CHAPTER - I

1.1 CORROSION AND ITS PREVENTION BY ORGANIC COATINGS

The term corrosion is derived from the Latin word 'Corrodere' which means eating away or destroying. With the exception of gold and silver very few metals are found in nature in the free state. The pure metals tend to revert to a more stable compound when they come into contact with the environment. A good example is rusting of iron. Corrosion takes place on both ferrous and non-ferrous metals but the ferrous metals pose greater problems. 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 localised. This reactivity, being fairly rapid at ambient temperatures, causes rust even beneath a coated surface [1,2].
The basic mechanism in these types of corrosion is electrochemical and involves the passage of electrons from areas of higher to lower electron density. When a plate of mild steel is exposed to atmosphere, a layer of oxide is formed very rapidly. If such a plate is immersed in water or chemical solution, differences of potential are set up between the oxide film and the metal. The following anodic and cathodic reaction will take place.

\[ 4 \text{Fe} \rightarrow 4 \text{Fe}^{2+} + 8e^- \text{(Anodic reaction)} \] \[ 4 \text{H}_2\text{O} + 2\text{O}_2 + 8e^- \rightarrow 8 \text{OH}^- \text{(Cathodic reaction)} \]

The ferrous and hydroxyl ions migrate towards the oppositely charged electrodes and react to form ferrous hydroxide.

\[ 4 \text{Fe}^{2+} + 8 \text{OH}^- \rightarrow 4 \text{Fe(OH)}_2 \] 1.3

This is then oxidised to hydrated ferric oxide (rust).

\[ 4 \text{Fe(OH)}_2 + \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} + 2 \text{H}_2\text{O} \] 1.4

The precipitation of ferrous hydroxide and subsequent oxidation takes place away from the metal surface.
1.2. CORROSION PREVENTION

Various methods used for the prevention of corrosion are given below:

a) Metallic coatings
b) Organic coatings
c) Electrochemical methods of protection
   1) Cathodic protection
   2) Anodic protection
d) Use of inhibitors.

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.

(i) Making the potential of iron sufficiently negative, and

(ii) 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.
1.3. CHEMISTRY OF ORGANIC COATINGS

1.3.1. 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.

1.3.1.(a) Binders [3]

A binder must get converted to a dense, solid, 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.

1.3.1.(b) Pigments [4]

Pigment 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 constituents 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 are used for colour and opacity, whereas extender 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.

1.3.1.(c) Solvent or thinner [5]

The importance of volatile component 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.
1.3.1.(d) Additives [6]

In addition to the major components paint may contain small quantity of driers, plasticizers, flexibilizer, anti-skinning agents, wetting agents, anti-settling agents, anti-fouling agents and fungicides. These additives 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. MECHANISM OF PROTECTION BY PIGMENTS

Pigments may be classified as inhibitive, non-inhibitive and metallic.

1.4.1. Inhibitive pigments

These pigments react with the moisture absorbed by the coating to form sufficient ions which react with the underlying metal surface to passivate it and make it more corrosion resistant. These pigments are used primarily as atmospheric coatings and not for constantly wet surfaces.

The inhibitive mechanism of lead and chromate pigments are explained in details by Leidheiser [7],
but the mechanism of zinc phosphate as an inhibitive pigment is not fully established.

1.4.2. Non-inhibitive pigment

The most important non-inhibitive pigments are micaceous iron oxide and aluminium flake. The important properties of this pigment is to reduce the permeability of oxygen and water through the coating.

The reduction of water or oxygen permeability may check the progress of corrosion and should improve other properties. These mechanism of protection have been reviewed by Funke [8].

1.4.3. Metallic pigments

Metallic pigments are metals which, except for zinc dust, are generally in the form of flakes or flat platelets. The flatplate like structure is important in that it tends to reinforce the binder.

The use of finely divided metallic zinc has increased rapidly in recent years due to its effective protection of iron and steel structures [9]. Zinc dust is a bluish-grey powder which is a reactive pigment. It gives zincates with alkalies. It gives corrosion resistance by sacrificial electrochemical reaction in preference
to the steel substrate [4]. It also absorbs ultraviolet radiation and so protects film former in exterior coatings [4]. The geometrics of zinc rich primer and associated effects on pigment loading have been reviewed by Hare et.al [10].

The aluminium pigment is available in two forms, leafing and non-leafing. From a corrosion resistant point, the leafing aluminium type pigment is most important. Aluminium pigmented coatings have the corrosion protective qualities almost irrespective of the binder.

The other leafing metallic pigment is stainless steel [11] and it acts in the same way as the aluminium pigment. It has recently been used as the main pigment along with some other pigments. The use of stainless steel pigment is not due to its rust inhibiting properties but because of its chemical resistance and exceptional resistance to moisture.

The manganese flake pigments [12] are also nowadays used as main pigment in the protective coatings because of its sacrificial action at the beginning and the barrier action in the latter stage to protect the iron or steel structures.

The other metallic powders used for protection
of steel structures are nickel, copper, magnesium and bronze, but gold and silver flakes are used in decorative applications such as sign writing, book binding and picture frames.

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 in turn 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 environmental 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. are secondary. If the coating is to be decorative, the resistance factors become secondary.

1.5.1. Pigment volume concentration and its importance

While formulating a paint with desirable properties, the relationship of ratio of pigment to non-volatiles in the paint must be known. This ratio is known as pigment volume concentration.
Pigment volume = \frac{\text{Volume of pigment concentration}}{\text{Volume of pigment + Volume of binder (PVC)}} \times 100

PVC is very important as it determines to a large extent the appearance and film properties of a paint. A low PVC paints generally have superior performance in washability, flexibility and durability. A high PVC paints generally have superior brushing, hiding power and low materials cost.

After certain PVC, the paint properties such as extensibility, rusting, adhesion etc., start falling. Hence the formulation of paint should not exceed critical pigment volume concentration (CPVC). Stieg [13] has traced the importance of both PVC and CPVC.

1.5.2. Selection of vehicles

Selection of vehicle 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.

1.6. COATING SYSTEM [3]

A proper surface coating system consists of three
main factors, they are 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 the intermediate coat, early failure occurs. Poor paint performance is mainly due to improper application and surface preparation.

1.6.1. 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 paint life showed that 10.3 years for sand blasting, 9.6 years for pickling and then hand cleaning.

1.6.2. Primer coat

The primer coat may contain rust inhibitive pigments such as zinc chromate and zinc dust and thereby providing another function in addition to acting as barriers. 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 primer has dual requirements, i.e., adhesion to the substrate and provision of a surface which will allow proper adhesion of the subsequent coats.

1.6.3. 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.

1.6.4. Top coat

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

i) Providing a resistant seal for the coating system
ii) Forming the initial barrier to the environment
iii) Providing a tough and wear-resistant surface
iv) 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 electrocoating, roller coating and fluidized bed methods.

1.7. EVALUATION OF ORGANIC COATINGS

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

1.7.1. Laboratory accelerated tests [14,15]

1.7.1.(a) Immersion test

Painted specimens with diagonal scratches, to expose the steel 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 constituents reach the metal surface by slow diffusion through the paint film.

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

The salt spray (fog) test 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.

1.7.1.(c) Humidity test

The swelling of paint by water and water vapour absorption and consequent formation of water and rust blisters could be tested by the exposure of painted steel to high humidities.

1.7.1.(d) 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 then 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 will give the quantitative value in short period.

1.7.2. Electrochemical techniques

1.7.2.(a) Potential-time measurements

The simplest of all the electrochemical tests is the measurement of the electrode potential of the
painted metal as a function of immersion time. The most useful and exacting study of this technique was done by Wormwell and Brasher using painted steel samples immersed in artificial sea water [16].

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.

1.7.2.(b) Galvanic current measurements

The painted metal under test can be made either anode or cathode in a galvanic current cell by coupling with a more anodic or more cathodic metal. For example, painted steel can be made anode by coupling to zinc cathode. The galvanic current flowing between anode and cathode can be monitored via a potentiostat wired as a zero resistance ammeter [17]. Galvanic current changes with immersion time in the test solution have been interpreted in terms of penetrant transport through the paint film and the electrochemical reactions occurring at the substrate metal/film interface. The lower galvanic current obtained with the painted steel/unpainted zinc couple indicated that protection by the paint film was attributed to polarisation of the cathodic reaction. This suggest that the galvanic current test is not a non-
destructive, repetitive test, and is more suited to mecha-
nistic studies than as a corrosion rating test [18].

1.7.2.(c) Polarisation or Tafel extrapolation method[19]

This method involves the measurement of overpoten-
tials for various current densities, and plotting of over-
potential against log current density made. The slope
gives tafel constants \((ba \text{ and } bc)\) and the intercept cor-
responds to corrosion current \((I_{corr})\). The charge transfer
resistance of a coated panel can be calculated from the
following equation.

\[
I_{corr} = \frac{ba \times bc}{2.303 (ba + bc)} \times \frac{1}{R_t} \quad \text{... 1.5}
\]

Where, \(ba\) and \(bc\) = Tafel constant

\(R_t\) = Charge transfer resistance

\(I_{corr}\) = Corrosion current

For non painted metals, under ideal condition,
corrosion rate can be calculated from polarisation curves
but in more complicated systems such as painted metals,
only qualitative information can be obtained from the
shape of the curves. For example, the slope of the polari-
sation curve shown in the figure 1.1 is similar in both
the anodic and cathodic directions. This indicates that
the high film resistance factor is controlling the rate
of the reaction [20].
Fig. 1.1. Polarisation diagram

where, \(a\) = anodic, \(c\) = cathodic
\(ba\) and \(bc\) = tafel constants.
\(I_{corr}\) = corrosion current.
\(E_{corr}\) = corrosion potential.
1.7.2.(d) A.C. Impedance method [21,22]

Impedance method has been widely used in recent years to measure the corrosion rate. The advantage of this method is that it completely eliminates the solution resistance. The equivalent circuit of a corroding system which has both anodic and cathodic activation controlled reaction may be represented as in the figure 1.2.

Solution resistance is represented by $R_S$, charge transfer resistance is given by $R_t$ and the double layer capacitance is shown by $C_{dl}$.

Using Stern and Geary equation, $I_{corr}$ is obtained from $R_t$, since

$$I_{corr} = \frac{ba \cdot bc}{2.303 (ba + bc)} \times \frac{1}{R_t}$$

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

$$Z = \frac{1}{R_S + \frac{j\omega C_{dl} + 1/R_t}{}}$$

$$= \frac{R_t}{1 + \omega^2 C_{dl}^2 R_t^2} - \frac{j\omega C_{dl} R_t^2}{1 + \omega^2 C_{dl}^2 R_t^2}$$

$$= Z' - jZ''$$

Thus the cell impedance $|Z|$ consists of real ($Z'$) and imaginary ($Z''$) parts. A plot of $Z'$ Vs $Z''$ for various
where, $Z'$ Real part
$Z''$ Imaginary part

Fig. 1-2. Schematic representation of impedance plot and its equivalent circuit.
frequencies is a semi circle. At high frequency, Z cor-
responds to $R_S$ and at low frequency, Z corresponds to $R_S +\ Rt$ and the difference between the two values gives $Rt$.

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.

$$f_{bl} = \frac{1}{2\pi (R_S + Rt) Cdl}, \quad f_{bh} = \frac{1}{2\pi R_S Cdl}$$

$$f_{(max)} = \frac{1}{2\pi Cdl \ Rt}$$

The rate of an electrochemical reaction can be strongly influenced by the diffusion of one or more re-
actants to the electrode surface. This situation can exist when the electrode surface is covered with a coating. Whenever diffusion effects dominate the reaction mechanism, the impedance to the reaction is called a "Warburg impe­
dance".

Thus the mechanism of protection by organic coat­
ing 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.
The corrosion current is influenced by cathodic reaction, anodic reaction and resistance of the electrolytic path. Attempts have been made to explain the protective action of paints also in terms of its influence on the various electrochemical parameters. Increase of anodic and cathodic polarisation is referred to as anodic and cathodic inhibition and increase of resistance is represented to as resistance inhibition. The anodic reaction may be inhibited by

a) Inhibitive action of soluble soaps  
b) Inhibitive action of soluble pigments  
c) Adsorption of polar molecules.

Cathodic reaction can not be prevented due to water, oxygen permeation through paint film. It was also shown by many workers that the increase in electrical resistance of paint film also gives protection. But the paint containing high percentage of Zn (above 80% by wt) gave cathodic protection.
References