydrochloric acid solutions using galvanostatic polarization technique. The results suggest that, in presence of inhibitors, the anode is preferentially polarized under the influence of an external current. The order of decreasing inhibition efficiency among the three groups of compounds is: oximes >  $\beta$ -diketones > hydrazides. The inhibitors appear to function through a Temkin adsorption isotherm.

The inhibitive effect of sodium silicate on the corrosion of aluminum-lithium alloy in alkaline medium was studied by weight loss and electrochemical methods <sup>(85)</sup>. The results show that sodium silicate significantly inhibits the corrosion of aluminum -lithium alloy in alkaline medium. The addition of small amounts of barium chloride further enhances the inhibition of corrosion of aluminum-lithium alloy due to synergistic effect. The suitable mechanism of corrosion, inhibition and synergism is discussed.

El Batouti et al <sup>(86)</sup> studied the inhibitive effect of surfactants compounds as corrosion inhibitors for corrosion of Al in HCl solution using weight loss method . These compounds are none ionic such as triton x -100 and ionic such as dodecyl sodium sulfate (**DSS**) and octyl sodium sulfate (**OSS**). The inhibition efficiency depends on the types of SAS and the inhibitor concentration and it was found to vary from 11.2 to 92.2 %. The activation energy of inhibition decreases in the same order as the percentage reduction in the rate of corrosion.



The inhibition of the corrosion of the aluminum alloy 3003 in a solution of 3% NaCl by  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{NO}_2^-$  and  $\text{CrO}_4^{2-}$  ions<sup>(87)</sup>. The methods used are the determination of the polarization curves and the metallographic examination of the surface condition. The tested ions inhibit the corrosion process. The comparative study of the effect of these ions shows that the  $\text{Mg}^{2+}$  ions are the most efficient ones at the temperature from 25 to 65°C. The inhibition efficiency increases with the concentration of these ions and reaches a maximum value of 86 % for  $5 \times 10^{-2} \text{M}$ . As a consequence, the gap between pitting and corrosion potentials becomes larger. At 75°C,  $\text{Mg}^{2+}$  ions tend to stimulate corrosion of alloy 3003 in the chloride solution considered.

Several epoxy ester resins inhibit the hydrogen evolution caused by aluminum pigment in aqueous alkaline media. At pH 8 less hydrogen is evolved than at pH 10<sup>(88)</sup>. One particular epoxy ester resin (EPE b) is an excellent corrosion inhibitor especially. At the high pH value of 10. An increase of epoxy ester addition results in a decreased hydrogen evolution, i.e., an increase of corrosion inhibition. Corrosion inhibition of aluminum pigment by the epoxy ester (EPE b) is not significantly affected by the addition of paint resins, saturated polyester or melamine resin.

The inhibitive influence of salicylic acid, as well as phthalic acid in conjunction with calcium acetate, on the corrosion of aluminum in 1.0 N NaOH was studied by weight. loss, gasometric and polarization measurements<sup>(89)</sup>. The inhibition efficiency values determined by these techniques showed close agreement. The combination of salicylic acid (or phthalic acid) and calcium acetate showed a synergistic inhibition effect. The shift in the steady OCP

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(open circuit potential) values for aluminum electrode dipped in 1.0 N NaOH, caused by the increasing addition of the inhibitor, was not considerable. Polarization studies revealed that the corrosion of aluminum in 1.0 N NaOH was predominantly under anodic control, in the presence as well as in the absence of the inhibitor.

The corrosion of commercial aluminum alloy sheets in different concentration of  $H_2SO_4$  and HCl solution was studied using the weight loss technique from 303 K to 313 K<sup>(90)</sup>. The difference in corrosion rate of aluminum in  $H_2SO_4$  and HCl solution without inhibitor was attributed to difference in activation energies of the metal acid solution reaction. Pre-exponential factors derived from the Arrhenius plot for both acids were observed to be approximately the same value at constant temperature and concentration. 2-Acetyl pyridine- (4-phenyl) thiosemicarbazone (PTSC) was used as corrosion inhibitor. The maximum inhibition efficiencies obtained were 76% and 28% in HCl and  $H_2SO_4$  solution respectively at concentration of  $5 \times 10^{-4}$  M at 303 K. Mechanism of physical adsorption is proposed. PTSC was found to obey the Langmuir isotherm at 303 K and 313 K in  $H_2SO_4$  solution but obeyed the Flory-Huggins isotherm at 323 K in HCl solution first order type of reaction mechanism was obtained from the kinetic treatment of the weight.

The inhibitive influence of tetra ethyl ammonium bromide was studied, in the absence as well as in the presence of CaO, on the corrosion of Al in 4.0 N NaOH by weight loss, gasometric and polarization measurements<sup>(91)</sup>. The values of percentage inhibition efficiency determined by the methods showed close agreement. The combination of tetraethyl ammonium bromide and CaO was found to show synergistic inhibition effect. The steady OCP value for Al

electrode, dipped in 4.0 N NaOH, was not considerably shifted by the increasing addition of the inhibitor. It was shown by polarization studies that the corrosion of Al in 4.0 N NaOH was predominantly under anodic control, in the presence and in the absence of the quaternary salt. A similar observation was made in the presence of the salt and CaO. The nature of inhibition was found to be of mixed type.

The electrochemical and surface properties of aluminum in 0.05M citric acid solutions of pH 2-8 were studied by open circuit potential (OCP), potentiodynamic polarization and potentiostatic current-time transient measurements<sup>(92)</sup>. The OCP reached a steady-state value very slowly, probably due to the slow rate of detachment of surface complexes into the solution. The corrosion kinetic parameters  $E_{corr}$ ,  $i_{corr}$  and  $b_a$  suggest that surface processes are involved in the dissolution kinetics, especially. In the pH range 3-6. Current-time transient measurements confirm that, in citric acid solutions of pH 3-6, the dissolution is controlled by surface processes, i.e., by the rate of detachment of surface complexes, while in solutions of pH 2, 7 and 8 dissolution is under mass-transport control. The addition of fluoride ions to citric acid changes the controlling steps of the dissolution process. Citrate and fluoride ions compete for adsorption sites at the oxide surface, and adsorption of these ions is a competitive and reversible adsorption.

The inhibition efficiency of vanillin towards the corrosion of aluminum in 5M HCl solution was measured using weight loss measurement, hydrogen evolution method, thermometry and potentiostatic polarization techniques<sup>(93)</sup>. The results drawn from the

different techniques are comparable and exhibit a small discrepancy. It was found that vanillin act as a good inhibitor for the corrosion of aluminum in 5 M HCl solution. The inhibition efficiency increases as the concentration of vanillin is increased . The adsorption on the aluminum surface follows Langmuir isotherm.

The inhibitive behavior of cadmium sulfate ( $\text{CdSO}_4$ ) on the corrosion of aluminum in 1M HCl was investigated using fluorospectrophotometry and mass loss techniques<sup>(94)</sup>. Results showed that  $\text{CdSO}_4$  was effective, especially at higher temperatures. Corrosion rate data obtained from the two techniques were consistent. The inhibition mechanism was investigated using X-ray photoelectron spectroscopy and scanning electronic microscopy.

The corrosion behavior of aluminum in 10% HCl was studied in the presence of transition metal sulfates such as iron, cobalt, nickel, copper, and zinc sulphate using galvanostatic and weight loss methods<sup>(95)</sup>. Iron and zinc sulphate retard the corrosion at all concentrations where as nickel and copper inhibit the reaction of aluminum in hydrochloric acid up to 100-ppm concentration. Cobalt sulphate accelerates corrosion at all studied concentrations. Polarization studies reveal the fact that iron and zinc are effective on cathodic sites.

The adsorption and corrosion inhibition of the anion surfactants such as dodecyl sulphonic acid sodium salt (DSASS), dodecyl benzene sulphonic acid sodium salt (DBSASS) and soduim dodecyl sulphate (SDS) on the aluminum surface in hydrochloric acid solution were studied using the weight loss method <sup>(96)</sup>. It was found that the adsorption of surfactant could prevent aluminum from dissolution and adsorption is according to Langmiur's isotherm. The

thermodynamic parameters such as adsorption heat, adsorption entropy and adsorption free energy were calculated. Also, the changes of the contact angles of aluminum sheets with and without surfactants were determined. corrosion inhibition of the anion surfactants on aluminum surface were discussed.

The inhibitive capabilities of Clotrimazole (CTM) and Fluconazole (FLC), two antifungal drugs, on the electrochemical corrosion of aluminum in 0.1 M HCl solution has been studied using weight loss measurements at 30 and 50 °C. The results indicate that both compound act as inhibitors in the acidic corroding. At constant acid concentration, the inhibition efficiency (%*I*) increased with increase in the concentration of the inhibitors. Increase in temperature increased the corrosion rate in the absence and presence of the inhibitors but decreased the inhibition efficiency <sup>(97)</sup>. CTM and FLC adsorbed on the surface of aluminum according to the Langmuir adsorption isotherm model at all the concentrations and temperatures studied. Phenomenon of physical adsorption is proposed from the activation parameter obtained. Thermodynamic parameters reveal that the adsorption process is spontaneous. The reactivity of these compounds was analyzed through theoretical calculations based on AM1 semi-empirical method to explain the different efficiencies of these compounds as corrosion inhibitors. CTM was found to be a better inhibitor than FLC.

The inhibiting effect of some Schiff bases on the corrosion of AA3102 aluminum in 0.1 M Hcl has been studied <sup>(98)</sup> by the means of the hydrogen evolution and electrochemical impedance spectroscopy .The Schiff bases 2-hydroxyacetophenone-etansulphonyihydrazone, Salicylaldhyde-etansulphonylhydrazone,5-bromosalicylaldehyde-

etansulphonylhydrazone and 5-chlorosalicyl aldehyde- etan sulphonylhydrazone were synthesized from salicylaldehyde and the corresponding amine. The hydrogen evolution tests showed that the corrosion resistance was greatly enhanced in presence of inhibitor these result were confirmed by the impedance measurements where it was observed that the effect of inhibitor addition appears by an increase in the resistance and by decrease in the capacity of the interface. Its suggest that their effect depend on their concentration and the molecular structures .the maximum inhibition efficiencies were obtained for 5-bromo salicyladehyde- etansulphony hydrazone and 5-chlorosalicylaldehyd-etansulphonylhydrazone by both method.

Chemical and electrochemical corrosion measurements are applied using bis-and mono-azo dyes as corrosion inhibitors for aluminum in hydrochloric acid <sup>(99)</sup>. The Frumkin's adsorption isotherm is found to be ideally applied .The higher inhibition efficiency of the azo dye additives in acidic solution may be due to the less negative potential of aluminum in HCl solution, favoring adsorption of the additive. The decrease in corrosion rate associated, with increase in the cathodic over voltage and a positive shift in the corrosion potential denotes inhibition of a mixed type and their adsorption in the double layer does not change the mechanism of the hydrogen evolution reaction.

A quantum chemical study of the corrosion inhibition proberites of pyridine and its derivatives at the aluminum electrode in hydrochloric acid was carried out <sup>(100)</sup> . Based on the calculated results the compounds were adsorbed on the metal surface mainly in their protonated forms .The models of the inhibitors adsorption on

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the Al-surface were discussed. The most favourable model is that the inhibitor molecule is adsorbed at the Al surface in an inclined state, and the electron of the Al-surface is transferred to the inhibitor. The coadsorption of the inhibitor,  $\text{Cl}^-$  and  $\text{H}_{\text{ads}}$  was discussed.

The inhibiting effect of tetradecyl-1,2-diolpropenoxyates on the dissolution of aluminum in 1M HCl was studied using weight loss and polarization measurements<sup>(101)</sup>. The inhibition efficiency increases with increasing concentration and number of propene oxide per molecule and with decreasing temperature. These compounds are adsorbed on the aluminum surface according to the Freundlich's adsorption isotherm. The values of the standard free energy of adsorption suggest that the adsorptive properties of the compounds under consideration approach those of the physical type. The effect of temperature on aluminum dissolution in 1M HCl was studied and the values of the activation energy in the presence and absence of the inhibitor compounds are calculated.

The inhibitive effect of some pyrazoline compounds on the dissolution of Al in 2 mol L<sup>-1</sup> HCl solutions was investigated by weight-loss and polarization measurements<sup>(102)</sup>. The inhibition efficiencies of these compounds were evaluated. It was found that the efficiency of the inhibitor decreases by increasing the temperature of the dissolution reaction indicating that the inhibition of Al occurs through physical adsorption of inhibitors. Addition of cations such as  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  or  $\text{Ni}^{2+}$  decreased the dissolution rate of Al in 2 mol L<sup>-1</sup> HCl. So when pyrazoline compounds were added the corrosion rate was decreased. This behavior was explained on the basis that the inhibitors form complex species with the added cations which are more adsorbed on Al surface.

The use of some p-substituted benzoic acid derivatives as a low cost inhibitors for the corrosion of Al in 60%  $\text{H}_3\text{PO}_4$  solution was expolred by weight loss and galvanostatic polarization measurements<sup>(103)</sup>. The inhibition efficiency of the compounds increase in the order : p-OH > p-NH<sub>2</sub> > benzoic acid > p-Br > p- NO<sub>2</sub>. This order is not affected by the variation of the temprature in the range 30-60 °C .The rate of corrosion is affected by both the concentration of inhibitors and the temprature of the medium . The reaction rate was propotional to the absolute value of Hammett constant ( $\sigma'$ ) .

The effect of the temprature on the corrosion behavior of the Al 6063 alloy in  $\text{H}_3\text{PO}_4$  was studied by cyclic voltametry, polarization and further electrochemical methods<sup>(104)</sup> .The corrosion processes were found to be depend strongly on the temprature (20-50°C) as will as the amount of CO<sub>2</sub> ,dissolved in  $\text{H}_3\text{PO}_4$  .In aerated  $\text{H}_3\text{PO}_4$  the corrosion of Al 6063 occurred at 30°C .The CO<sub>2</sub> dissolved in  $\text{H}_3\text{PO}_4$  retarded the cathodic and anodic reactions which was explained by the formation of a passivating surface layer on Al 6063.At > 30°C, accelerated reactions occurred on the metal/oxide or oxide/solution interface resulting in a reduced anticorrosive effect of the surface film.

The inhibiting effect of N,N-bis (chloro-bromo-and flouro),phenyl-4,4bipyridiniumchlorides on the corrosion of Al in 1.5 M HCl was studied.Hydrogen evolution,weight loss and polarization measurements were employed<sup>(105)</sup> . The three diferent teqniques demonstrate the agreement and conformity of the expected results as to the type of inhibition and sequence of effeciencies of the studeid compounds.



Inhibition of the corrosion of aluminum in hydrochloric acid by sulfonic acid (SA), sodium cumene sulfonate (SCS), and sodium alkyl sulfate (SAS) has been studied<sup>(106)</sup>, using weight loss and potentiostatic polarization method. The results drawn from the two techniques are comparable and exhibit small discrepancy. The inhibition action depends on the chemical structure and the concentration of the inhibitor, the concentration of the corrosive media, and the temperature. The efficiency of inhibitor increases in the order: SAS < SCS < SA in the study of the concentration range. Results for weight loss indicated inhibitor efficiency (I%) increased with increasing inhibitor concentration, the inhibitor efficiency (I%) decreased as the concentration of HCL increased. For the tested additive, the increase in temperature resulted in decreasing of the inhibitor efficiency (I%) and decrease in degree of surface coverage ( $\theta$ ). The degree of surface coverage ( $\theta$ ) increased linearly with the logarithm of the inhibitor concentration fitting a Temkin isotherm.

A novel series of self-assembled nonionic Schiff bases amphiphiles was synthesized and their chemical structures were confirmed<sup>(107)</sup> using elemental analysis, FTIR spectroscopy and <sup>1</sup>H NMR spectra. The surface activities of these amphiphiles were determined based on the data of the surface and interfacial tension, critical micelle concentration, effectiveness, efficiency, maximum surface excess, minimum surface area. Thermodynamics of adsorption and micellization processes of these amphiphiles in their solution were also calculated. The surface and thermodynamic data showed their higher tendency towards adsorption at the interfaces. The synthesized amphiphiles were evaluated as corrosion inhibitors for aluminum (3CR) at different doses (400-10 ppm) in acidic

medium (4N HCL) using the weight loss and hydrogen evolution techniques. The corrosion measurements showed that the synthesized nonionic Schiff bases could serve as effective corrosion inhibitors. The surface and corrosion inhibition activities were correlated to the chemical structures of the inhibitors.

Aluminum and zinc pigments undergo corrosion in aqueous alkaline media (e.g., water-borne paints) with the evolution of hydrogen <sup>(108)</sup>. The corrosion inhibiting effect of 2-amino and 2-nitrophenol is excellent for aluminum pigment whereas 4-nitro- and 4-aminophenol don't inhibit this corrosion reaction. For zinc pigment the corrosion inhibiting effect decreases in the following order: 2-nitrophenol > 2-aminophenol > 4-nitrophenol > 4-aminophenol. So, for aluminum pigment the possibility of chelate formation (2-substituted phenols) seems to be a basic requirement for corrosion inhibition by phenol derivatives. For zinc pigment possible chelating effect of the inhibitor improves corrosion inhibition but is not a basic requirement. The best overall corrosion inhibitor both for aluminum and zinc pigments is 2-nitrophenol (protection factor 96-99.9%).

Quantum chemistry has been applied to study the possible inhibition efficiency of some aliphatic amines in the corrosion of aluminum in (1N HCL)<sup>(109)</sup>. Results of HOMO- LUMO calculations were correlated with data obtained from electrochemical investigations. The electron donor and electron acceptor action of inhibitors are discussed. Results of this study may also be used in the general evaluation of inhibition corrosion.

Some inorganic compounds have been tested as corrosion inhibitors for 6063 aluminum alloy in 3 % NaCl<sup>(110)</sup>. Li<sup>+</sup> and Mg<sup>2+</sup>

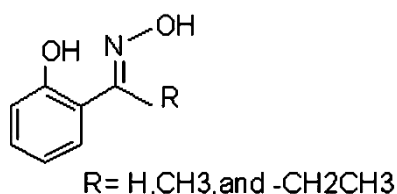
metallic by electrochemical and metallographic methods. The compounds were  $\text{MoO}_4^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{NO}_2^-$  oxo-anions and cations. Results obtained show that these compounds inhibited corrosion of 6063 aluminum alloy in the absence of  $\text{Li}^+$ . However, in the presence of these cations, % inhibition efficiency decreased at elevated temperature.

The effect of benzaldehyde, 2-hydroxybenzoyl hydrazone derivatives on the corrosion of aluminum in hydrochloric acid has been investigated using thermometric and polarization techniques<sup>(111)</sup>. The inhibitive efficiency ranking of these compounds from both techniques was found to be: 2>3>1>4. The inhibitors acted as mixed-type inhibitors but the cathode is more polarized. The relative inhibitive efficiency of these compounds has been explained on the basis of structure of the inhibitors and their mode of interaction at the surface. Results show that these additives are adsorbed on an aluminum surface according to the Langmuir isotherm. Polarization measurements indicated that the rate of corrosion of aluminum rapidly increases with temperature over the range 30-55°C both in the absence and presence of inhibitors. Some thermodynamic data of the adsorption process are calculated and discussed.

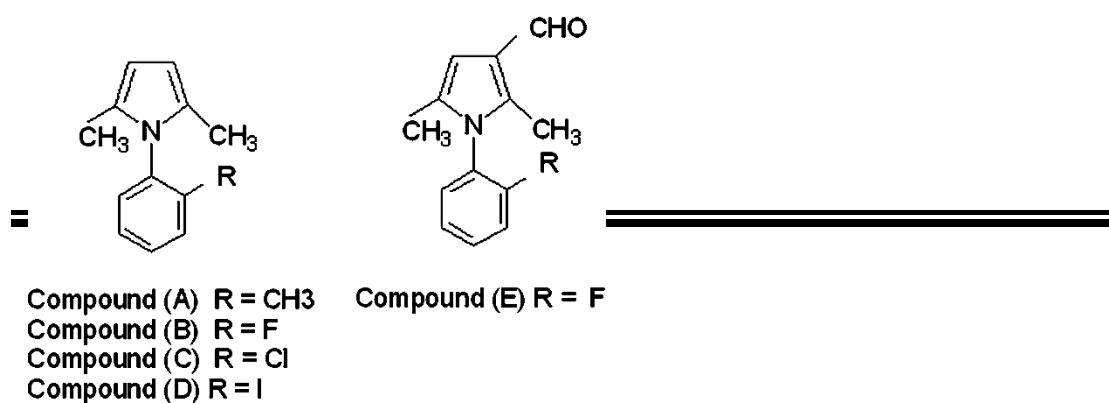
A kinetic-thermodynamic study was made on the dissolution of aluminum in 2 M HCl and 2 M NaOH solutions in the presence of some bis- and mono-azodye derivatives as corrosion inhibitors<sup>(112)</sup>. Chemical and electrochemical corrosion measurements are applied. The three methods gave consistent results. The mechanism of inhibition process is discussed on the basis of an adsorption isotherm, as well as the calculated kinetic-thermodynamic model. The Frumkin adsorption isotherm is found to be ideally obeyed. The

higher inhibition efficiency of the azodye additives in acidic than in alkaline media may be due to the less negative potential of aluminum in hydrochloric acid solution, favoring adsorption of the additive. The decrease in corrosion rate associated with an increase in the cathodic overvoltage and a positive shift in the corrosion potential, in the presence of the investigated azodyes, denotes inhibition of a mixed type (predominantly anodic) and their adsorption in the double layer does not change the mechanism of the hydrogen evolution reaction.

Aluminum and zinc pigments react in aqueous alkaline media (e.g., water-borne paints) with the evolution of hydrogen. The corrosion inhibiting effect by addition of 2-hydroxy oximes gives protection factor up to 99.9% for aluminum more than zinc <sup>(113)</sup>.



The inhibitory activity of some substituted N-arylpyrroles on aluminum corrosion in hydrochloric acid was studied in relation to inhibitor concentration, using potentiodynamic and impedance spectroscopy techniques<sup>(114)</sup>. All investigated compounds were found to act as cathodic -type inhibitors and inhibition was ascribed to the adsorption of inhibitor onto the electrode surface. The inhibiting efficiency of the additives depended on the inductive power of the groups attached to the benzene and/or pyrrole ring. The



carbaldehyde group showed better inhibiting power due to additional condensation on the Al electrode surface.

The impedance results analysed in term of the polarization resistance showed that EIS technique can be successfully applied in the determination of corrosion resistance.

The electrochemical corrosion behavior of wrought Al alloys 2011-T8, 6061-T4 and 6061-T6 was studied in aerated and deaerated 3.5 % NaCl solution at 23°C and compared with that of aluminum <sup>(115)</sup>. The microstructural examination was performed by light and scanning electron microscopy, while open-circuit potentials (OCP), corrosion rates and pitting potentials of the alloys were determined using potentiodynamic and cyclic polarization techniques. The OCP values for all the alloys increased towards the negative in the deaerated compared to aerated solutions. The OCP values in the aerated solutions were generally stable within a 100 mV range.

The corrosion of aluminum was studied in 0.1M halide solution in various concentrations decyl and dodecyl sodium sulphate<sup>(116)</sup>. The results obtained from the potentiodynamic measurement show that the pitting corrosion is inhibited by the presence of organic compounds in the medium. The percentage inhibition was found to increase with increasing the concentration of organic compounds in the medium at constant halide concentration. It was found that the efficiency of inhibition for a given halide concentration decreases in the order of dodecyl sodium sulphate > decyl sodium sulphate. At constant inhibitor concentration, the pitting corrosion was found to decrease in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ .

The inhibitive action of the mucilage extracted from the modified stems of prickly pears, toward acid corrosion of aluminum, was studied using weight loss, thermometry, hydrogen evolution and polarization techniques <sup>(117)</sup>. It was found that the extract acts as a good corrosion inhibitor for aluminum corrosion in 2.0 M HCl solution. The inhibition action of the extract was discussed in view of Langmuir adsorption isotherm. The inhibition efficiency (IE) increases as the extract concentration is increased. The effect of temperature on the (IE) was studied. It was found that the presence of extract increases the activation energy of the corrosion reaction. It was found also that the *Opuntia* extract provides a good protection to aluminum against pitting corrosion in chloride ion containing solutions.

The inhibition of three ethoxylated fatty acids of different molecular weights on the corrosion of aluminum in both 1.0 M HCl and 1.0 M H<sub>2</sub>SO<sub>4</sub> solutions have been studied at different temperatures (25–55 °C) by means of weight loss and potentiodynamic polarization techniques <sup>(118)</sup>. The inhibition efficiency for the three fatty acids increase with the increase in the inhibitors concentration but decreases with increasing temperature. The inhibition efficiency for the three inhibitors decreases in the order (n=20, 40, 80 ):

$$\text{OL [EO]80} > \text{OL [EO]40} > \text{OL [EO]20}$$

The inhibition occurs through adsorption of the inhibitor molecules on the metal surface without modifying the mechanism of corrosion process. Frumkin adsorption isotherms fit well the experimental data of dissolution and adsorption were calculated and discussed.

The inhibition of aluminum corrosion in oxalic acid solution by three cationic surfactants was studied using potentiostatic and potentiodynamic anodic polarization <sup>(119)</sup>. The role of some surfactants in the corrosion of Al in 1 M HCl has been studied using weight loss and galvanostatic polarization techniques. Results showed that the inhibition occurs through adsorption of the inhibitor molecules on the metal surface. The inhibition efficiency was found to increase with increasing inhibitor concentration and decreased with increasing temperature which is due to the fact, that the rate of corrosion of Al is higher than the rate of adsorption. The adsorption of the these compounds on the metal surface is found to obey Freundlich adsorption isotherm. The inhibiting action of these compounds are considerably enhanced by the addition of KI, due to the increase of the surface coverage and therefore indicate the joint adsorption of these compounds and iodide ions.

Thermodynamic parameters for adsorption and activation processes were determined. Galvanostatic polarization data indicated that these compounds act as mixed-type inhibitors. Results obtained from the two techniques are in good agreement<sup>(120)</sup>. Exudates gums from *Pachylobus edulis* (PE) and *Raphia hookeri* (RH) were evaluated as corrosion inhibitors for aluminum in HCl using weight loss and thermometric measurements at 30 – 60 °C. The exudates were found to retard corrosion rate of aluminum. The inhibition efficiency (%1) increased with increaseing in concentration of the exudates. Increase in temperature increased the corrosion rate in the absence and presence of inhibitors but decreased the inhibition efficiency. Both PE and RH exudates gums were found to obey Temkin adsorption isotherm and Kinetic-Thermodynamic.

Model of El-Awady<sup>(121)</sup> et al. at all the concentrations and temperatures studied.

Phenomenon of physical adsorption is proposed from the activation parameters obtained.

Thermodynamic parameters reveal that the adsorption process . Exudate gum from RH was found to be a better inhibitor than PEClotrimazole (CTM)[1-[(2-chlorophenyl)-diphenyl-methyl imidazole], an antifungal drug, was investigated as a corrosion inhibitor for aluminum in HCl using weight loss method. CTM inhibited the corrosion of aluminum in HCl. The inhibition efficiency increased with increase in the concentrations of CTM to reached 90.90% at  $1 \times 10^{-4}\text{M}$ , but decreased with increase in temperature.

Phenomenon of physical adsorption is proposed for the inhibition and the process followed the Langmuir adsorption isotherm and kinetic / thermodynamic model of El-Awady et al. The mechanism of adsorption inhibition and type of adsorption isotherm were proposed from the trend of inhibition efficiency with temperature,  $E_a$ ,  $_{Gads}$ , and  $Q_{ads}$ . Quantum chemical calculations results show that CTM possesses a number of active centres concentrated mainly on the imidazole moiety of the molecule. The highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) were also found around the nitrogen atoms and the cyclic of the benzene rings<sup>(122)</sup>.

Crystal violet dye (CV) was studied as a corrosion inhibitor for aluminum in hydrochloric acid ( $1 \text{ mol dm}^{-3}$ ) and potassium hydroxide ( $0.5 \text{ mol dm}^{-3}$ ) solutions in the temperature range  $30^{\circ}$ - $60^{\circ}\text{C}$  using the gravimetric technique. The effect of iodide ions on the inhibiting efficacy of CV was also assessed. CV was found to inhibit Al corrosion in both aggressive media, exhibiting greater inhibition



efficiency in 1 M HCl (83.6%) than in 0.5 M KOH (23.0%). Inhibition efficiency in 0.5 M KOH was, however, synergistically increased in the presence of iodide ions to attain values up to 85.3%. Inhibition efficiency in the acidic and alkaline solutions increased with CV concentration but decreased with rise in temperature, suggesting physical adsorption of CV on the Al surface. The calculated values of activation energy ( $E_a$ ), free energy of adsorption ( $\Delta G_{ads}$ ), and heat of adsorption ( $Q_{ads}$ ) confirm the physisorption mechanism. The inhibitor adsorption characteristics were approximated by the Freundlich adsorption isotherm <sup>(123)</sup>.

It was found that the addition of the three used surfactants resulted in a decrease of the corrosion current, demonstrating the inhibiting nature of these surfactants. The inhibition efficiency increases with increasing surfactant concentration as well as the number of ethylamine units. It was found that the adsorption of surfactant molecules on the aluminum surface follows the Langmuir adsorption isotherm. The effect of temperature on the inhibition efficiency decreases with increasing temperature. The activation energy of the system increases with the addition of surfactant. On the other hand, it was found that the addition of surfactant shifts the pitting corrosion potential of aluminum toward the active direction, indicating the accelerating effect on pitting corrosion.

The effect of polyamide compounds on the corrosion behavior of aluminum electrode in oxalic acid solution was investigated using potentiostatic and potentiodynamic anodic polarization techniques <sup>(124)</sup>. The inhibition efficiency increases with increasing polyamide concentration until a critical value and then starts to decrease in high polymer concentration indicating a low inhibition efficiency. The

inhibitive action of the polyamide compounds was explained in terms of adsorption of the polyamide compounds on the metal surface and formation of insoluble complexes. The adsorption process was found to obey Temkin adsorption isotherm. The addition of polyamide compounds shift the pitting potential of aluminum electrode to more positive potentials, indicating an increased resistance to pitting attack.

The corrosion behavior of aluminum in 2 M HCl solution in the absence and presence of four compounds of antibacterial drug was investigated using hydrogen evolution, weight loss, and potentiostatic polarization techniques <sup>(125)</sup>. It was found that, the inhibition efficiency of these compounds depends on their concentration and chemical structure. The inhibitive action of these compounds was discussed in terms of blocking the electrode surface by adsorption of the molecules through the active centers contained in their structure. The adsorption process follows Langmuir adsorption isotherm. The effect of temperature on the rate of corrosion in the absence and presence of these compounds was also, studied. Some activated thermodynamic parameters were computed.

The effect of methylene blue (MB) dye on the electrochemical corrosion of aluminum in HCl solutions was studied using gravimetric techniques at 303 and 333 K <sup>(126)</sup>. The results indicate that MB acts as an inhibitor in the acidic corrodent. The inhibition efficiency was observed to be sensitive to acid concentration and increased with an increase in MB concentration but decreased with rise in temperature. Synergistic effects increased the inhibition efficiency on addition of halides namely: KCl, KBr and KI. The experimental data were corroborated with the Langmuir as well as

Flory–Huggins adsorption isotherms. The activation energy values of 19.39 and 30.53 kJ mol<sup>-1</sup> calculated for the corrosion process in the absence and presence of MB, respectively, suggest that the inhibitor molecules are physically adsorbed on the Al surface.

The results of investigations by scanning electron microscopy (SEM) and Auger electron spectroscopy (AES) to study the surface morphology, the composition and thickness of the adsorbed film formed on the surface of aluminum samples in 2 M hydrochloric acid solution containing optimum doses of the blends hexamine–KI and hexamine–CaCl<sub>2</sub> as inhibitors are discussed <sup>(127)</sup>. It is concluded that much higher corrosion resistance and improvement in the surface morphology of aluminum observed due to the marked layer enrichment on the aluminum surface from the blends additives. The results could also explain the effectiveness of the halide ions to facilitate the adsorption of hexamine.

Corrosion inhibition of aluminum in hydrochloric acid solution by hexamine–halide blends (HA–KI and HA–CaCl<sub>2</sub>) was investigated using gravimetric method, open circuit potential and polarization measurements <sup>(128)</sup>. Results showed that single additives HA and KI are moderate inhibitors, while CaCl<sub>2</sub> is poor inhibitor for corrosion inhibition of Al in 2 M HCl solution. In the presence of blends HA–KI and HA–CaCl<sub>2</sub>, the corrosion resistance of aluminum is improved and the corrosion rate (CR) and corrosion current (I<sub>c</sub>) are reduced significantly, so the inhibition efficiency (IE) and polarization resistance (R<sub>p</sub>) are increased. With the mixed inhibitors, there is a compact adsorbed film formation on the surface of Al, due to a synergistic action between the halides ions and HA.

Aluminum pigments corrode in aqueous alkaline media (e.g., water-borne paints) with the evolution of hydrogen<sup>(129)</sup>. The hydrogen corrosion of aluminum pigment can be inhibited by the chelating agent citric acid, which is a renewable raw material and absolutely non-toxic. At pH 8 more hydrogen is evolved as at pH 10 which can be explained with the isoelectric point of aluminum oxide (pH 9) and a chemical reaction of citrate with aluminum. The product of this reaction should be aluminum (III)–citric acid-chelate which is assumed to be the actual corrosion inhibitor. This assumption can be corroborated by tests with aluminum (III)–citric acid-chelates. With increasing addition of citric acid the hydrogen volumes evolved increase, which could also be explained with a chemical reaction of citrate with aluminum.

The molecular behavior of some pyridine derivatives as corrosion inhibitors of iron and aluminum in acid media, were studied quantum electrochemically <sup>(130)</sup>. The calculations were made for three conditions; isolated inhibitor molecule, metal cluster, and finally polarized continuum media. It is concluded that for aluminum the vertical adsorption through nitrogen atom is prevailing, while for iron both vertical and planar adsorptions (through  $\pi$ electrons of aromatic ring) are possible, but the vertical is predominant. The inhibitor chemical potential ( $\mu$ ) and the extent of charge transfer ( $\Delta N$ ) to the metal were determined. A linear correlation between each of these and the inhibition efficiencies are demonstrated. Finally, from the calculated desolvation free energy values as a function of dielectric constant, it is observed that there is an abrupt decrease in the free energies as the inhibitor molecule enters EDL.

Also the calculated desolvation free energies show a linear correlation with experimental inhibition efficiencies.

Sol-gel derived organo-silicate hybrid coatings preloaded with organic corrosion inhibitors have been developed in order to provide active corrosion protection when integrity of the coating is compromised <sup>(131)</sup>. The incorporation of organic corrosion inhibitors into hybrid coatings has been achieved as a result of physical entrapment of the inhibitor within the coating material at the stage of film formation and cross-linking. Entrapped corrosion inhibitor becomes active in corrosive electrolyte and can slowly diffuse out of the host material. To ensure continuing delivery of the inhibitor to corrosion sites and long-term corrosion protection, a sustained release of the inhibitor is achieved by a reversible chemical equilibrium of either ion-exchange of the inhibitor with the coating material or through cyclodextrin-assisted molecular encapsulation. Several organic compounds, such as mercapto benzothiazole, mercapto benzimidazole, mercaptobenzimidazole sulfonate, and thiosalicylic acid, have been selected to evaluate the effectiveness of these two approaches. Corrosion protection performance of the coatings on aluminum alloy 2024-T3 has been examined using electrochemical methods including scanning vibrating electrode technique, potentiodynamic scan, and electrochemical impedance spectroscopy.

The inhibition effect of some amino acids towards the corrosion of aluminum in 1 M HCl + 1 M H<sub>2</sub>SO<sub>4</sub> solution was investigated using weight loss measurement, linear polarization and SEM techniques<sup>(132)</sup>. The used amino acids were alanine, leucine, valine, proline, methionine, and tryptophan. The effect of inhibitor

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concentration and temperature against inhibitor action was investigated. It was found that these amino acids act as good inhibitors for the corrosion of aluminum in 1 M HCl + 1 M H<sub>2</sub>SO<sub>4</sub> solution. Increasing inhibitor concentration increases the inhibition efficiency and with increasing temperature the inhibition efficiency decreases. It was found that adsorption of used amino acids on aluminum surface follows Langmuir and Frumkin isotherms.

An electrochemically integrated multi-electrode array namely the wire beam electrode (WBE) has been applied in novel experiments to study the anodic dissolution behavior of aluminum (AA1100), which was exposed to corrosive media with and without the presence of corrosion inhibitor potassium dichromate <sup>(133)</sup>. The objective of this work is to demonstrate the applicability of the WBE for investigating corrosion processes under anodic polarization. Anodic current measurements and mapping have been made, for the first time, with the WBE surface being anodically polarised. Pitting potential as well as anodic dissolution profile has been successfully determined by mapping anodic dissolution currents over the anodically polarised WBE surface. The pitting potential determined using the WBE method was found to correlate well with that determined using the conventional pitting scan method; and the anodic dissolution profile determined using the WBE method was found to correlate with maps obtained using the scanning reference electrode technique (SRET). Potassium dichromate was found to significantly affect the pitting potential, anodic dissolution profile and pitting initiation characteristics of aluminum. Two mechanisms of localized corrosion initiation have been identified. For WBE surface under free corrosion or low anodic polarization conditions, the

initiation of localized corrosion was found to be due to the disappearance of minor anodes, which lead to accelerated dissolution of a few major anodes. For WBE surface under large anodic polarization,. This work suggests that the WBE method is useful for understanding the electrochemical behavior of localized anodic processes.

It has been characterized and evaluated the 2024-T351 and 7050-T7451 aluminum alloys pitting corrosion in naturally aerated chloride aqueous solutions containing chromate, molybdate and tungstate <sup>(134)</sup>. It has been carried out electrochemical and non-electrochemical immersion corrosion tests accompanied by surface metallography analysis using an optical microscopy. Chromate for the two alloys and in molybdate for 7050 has corrosion inhibiting effects, whereas tungstate promotes the pitting corrosion for these alloys. Despite inhibitor presence, when pits have been nucleated, they grow with the same intensity.

Most high strength aluminum alloys used in the aircraft industries are susceptible to corrosion. Up to now hexavalent chromium is the conventional corrosion inhibitor <sup>(135)</sup>. Because chromium in hexavalent state is carcinogenic, it is necessary to develop effective alternative inhibitor systems. We investigated magnetron sputtered substoichiometric and stoichiometric aluminum nitride ( $\text{AlN}_x$  with  $x \leq 1$ ) coatings for corrosion protection of aluminum alloys 2024-T3, 6061-T4 and 7075-T6. The corrosion behavior of the treated surfaces was tested by anodic polarization scanning and salt spray testing.

From the polarization curves it can be concluded that magnetron sputter coating with  $\text{AlN}_x$  leads to a higher pitting potential of the

three aluminum alloys investigated. The salt spray tested samples also confirm the protective effect of the coatings. In addition we found that AlN<sub>x</sub> layers with high nitrogen content lead to a stronger shifting in pitting potential than those with low nitrogen content. Anyway, the results of the salt spray testing show that particularly nitrogen-rich AlN<sub>x</sub> layers are less stable towards NaCl electrolyte.



# AIM OF THE PRESENT WORK

## The Present Work Was Aimed To:

- 1-Investigate the inhibiting effect of 4-aminophenazone and phenazone as corrosion inhibitors for aluminum and aluminum-silicon alloy in 1 M HCl.
- 2-Determine the rate of corrosion of aluminum and Al-Si alloy, in absence and presence of these organic compounds by weight-loss method (chemical method) at 30 °C.  
and Determine the rate of corrosion of aluminum and aluminum – silicon alloy by potentiodynamic polarization method and impedance method (electrochemical method) at 25 °C
- 3-Study the effect of the temperature on the corrosion rate by one of the two methods to:
  - (a) Calculate the thermodynamic parameters related to the corrosion process.
  - (b) Determine the type of adsorption isotherm and the kind of adsorption (physical or chemical).
- 4-Determine the mechanism and percentage inhibition of these investigated compounds.
- 5-Investigate the synergistic effect of KI, KBr, and KSCN on the corrosion inhibition of the investigated compounds.
- 6-Finally, ordered these organic compounds according to their percentage inhibition efficiencies.