Chapter 1

INTRODUCTION
CHAPTER 1: INTRODUCTION

Corrosion, the deterioration caused by chemical reaction with the environment, affects materials as different as structural metals, ceramics, and wood, as well as works of art and artifacts from past civilizations. Corrosion technology is a field of study that focuses on the mechanisms of corrosion and on the design of protective schemes to prevent it or limit its extent.

Corrosion comes from the Latin word 'corrodere' - to gnaw away. The word implies the destructive alteration of the metal caused by the chemical or electrochemical action of its environment [1]. The metals are not thermodynamically stable and will return to stable metallic compounds when exposed to the environment.

For example, metallic iron is oxidized to ferric oxyhydroxide, a thermodynamically stable state: i.e. iron in the higher level of free energy is changed to lepidoerocite.

\[ \gamma-\text{FeOOH}, \text{in the lower level.} \]

\[
4\text{Fe} + 3\text{O}_2 + 2\text{H}_2\text{O} \quad \longrightarrow \quad 4\text{FeOOH} \quad \Delta G^\circ = -81 \text{ K cal/mole}
\]

Corrosion is the deterioration of a material as a result of reaction with its environment, especially with oxygen. Although the term is usually applied to metals, all materials, including ceramics, plastics, rubber and
wood, deteriorate at the surface to some extent when they are exposed to certain combinations of liquids and/or gases. Common examples of metal corrosion are the rusting of iron, the tarnishing of silver, the dissolution of metals in acid solutions, and the growth of patina on copper. Most research into the causes and prevention of corrosion involves metals, since the corrosion of metals occurs much faster under atmospheric conditions than does the corrosion of nonmetals. The cost of replacing equipment destroyed by corrosion in the United States alone is in the billion-dollar range annually. Since iron is the most widely used construction material which needs protection, this chapter will deal with the corrosion preventive methods and the mechanism of protection by organic coatings.

It has been established that the factors essential for the corrosion of iron and steel are water, oxygen, chemicals and a potential difference between the iron and other bodies with which it is in contact. The corrosion may be uniformly distributed over the surface or highly localized. This reactivity, being fairly rapid at ambient temperatures, causes rust even beneath a coated surface [2,3].

1.1 TYPES OF CORROSION

From the mechanism of corrosion process, corrosion can be classified into two types: chemical corrosion and electrochemical corrosion.
(a) Chemical corrosion

Chemical corrosion is subject purely to the basic laws of chemical kinetics of heterogeneous reactions and refers to the causes of corrosion that are not accompanied by generation of electric current.

(b) Electrochemical corrosion

Electrochemical corrosion is subject to the basic laws of electrochemical kinetics and generally refers to the cases of corrosion with generation of current, due to microgalvanic cells on the surface.

Corrosion is usually an electrochemical process in which the corroding metal behaves like a small electrochemical cell. Since the corrosion of iron by dissolved oxygen is, from an economic standpoint, the most important redox reaction occurring in the atmosphere, it will be used here to illustrate the electrochemical nature of the process. A sheet of iron exposed to a water solution containing dissolved oxygen is the site of oxidation and reduction half reactions, which occur at different locations on the surface. At anodic areas, iron is oxidized according to the reaction:

At the same time, oxygen molecules in the solution are reduced at the cathodic areas:
The two process produce an insoluble iron hydroxide in the first step of the corrosion process:

Generally, this iron hydroxide is further oxidized in a second step to produce Fe(OH)$_3$, the flaky, reddish-brown substance that is known as rust. Unfortunately, this new compound is permeable to oxygen and water, so it does not form a protective coating on the iron surface and the corrosion process continues.

All metals exhibit a tendency to be oxidized, some more easily than others. A tabulation of the relative strength of this tendency is called the electromotive series of metals. Knowledge of metal’s location in the series is an important piece of information to have in making decisions about its potential usefulness for structural and other applications.

(c) Mechanism of ElectroChemical Corrosion

This mechanism suggests that the corrosion is caused by the presence of micro-galvanic cells on the metal surface, which arise when the metal is exposed to the environment. The electric current that flows through such galvanic cells causes corrosion/dissolution of the metal.

The electrochemical reactions in the corrosion cell are written in the general forms:
Anodic reaction

\[ M \rightarrow M^{n+} + ne^- \quad (M: \text{metal}) \]

1.2

Cathodic reaction - in acidic solution

\[ 2H^+ + 2e^- \rightarrow H_2 \]

1.3

- in neutral and alkaline solutions

\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]

1.4

The corrosion of metal in hydrochloric acid is an electrochemical process. That is, any reaction that can be divided into two (or more) partial reactions of oxidation (1.2) and reduction (1.3) is termed electrochemical. The composite reaction involving charge transfer or exchange of electrons is shown schematically in figure 1.1. The metal dissolves by (1.2) liberating electrons into the bulk of the metal which migrate to the adjoining surface, where they react with \( H^+ \) in solution to form \( H_2 \) by (1.3). The hydrogen evaluation depicts that the metal is corroded by hydrochloric acid.

Figure 1.1 : Schematic diagram of metal M dissolution, liberating into solution a metal ion \( M^{2+} \) and into the metal electrons, \( e^- \), which are consumed by reduction of \( H^+ \) to \( H_2 \).
1.2 FORMS OF CORROSION

Corrosion is a natural process and is a result of 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 added to the ore, to produce the metal. It is the same energy that provides the driving force causing the metal to revert back to the more stable compound. Corrosion comes in different forms depending on the environment to which the metal is subjected to each form of corrosion is briefly described below.

<table>
<thead>
<tr>
<th>General / Uniform Corrosion: Corrosive attack dominated by uniform thinning due to even regular loss of metal from the corrosion surface.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric</td>
</tr>
<tr>
<td>Galvanic</td>
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<tr>
<td>Stray - current</td>
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<tr>
<td>General biological</td>
</tr>
<tr>
<td>Molten salt</td>
</tr>
<tr>
<td>Liquid metals</td>
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<tr>
<td>High-temperature</td>
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</tbody>
</table>
Figure 1.2: High temperature tensile/rupture from cumulative thermal cycling in hydrogen reformer tubes.

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<thead>
<tr>
<th>Localized Corrosion: all or most of the metal loss occurs at discrete areas</th>
<th>Film form</th>
<th>occurs on metallic surfaces coated with thin organic film, typically 0.1mm thick, characterized by the appearance of fine filaments in semi-random directions from one or more sources.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crev ice</td>
<td>corrosion in narrow openings or spaces in metal to metal or non-metal to metal component sites.</td>
<td></td>
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<tr>
<td>Pitting</td>
<td>extremely localized corrosion marked by the development of pits.</td>
<td></td>
</tr>
<tr>
<td>Localized microbiological</td>
<td>cases where biological organisms are the sole cause or an accelerating factor in the localized corrosion</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Metallurgically influenced corrosion: form of attack where metallurgy plays a significant role.</th>
<th>Intergranular</th>
<th>occurs when the corrosion rate of the grain boundary areas of an alloy exceeds that of the grain interiors.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dealloying</td>
<td>a form of corrosion characterized by the preferential removal of one constituent of an alloy leaving behind a altered residual structure.</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1.3: Crevice Corrosion of stainless steel

Figure 1.4: Pitting Corrosion in aluminum flats on a storage tank roof

Figure 1.5: Microbiologically induced Corrosion in a sour gas pipeline
<p>| | |</p>
<table>
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<th></th>
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<tbody>
<tr>
<td><strong>Mechanically assisted</strong></td>
<td><strong>Erosion</strong> Removal of surface material by the action of numerous individual impacts of solid or liquid particles.</td>
</tr>
<tr>
<td><strong>degradation</strong>: form of attack where velocity, abrasion, hydrodynamics etc., play a major role</td>
<td><strong>Fretting</strong> Combined wear and corrosion between contacting surfaces when motion between the surfaces is restricted to very small amplitude oscillations.</td>
</tr>
<tr>
<td></td>
<td><strong>Cavitation &amp; Water drop impingement</strong> Occurs on a metal surface in contact with a liquid, pressure differentials generate gas or vapor bubbles which upon encountering high pressure zones.</td>
</tr>
<tr>
<td></td>
<td><strong>Fatigue</strong> Occurs in metals as a result of the combined action of a cyclic stress and cause explosive shocks to the surface.</td>
</tr>
<tr>
<td><strong>Environmentally induced cracking</strong>: forms of cracking that are produced in the presence of stress</td>
<td><strong>Stress cracking</strong> Service failures in engineering materials that occur by slow environmentally induced crack propagation.</td>
</tr>
<tr>
<td></td>
<td><strong>Hydrogen damage</strong> Results from the combined action of hydrogen and residual or tensile stress.</td>
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<tr>
<td></td>
<td><strong>Liquid metal embrittlement</strong> Brittle failure of a normally ductile metal when coated with a thin film of a liquid metal and subsequently stressed in tension.</td>
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<tr>
<td></td>
<td><strong>Solid metal embrittlement</strong> Occurs below the melting of the solid in certain liquid metal embrittlement couples.</td>
</tr>
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</table>
Figure 1.6: stress corrosion cracking

Figure 1.7: stress oriented hydrogen induced corrosion

Figure 1.8: hydrogen induced corrosion
The corrosion cell

In the case of a corroding metal it is envisaged that innumerable microscopic cells (in otherwords miniature dry cells) is electrically short circuited through the body of the metal. The heterogeneities present in the metal give rise to such micro cells. The corrosive environment provides the electrolyte (acid-or alkali or salt solution). Soil as well as a thin film of condensed moisture constitutes an electrolyte. Water is an electrolyte containing at equal number of H⁺ ions and OH⁻ ions.

At the anode corrosion takes place.

Example: \[ \text{Fe} \rightarrow \text{Fe}^{++} + 2e \] \[ \text{Zn} \rightarrow \text{Zn}^{++} + 2e \] \[ \text{Al} \rightarrow \text{Al}^{+++} + 3e \]

At the cathode, equivalent electrons are consumed as follows by reduction:

i) In acids:

\[ 2 \text{H}^+ + 2e \rightarrow \text{H}_2 \text{ (acid)} \]

(ii) In aqueous alkaline or neutral solutions and in acids containing dissolved air or oxygen:

\[ 2 \text{H}_2\text{O} + \text{O}_2 + 4e \rightarrow 4\text{OH}^- \text{ (alkaline or neutral solutions)} \] \[ 4\text{H}^+ + \text{O}_2 + 4e \rightarrow 2\text{H}_2\text{O} \text{ (acid)} \]
(iii) In solution containing other cations or oxidizing ions:

$$\text{Cu}^{2+} + 2e \rightarrow \text{Cu} \quad \text{(1.11)}$$

(iv) Metal ion reduction:

$$2\text{Fe}^{3+} + 2e \rightarrow 2\text{Fe}^{2+} \quad \text{(1.12)}$$

(v) In soil in presence of anaerobic sulfate reducing bacteria,

$$\text{CaSO}_4 + 8\text{H}^+ + 8e \rightarrow \text{CaS} + 4\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + 2\text{H}_2\text{O}$$

$$\quad + \text{H}_2\text{S} \quad \text{(1.13)}$$

Formation of visible corrosion product

In acid solutions, the dissolved ions remain in solution. But in neutral solutions usually solid corrosion products are formed by the interaction of cations and anions moving away from the anode and cathode areas respectively. Normally oxide or hydroxide of the metal are formed. For example, in the case of iron in aerated water or neutral solution, the formation of familiar red -brown rust occurs as follows.

$$4\text{Fe} \rightarrow 4\text{Fe}^{++} + 8e \quad \text{(1.14)}$$

$$2\text{O}_2 + 4\text{H}_2\text{O} + 8e \rightarrow 8\text{OH}^- \quad \text{(1.15)}$$

Similarly other metals form their corrosion products. The type of corrosion product to be formed is dependent on the pH of the corrosive solution, its chemical composition and the electrode potential of the corroding metal.
**Electrode Potential**

When a metal is in contact with an electrolyte, a potential difference is developed known as the single electrode potential at the metal/electrolyte interface. The electrode potential is practically measured by using a dc voltmeter and a reference electrode (i.e. whose electrode potential is of known value) placed close to the surface.

1.3 **CORROSION CONTROL**

In the field of combating corrosion both economic and scientific considerations are involved. Modern technology for combating corrosion provides a number of effective methods for the protection of metals and metallic structures. They are broadly subdivided into four categories.

<table>
<thead>
<tr>
<th><strong>Barrier Films</strong></th>
<th>either organic coatings or electro plating</th>
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</thead>
<tbody>
<tr>
<td><strong>Change of Materials</strong></td>
<td>complete or partial change of materials used</td>
</tr>
<tr>
<td><strong>Change of Environment</strong></td>
<td>either a complete change in environment or a partial alteration by modification of pH etc.</td>
</tr>
<tr>
<td><strong>Electrochemical Techniques</strong></td>
<td>sacrificial coatings, cathodic or anodic protection etc.</td>
</tr>
<tr>
<td><strong>Design</strong></td>
<td>allowances for general corrosion and control of factors such as temperature, velocity etc.</td>
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</tbody>
</table>

**Barrier Films**

If the metal has a poor resistance to corrosion in the environment under consideration, provision has to be made in the design for applying
appropriate coatings such as organic coatings [4-8], inorganic coatings [9-12] or metallic coatings [13-14]. The role of coating is either to isolate the base metals from the corrosive environments or provide corrosion inhibition through passivation or provide cathodic protection. In all cases of protective coatings, the defects in the coating (caused either during production or service) may lead to corrosion and hence has to be taken care of.

Change of Materials

The exposure of metallic structures or operation of components in severe conditions, such as high temperatures, pressure, or highly corrosive media, demands the use of highly corrosion resistant material. This has become possible by suitably alloying the metals. The examples being stainless steel, monels and super alloys.

Change of Environment

Many of the constituents present in the environment are capable of producing severe corrosion of metals and alloys though the degree of severity may vary in each case. It is possible to prevent corrosion by modifying the environment either with addition of certain chemicals (inhibitors) or be made less aggressive by other methods such as removal of oxygen and dehumidification. The most important corrosive agents to be considered are water vapor, acid fumes, salts and hydrogen sulfide. The chemical substances which are added to reduce corrosion rates are called
corrosion inhibitors [15-17]. The use of inhibitors has become the most widely used technique of combating corrosion in cooling water system. A large section of organic compounds such as aldehydes, amines and sulfur compounds are used as effective inhibitors. Tin, arsenic, phosphorous and chromium compounds are examples of inorganic corrosion inhibitors.

**Electrochemical Techniques**

Cathodic protection and anodic protection are the two methods which are used to reduce the corrosion of metals in contact with electrolytes.

**Cathodic protection** [18]

"*Reduction or elimination of corrosion by making the metal a cathode by means of an impressed d-c current or attachment to a sacrificial anode (usually Mg, Al or Zn)*"

In this method, the potential of the metal is shifted to sufficiently negative value such that the system is in the thermodynamically stable region (region of immunity). This is achieved by one of the two methods viz., impressed current system or sacrificial anode system.

In the impressed current method, an auxiliary electrode is connected to the positive of the external power source and the structure(metal) to the negative and the current is passed to make the potential of the structure sufficiently negative. DC power is impressed from a DC power source on to
the structure using expendable anodes. The basic requirements for impressed current systems are a DC power source, anode bed comprising of group of anodes, and insulated lead wire. The power source is normally a rectifier. A wide range of anode materials are available for impressed current system. Impressed current anodes include, scrap steel, graphite, aluminum, high silicon, lead silver alloys and titanium insoluble anodes [TSIA]. The choice of the anode material is determined by the nature of the environment, the current density discharge limitations and economics. When impressed current system is opted for protection in soil the anode materials are surrounded by carbonaceous backfills like coal, coke-breeze, calcined petroleum coke breeze or natural graphite particles are commonly used.

In the sacrificial anode method, the anode material and the metal to be protected electrically form a cell. The anode material should possess a more negative corrosion potential than the structure. This method provides protection by the principle of galvanic corrosion or bimetallic corrosion. The current is generated by coupling a metal or alloy and the material to be protected in a corrosive or conductive media. Magnesium, Zinc or Aluminum alloys are used to cathodically protect steel structures in natural media. High purity zinc and magnesium alloys are used to protect steels in soil and fresh waters, water and oil carrying pipelines, underground storage tanks receive protection by magnesium and high zinc anodes. In these circumstances aluminum alloy anode develops surface films and reduces current output. Aluminum alloy anodes find applications in protecting structures in sea water and saline waters such as ship hulls, steel piles.
supporting platforms etc. For underground applications both high purity zinc and magnesium alloy anodes are surrounded by backfill generally consisting of 75% gypsum, 20% bentonite and 5% sodium sulfate. The backfill provides a uniform environment around the anode, reduces anode to soil resistivity and retains moisture.

Criteria for cathodic protection

(1) A negative (cathodic) potential of at least 850mV as measured between the structure and a saturated copper/copper sulfate electrode contacting the environment. This potential is determined when protective current is applied.

(2) A negative (cathodic) potential shift of at least 300mV as measured between the structure and copper/copper sulfate electrode in the environment. This shift is the difference between the unprotected potential and the potential when cathodic current is applied.

(3) A negative polarization potential shift of at least 100mV measured between the structure and a saturated copper/copper sulfate electrode contacting the electrolyte. This potential is determined by interrupting the protective current and measuring the polarization decay.
Anodic protection [19]

This method is applicable only in cases where the metal/alloy can be passivated anodically in the given medium. The structure to be protected is made the anode and the potential is set in the passive region. The current density in the passive region is extremely small and so the electric power needed for anodic protection is much smaller than that required for cathodic protection.

1.4 SURFACE COATINGS

The development of new and improved coatings has been increasing over the past few years. The new technologies are finding wider applications.

By applying these coatings on the substrate having the required physical and mechanical properties, it is possible to obtain the desired strength and optimum corrosion resistance at an economical cost. The available coatings, viz. organic, inorganic and metallic coatings have their own specific areas of application, with a range of properties dependent on the specific material.

1.4.1 ORGANIC COATINGS

The most commonly used organic coating [20,21] is 'Paint'. When applied for corrosion resistance, paints are referred to as coatings.
The protection of metals by organic coating is regarded as one of the most economical and largely adopted method. Organic coatings are used as a barrier layer to prevent the contact of the corrosive ions to the metal surface.

The corrosion (anodic) reaction consists of the passage of ions from the metallic lattice to the solution with the liberation of electrons, which are consumed at the cathode with water and oxygen. There are two ways by which anodic reaction could be suppressed.

By

a) Making the potential of iron sufficiently negative, and
b) Making the surface of the iron a passive one by forming a film over it which will be impervious to the passage of iron ions.

1.4.2 CHEMISTRY OF ORGANIC COATINGS

Constitution of paint

*Paint can be defined as a fluid material which when spread over a surface in the form of a thin layer, will form a solid, adherent and cohesive film.*

The fluid paint contains three major ingredients - binder or film former, pigment and solvent. The relative proportions of these materials can be varied to produce films with any desired physical and application characteristics.
(a) **Binders**

A binder [21] must get converted to a dense, solid, and adherent film with all substrates. It provides uniformity and coherence to any coating system. The binder's ability to form a dense, packed film is directly related to its molecular size and complexity. It binds the pigment particles into a film and adhere to the substrate.

Examples: Alkyd, epoxy and silicone etc.

(b) **Pigments**

Pigment [22] may be defined as a material available as solid particles largely insoluble in the film former and in the solvents used in the paints and capable of being dispersed in the paint constitutions to give maximum benefits in terms of the required paint properties.

Under this general definition of pigments, there are two classes, true pigments and extender pigments. The former being used for colour and opacity (or hiding power), while the latter may be added to paints to modify the gloss. They are also added to paint to provide economics. Further the pigments have been classified as inorganic and organic. The inorganic pigments include all the whites and extenders and a useful range of colours, both synthetic and naturally made. The organic pigments are generally synthetic.

Examples: Titanium di-oxide, silica and mica etc.
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Examples: Titanium di-oxide, silica and mica etc.
(c) Solvent or thinner

The importance of volatile component or solvent [23] of a coating has been rather neglected but it is certain that it plays an active role in dissolving the resin, reducing the viscosity of the polymer to the consistency suitable for application, helping in wetting the substrate, controlling the rate of drying or setting of the coating film after application, thus having a profound effect on the durability of the coating.

A single solvent is never used for a resin system. Usually a mixture of solvents (solvent blend) are used.

Examples: Xylene, toluene and butanol etc.

(d) Additives

In addition to the major components, the paint may contain small quantity of drier, plasticizers, flexibilizer, anti-skinning agents, wetting agents, anti-settling agents, anti-fouling agents and fungicides. These additives [24] play an important role in the paint formulations. Different types of additives are added for different purposes. They are usually in small quantities, (1-2%) of the entire formulation. These additives contribute package stability, ease of application, appearance and corrosion resistance quality to the coating.
1.4.3 CORROSION CONTROL BY ORGANIC COATINGS

Organic coatings, along with proper surface pretreatment, are the most common and cost effective mode of corrosion protection for metallic objects and structures. From automobiles to jet aircraft, from chemical factories to dishwashers, exterior surfaces of corroidable metals such as steel and aluminum alloys are effectively protected from their environment by a coating system. Professor W. Funke [25-29] has had much of his research focus on pursuit of understanding the properties of the organic coatings.

There are three main modes of corrosion protection that coatings provide:

(i) barrier protection
(ii) cathodic / sacrificial protection (i.e. zinc rich coatings) [30-32]
(iii) inhibitive / passivation protection (i.e. coatings formulated with inhibitive pigments and / or additives).

The latter two modes are what may be designated as 'active' protection, that is provided to the metal substrate by damaged areas of a coating.

Barrier protection is the mode by which intact coatings provide protection to metal substrates, and is a protection provided by the reduction of the transport of materials, ions or charge [33-35]. Barrier properties that are important for coatings are the resistance to transport (small diffusion coefficients) for the chemical species of the corrosion reactions, in most
cases H₂O, O₂ and electrolyte ions, usually Cl⁻. The barrier properties of polymer and paint films are known to be altered by their exposure to various gases and liquids [36].

1.4.4 BARRIER PROPERTIES AND CORROSION PROTECTION

The paint film protects the metallic surface by acting as barrier between the metal and environment. The film also act as the insulator and prevents the flow of electric current there by suppressing electrochemical reaction.

The barrier properties of organic coatings are of primary interest in the design of high performance coatings for long term protection of metal surface. It was also an emphasis of the work of Funk [37] relative to his analyses of corrosion protection. According to the present thinking, which dates from the contributions of Funk, it is very difficult to maintain a complete barrier to oxygen or water by an organic coating film, but the barrier effects towards ionic materials and charge appear to be those that are important to the protective performance of the coating. It can be said that this set of barrier properties is the one that appears to distinguish a good coating from a bad one with respect to corrosion protection. This ability to provide a uniform set of barrier properties across the total film surface with minimum of weak points in the film to destroy the barrier between the environment and the metal substrate. It must be emphasized here that these comments are made concerning intact, undamaged, coating films, and does not relate to corrosion protection provided by inhibitive pigments, zinc rich primers, and galvanizing. The barrier
properties also seem to fail when there is a lack of adhesion between the film and the substrate, so what has been come to be known as 'wet adhesion' is part of what is an effective barrier coating. This means that the properties of the coating / metal substrate interface are closely tied to the barrier properties of the coating system.

1.5 PRINCIPLES OF PAINT FORMULATION

The success of the paint depends on its formulation. It is very important to know exactly what properties are desired in the specific coating and this intern depends on the function for which the paint is intended to be used. This forms the basis on which one can choose the pigment, binder and other ingredients. If the basic function of the paint is to protect a surface from harmful environment agents, such as weathering, attack of chemical agents etc. The paint should have good resistance to these factors. The factors such as gloss, appearance etc. being secondary. If the coating is to be decorative, the resistance factors become secondary.

Pigment Volume Concentration and its importance

While formulating a paint with desirable properties, the ratio of pigment to non-volatile in the paint must be known. This ratio is known as pigment volume concentration.

\[
Pigment\,\,\,volume\,\,\,concentration = \frac{\text{Volume of pigment}}{\text{Volume of pigment} + \text{Volume of binder}} \times 100
\]
PVC is very important as it determines to a large extent the appearance and film properties of a paint. A low PVC paint generally have superior performance in washability, flexibility and durability. A high PVC paint generally have superior brushing, hiding power and low materials cost. A number of properties such as gloss, flexibility, scratch hardness, resistance to corrosion are mostly determined by pigment volume concentration (PVC).

Upto a certain PVC, the paint film will have required film properties. After a certain PVC, the film properties such as flexibility, water adsorption, adhesion etc. will drastically fall. The PVC after which, the drastic fall in the properties of the paint film occur is called critical pigment volume concentration (CPVC). The values of CPVC is characteristic of a particular system and varies from one system to another. Hence the formulation of paint should not exceed critical pigment volume concentration. Stieg [38] has traced the importance of both PVC and CPVC.

**Selection of vehicles**

Selection of vehicles is more difficult than the selection of pigment. We have to select the resins, solvents, driers and other additives that might enter into the formulation. Depending upon the environmental condition, we have to select the vehicles. The properties desired in the film and the method of drying will determine the type of vehicle used.
Coating system

A proper coating system [21] consists of main factors, like primer, intermediate and top coats. If the metal surface is not properly cleaned, the paint may peel off because of poor bonding. If the primer does not have good adherence with intermediate coat, early failure occurs. Poor paint performance is mainly due to improper application and surface preparation.

Surface preparation

Surface preparation involves surface roughening to obtain mechanical bonding as well as removal of dirt, rust, mill scale, oil, grease and other impurities. The best method to obtain clean rough surface is grit blasting or sand blasting. The other methods are chemical treatments, wire brushing, flame cleaning etc. A study of surface preparation on the paint life showed 10.3 years for sand blasting, 9.6 years for pickling and then hand cleaning.

Primer coat

Primers are the first coats applied to meet the requirements of the surface. The primary purposes of a primer is to give strong bonding to substrate, high order of internal strength and also strong resistance to corrosion and chemicals. The primer must also provide a proper and compatible base for the top coats. Thus the primer has dual requirements, i.e., adhesion to the
substrate and provision of surface which will allow proper adhesion of the subsequent coats.

**Intermediate coat**

Intermediate coats are usually used in coating systems which are designed for specific purposes. The primary purposes of an intermediate coat is to provide thickness for total coating, strong chemical resistance, increased electrical resistance, strong cohesion and strong bond to primer and top coat. The intermediate coat usually has rather high pigment to vehicle ratio, so that it is a flat coat with good adhesion.

**Top coat**

The top coat selection is important because it has to perform functions such as:

(a) Providing a resistant seal for the coating system.
(b) Forming the initial barrier to the environment
(c) Providing a tough and wear-resistant surface
(d) Providing a pleasing appearance.

The top coat is more dense than the intermediate coat because it is formulated with a lower pigment to vehicle ratio. The paint is usually applied by brush or spray and some special methods such as electro coating, roller coating and etc.
1.6 TYPES OF DRYING MECHANISM

Evaporation

Whitewash may conveniently be employed as the simplest example of material in which evaporation is the sole drying mechanism involved. Drying by evaporation alone is also encountered in certain paints in which the carrier solvent is not water but an organic solvent such as alcohol, xylene, MIBK and etc.

Oxygen-Activated Drying and Hardening

The drying of linseed oil type paints is a two stage process; in the first stage the solvent (thinner) evaporates from the film, and in the second the film hardens by molecular growth due to reaction with the oxygen in the atmosphere above the film. It was found long ago that the rate of drying of a linseed oil paint was too slow for practical purposes unless certain accelerating agents were added to the paint. These are chemical compounds which are in effect oxygen carriers. They are known as driers and belong to the class of chemical activators called catalysts.

Heat Activated Hardening

Heat has the effect of stimulating chemical reaction. The reaction responsible for the hardening of a paint coating can be accelerated by
heat. Paints depending for their power of drying and hardening on the degree to which they receive heat from an external source are referred to as stowing or baking types. The effect of heating is first to hasten the evaporation of solvent from the coating and finally to speed up molecular growth until the desired hardness and tenacity are developed in the coating.

1.7 EVALUATION OF ORGANIC COATINGS

The protective behavior of the organic coatings can be evaluated by accelerated tests and electrochemical techniques.

1.7.1 LABORATORY ACCELERATED TESTS [39,40]

(a) Immersion test

Painted specimens with diagonal scratches, to expose the steel surface are completely immersed in distilled water or salt solution. If scratches do not show rust, it can be concluded that the paint gives protection even if corrosive constitutions reach the metal surface by slow diffusion through the paint film.

(b) Salt spray test (ASTM - B 117)

The salt spray (fog) test is one in which the painted steel is continuously exposed to salt fog and the spray tests in which the specimen is
intermittently sprayed with 5% sodium chloride or sea water solution. These tests are severe and such conditions are not normally obtained in actual exposure except on the beach, but the resistance to salt diffusion and the prevention of spreading of rust scratches are well tested by them.

(c) Outdoor exposure tests

Laboratory paint testing offers convenience and gives quick results, but it will not reveal which paint will be most suitable for a given location. To obtain more definite results, the coating system must be applied to test panels which are placed on test racks at various plant locations. After several months of field exposure the paint failure is examined by comparing with the ASTM standard photographs.

Accelerated test will give the qualitative picture of the coatings but it is a time consuming method, the electrochemical tests giving the quantitative value in short period.

1.7.2 ELECTROCHEMICAL TECHNIQUES

(a) Potential-Time measurements

The simplest of the electrochemical tests is the electrode potential measurement of the painted metal as a function of immersion time. The measurement of potential is quite a useful method owing to its simplicity
and ease of measurements. The potential is measured by using a saturated calomel electrode and a multimeter.

The corrosion potential of a metal in an aqueous solution, in combination with other facts, can often provide information about the mechanism of the reaction and the rate of controlling factor. The value of the corrosion potential by itself provides little information, but its change with time and its value in reference to other samples may be usefully applied. In the case of painted metals the area of metal exposed to the electrolyte is a function of the permeability of the paint to water and to ions and the integrity of the coating. Any electrical measurement must be made with negligible current flow or else the very fact of current flow may induce irreversible changes in the coating. For corrosion potential measurements a very high impedance voltmeter is an absolute necessity.

A review of the corrosion potential of painted metals covering the literature has been prepared by Wolstenholme [41]. The early work of Burns and Haring [42], Haring and Gibney [43], Whitby [44] and Zahn [45] focused on the magnitude of the corrosion potential and how it changed with time. The summation of all these studies on steel substrates was that negative potentials were indicative of corrosion beneath the paint and positive potentials were indicative of the absence of corrosion. The most useful and exact study of this techniques was done by Wormwell and Brasher using painted steel samples immersed in artificial sea water [46] or 3% sodium chloride solution.
(b) Electrochemical impedance measurements

Electrochemical impedance [47,48] methods offer a convenient way of evaluating the performance of organic coating/metal systems.

The single-frequency a.c method can supply only limited information on the mechanism of paint degradation because true paint resistance and capacitance are frequency-dependent [49]. Electrochemical impedance spectroscopy (EIS) is the method in which the impedance of an electrochemical system is studied as a function of the frequency of an applied a.c. wave.

When a steady-state system is perturbed (say by an applied a.c. voltage) it relaxes to a new steady state. The time (in seconds) taken for this relaxation is known as the time constant, \( \tau \), and given by:

\[
\tau = \frac{1}{RC}
\]

where \( R \) is the resistance and \( C \) the capacitance of the system. The analysis of this relaxation process would provide information about the system. The ratio of the response to the perturbation is the transfer function. When the applied perturbation is an a.c. potential and the response in a.c. current, the transfer function is the impedance. To simplify calculations further, the perturbation and response are transformed from a function of time into the frequency domain via a Laplace transformation. In the frequency domain, fast processes (with low \( \tau \)) occur at high frequencies
while slow processes (with high $\tau$) occur at low frequencies. The frequency around which a process occurs may be ascertained by:

$$ f = \frac{1}{2\pi\tau} \quad \quad \quad 1.17 $$

Thus dipolar properties may be studied at high frequencies, bulk properties at intermediate frequencies and surface properties at low frequencies. Impedance may also be considered as the 'resistance' to the flow of alternating current,

$$ E = iZ \quad \quad \quad 1.18 $$

where $E$ and $I$ are waveform amplitudes for potential and current, respectively, and $Z$ is the impedance. Two different components contribute to impedance. One is due to resistors and is known as the reactive or real component and represented by the letter $Z'$. The other arises from a.c. circuit elements such as capacitors, inductors etc. and is known as the reactive or imaginary component and represented by the letter $Z''$. Unlike the resistive impedance, the reactive impedance affects not only the magnitude of the a.c. wave but also its time-dependent characteristics (phase). For instance, when an alternating voltage wave is applied to a capacitor, the resulting current wave form will lead the applied voltage waveform by $90^0$. Due to this reason, it is convenient to introduce complex notation by incorporating the complex number $j$ where

$$ j^2 = -1 \quad \quad \quad 1.19 $$

Thus, if a system is perturbed by a sinusoidal potential varying with time $t$ as

$$ E(t) = E_0 \exp(j\omega t) \quad \quad \quad 1.20 $$
its response would be
\[ l(t) = l_0 \exp(j(\omega t - \theta)) \quad \text{------} \quad 1.21 \]
provided it is linear. E(t) and I(t) are the instantaneous values and \( E^0 \) and \( I^0 \) the maximum values (peak amplitude) of the potential and current wave forms, respectively. \( \theta \) is the phase angle difference and \( \omega \) the angular frequency in radians given by
\[ \omega = 2\pi f \quad \text{------} \quad 1.22 \]
where \( f \) is the frequency. Usually a low a.c. voltage of about 10 mV is applied to keep the system linear.

Introducing the complex notation enables the impedance relationships to be presented as Argand diagrams (Figure 1.9) in both Cartesian \((Z', Z'')\) and polar coordinates \((r, \theta)\). The former leads to the Nyquist impedance spectrum where the real impedance is plotted against the imaginary and the latter to the Bode spectrum where both \( r \), the modulus of impedance, and the phase angle are plotted as a function of the frequency.

![Figure 1.9: Argand diagram showing impedance vectors](image)
its response would be

\[ I(t) = I_0 \exp(j \omega t - \theta) \]

---

1.21

provided it is linear. \(E(t)\) and \(I(t)\) are the instantaneous values and \(E^0\) and \(I^0\) the maximum values (peak amplitude) of the potential and current waveforms, respectively. \(\theta\) is the phase angle difference and \(\omega\) the angular frequency in radians given by

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![Argand diagram showing impedance vectors](image)

**Figure 1.9**: Argand diagram showing impedance vectors
Mansfeld recommends the use of the Bode plots for three reasons [50]: in Bode, all measured points are displayed equally while in Nyquist the majority of the points are located together at both ends of the spectrum; labeling of the curves in a Nyquist plot with frequency marks is quite cumbersome; and in Bode plots, R and C regions are clearly distinguished and together with the information provided by the frequency dependence of the phase angle, which is a very sensitive indicator of small changes in the spectra, a quick survey of the type of spectrum recorded is possible. However, most EIS spectra have been presented as Nyquist plots [51].

Irrespective of the way the results are present, the equipment for EIS should obtain four parameters $Z'$, $Z''$, $\tau$, and $\theta$. These are computed from the raw data obtained which consists of the real and imaginary components of the voltage and current at each frequency applied.

Impedance method has been widely used in recent years to measure the corrosion rate of the metals, resistance and capacitance behavior of the coated metal substrates. The advantage of this method is that it completely eliminates the solution resistance.

Solution resistance is represented by $R_s$, Charge transfer resistance is given $R_{ct}$ and the double layer capacitance is shown by $C_{dl}$.

Using Stern and Geary equation, corrosion rate ($I_{corr}$) is obtained from $R_{ct}$ since

$$I_{corr} = \frac{b_a \times b_c}{2.303 \left( b_a + b_c \right)} \times \frac{1}{R_{ct}}$$

1.23
The impedance of the above circuit for the given \( \omega \). \((\omega = 2\pi F)\) is

\[
Z = R_s + \frac{1}{j\omega C_{dl} + 1/R_{ct}} \\
= R_s + R_{ct}/i + \omega^2 C_{dl}^2 R_{ct}^2 - j\omega C_{dl} R_{ct}^2/i + \omega^2 C_{dl}^2 R_{ct}^2 \\
= Z' - jZ'' ------ 1.24
\]

Thus the cell impedance \( Z \) consists of real (\( Z' \)) and imaginary (\( Z'' \)) parts. A plot of \( Z' \) Vs \( Z'' \) for various frequencies is a semi circle. At high frequency, \( Z \) corresponds to \( R_s \) and at low frequency, \( Z \) corresponds to \( R_s + R_{ct} \) and the difference between the two values gives \( R_{ct} \).

The double layer capacitance value is determined from break point frequencies of the log \( Z \) Vs log \( F \) (bode plots) or from the frequency at which \( Z'' \) is maximum.

\[
F_{dl} = \frac{1}{2\pi (R_s + R_{ct}) C_{dl}} \quad ------ 1.25 \\
F_{bh} = \frac{1}{2\pi R_s C_{dl}} \quad ------ 1.26 \\
F_{(\text{max})} = \frac{1}{2\pi C_{dl} R_{ct}} \quad ------ 1.27
\]

The coating system resistance generally degraded with time. A lower limit of about \(10^6\) ohms/cm\(^2\) existed, below which corrosion occurred beneath the coating [52]. This generality was found with both AC and DC resistance measurement techniques. The degradation was associated with ion and water penetration into the coating, transport of ions through the coating, and the subsequent electrochemical reactions (corrosion) at the coating-metal interface.
Capacitance measurements were used to estimate water uptake rates by coatings. The rates were correlated with coating performance and were useful in calculating minimum protective coating thickness.

Thus the mechanism of protection by organic coating has been evaluated by accelerated laboratory tests, and electrochemical measurements. The paint film gives protection by barrier effect, suppressing the anodic and cathodic reaction of the metal substrate and offering high resistance to the flow of corrosion current.

1.8 HIGH TEMPERATURE CORROSION

"High temperature corrosion by direct reaction of exposed metals to oxidizing agents at elevated temperatures"

As the demand for high temperature thermal and corrosion resistance inexorably increases the need for developing various heat resistant coatings to solve problems pertaining to corrosion science and technology. The areas in which materials limitations are holding back industrial progress are increasing in the high temperature technologies (processing and power industries) where process economics, increasingly dirty fuels and limitation of natural reserves makes high temperature materials a very important field in which, increasingly, the high temperature corrosion is the vital factor.
It has been proved that coatings and claddings offer the best possibility for achieving corrosion resistance beyond the scope of any viable alloy candidate. Specifically tailored coatings can offer cost-effective as well as optimized corrosion resistance and strength. However, the heat resistant coatings stand where the above said merits pose the technological challenges ahead in solving the setbacks in developing such new corrosion resistant materials at high temperature.

For the past forty years, or more, the coating industry has had a wide variety of resins and pigments to manufacture coatings for protection and decoration of hot surfaces. Review of some of the work done reveal that many newer materials can be used with success at various temperatures and atmospheric conditions[53]. High temperature heat resistant protective coating has considerably attracted the research groups during the past twenty years with the advent of high speed jets, rockets and space vehicles, which develop very high skin temperature on launch and re-entry into the earth's atmosphere. The existing structural materials at high temperature have the limitation due to oxidation, chemical reaction, erosion, etc. These limitations are being overcome by high temperature heat resistant protective coatings as a method of providing improved reliability and higher operating temperature capability[54]. Heat resistant coatings are also required for use on surfaces such as exterior of a steel chimney, interior of furnace doors, refinery equipment, space heaters, exhaust, jet engine tail pipes, boilers, motors, etc. besides being used in heat exchangers, steam lines, cars, buses, lorries, engines exhaust pipes and mufflers.
The exact requirements are now met mostly by the use of silicone resin based coatings [55-58]. It is obvious that the high temperature environment indeed demands special class of paints. The heat stability (tolerance) limit of a commonly available coating system falls well within 333 K ($60^\circ$ C). When the operating temperature rises, deterioration becomes rapid. Currently silicone resin based coatings are widely used in the design of heat resistant, heat and corrosion resistant, and weather resistant coatings. In the above instances, the silicone finishes have replaced either more organic finishes or inorganic finishes [59,60].

The silicon element was first studied in 1824 Berzelius and later by Friedel and Krafts. The first systematic investigation of silicon and silicones was carried out by Kipping between 1899 and 1944. The first silicone products were made in USA in the early 1950s. The practical considerations of these silicone resin based protective heat resistant coatings have recently been reviewed by Staples [61]. The chemistry of silicone resins has also been reviewed by several workers [62-66]. Manufacture of silicone resins generally involves four steps: (1) hydrolysis of chlorosilanes, (2) neutralization, (3) bodying, and (4) curing.

Chemically, silicones are polymers comprising alternate silicon and oxygen atoms linked to organic molecules (methyl or phenyl groups). Silicone may also be thought of as hybrid polymers, i.e. a cross between organic and inorganic substances and it has peculiar chemistry since the Si-C bond of silicones is not found in any other materials. It is quadrivalent as is carbon
Si-O-Si-O. This result provides high extreme resistance to low and high temperature, resistance to weathering and oxidation, water resistance and superior adhesive properties[67]. The chemical structure of silicone is shown in figure 1.10.

![Chemical structure of silicone resin](image)

**Figure 1.10 : Chemical structure of silicone resin**

More recently Deborah Wiebe et. al [68] reveals that the silicone based coatings are very useful to protect the concrete structures in immersion service from Biological Fouling. In 1989, the Electric Power Research Institute (EPRI) published a technical report summarizing an extensive evaluation of several types of nontoxic coatings at eight coastal utility sites in the US[69]. Other types of toxic coatings had been evaluated in previous studies at six of those locations[70]. More than 30 coatings, including silicone coatings were included in the study. After two years, the results showed that the silicone based coatings generally performed well
over all ranges of environmental conditions and, depending on full scale performance and longevity, could be a cost-effective solution.

1.9 WHY SILICONES?

Silicones are used in the organic coatings for protecting the metal substrates at high temperature environment because of its typical properties are mentioned below:

- thermal stability due to excellent of 
  - Si - O - Si - bond and
- good solidity of 
  - Si - C - bond
  even in an oxidizing atmosphere,

- good low temperature properties due to a relatively low glass transition temperature (≤ - 100° C)
- water-repellency and release properties due to low surface tension
- good weathering properties due to oxidation resistance and virtual transparency to ultraviolet rays
- chemical and biological inertness
- good dielectrical characteristics, particularly when associated with the other above properties.
1.10 SILICONES IN COATING INDUSTRY

Silicones are needed in coating preparations:

- as binder,
- as additives.

In the first case, the resins commonly used, take the place of organic resins, or as modifiers. It is interesting to note that silicone resins will not contaminate organic resins, and so segregation of equipment is unnecessary.

In the second case of fluids, used in very small quantities, give special effects (hammertone finishes), or act as antifoams against bubble formation, craters and orange peel, floating and flooding, or impart mar resistance to coating. These fluids offer great opportunities. It is necessary to take some precautions in use: the bad reputation of silicones stems from errors made in the past, when using these products.

They are now well known and generally used carefully and successfully.

In the coating industry, silicone resins are often modified with organic resins, usually for one of the following reasons:

- to improve film properties (hardness, flexibility, adhesion, abrasion resistance)
- to produce faster cure
- to reduce thermoplasticity.