CHAPTER I
INTRODUCTION

Introduction

Over the recent years, water-based paints have extendedly been produced, under increasing environmental restrictions. These coatings are widely recognized as the environmental friendly paints due to their water-based resin composition and low level of volatile organic compounds (VOC). Stricter environmental laws in 1950s have intensified researches on water-based paints, leading to a gradual substitution of solvent-based counterparts since 1970s [1-4]. Less volatility, more safety especially against fire risk and better hygienic conditions during production and application are the main advantages of using water-based paints [5].

Also in the early 1990's the US Environmental Protection Agency (EPA) issued guidelines to limit the use of volatile organic compounds (VOC) in order to reduce air pollution as set by the Clean Air Act, leading to significant changes in anti-corrosive paint formulations which include relatively large amount of VOCs [6]. The toxic nature of some VOCs, in addition to the toxicity of the most traditional anti-corrosive pigments, which contain essentially heavy metals e.g. Pb, Cr, Ba …etc., has been another driving force for change in paint formulations. Consequently, paints manufacturers have found themselves caught between the anvil of environmental regulations and the hammer of the consumers whom will not settle with a lesser level of performance. Therefore, they have been exerting great efforts to comply with environmental legislations, which are expected to be stricter and more exacting in the future [7]. These efforts come in switching from using solvent-borne coatings to the use of more friendly to the environment coatings as water-borne, powder, high solids or low VOC coatings, and radiation curable coatings. In addition, more safe organic corrosion inhibitors can be introduced in paint formulations, in additive levels, instead of the aforementioned toxic anti-corrosive pigments.

1.1. Corrosion

1.1.1. Definition of corrosion

Corrosion can be defined as a naturally occurring physical and chemical deterioration of a metal due to reaction with its environment, especially with oxygen [8].

Corrosion is a natural process, which takes place due to the inherent tendency of metals to revert to their more stable compounds, usually oxides. Most metals are found in nature in the form of various chemical compounds called ores. In the refining process, energy is required to produce the metal in the pure state. It is the same energy that provides the driving force causing the metal to revert back to the more stable compound [9].

1.1.2. Corrosion mechanism

According to the mixed potential theory [10], corrosion of metal is a result of an electrochemical reaction, and the corroding metal behaves like a small galvanic cell. This reaction can be divided into two or more oxidation and reduction reactions, which take place simultaneously on the metal surface. Two main partial reactions occur in electrochemical corrosion:

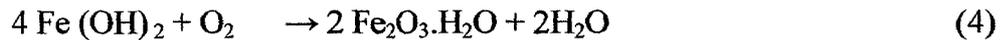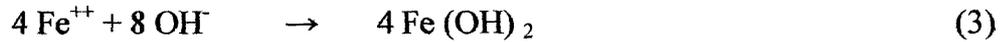#### 1.1.2.1. Anodic dissolution reaction

In all the proposed mechanisms, the initial anodic reaction is the oxidation of metal. In this reaction, the metal will dissolute as a result of electrons loss, and metal ions pass into solution.

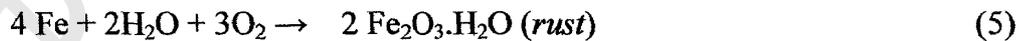#### 1.1.2.2. Cathodic reduction reaction

The nature of cathodic reduction reaction depends on the system under investigation, e.g. hydrogen evolution reaction in acid medium in de-aerated solutions, and oxygen reduction reaction in aerated solutions.

During the overall reaction of corrosion there can be no accumulation of electrical charge. This electrochemical reaction is taking place in the absence of any externally applied potential and the net measurable current is zero.

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A simplified representation of the reactions that occur between iron, water and oxygen to produce rust is given below:

$$4\,Fe \rightarrow 4\,Fe^{++} + 8e^{-}$$ ------------------------------------ *Anodic reaction* (1)

$$4\,H_2O + 2O_2 + 8e^{-} \rightarrow 8\,OH^{-}$$ ------------------------- *Cathodic reaction* (2)

$$4\,Fe^{++} + 8\,OH^{-} \rightarrow 4\,Fe\,(OH)_2 \qquad\qquad (3)$$

$$4\,Fe\,(OH)_2 + O_2 \rightarrow 2\,Fe_2O_3.H_2O + 2H_2O \qquad\qquad (4)$$

Overall reaction

$$4\,Fe + 2H_2O + 3O_2 \rightarrow 2\,Fe_2O_3.H_2O\ (rust) \qquad\qquad (5)$$

1.1.3. Atmospheric corrosion

Atmospheric corrosion can be defined as the corrosion of materials exposed to the air and its pollutants, rather than immersed in a liquid [11]. Atmospheric corrosion severity tends to vary significantly in different locations and, historically, it has been customary to classify environments as rural, urban, industrial, marine, or combinations of these. These types of atmospheres have been described as follows [12]:

1.1.3.1. Rural

Generally, this category is the least corrosive and normally does not contain chemical pollutants, but does contain organic and inorganic particulates. The principal corrodents are moisture, oxygen and to a lesser extent carbon dioxide.

1.1.3.2. Urban

This type is similar to the rural one in that there is little industrial activity. Additional contaminants are of the SO_χ and NO_χ variety, which produced from motor vehicle and domestic fuel emissions.

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1.1.3.3. Industrial

These atmospheres are associated with heavy industrial manufacturing facilities and can contain concentrations of sulfur dioxide, chlorides, phosphates, and nitrates.

1.1.3.4. Marine

Fine wind swept chloride particles, which deposited on surfaces, characterize this type of atmosphere. Marine atmospheres are usually highly corrosive, and the corrosive tends to be significantly dependent on wind direction, wind speed, and distance from the coast.

1.1.4. Corrosion in sea water

In the presence of an electrolyte solution, such as sodium chloride, the anodic and cathodic reactions are modified, and then ferrous chloride will be formed at the anode and sodium hydroxide at the cathode [13], as follow:

$$4Fe + 8Cl^- \rightarrow 4FeCl_2 + 8e^- \qquad (6)$$

$$4H_2O + 2O_2 + 8Na^+ + 8e^- \rightarrow 8NaOH \qquad (7)$$

These two compounds are very soluble and easily acted by oxygen, so that they diffuse away from the metal surface to form ferrous hydroxide or basic salt, which then combine with oxygen to form rust, with the generation of sodium chloride, as represented in the following equations:

$$FeCl_2 + 2NaOH \rightarrow Fe(OH)_2 + 2NaCl \qquad (8)$$

$$4Fe(OH)_2 + O_2 \rightarrow 2Fe_2O_3 \cdot H_2O + 2H_2O \qquad (9)$$
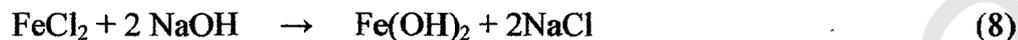
1.1.5. Corrosion in acids

When metals are dissolved in mineral acids, the metal atoms react with hydrogen ions in the water to produce metal ions and hydrogen atoms. Hydrogen atoms may combine to form hydrogen molecules, which may form a layer on the

metal and inhibit the corrosion reaction, or it may be evolved as a gas. Also, hydrogen atoms may react with the dissolved oxygen to form water molecules, as shown in the following equations:

$$Fe + 2H^+ \quad \rightarrow \quad Fe^{++} + 2H \tag{10}$$

$$2H \quad \rightarrow \quad H_2 \tag{11}$$

$$H_2 + \tfrac{1}{2} O_2 \quad \rightarrow \quad H_2O \tag{12}$$

1.1.6. Types of corrosion [14]

There are two main classes of corrosion; the first is the dry corrosion, and the second is the wet corrosion. Both types are electrolytic in nature and depend on the operation of the electrolytic cell at the metal surface.

1.1.6.1. Dry corrosion

The term dry means the absence of water or an aqueous solution. This type is generally metal/gas or metal/vapor reaction involving nonmetals such as oxygen, halogens, hydrogen sulphide, sulphur vapor, etc., and oxidation, scaling and tarnishing are the most important forms. The main characteristic of this reaction is that the initial oxidation of the metal, reduction of the non-metal, and formation of compound occur at the same place (the metal/non-metal interface). If the compound be volatile or discontinuous, further interaction at the interface (or through a thin film of constant thickness) is possible and in most cases the reaction rate will tend to remain constant with time (linear law). If the film is continuous it will present a barrier to the reactants and further interaction will necessitate passage of the reactants through the film by: (a) Diffusion of the non-metal or, (b) Diffusion and migration of ions of the reactants.

1.1.6.2. Wet corrosion

The term wet includes all reactions in which an aqueous solution is involved in the reaction mechanism. In wet corrosion, the oxidation of the metal and reduction of a species in solution (electron acceptor or oxidizing agent)

occur at different areas on the metal surface with consequent electron transfer through the metal from the anode (metal oxidized) to the cathode (electron acceptor reduced). The thermodynamically stable phases formed at the metal/solution interface may be solid compounds or hydrated ions (cations or anions) which may be transported away from the interface by processes such as migration, diffusion and convection (natural or forced). Examples of wet corrosion are corrosion of iron in sea water and acidic solution.

1.1.7. Classification of corrosion [15, 16]

1.1.7.1. Electrochemical corrosion

Electrochemical corrosion can be further separated into:

a- *Separable anode / cathode type*

In these cases certain areas of the metal can be experimentally identified as predominantly anodic or cathodic. The distances of separation of this area may be very small (of the order of fractions of a millimeter). There is a macroscopic flow charge through the metal.

b- *Interfacial anode / cathode type*

In this type, one entire interface will be cathode and the other will be anode. In this case the charge is transported through a film of reaction product on the metal surface.

c-*Inseparable anode / cathode type*

Here the anodes and cathodes cannot be distinguished by experimental methods e.g. the uniform dissolution of metal in fused salt non-aqueous solution, acidic, alkaline or neutral solutions.

1.1.7.2. Chemical corrosion

Chemical corrosion involves direct chemical reaction of metal with its environment. There is no transport of electric charge, and the metal remains film

free. This would include corrosion in gaseous environment when the reaction product is volatile.

1.1.8. Forms of corrosion

1.1.8.1. Galvanic corrosion [17]

Galvanic corrosion is an electrochemical reaction between two dissimilar metals in the presence of an electrolyte and an electron conductive path. It occurs when the two are put together in the same electrically conductive medium. The metal that is more oxidation resistant becomes the cathode, while the less resistant metal becomes the anode that undergoes rapid corrosion. For example, when aluminum alloys are in contact with steel, galvanic corrosion may occur.

1.1.8.2. Filiform corrosion [18]

Filiform corrosion is a unique type of galvanic corrosion occurring under the painted or plated surfaces that do not exhibit good adhesion under gaskets. Also, this type of corrosion occurs under painted or plated surfaces when moisture permeates the coating. It appears as a radial (worm-like) corrosion path emanating from a central core as corrosion.

1.1.8.3. Crevice corrosion [19]

Crevice or contact corrosion produced from the contact of metals with metals or nonmetals. It may begin through the action of an oxygen concentration cell and continue to form pitting. Also crevice or contact corrosion occurs when surfaces of the metals, which are in contact with other materials and the surfaces, are wetted with corrosive medium.

1.1.8.4. Pitting corrosion [20]

Pitting is a type of corrosion that may be described as a condition intermediate between general corrosion and passivity (no corrosion). It takes the form of many small holes over the surface of the metal. It may occur from

concentration cell corrosion or where the coating of the metal is absent or at the sites of deposits of various types. Pitting is most likely to occur in the presence of chloride ions, combined with oxygen or oxidizing salts.

1.1.8.5. Uniform corrosion [21]

This type of corrosion attacks the entire piece of metal, and it can be caused by exposure of the metal to direct chemicals such as strong acids. It is first seen as a general dulling of the metal surface and if it is allowed to continue, the surface becomes rough and possibly frosted in appearance.

1.1.8.6. Intergranular corrosion [8]

Intergranular corrosion occurs at the grain boundaries of the metal due to the presence of impurities or stresses. A highly magnified cross-section of any commercial alloy will show its granular structure. This structure consists of quantities of individual grains, and each of these tiny grains has a clearly defined boundary that chemically differs from the metal within the grain center. Corrosion occurs on exposure of the metal's surface to a corrosive medium. The grain boundaries become the anodes, while the grains themselves are the cathodes.

1.1.8.7. Hydrogen embrittlement corrosion [22]

Hydrogen induced damage describes any number of forms of degradation of metals caused by exposure to environments (liquid or gas) which cause absorption of hydrogen into the material to cause degradation in mechanical performance. Examples of hydrogen induced damages are:

- Formation of internal cracks, blisters or voids in steel.
- Embrittlement (loss of ductility).
- High temperature hydrogen attack (surface decarburization and chemical reaction with hydrogen).

1.1.8.8. Stress corrosion cracking (SCC) [8]

This type of corrosion is caused by a combination of internal or external stresses that occur during processing of the metal with corrosion. In this case, corrosion proceeds very rapidly at the spot where the stresses are concentrated and the failure of the metal may be very sudden. For example, stainless steel pipes, one foot in diameter and 5/8 inch thickness, have been known to fail after less than a month of underground service. In addition, certain types of formed brass develop corrosion cracks on exposure to relative dry industrial atmosphere.

1.1.8.9. Concentration cell corrosion [23]

Concentration cell corrosion occurs when the conductive fluid that surrounds the metal is not homogeneous. Cathodes and anodes are formed due to the differences in ionic concentration between different regions of the medium. The resulting corrosion is highly localized and often results in pitting. There are three different types of concentration cell corrosion:

- Metal ion concentration cell.
- Oxygen concentration cell.
- Active- passive cell.

1.1.8.10. Erosion corrosion [8]

In this case the metal may be attacked by a combination of erosion and corrosion. For example, some abrasive action may constantly erode the covering of the metal, leaving it open to further corrosion.

1.1.8.11. Microbiological corrosion [24]

Microbiological corrosion refers to corrosion and ensuring loss of metal caused by biological organisms. It is considered as a common problem in industrial processes due to the presence of microbes, adequate nutrients, and corrosive by products. There are several types of microorganisms, which can cause corrosion of pipelines and other steel structures when placed under ground. Fairly specific conditions of the soil are necessary such as high content of

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organic matter, the presence of sulfate, thiosulfate, sulfur, ferrous carbonate and nitrates. One type of microorganisms cannot live in the presence of free oxygen, is referred as anaerobic. It derives the energy for its existence from the reduction of sulfate to hydrogen sulfide. Organic matter is necessary to serve as the hydrogen donor. Iron tends to go into solution and ferrous ions react with hydrogen sulfide to produce ferrous sulfide. Ferrous hydroxide is also a product of the overall reaction, which may be shown as follows:

$$4Fe + CaSO_4 + 4H_2O \rightarrow FeS + 3Fe\,(OH)_2 + Ca\,(OH)_2 \qquad (13)$$
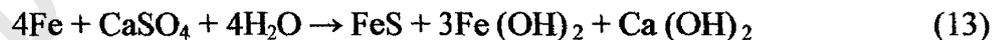
There are also aerobic microorganisms, which oxidize sulfide to sulfate when the conditions in the soil change, and the sulfuric acid is the final product, the acidity attacks the steel and corrosion is accelerated.

1.1.8.12. High temperature corrosion [8]

When metals are exposed to oxidizing gases at elevated temperatures, they can be corroded by direct reaction with these gases in the absence of any liquid electrolyte. This type of corrosion is referred to as tarnishing, high temperature oxidation, or scaling. The rate of such corrosion attack is a function of the temperature and it increases substantially by increasing temperature.

1.1.9. Corrosion prevention

Any corrosion cell consists of an anode (the positive pole), a cathode (the negative pole), a continuous conductive medium (the electrolyte), and a conductor that carry the flow of electrons from the anode to the cathode. To prevent corrosion, this cell must be inhibited; that is, one or more of its parts rendered ineffective [8]. This can be achieved by:

1. Making the electrolyte nonconductive,
2. Breaking the electrical connection between the anode and cathode,
3. Insulating either cathode or anode from the electrolyte, or
4. Removing the electrical potential from the system.

Practically, the most commonly used combating methods of corrosion come in the form of metal purification, cathodic protection, anodic protection, corrosion inhibitors, or paints [25].

1.1.9.1. Metal purification

The corrosion resistance of pure metal is usually better than that of one containing impurities or small amount of other elements. However, pure metals are usually expensive and relatively soft and weak. In general, this category is used in few cases, which are more or less special [26]. Before any coating process of metal surface, it is essential that the latter's surface shall be in a suitable condition to receive the coating. In order to achieve this, one or more pretreatment processes must be employed. Pretreatment fulfill one or more of three purposes [27]:

1. Removing the metal surface contaminants, like oils, greases, waxes, etc.
2. Removing the superficial corrosion, using chemical or physical means. Chemical means include treatment of metals by dilute acids (pickling process); while physical cleaning can be achieved by polishing or abrading the metal surface using manual or mechanical means.
3. Controlling the physical nature of the metal surface, that affects the corrosion, such as temperature, pH, and the presence of oxygen.

1.1.9.2. Cathodic protection

This is an electrochemical method of corrosion control; it has found wide applications in the protection of carbon steel structures underground, such as pipelines and tanks, from external soil corrosion. It is widely used in water systems to protect ship hulls, offshore structures, and water-storage tanks.

Two methods of providing cathodic protection for minimizing corrosion of metals are used today. Both depend on making the metal to be protected the cathode in the electrolyte involved [28]. They include:

1.1.9.2.1. Sacrificial anode method

In this method, the metal to be protected is connected to another more active metal, which act as a sacrificial anode. For example, Zinc, Magnesium, or Aluminum can be used as anodes in electrical contact with the metal to be protected like iron. The current required is generated by corrosion of the sacrificial anode material. Another example is paints or primers, which contain zinc dust; they are widely used for protection of steel against corrosion, in which the zinc is in contact with the metal surface which acts as a sacrificial anode.

1.1.9.2.2. Impressed current method

This method requires the maintenance of a constant cathodic current flowing into the metal to be protected. This direct current is provided by using an external electrical source, such as rectifiers.

1.1.9.3. Anodic protection

Anodic reaction is the passage of metal ions from the metal surface into solution with liberation of electrons, which are consumed at the cathode by reaction with water and oxygen or with hydrogen ions:

$$M \rightarrow M^{+n} + n\,e^{-} \tag{14}$$
$$2H^{+} + 2\,e^{-} \rightarrow H_2 \tag{15}$$

Anodic reaction can be suppressed by two ways; they are:

1. Cathodic protection, as mentioned before, and
2. Anodic passivation.

Anodic passivation is an electrochemical method relies on an external potential control system (potentiostat) to maintain the metal or alloy in a non-corroding (passive condition) state [29]. Anodic passivation can be achieved by:

1.1.9.3.1. Passivation by anodic current

This method was firstly suggested by *Endeleanu* [30] in 1954. This technique was developed using electrode kinetic principles. Simply, the anodic protection by anodic current is based on the formation of a protective film on metals by externally applied anodic current. Considering the preceding two equations, it appears that the application of anodic current to the structure should tend to decrease the dissolution rate of metal and consequently decrease the rate of hydrogen evolution. This usually does occur except for metals with active-passive transition such as nickel, iron, chromium, titanium and their alloys. If carefully controlled anodic current is applied to these metals, they are passivated and the rate of metal dissolution is decreased [31, 32].

1.1.9.3.2. Passivation by surface coatings

Some metals when exposed to the environment develop an outer passive layer, which inhibits further corrosion. In other cases, the passive layer can be formed by treatment with certain chemicals. In case of iron metal, the reddish oxide layer formed does not normally adhere well to the metal surface and slowly flakes off, exposing further metal to corrosion.

Surface coatings can make anodic passivation for metals, especially with iron metal. Thus, one of the most widely used methods for suppressing the corrosion of steel is paints, especially those containing anti-corrosive pigments.

1.1.9.4. Corrosion protection by surface coatings

The protective surface coating industry was formed actually after the World War II. Steel bridges were the most important things requiring maximum corrosion protection. One of the most effective systems consisted of a red lead-linseed oil primer plus a linseed oil-graphite topcoat. This was the first real

protective coating. Phenolic resin, the first synthetic resin used for coating systems, was the next important technology, which made varnishes more durable to water and weather. Since then, chlorinated rubber, vinyls, silicones, alkyds, acrylics, epoxies, polyurethane resins and ethyl silicates inorganic zinc have become important for protective coatings [33, 34]. An ideal protective coating is a material composed of a perfect film that will resist industrial or marine environment and prevent serious breakdown of basic structure. Also, protective coating film must resist the penetration of ions and prevent it from reaching the metal, resist the action of moisture osmosis, and maintain a good appearance under various weathering conditions in reasonable time [35]. The design of effective anti-corrosive coatings is a complex art. It requires an extensive knowledge of corrosion principles in addition to the chemistry of coating formation and formulation. It would be impossible to develop effective corrosion resistant coatings without such inclusive information [36].

1.1.9.4.1. Concepts of protection by organic coatings

Coatings protect the metals from corrosion by using one or more of the following basic coating concepts:

1.1.9.4.1. a. Impermeability (barrier protection)

An impervious coating must be inert to all the surrounding conditions such as air, oxygen, carbon dioxide and the passage of ions and electrons [37]. Barrier coatings are designed to reduce permeability to water and ionic species. The selection of binder, pigment/binder ratio and type of pigment is important. However, the efficiency of coatings, which should protect by a barrier mechanism, is seriously imparted by the hydrophilicity of the binder matrix [38]. Proper pigmentation can significantly lower moisture transport in coatings. However, factors like incomplete dispersion, flocculation, and poor binding between pigment and resin may diminish this effect substantially and may even lead to an overall rise in moisture transport compared to non-pigmented films [39]. The use of barrier pigments is also a useful technology. The term "barrier

pigment" is used to refer to lamellar or platy pigment [40]. A lamellar pigment may reduce the water permeability of a coating by creating a long and curving route through which the water, dissolved electrolytes and oxygen must travel to reach the substrate. The barrier effect of lamellar pigments is shown in Fig. (1.1). Lamellar pigments include aluminum flakes, graphite, kaolin, micaceous iron oxide (MIO), and mica.

Funke [41] reported that a coating containing 15% by volume of aluminum flakes outperformed the un-pigmented coating.
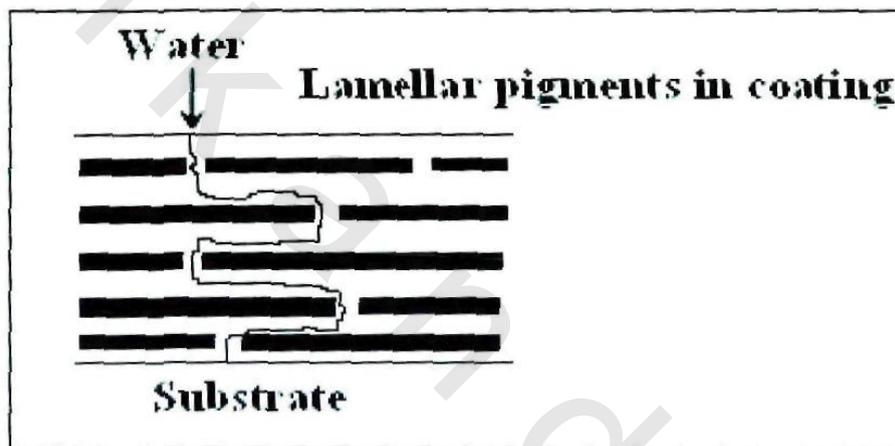

Fig. (1.1): Barrier effect created by lamellar pigments

1.1.9.4.1. b. Cathodic protection (Zinc-rich coatings) [42]

Zinc is more active than steel/iron and sacrifice itself as an anode to protect iron from corrosion. Today, zinc-rich coatings, in which zinc dust is loaded at high level (about 85% of the total paint mass), are widely used in the protection of steel against corrosion.

1.1.9.4.1. c. Inhibition (metal passivation)

It is believed that the inhibiting agents in paints involve the formation of passivation films on metal surface. The passivation type inhibitors function by

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migrating to the metal interface and making the naturally formed oxide layer more dense, and adherent. As a result, it would be more protective.

Some metals when exposed to the environment develop an outer passive layer, which inhibit further corrosion. In the case of Aluminum, it forms an oxide film in air that is highly adhered and quitly impervious, which protects the metal from corrosion within a pH range of 4.5 to 8.5. Above and below this range, the oxide film breaks down, and then the Aluminum corrodes rapidly. Unlike aluminum, the initial air formed oxide film on iron and steel is usually quite porous, water soluble and not very adhesive. By using corrosion inhibitors, it is possible to produce a thin and highly adhered impermeable film, which passivates the metal surface. The passivated metal behaves as if its electrical potential was far less active [43, 44].

1.1.9.5. Corrosion inhibitors

Corrosion inhibitors are chemical compounds that inhibit corrosion. The effectiveness of inhibitors is as a result of the controlling influence on the cathodic or anodic area reactions. The effectiveness of a given inhibitor generally increases with an increase in its concentration to a certain limit. In some instances, the amount of inhibitor present is critical in that a deficiency may result in localized or pitting attack, with the overall results being more destructive than when none of the inhibitors is present [45].

Corrosion inhibitors can be classified as inorganic (anti-corrosive pigments) corrosion inhibitors, and organic corrosion inhibitors.

1.1.9.5.1. Inorganic corrosion inhibitors

From the toxicological point of view anti-corrosive pigments can be classified into toxic and low toxic types. Lead and chromate pigments are underlain the category of toxic type. In the past twenty five years, public concern over toxicological aspects of lead and chromate pigments resulted in its major limitation or elimination of their use. Nowadays, new inhibitors of reduced or low toxicity have been introduced; such as phosphates (zinc phosphate and its

various forms), borates, molybdates, and metal oxides as well as some semi- or totally organic corrosion inhibitors. [46-49]

1.1.9.5.1.1. Toxic anti-corrosive pigments

i) Lead pigments

Important lead pigments used for anti-corrosive primers are basic pigments such as red lead and basic lead silicochromate [50]. There are several mechanistic theories suggested for the function of corrosion protection by lead pigments [51, 52].

Rammelt et al [53] suggested that a basic lead pigment provides protection via its reaction with mono and dicarboxylic acid breakdown products of oxidizing vehicle systems such as alkyds and oils. They form lead soaps/salts with the long chain breakdown products, which are highly inhibitive. They can thicken the naturally formed oxide layers on the metal surface beneath the coating.

ii) Chromate pigments

The most important inhibitive chromate pigments are the metals of hexavalent chromium such as zinc chromate (zinc tetraoxychromate) and strontium chromate. Unfortunately, the hexavalent chromates are toxic and carcinogenic in nature. The chromates are strong oxidizers and inhibit corrosion by passivation the steel surface via the formation of ultra-thin films of mixed ferric and chromic oxides. Hexavalent chromates can raise the anodic current density above the value required for the formation of passive films. In this case, the film is less soluble, and contains the more passive ferric rather than ferrous oxide. The effectiveness of chromate may be due to its incorporation into the natural oxide on the surface of the inhibited metal as chromium hydroxide or chromium oxide, which then protect the underlying metal by its very low solubility [54]. Zinc chromate is not usually recommended in linseed oil modified primers, probably because of its high water solubility.

1.1.9.5.1.2. Low toxic anti-corrosive pigments

i) Phosphate pigments

Phosphates are precipitation type inhibitors. They form films at both anodic and cathodic area sites [55]. Zinc phosphate is a lamellar (platy) and function as both an inhibitive pigment and barrier pigment [56]. The accelerated performance tests (e.g. salt spray) of phosphates are poor due to their sluggish solubility. Many modified forms of zinc phosphate have been developed to decrease particle size and changing of its shape for improvement of its water solubility [57, 58]. *Amo, B. et al* [59] reported that several modified phosphate pigments provide significantly improved performance when compared with unmodified zinc phosphate. Calcium zinc phosphate pigments take part in the passivation of steel, which has been proved by the results of electrochemical investigations and by the presence of the passive layers as has been found out by X-ray diffraction (XRD) technique [60].

ii) Silicate pigments

Silicates, similar to phosphates, are also precipitated pigments. Phosphosilicates are the most famous type [61]. This family of pigments includes basic phosphate or borate of aluminum, barium, strontium, zinc and lead. Calcium is of high interest because it is not a heavy metal.

iii) Borate pigments

The earliest and the most important borate is barium metaborate. Inhibition by borates is attributed to its alkalinity and anodic passivation of the metaborate ion [62]. There is a growing concern over the toxicity of barium, which may limit the use of this material. Zinc borate is another important member of this family [63]. The borates are particularly effective in medium and long oil alkyds. The mechanism is most anodic and to some extent cathodic.

iv) Molybdate pigments

Molybdates are oxidizing type anodic inhibitors. *Simpson, C.* [64] proposed that a protective layer of iron (III) molybdate is formed on the iron surface and it is insoluble in neutral and basic solutions. The most important types include basic molybdates (zinc, zinc-calcium…etc.), and zinc molybdenum phosphate. Molybdates are expensive compared to most other inorganic inhibitors, which limit their use.

v) Ion exchange pigments

The inhibition function of these pigments is based on the principle that the inhibitive ions are released from the pigment in exchange with corrosive ions such as sulfates [65]. They are not soluble in water and should not reduce humidity resistance of coatings. It should be interesting to use the concept of combining electrochemical mechanisms to achieve synergism. These materials are also relatively expensive.

1.1.9.5.2. Organic corrosion inhibitors

Organic corrosion inhibitors have long been used in technological applications other than coatings. These areas include oil-based applications (functional fluids, lubricants), aqueous applications (water treatment, pickling, descaling, metal cleaning, cooling water, and circulating systems), concrete protection, and repair [66-74].

Recent literature and patent activity indicate an increasing interest in using organic compounds as corrosion inhibitors in surface coatings. Such compounds may be used alone or in combination with other inhibitive pigments such as zinc phosphate, to enhance the latter material's activity. Using of organic corrosion inhibitors in coating applications has been very limited so far [75, 76]. Only some of them are commercially significant in surface coating industries. Very few are totally organic, and the most are metal salts of organic compounds containing heavy metals like lead and barium.

The most important classes of organic corrosion inhibitors, which had found wide applications in oil well refineries and surface coatings, are [77]:

- Saturated and unsaturated heterocyclic compounds containing one or more hetero atoms as sulfur, nitrogen, or oxygen atoms.
- Thioamides and thiosemicarbazides.
- High molecular weight alcohols and aldehydes.
- High molecular weight amines and amides.
- Sulphonic acids and their derivatives.
- Fatty acids and their derivatives.
- Thiourea and their derivatives.
- Thiols.
- Quaternary nitrogen compounds.
- Thiazines.
- Mercaptans and sulfides.
- High molecular weight nitriles.
- Organic phosphate compounds.
- Carboxylic acids and their derivatives.

1.1.9.5.2.1. Corrosion protection mechanism

Both anodic and cathodic effects are sometimes observed in the presence of organic inhibitors, but as a general rule, organic inhibitors affect the entire surface of a corroding metal when they are present in sufficient concentration. Organic inhibitors, usually designated as film forming, protect the metal by forming a hydrophobic very thin film on the metal surface. Their effectiveness depends on the chemical composition, their molecular structure, and their affinities for the metal surface.

Organic inhibitors provide metals protection by various mechanisms. The functional groups of organic compounds play an important role in their activity. Among the more important types of functional groups are amines, hydroxyls, mercaptans, sulfonates and nitrogen in heterocyclic compounds [78-87].

Mechanism of action of organic inhibitors is function by physical adsorption (*Van der Waal's* forces), chemisorptions, or by π-bond orbital adsorption. The variation of electron density at the reactive center can affect the chemisorptions bond strength between the inhibitor and the metal [62, 88-92].

Organic corrosion inhibitors can be classified as cathodic site adsorbers, and anodic site adsorbers, or those that serve both functions. Examples of cathodic adsorbers are aliphatic and aromatic amines. Anodic inhibitors include mercaptans. Aminobenzenethiol that contains both an amino group and a thiol group serve both purposes. According to the electrochemical corrosion mechanism, it is useful to have both functions in a compound [34, 93-97]. However, in real applications, this concept is not so simple.

1.2. Emulsion systems
1.2.1. Definition

An emulsion can be defined as a stable dispersion of two immiscible liquids, by using surface active agent (emulsifier). Since almost invariably one of them is aqueous in nature, the two common types of emulsions are oil-in-water (O/W) and water-in-oil (W/O). The term oil is used as a general word denoting the water insoluble fluid. If the oil is the dispersed phase, the emulsion termed as oil-in-water emulsion, and if the aqueous medium is the dispersed phase, the emulsion termed as water-in-oil emulsion [98, 99].

The type of the prepared emulsion is greatly depends on the relative volumes of the two phases, the nature of emulsifying agent, preparation method, and temperature [100].

1.2.2. Classification of emulsions

Investigators tend to divide emulsions into three categories [101-104]:

1. Macro-emulsions: These are opaque emulsions with particle size range (1-10 μm), and they tend to aggregate and separate out.

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2. *Micro-emulsions:* They are transparent dispersions with particle size range (0.01-0.1 μm). These emulsions are thermodynamically stable systems, but the amount of used surfactant is usually high.

3. *Mini-emulsions:* They have an intermediate particle size (0.05-0.1 μm), and they are stable with respect to aggregation and sedimentation.

1.2.3. Surfactants and interfacial tension [105]

In homogenous solution, each molecule is exposed to an equal attraction in every direction. At the interface between two immiscible liquids, the molecules of each liquid at this interface are subjected to an unbalanced net force directed normal to the surface pulling them inward and away from the second liquid. The barrier produced by the exhibited interfacial tension prevents one of the liquids from becoming emulsified into the second. Surfactants serve the purpose of stabilizing the normally immiscible mixture by reducing the interfacial tension between the fluids. A surfactant molecule is comprised of a hydrophilic head and a hydrophobic tail. Thus, when a surfactant molecule adsorbs at the oil-water interface, the hydrophobic tail adsorbs onto the oil droplet and the hydrophilic head adsorbs or orients itself toward the water.

1.2.4. Factors affecting emulsion stability

Actually, there are many factors which affect the stability of an emulsion. They include the followings:

i) Type of emulsifier [106]

One of the most critical steps in the preparation of a given emulsion is the choice of the emulsifying agent. The functions of the emulsifying agents, which are a type of surfactants, are to facilitate the emulsification and to promote stability.

Surfactants are chemical compounds, which contain hydrophilic and hydrophobic groups in their structures. The emulsion stability depends greatly on the strength of the interfacial film produced by the emulsifying agent. Higher

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emulsifier concentration leads to a close-packed arrangement of these molecules on the surface of the droplets and strengthens the interfacial film. Surfactants are often named according to their technological application; hence name such as detergents, wetting agents, emulsifiers, and dispersing agents [107, 108].

They are classified as anionic, cationic, and non-ionic or amphoteric according to the charge carried by the surface-active part of the molecule [109].They may enhance emulsion stability by:

1. Reducing interfacial tension between the two immiscible liquids, so that the increase in energy associated with the increase in area is reduced.
2. Decreasing the rate of coalescence of the dispersed liquid droplets by forming mechanical, steric, and/or electrical barriers around them which prevent the droplets from getting close enough to coalesce.

A good emulsion, which will not crack or cream, is dependent on the proper blend of water phase, oil phase and emulsifiers. To determine the type and amount of an emulsifying agent to be used in a preparation, the HLB (Hydrophilic-Lipophilic-Balance) system is utilized. This system assigns an empirical value to the oil phase and to the emulsifying agents; this value is determined by the type and the number of the individual hydrophilic and lipophilic components in the chemical structure of each agent. It is supposed to give an indication to the behaviour characteristics of an emulsifier, and it determines the type of an emulsion that tends to be formed.

The concept of HLB was firstly introduced by *Griffin* [110, 111] to classify a select surfactant. According to *Griffin* classification, the surfactant that was lipophilic (hydrophobic) in character was assigned a low HLB number, and the hydrophilic surfactant was given a high HLB number. Thus, emulsifiers with low HLB values tend to make W/O emulsions, and that of high HLB values tend to make O/W emulsions.

Many attempts have been made to determine the HLB number of surfactants [112-116]. *Davies* [117] examined the chemical structure of the emulsifiers and found that each group has a negative or positive contribution to the HLB of the emulsifier. He suggested a number for each group. These group numbers are obtained from several known structure of defined HLB. For a given structure, the HLB number was calculated by substituting the group numbers into the following equation:

HLB = Σ(hydrophilic group number) - Σ (hydrophobic group number) + 7

The emulsifying agents that favor W/O type emulsions have HLB values 3-5 and that favor O/W type emulsions have HLB values 8-15.

ii) Viscosity of continuous phase [118]

Emulsions can be thin or thick fluids, pastes, or gels and may exhibit thixotropy or dilatency. Viscosity is influenced by:

1. The characteristics of the external phase, including additives.
2. The volume ratio of the two phases.
3. The particle size.

If the continuous phase has a high viscosity, then the motion of the dispersed phase will be slowed, thus minimizing the rate of coalescence. Emulsion viscosity can be increased by adding thickeners such as soap gels, lipophilic fatty acid esters, or gums to the continuous phase, raising the proportion of the internal phase, reducing the particle size of existing particles, and by incorporating fine air particles as a third phase.

iii) Temperature

Change in temperature cause changes in interfacial tensions, viscosity, nature (hydrophilicity/hydrophobicity) of the surfactants, vapor pressures of the

liquid phases, and thermal agitation of the molecules. Thus, emulsions tend to be very sensitive to temperature changes.

Emulsions are more stable when the temperature is near the point of minimum solubility of the emulsifier [119].

iv) Particle size distribution

The more uniform the distribution, the more stable the emulsion; the larger oil droplets grow at the expense of the small ones [120].

The particle size of an emulsion may be reduced by increasing the amount of emulsifier, improving its HLB, preparing the emulsion by phase inversion to provide an extended internal phase at the time of inversion to the final emulsion type, and by improving agitation [121].

v) Volume of dispersed phase

A low-internal-phase (LIP) emulsion assumes the overall characteristics of the external phase. Very dilute (LIP) emulsions are often difficult to handle because of the dilution effect on the emulsifier. On the other hand, high-internal-phase (HIP) emulsions exhibit higher apparent viscosity, as the internal phase volume ratio increases, and finally a thick, non-flowing paste is formed. However, increased viscosity may improve stability somewhat [122].

1.2.5. Methods of emulsification

i) HLB optimization method

The HLB value is related to emulsion performance. With increasing HLB, the performance factor increases to a maximum and then decreases. The HLB value at which the maximum occurs is called the required HLB for the oil in that system (O/W or W/O). In fact, the most stable emulsion systems usually consist of blends of two or more emulsifiers for attaining better emulsion stability. In this case, the HLB value of emulsifier blend can be calculated by using the following equation [123-125]:

$$\mathbf{HLB_{mix} = HLB_A . A\% + HLB_B . B\% + HLB_C. C\% + ..., etc.}$$

Where HLB_A, HLB_B and HLB_C are HLB values of surfactants A, B and C while A%, B% and C% are the weight percentage of A, B and C in the surfactant mixture, respectively.

ii) Phase inversion method

Dai et al [126] studied the emulsification of two immiscible liquids. They showed that at a certain ratio of the two liquids, inversion takes place, and the external phase becomes the internal phase. The phase volume ratio at the point of inversion was found to be equal to the square root of the ratio of the viscosity of the two components.

However, an emulsifier exerts a controlling effect on the inversion. The inversion phase ratio seems to depend on the concentration of the emulsifier, its chemical nature, and its HLB value. At a certain HLB, inversion occurs most easily. On changing the HLB to either higher or lower value, the stability of the O/W or W/O emulsions increases, reaches a maximum, and then decreases. Inversion and especially phase inversion temperatures are related to the choice of emulsifier [127, 128].

iii) Maximum solubilization method

This developed method looks at the fact that the greater the amount of the aqueous phase that can be solubilized in the oil phase, the smaller the average droplet size in an O/W emulsion subsequently formed when a W/O emulsion inverts by continual addition of water. So, the surfactant system that provides maximum solubilization capacity for water in the W/O system, without causing inversion, will be the best for making the O/W emulsion [129].

iv) Emulsification equipment

The purpose of the emulsification equipment, whether simple or complex is to break up or disperse the internal phase in the external phase, so

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that the particle size of the resulting emulsion is sufficiently small to retard coalescence. The major concerns in the choice of emulsifying equipment are the apparent viscosity in all stages of manufacture, the amount of the mechanical energy input required, and heat exchange demands. Preparation of emulsions is greatly affected by the type of agitation. A good manufacturing process is based on a properly developed laboratory procedure. Scale-up introduces problems of agitation, incorporation of air (particularly via vortices in large tanks), surface-volume ratios, addition rates of ingredients (especially at inversion points), cooling rates, and raw materials control [130].

1.3. Water-borne coatings

The main group of industrial environmentally friendly coatings includes water-borne systems, high solids systems and solvent free systems [131]. Their development had a spin-off, leading companies to gain good public relations, being seen as firms that care for environment by producing less harmful products. Indeed, new national and international environmental management systems are now in place to allow companies to have formal structures to demonstrate such awareness and compliance [132]. There are four major types of compliant coatings that exist in market place. They include water-borne coatings, high built coatings (low VOC's or solvent free), radiation curable coatings and powder coatings [133].

Nowadays, water-borne coatings that currently account for more than 60% of the total volume of coatings produced globally are projected to grow with annual rate of 5-7% through the next years, due to the hard application of environmental laws. The largest portion of water-borne paints produced worldwide is sold in the architectural market category, while, coatings applied to cans and automobiles represent the next largest areas for water-borne coatings. Other applications in which water-borne coatings are used include aerospace, marine, wood products, and traffic coatings [134, 135].

Coatings that utilize water as the major liquid have been described by a variety of different terms, including water-borne, water-soluble, emulsion, latex, and water reducible [136].

Water-borne coatings generally define the broad category of coatings that utilize water as the main volatile liquid component. Each of the other terms has a specific meaning in relation to water-borne coatings. The term water reducible describes specific water-borne coatings whose viscosity can be easily reduced upon the addition of more water. A water-soluble coating refers to the ability of water to dissolve the binder forming a true solution. Finally, the term emulsion refers to a dispersion of liquid (polymer particles) droplets in a water medium [137].

1.3.1. Composition of water-borne coatings

Actually, emulsion coatings are complex mixtures of organic and inorganic ingredients. Among these ingredients that might be present in paint formulation are polymer particles (resin), surfactants, pigments and extenders, thickeners, coalescing solvents, preservatives, and corrosion inhibitors. These ingredients comprise approximately half of the paint formulations; the other half is water. Titanium dioxide is the most commonly used pigment that provides white color and opacity. Since the pigment must be dispersed in water along with the resin, wetting and dispersing agents are required. Thickeners or protective colloids must be added to raise the viscosity that is acceptable for application. Preservatives or biocides are added to prevent growth of microorganisms, which may degrade the additives. The resins, which commonly used in conventional solvent-borne coatings, are usually modified by increasing their hydrophilic nature prior to being incorporated into water-borne coating formulations. Typical resins or binders include acrylics, alkyds, polyesters, epoxies, polyurethanes, and vinyls [138, 139].

Co-solvents, who are added in small amounts to paint formulations, are commonly used to provide adequate flow, film formation, wetting, and drying behaviour of the paint [140].

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1.3.2. Surfactants in water-borne coatings

All water-borne coatings need surfactants in order to reduce the free energy of the various interfaces of the system, thus providing kinetic stability to the formulation. Surfactants are used as binder emulsifiers and as pigment dispersants, they are needed to improve wetting on low energy substrate, to control foaming during application and processing, and to prevent film defects caused by surface tension gradients [141].

In addition, surface-active polymers, often referred to as associative thickeners, are widely used to optimize the rheological properties of the formulation, and anionic polyelectrolyte such as polyphosphates are commonly used as pigment dispersing agents. Lately, the majority of surfactants used in coatings formulations are standard anionic and nonionic such as fatty alcohol sulfates, alkylaryl sulfonates and alcohol ethoxylates. Cationic and amphoteric surfactants are rarely used. In water-borne coatings the presence of hydrophilic surfactants in the dry paint film can facilitate the passage of water through the film and consequently, the water up-take may be five or six times higher than that in conventional paints [142, 143].

In recent years, polymerizable surfactants have become of interest as emulsifiers in emulsion and suspension polymerization. By using surfactants that become covalently attached to the latex particle, many of the problems encountered with conventional emulsifiers can be avoided or at least minimized. Positive effects may be obtained both on the stability of the latex and on the properties of the dry film [144].

1.3.3. Recommended pigments in water-borne coatings

In developing paint formulations, the type of pigmentation packages that are acceptable for water-borne systems are taken into consideration. For white gloss enamels, titanium dioxide is used as the main pigment and talc is often used as an extender pigment. Due to environmental concerns the use of lead and chromate based corrosion inhibiting pigments is no longer acceptable [145]. In an

extensive study conducted by *Jackson, M.A.* [146], anti-corrosive pigments that function well in water-borne epoxy primer are those that are relatively inert and don't release large amount of water soluble salts which adversely affect the cationic character of the water miscible amine functional curing agent.

In choosing the extender pigments, good results are often obtained if a combination of particle size, shape, low oil and water absorption are employed, which may improve barrier protection. Typical pigments used include calcium metasilicate, barium sulfate, talc, micaceous iron oxide, and mica [147].

1.3.4. Organic corrosion inhibitors in water-borne coatings

The most effective anti-corrosive pigments, used today in coatings for metals protection, are based on heavy metals such as lead, chromium and barium; these pigments are classified by Environmental Protection Agency (EPA) as toxic pigments [148]. High performance is not enough to isolate heavy metals based system from regularity demands for reductions in solvents emissions and in the used of toxic heavy metals. Thus, on the new cusp of the new millennium, the coatings industry is facing a true challenge in replacing toxic pigments with responsible alternatives without sacrificing the performance. Water-borne coatings are expected to play a more than significant role in the future.

They have certainly come a long way in their development to become effective in corrosion protection, passing through several stages. In the first stage, single pack anti-corrosive coatings, based on styrene-butadiene, vinyl acrylic and alkyd emulsions were developed. In the following stage, two pack epoxy anti-corrosive coatings, largely dependent on the synthesis of new binders, were developed. Special attention is currently being paid to other binders such as fluoropolymers and polyurethane dispersions [149-152].

Corrosion protection by organic corrosion inhibitors can be achieved by various mechanisms [153, 154]. Amongst these is the improvement of the barrier function of the paint film, which means a decrease of the porosity and

permeability for water, oxygen and aggressive ions. Other possible mechanisms would be an improved adhesion between coating and substrate, adsorption of the inhibitor onto the metal surface forming a protective layer, and/or interaction with either cathodic or anodic corrosion sites on the metal surface. In addition, appropriate secondary properties and excellent compatibility with the various resin systems will largely determine the effectiveness of organic corrosion inhibitors in water-borne technology [155].

Therefore, an efficient corrosion inhibitor should meet the following properties [156, 157]:

1. High long-term efficiency at low concentrations.
2. Low water solubility.
3. Non-acidic.
4. High purity.
5. High efficiency at wide pH range.
6. Low toxicity.
7. Compatible with all major resin technologies.
8. Sufficient thermal stability.
9. Easy incorporation.
10. Useful as the sole inhibitor.

1.4. Gel permeation chromatography

1.4.1. Basic of gel permeation chromatography

Gel permeation chromatography (GPC) is a form of size-exclusion chromatography, where the mechanism of separation in GPC is based on volume exclusion [158]. The results of separation in GPC are achieved due to the hydrodynamic volume, V_h, of the sample molecules [159].

The separation in GPC is also based on the molecular size and not the molecular mass of the sample molecule, which involves passing a dilute polymer solution through a tubular column packed with macro-porous polymer gel (cross linked) beads. The diffusion of molecules between mobile phase and pore is the basis for separation mechanism and performance. Since for smaller molecules more pores are accessible, these molecules are more strongly retarded and consequently elute later than the higher molecular fractions. The selectivity of this process for molecular weight is outstanding and the range of molecular weights which can potentially be characterized by this technique is only limited by the ability to produce controlled spaced gels. GPC is by far the most versatile technique for the determination of molecular weight in a polymer sample [160].

1.4.2. Definitions

Low molecular weight is arbitrarily defined as a molecular weight below 1000 dalton. The number-average molecular weight ($\overline{M}_n$) and the weight average molecular weight ($\overline{M}_w$) are determined as the following:

$$\overline{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \qquad\qquad \overline{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

where N_i is the number of molecules of molecular weight M_i.

The weight-average molecular weight is larger than or equal to the number-average molecular weight. The ratio of the weight-average and number average molecular weight is known as *(PDI) polydispersity index.*

$$PDI = \frac{\bar{M}_w}{\bar{M}_n}$$

The (PDI) is a measure of the distribution of individual molecular weights in a batch of polymers. The PDI has a value always greater than 1.

In the present work, new organic compounds are prepared by the reaction of epoxidized soybean oil with different thiol compounds. The produced adducts are emulsified and added to different water-borne paint formulations as corrosion inhibitors for mild steel, instead of the anti-corrosive pigments. These inhibitors will not constitute more than 0.1 % of the total mass of paint. This means that, cheap, friendly to environment anti-corrosive water-borne paints are prepared.