INTRODUCTION
CHAPTER I
GENERAL INTRODUCTION

Historical Developments

Organic surface coatings are generally applied over metallic substrates for various purposes including decoration, corrosion protection, insulation and certain definite functional applications.

The use of paints dates back to prehistoric times [1,2]. Paints applied fifty thousand years ago have been identified, but these were used essentially for decorative application. Though the present day paint systems accommodate a large number of ingredients for taking care of so many aspects of the coating the olden days' paints were containing only the essential three components namely the binder, pigment and the thinner. Paintings of this type were in existence before the age of metal. At a later stage Egyptians developed the art of decorative and protective paints to a remarkable degree and they developed wider colour range of pigments. All these came into use during the period 3000–600 B.C. Excellent varnishes were used and though the compositions of these varnishes were not definitely known invariably they were heated combinations of oils and natural resins. During 600 B.C. - 400 A.D. varnishes incorporating drying oils were introduced.
Protective coatings were made use of as early as second century by Greeks. The protective value of drying oils began to be recognized in Europe only during thirteenth century. The industrial revolution had a major effect on the development of the paint industry. The increasing use of iron and steel for construction and engineering purposes resulted in the need for anticorrosive primers which would delay or prevent rusting and corrosion. Lead and zinc based paints were developed during this period which are still in very much use as anticorrosive primers. Prussian blue, the first artificial pigment with a known chemistry was discovered in the early 18th century and later turpentine was brought in as a paint solvent. During 1850 to 1890 formaldehyde resins were developed but it was used in paints only in the 20th century. Nitrocellulose was widely used as coating material especially for the automobiles in 1920s. Even earlier, paint manufacture using linseed oil had begun and the pigments used were iron oxide, chrome yellow etc. Later China wood oil with its superior drying property was made use of. Titanium dioxide which was to replace white lead was introduced in 1918. New coloured pigments and dyestuffs manufactured synthetically became available during this period. Since then much work had been undertaken in the direction of various synthetic resins and pigments and a variety of paint systems for decorative, protective and other special applications had been formulated.
New application techniques by which paints could be applied to get uniform coatings and also varying thicknesses were developed. Phenolic resins and polyesters were introduced which are even now found as good coating materials. In the early years of the 20th century alkyd resins were commercially produced and this was followed by the development of other classes of resins like melamines, ureas, vinyls, acrylics, epoxies and polyurethanes. The synthetic resin developments became the basis for protective coatings used and from that time on the development of solvents and plasticizers was taking place. The chemical resistant vinyl coatings and chlorinated rubber products were developed in 1930s. Chlorinated rubber was the most resistant protective coating until early 1940s. Newer pigments were also being developed and so also other additives for imparting various desirable properties to the coating. Shortly after World War II epoxy resins were developed which had a major impact on the protective coating field. These resins could be used as protective paint binders which was easier to apply and had good adhesion and resistance to corrosion. Polyurethane coatings were also developed during this period but were considered inferior to epoxy because of their lesser water resistance and tendency to yellow. Most of the coating products developed during the World War II period are being used even now. The solvent based paints though abundantly used, due to the pollution problem and toxic
and fire hazard nature, alternate methods of formulations and applications were to be thought of. The development of water soluble paint compositions, electrodeposition of paints from aqueous systems, powder coating (solventless systems) and high solids coatings are some of the alternatives which have been developed for minimising the use of solvent based coating compositions. At present all these systems are being used including the conventional paints but there is an emphasis for adopting these modern methods and work in this direction is progressing.

Chemistry of Organic Coatings

Organic coatings generally consist of polymeric materials with various additives to impart the required properties [3]. The basic film forming material is the polymer/resin. The additives include pigments, dyes, extenders, driers and other materials for incorporating specific properties to the basic polymer film. The chemistry of the film formers is basically concerned with the preparation of the polymers that are used for the liquid coatings and also with the mechanism by which these liquid coatings form dried films. Both clear coatings and pigmented coatings are applied depending on the requirements of the coating. A variety of resins are used for these coatings both natural and synthetic [4-6]. As a paint film dries, these vehicles change
from a liquid to the solid film by one or more of several mechanisms; evaporation of solvents, oxidation, polymerization through application of heat, addition of catalyst or combination of reactive components. It is generally found that the film properties of a surface coating improve as the molecular weight or molecular complexity of the final polymer increase [7]. If the polymer used is of sufficiently high molecular weight to give the desired film properties without further chemical or molecular weight change they are applied as solutions or dispersions and the film formation results from evaporation of the solvent or diluent. These systems referred to as thermoplastic or lacquer type formulations are used as coating materials to some extent [8].

The second method of obtaining a desirable film is to use a polymer system with a complex molecular structure. Since such polymers would be insoluble in common solvents this structure must be formed from predominantly linear but reactive polymers during or after the time the solvent evaporates from the applied films. These thermosetting or enamel type coatings find wide application in the coating industry [9]. The selection of the coating depends on the properties desired in the final film.

The properties of the coatings are decided by the main constituents of the paint film namely the binder (resin/polymer) and the pigment. There are several class of resins
suitable for use in the surface coating industry and each has got its own specific properties for making it suitable for certain specific applications [10].

Synthetic resins are polymeric substances of high molecular weight made up of repeating molecular structural units usually in the form of chains with terminating group at each chain end. The polymer chain may be linear, branched or cross linked or some combination of these forms, depending on functionality and reactivity of the monomers from which they are formed and on the manner of polymerisation [11 - 13]. The physical properties of the polymer are largely determined by the structure of the polymer chains, their molecular weight and the nature of the intermolecular forces that are in effect between chains in close proximity. The chemical properties of the polymer depend upon its chemical composition and structure. Polymers themselves are in different forms according to their structural arrangements like linear polymers, branched polymers, cross linked polymers and copolymers. In the linear polymers, the molecular chains though closely entangled are separate entities. They are described as thermoplastic materials. Branched polymers are those in which basically linear molecular chain acquire long chain side groups as a result of random activation of sites along the already polymerized main chain or by the introduction of occasional trifunctional groups during the polymerization.
process. The side chains are similar in molecular structure to the parent chain and may grow to considerable length with side chains of their own so that a highly branched structure with properties resembling cross linked polymers may be built up. In cross linked polymers the molecular chains are tied together and their mobility reduced by the many primary valence bonds between chains. Such polymers are called thermoset materials and are infusible and insoluble except by chemical attack or degradation. Copolymers are the products formed by the polymerization of two or more different monomers e.g. vinyl chloride-acetate. Each monomer imparts specific properties to the polymer. Vinyl chloride imparts hardness whereas vinyl acetate imparts flexibility and solubility.

Different types of polymerization are involved in the formation of resins. Autooxidative polymerisation is the process whereby certain monomeric molecules absorb oxygen so that hydroperoxides are formed which decompose to produce primary valence bonds between the monomers to give a polymeric structure. Condensation polymerisation is the process whereby a small molecule, generally water, is eliminated in the reaction between molecular units so as to produce primary valence bonds between the monomers to give a polymeric structure.
In addition polymerisation reactive monomers add on to each other to form homopolymers, copolymers and heteropolymers. Homopolymers contain the same monomer repeated while in copolymers different monomers add on but each monomer should be capable of forming homopolymers. In heteropolymers different monomers combine together, but some of the monomers may not be able to form polymer by themselves.

The principal methods of polymerization which are in general use are bulk polymerization, solution polymerization, emulsion polymerization and suspension polymerization. In bulk polymerization the catalyst and initiator are added to the monomer. Most of them are exothermic which makes the reaction difficult to control. In the solution polymerization the monomer and the catalyst along with initiator are dissolved in an inert liquid which may or may not be a solvent for the polymer. It can be more easily controlled than the bulk polymerization. The method is used for both condensation polymers and addition polymers. In emulsion polymerization the monomer which is insoluble in water is emulsified with a surfactant. The polymerization proceeds very rapidly yielding high molecular weight product in finely divided form. Since the polymer is obtained in dispersed phase, there is no appreciable change in the viscosity. The process may be used for addition polymerization. In suspension polymerization, the monomer is dropped into water
and polymerized. No emulsifying agent is used and the monomer droplets are much larger than those in emulsion polymerization.

**Classification of Organic Coatings**

Organic finishes can be classified as paints, enamels and lacquers. A paint consists of a dispersion of a pigment or a combination of pigments in a vehicle consisting of a resin or polymer with addition of thinner or solvent to adjust to the proper viscosity for application. Film formation involves evaporation of the solvent. Pigments are ground with the binder by using solvents and paints are formulated.

An enamel consists of intimate dispersion of pigments in a resin vehicle. The drying of these systems occurs at room temperature by oxidation. The enamel vehicle may be an oil-resin mixture containing either natural or synthetic resin or it may be a straight synthetic resin medium. Enamel coatings are harder and tougher. With a number of synthetic resins now available it is possible to produce coatings with different physical properties and resistance to moisture, chemicals etc. Hard resins and hard pigments favour non-chalking coatings.

Lacquers and solvent type resin finishes are mainly used for prevention of tarnish and oxidation of polished
surfaces. Due to their quick drying characteristics lacquers or solvent type resin finishes find wide use in the protection and decoration of almost any product where spray or dipping application is feasible. Majority of lacquer resins remain soluble in the solvents used for application. Binder, pigment and the solvent make the most important parts of any type of paint.

Binders or film formers may be classified according to their molecular weight [14,15]. Low molecular weight polymers that will not form solid films normally without further chemical reaction form one class. High molecular weight polymers that will form useful films without further chemical reaction form the second class. There are a number of resins available for the surface coating application. The characteristics of a few important resins are described below.

The binders used as surface coatings were originally based on natural oils and resins and gums. Shellac, rosin etc. come under this class. Modified vegetable oils like linseed oil, dehydrated castor oil and tung oil are widely used as coating materials. Alkyd resins form a class of resins which are used in the surface coating industry for different purposes [16]. Alkyds with different oil lengths offer varying properties. These resins can be blended with other resins like amino resins for modifying some of their properties. They give good enamel paints.
Phenolic resins, formed by reacting phenol with formaldehyde, find use as industrial coatings mainly because of the good insulation property and good chemical resistance. They are invariably used in combination with other resinous film formers.

Epoxide resins, a large group of which is based on the reaction product of bisphenol A and epichlorohydrin find very good potentiality in the surface coating industry \([17,18]\). They have got very good corrosion resistance apart from hardness, toughness, adhesion to basis metal and alkali resistance when they are crosslinked with polyamines or polyamide resins. Epoxy resins may be esterified with unsaturated fatty acids to give epoxy esters. Both epoxy esters and crosslinked epoxy resins are used as coating material. Epoxy ester though slightly inferior in quality compared to epoxy polyamide is used as a primer which offers better protection than alkyds. Epoxy resins crosslinked with polyamide is widely used for giving protective coatings over steel structures especially for aggressive corrosive environments.

Amino resins are reaction products of urea or melamine and formaldehyde \([19]\). The amino resins are having good crosslinking capability. Some of the resin systems like acrylics are blended with amino resin for getting the crosslinked species which offer good adhesion and flexibility.
Acrylic polymers are widely used as decorative and protective coatings because of their excellent properties of strength, chemical and weather resistance and fade resistance [20]. The term acrylic has come to represent those polymers containing acrylate and methacrylate esters in their structure along with certain other vinyl unsaturated compounds. Both thermoplastic and thermosetting systems are available, the latter formulated to include monomers possessing additional functional groups that can further react to form crosslinked resin. Acrylic coatings have got very good colour retention properties and are widely used as topcoats in the automobile and other industries especially for good gloss and fade resistance. At the same time it has got sufficient hardness, toughness and corrosion resistant properties also.

Polyurethane resin [21] which is the addition product of isocyanate and polyol is available as two pack system or single pack cured by moisture, air or oxygen. These resin coatings have got very good properties of toughness, hardness, chemical resistance and corrosion resistance. They are widely used in coating industry especially as topcoats taking into account their resistance to weathering.

There are other types of resins which are used as coatings for specified applications, e.g., silicone resins for heat resistance. Apart from these a good number of resins
can be used as combinations to impart certain properties of one resin to the other so that the coating quality will be superior.

The reactions involved in the preparation of some of these resins are indicated below.

**Epoxy resin**

\[
\text{HO} - \text{C} - \text{C} - \text{OH} + 2 \text{CH}_2 - \text{CH} - \text{CH}_2 \text{Cl} \rightarrow
\]

\[
\text{CICH}_2 - \text{CH} - \text{CH}_2 - \text{O} - \text{C} - \text{O} - \text{CH}_2 - \text{CH} - \text{CH}_2 \text{Cl}
\]

\[\text{NaOH}\]

\[
\text{CH}_2 - \text{CH} - \text{CH}_2 - \text{O} - \text{C} - \text{O} - \text{CH}_2 - \text{CH} - \text{CH}_2
\]

\[\text{(Bisphenol A diglycidyl ether)}\]

\[
\text{CH}_2 - \text{CH} - \text{CH}_2 - \text{O} - \text{C} - \text{O} - \text{CH}_2 - \text{CH} - \text{CH}_2
\]

\[\text{+ bisphenol A + epichlorohydrin}\]

\[
\text{CH}_2 - \text{CH} - \text{CH}_2 - \text{O} - \text{C} - \text{O} - \text{CH}_2 - \text{CH} - \text{CH}_2
\]

\[\text{(epoxy resin)}\]
Urethane

\[ R-N=C=O + HO - R_1 \rightarrow R-N-C-OR_1 \]
(Isocyanate) (Alcohol) (Urethane)

Acrylic resin

\[
\begin{align*}
\text{CH}_3 & \\
\text{CH}_2 - C - C & \equiv O \\
\text{CH}_2 = C & \equiv O - \text{CH}_3
\end{align*}
\]
\[
\begin{align*}
\text{CH}_3 & \\
\text{CH}_2 - C - C - CH_2 & - C - CH_2 - C - \\
\text{CH}_3 & \\
\text{CH}_2 - CH & - COOCH_3 & \text{COOCH}_3 & \text{COOCH}_3
\end{align*}
\]
(Methyl Methacrylate) (Polymethacrylate)

Phenolic resin

\[
\begin{align*}
\text{OH} & \\
\text{\text{Phenol}} & + 2\text{CH}_2 \text{OH} \rightarrow \\
\text{OH} & \\
\text{CH}_2 \text{OH} & \rightarrow \\
\text{\text{Phenol formaldehyde resin}}
\end{align*}
\]
Amino resin

\[
\begin{align*}
\text{NH}_2 & \quad \text{CO} & \quad \text{HCHO} \\
\text{NH}_2 & \quad \text{Formaldehyde} & \\
\text{(Urea)} & \\
\text{NH - CH}_2 \text{OH} & \\
\text{CO} & \\
\text{NH}_2 & \\
\text{-N - CH}_2 \text{- N - CH}_2 \text{- N - CH}_2 \text{- N-} & \\
\text{CO} & \quad \text{CO} & \quad \text{CO} & \quad \text{CO} & \\
\text{NH}_2 & \quad \text{NH}_2 & \quad \text{CH}_2 & \\
\text{(Urea formaldehyde resin)}
\end{align*}
\]
Pigments are incorporated in paints to obscure the underlying surface and to decorate the surface [22,23]. Other than these there are some definite purposes for the incorporation of pigments which include enhancing corrosion protection, hardness, toughness, durability etc. of the film. Some pigments are added for changing the consistency of the paint, e.g., the thixotropy. The type of finish which is obtained from a paint is controlled to a degree by pigmentation.

Primary pigments comprises solid particulate material which is dispersed in binder or film former. Among the white pigments titanium dioxide is very widely used. Coloured pigments fall into two main groups, inorganic and organic. Some of the pigments abundantly used earlier are now replaced because of the toxicity, e.g., lead based pigments. Some of the commonly used pigments are listed below.

<table>
<thead>
<tr>
<th>Colour</th>
<th>Inorganic</th>
<th>Organic</th>
</tr>
</thead>
<tbody>
<tr>
<td>White</td>
<td>Titanium dioxide</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zinc oxide</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Antimony oxide</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lead carbonate (basic)</td>
<td></td>
</tr>
<tr>
<td>Red</td>
<td>Red iron oxide</td>
<td>Toluidine red</td>
</tr>
<tr>
<td></td>
<td>Cadmium Selenide</td>
<td>Quinacridones</td>
</tr>
<tr>
<td></td>
<td>Red lead</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chrome red</td>
<td></td>
</tr>
<tr>
<td>Color</td>
<td>Pigment</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>----------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Green</td>
<td>Chromium Oxide</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phthalocyanin green</td>
<td></td>
</tr>
<tr>
<td>Blue/violet</td>
<td>Ultramarine</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phthalocyanin blue</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Prussian blue</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cobalt blue</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Carbazol violet</td>
<td></td>
</tr>
<tr>
<td>Yellow</td>
<td>Lead, Zinc and Barium Chromate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cadmium Sulfide</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Iron oxide</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nickel azo yellow</td>
<td></td>
</tr>
<tr>
<td>Black</td>
<td>Carbon black</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Aniline black</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Copper carbonate</td>
<td></td>
</tr>
</tbody>
</table>

Pigments are used to provide aesthetic appeal, surface protection and some auxiliary properties like film reinforcement, hardness, fire retardance, anticondensation, nonskid surfaces etc.

True pigments are used for colour or opacity and extender pigments as filler material. Extender pigments are normally cheap materials and some of the examples of this category are barytes, chalk, calcite, talc, mica etc. The main qualities required for the pigments are appearance, resistance to attack by the other constituents, durability and corrosion protection. Corrosion resistance provided by paint coatings is a particularly important feature and corrosion inhibiting pigments and techniques of anticorrosive paint design form a technology of their own.
In selecting pigments for paints the type and end use of the paint should be taken into consideration. The properties like hardness, toughness, corrosion protection etc. which will contribute to the bare resin film should be taken into account. The type of the film former which is used for the paint formulation should be first considered before selecting the pigment because some of the films are affected by the chemical nature of the pigment. Another factor that should be considered for the pigment selection is the solid colour, special effect or transparency required for the finish. For getting mixed colours blending of pigments is also resorted which should be done carefully. Organic and inorganic coloured pigments can be blended to produce subtractive colours.

Corrosion inhibiting pigments are effective in preventing rusting of surface by

1) helping to provide a physical barrier to the passage of water and oxygen necessary for corrosion
2) being sacrificially dissolved as an anode thus protecting the anodic sites that would have pitted
3) providing soluble passivating ions to protect the metal or
4) producing insoluble films which prevent active corrosion.
The main corrosion inhibiting pigments are red lead, basic lead silico chromate, zinc chromate, strontium chromate, zinc molybdate, calcium plumbate, zinc phosphate, zinc dust, barium chromate and micaceous iron oxide. Inhibitive pigments are mainly used in primers or first coat and in coatings which use the concept of inhibition rather than impermeability. These are pigments which 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. This class of pigments include zinc chromate, strontium chromate, lead chromate, red lead, zinc powder etc.

Solvents or thinners are volatile organic liquids for dissolving the resin and for reducing the viscosity of the paint [24], e.g., toluene, xylene, methyl ethyl ketone etc. The important properties of the paint solvent include solvent power, rate of evaporation, boiling point, distillation range, flash point, inflammability and toxicity.

Many a solvent used in paint industry are obtained from petroleum products. Depending on the solubility required solvents are used. If sufficient solubility is not achieved, mixtures of solvents can be used which will have more solvent power.
Corrosion and its Control

Huge amounts are being spent by every country for corrosion protective measures. The total investment on this will be around 2-3% G.N.P. Out of this large sums 30 to 40% goes towards protective coatings. Quality improvement for better decorative properties and better protection brought under control the corrosion problem in a technical sense. The required combination of properties for a given coating is determined in every case by the special nature of the coating property. There are countless variation of coating needs and any particular need may have a variety of solutions in terms of materials and coating methods. A solution to a specific problem can be arrived at only by a cooperative effort by both the user and the supplier of coatings. For example, for a corrosion protective coating in a given environment many coating systems may be suitable, but the choice can be made by the factors prevailing in the specific atmosphere.

1. Mechanism of Corrosion

Corrosion is an electrochemical phenomenon. Since the different regions of the same metal surface have different electrode potentials with respect to the same environment, microgalvanic cells are formed leading to corrosion of metal at the regions with more negative potential and
formation of OH$^-$ or evolution of hydrogen gas (reduction) at the region with more positive potential [25,26].

Thus the dissolution of a metal in a liquid environment occurs at discrete sites (anodes) and may be represented for a divalent metal by the oxidation reaction.

$$\text{M} \rightarrow \text{M}^{++} + 2\text{e}^-$$

which represents the formation of the ion M$^{++}$ in solution from the atom, M having two electrons e, in the metal. To maintain electrical neutrality in the metal there must be a simultaneous cathodic reaction in which electrons are consumed. The likely cathodic reactions are, in acid solution,

$$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$$

in acids containing dissolved oxygen

$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$$

in neutral and slightly alkaline media

$$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$$

A corrosion cell consists of an anode and cathode in contact with each other and with a common electrolyte. The driving force for the corrosion reaction is determined by the difference in potential or the e.m.f. between the anode and cathode.
At the corrosion potential the metal dissolution rate \( i_a \) is equal to hydrogen ion or oxygen reduction rate \( i_c \) and this again corresponds to the corrosion rate \( i_{corr} \). Thus

\[ i_a = i_c = i_{corr} \]

The behaviour of the micro galvanic cell at the corroding metal can be schematically represented by the polarisation curves of the Evan's diagram (Fig.1). These diagrams will also help in understanding the mode of control of the corrosion processes in terms of the anodic or cathodic reactions or both, as well as in understanding the mechanism of corrosion control under different conditions.

At a corroding surface corrosion current flows involving anodic and cathodic reactions, metal ions accumulate in the immediate vicinity of the anode while near the cathode \( \text{OH}^- \) ions accumulate and dissolved oxygen is consumed. The speed with which the reactions occur is very fast compared with the secondary processes of diffusion and convection by means of which the ions are removed and dissolved oxygen replenished. The resulting changes in the composition of local environments change the reversible electrode potentials. The greater the current density, the greater the potential change. The polarization shifts the cathode potential in the active direction and the anode potential in the noble
Fig. 1. Polarisation diagram for two metals immersed in a solution (Evans diagram)
direction, thus acting as a counter e.m.f. that reduces the effective cell potential. Polarization may also occur if an activation energy is required for the electrode reaction to occur. It is often observed that the cathodic reaction of hydrogen formation does not occur even though conditions are thermodynamically favourable; the potential at which hydrogen is evolved from the cathode of a corrosion cell is often more active than the reversible value predicted by the Nernst equation. Activation polarization of any kind increases with current density according to the Tafel equation

$$\eta = \beta \log \frac{i}{i_0}$$

where \(i\) is the current density and \(\beta\) and \(i_0\) are constants for a given metal and environment. The polarization behaviour of corrosion cells largely determines the rate of corrosion. The effective voltages of corrosion cells may be reduced by polarization virtually to zero in which case the rate of corrosion is limited to that required to maintain this polarization. The progress of corrosion may be controlled by the extent either of anodic polarization or cathodic polarization.

The anodic and cathodic areas may be of very small dimension and may shift with time in which case corrosion will be nearly uniform over the corroding surface. Zinc
attacked by hydrochloric acid; or mild steel exposed to the atmosphere suffer uniform corrosion. If most of the surface behaves as cathode with the anodic reaction confined to a relatively few active areas pitting occurs. The pitting of aluminium happens in this manner. The corrosion rate is determined by the anodic current density. Foreign metal inclusions obviously provide small anodes or cathodes depending on whether they are active or noble relative to the parent metal.

In atmospheric environments moisture is available from rain, dew or water vapour frequent in the air. At sufficiently high humidities moisture may be absorbed by corrosion products to produce conditions necessary for wet corrosion. Atmospheric contaminants e.g. sulphur dioxide dissolved in moisture cause wide variations in observed corrosion rates.

The direct oxidation or tarnishing of metals may be viewed as consisting of the metal surface acting as anode and a monomolecular layer of oxygen, sulphur or other non-metallic element in contact with the surface serving as cathode. In the action of this cell both metallic ions and electrons migrate from the metal into the interfacial region where the electrons ionize the adsorbed nonmetallic elements. These in turn unite with the migrating cations to form a solid state lattice structure on the metal surface.
2. Corrosion of iron and steel

It has been established that the three factors that control the corrosion of iron and steel are moisture, oxygen and potential difference between iron and other bodies with which it is in contact [27]. There can be scale or rust on the surface or carbon as a constituent of the steel. The presence of dissolved salts (Cl⁻ or SO₄²⁻) or carbon dioxide dissolved in moisture will catalyse the corrosion reaction. The corrosion may be uniformly distributed over the surface (general rusting) or highly localized (pitting). 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 clean mild steel plate is exposed to the atmosphere a layer of oxide is formed very rapidly. At the base of a fissure in the oxide film there is iron or a very thin oxide film. At this point iron will tend to go into solution as ferrous ions and electrons will be liberated on the metal. The reverse reaction will also take place and in the absence of other factors a state of equilibrium will be reached.

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e} \quad \text{(anode reaction)} \]

Electrons will flow to the oxide film and then in the presence of water and oxygen are consumed in the formation of hydroxyl ions.
The flow of electrons away from iron upsets the equilibrium and the metal dissolves at the base of the fissure. The rate of dissolution of the iron anode will depend on the rate of removal of electrons and this will in turn depend on the rate of supply of oxygen at the oxide surface (cathode). If this is sufficient and the cathode is large, reaction will be rapid and severe pitting of the steel will take place. The ferrous and hydroxyl ions migrate towards the oppositely charged electrodes and ultimately react to form ferrous hydroxide

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

This is then oxidized to hydrated ferric oxide

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

The precipitation of ferrous hydroxide and subsequent oxidation takes place away from the metal surface and consequently the rust does not protect the metal from further attack.

In the presence of a neutral electrolyte such as sodium chloride the rate of corrosion is considerably increased but in the presence of oxygen the electrode reactions are substantially the same. Sodium ions are not discharged at the cathode since this is not sufficiently negative due
to the cathode reaction with oxygen. However, in the absence of oxygen, hydrogen is discharged.

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

This can lead to accumulation of hydrogen on the cathode and the rate of cell reaction will gradually decrease (by polarization). Methods for the prevention of corrosion are designed to suppress one or both of the electrode reactions or to provide a complete barrier between the steel and the environment.

The essential point of corrosion process is that it involves the movement of electrons through the metal, the circuit being completed through the water. If the water contains dissolved salts such as salt from sea water, the transfer of electron is made easier and the extent of corrosion is proportionally increased. In addition to increasing the conductivity of solutions, the chloride ion is especially aggressive and has a very damaging effect upon the corrosion of steel.

3. Corrosion protection by organic coatings

As already mentioned paint coatings are applied for protection of metals from corrosion. They are applied in two or three coats. The primer coat should have good adhesion, and should be anticorrosive and it should form a suitable base for the intermediate coat. The adhesion to the
basis metal is primarily a function of the resin binder in the primer, the anticorrosive nature is largely contributed by the pigments where as the formation of a good base for the top coats is partly a function of the binder. The choice of the type of binder for the primer is also governed by the choice of top coats. For a paint coating to prevent the onset of corrosion the following factors either alone or in combination may be considered. They are barrier effect, chemical inhibition, adsorption of polar molecules and electrical resistance.

Organic protective coatings can be classified as barrier coats which provide a purely physical barrier to the ingress of moisture and oxygen and paints (including primers) in which the barrier effect is augmented by corrosion inhibiting pigments. The line of demarcation is often indistinct. Organic barrier coats can be used for either temporary or permanent protection. Temporary coats (also known as temporary rust preventives) e.g., jellies, grease/resin mixtures etc. Permanent barrier coats are required to resist penetration by moisture and oxygen and are applied in thicker films than normal paints, e.g., bituminous coatings, chlorinated rubbers, epoxies etc.

The use of corrosion-suppressing primers is by far the most widely used method for protecting steel and it
is now universally accepted that the protection afforded by any primer is influenced by the condition of the surface to which it is applied [28]. Good protection is associated with good adhesion and this requires a clean surface. The primer should ideally possess the following properties.

- suitability for application by the specified method under the required conditions;
- effective solvent release enabling it to dry within the specified time;
- good adhesion to the metal surface under both dry and wet conditions;
- the surface must provide a good key for subsequent coats;
- a high degree of impermeability to moisture and oxygen.

Examples of commonly used pigments for primers are red oxide, zinc chromate, lead chromate, lead silico-chromate, zinc powder etc. [29].

The incorporation of inorganic or metallic pigments into polymer films or paint coatings is a well established means of decreasing permeability and avoiding corrosion. There are three requirements for maximum effectiveness [30,31].

1. The pigments should be essentially impermeable.
2. Platy or pigments of high aspect ratio should be used.

The pigment in the coating should be aligning in the
plane perpendicular to the diffusion path, i.e., parallel to the paint/substrate interface.

3. There must be excellent adhesion between pigment and binder in both dry and wet conditions.

The properties of paint coating can change with pigmentation. Above the critical pigment volume concentration there is insufficient binder to fill the interpigment spaces and the coating will be porous and much more permeable. The optimum pigment volume concentration for minimum permeability, is just below the critical pigment volume concentration. Micaceous iron oxide, mica, glass flakes, aluminium flakes, stainless steel etc. are the main lamellar pigments. Aluminium flake has been shown to be particularly successful as a barrier pigment in paint coatings.

**Essential coating properties**

The essential properties which a corrosion protective coating should possess are water resistance, chemical resistance, proper adhesion, abrasion resistance, ability to expand and contract and weather resistance.

Resistance to water is the most important property of a coating as there is the possibility of coming into contact with water by any coating in one form or the other[32]. For a high performance corrosion-resistant coating to also have excellent water resistance means it must not only
withstand continuous immersion in water or sea water, but it must do so without blistering, cracking, softening, swelling or loss of adhesion. It must also withstand repeated cycles of hot and cold adhesion. The water absorption refers to the amount of water which is picked up and retained within the molecular spaces of the coating. If the coating is strongly adherent to the basis metal the moisture will remain as an inert material. If the coating has poor adhesion there is an interface between the coating and the steel (or any substrate) and the moisture passes into the direction of poor adhesion, condensing in the space. If there is increase in temperature the moisture creates blisters. The mechanism of osmosis also concerns the passage of moisture through a coating. All organic coatings will transmit moisture vapour which make them semipermeable membranes and therefore subject to this mechanism. To prevent the bad effect of osmosis the coating surface should be clean before immersion or exposure to high humidity. Another important property for the organic coating is the dielectric strength as the coating must break the electrical circuit set up during a corrosion reaction in order to be corrosion resistant. It does so by resisting the passage of any electrons and prevents any metal from going into solution at the anode. If the electrons can not travel to the cathode the corrosion mechanism is not possible. The property is also a key one wherever the coatings are to be used along with cathodic protection.
Another important property required for a corrosion resistant organic coating is the resistance to ionic passage. A coating which has a very high molecular weight and dense molecular structure would have the least ionic transfer through the coating. Resins used for coating have varying degrees of resistance to ionic and electron passage. Epoxy and vinyl coatings have good resistance to ions and at the same time epoxies have some tendency to pass electrons.

Chemical resistance of a coating is a property of the resin and also the additives including the pigments. A corrosion resistant coating especially primer coating should be showing good resistance to alkalies, acids and salts over a wide range of pH. Alkali resistance is extremely important in a primer. One of the chemical reactions in the corrosion process is the formation of strong alkali at the cathode. Any primer which is not highly resistant to alkali will tend to fail in the cathode area. A coating should have very good adhesion also and it is created by the physical and chemical forces which interact at the interface of the coating and the substrate. Several other properties including abrasion, weather resistance etc. are also very important as far as the coating performance is concerned [33].

The basic properties a coating should possess depend on the purpose for which coating is applied. For example,
a coating applied to protect from corrosion should have the basic property of withstanding the corrosive environment. The fundamental concepts involved in corrosion resistant coatings include those of coating protection, component design, component function and coating formulation. Many coatings contain a large number of ingredients each of which has its own function in the overall performance of the coating.

Impermeability is a concept basic to most available anticorrosive coatings. An impermeable coating contains no material which will react with moisture vapour. Each ingredient is designed to be unaffected by moisture vapour and allow only for the moisture to get accumulated. An impervious coating is often used as an immersion coating and hence should be inert to the surrounding immersion medium.

Inhibition is another concept which normally goes with the primers [34,35]. An inhibiting primer contains pigments that can react with the moisture/water content within the coating which then react with the metallic substrate to passivate, preventing from further corrosion of the substrate. The inhibitive coatings are mostly used in atmospheric exposures of steel or other metals. Many resin systems can be used for inhibitive primers which include vinyls, epoxies and urethanes. The commonly used pigments for this purpose are zinc chromate, strontium chromate, barium chromate, red lead etc.
Application of organic coatings

Success in industrial painting to specification demands the correct technique and the skill in the application of paints. Uneven layers of paint produce stresses that are liable to promote cracking, blistering, peeling and other defects. Some of the methods of paint application now in vogue are described in this section.

The method of application by dipping is widely used [36] for undercoats where uniformity in film thickness and appearance are not very important. In the dip application there is economy in paint and labour. Large dip tanks of paint however present serious fire hazards. For this reason water based paints are being formulated. In the 'roto dip' process special machinery [37] consisting of a rotating framework for taking the article in and out of the paint is used. This method is applicable especially for car bodies.

In brush application which is still the most widely used among conventional application techniques care has to be taken in the use of specific brushes to obtain uniform acceptable coatings [38].

In the flow coating process the articles to be finished are given an excess of paint coating which subsequently pass through a solvent chamber for getting good flow and setting of the paint film. In curtain coating, the articles
to be painted are placed on a conveyor and passed through a curtain of paint on to a second conveyor, the thickness depending on the speed of the conveyor and the thickness of the paint curtain.

In the roller coating process, flat articles are easily coated, the thickness being controlled by the pressure of application of the roller.

In the compressed air spraying method, paint is atomized by compressed air; the method can be adapted for rapid application on complex shaped articles [39]. However, there is paint wastage and also health hazard due to overspray, spray bounce and spray fog. In the steam spraying process compressed air is replaced by super heated steam in the pressure range of 1-3 kg cm\(^{-2}\) with 105-110°C temperature at the spray gun. The method has the advantage of reducing spray fog and spray bounce. The same advantages are present in the hydraulic spraying process. In this process atomization is effected by applying high pressure to the liquid paint using special spray guns. Airless spraying (hydraulic spraying) is a high production method for applying decorative maintenance paints and protective coatings. Airless spray painting is cleaner and faster [40] than the other conventional spraying methods. The former greatly reduces the fog often to 50% of that experienced with the other conventional spraying systems. In the hot hydraulic spraying process,
the paint is heated to about 80°C, the spray pressure is kept at about 40 kg cm\(^{-2}\). Due to the absence of compressed air and high spray pressures, spray bounce and spray fog are reduced so much that hot hydraulic spray can be carried out in well ventilated shops without undue discomfort to workers in the near vicinity. In the airless spray method of painting because of the high velocity at the nozzle the spray can cause serious injury within a range of several feet and the gun should be handled with great precaution. Airless spraying can also cause electrostatic fire and explosion hazards [41].

Methods of paint application such as brushing, dipping, roller coating and others result in atmospheric pollution by solvents. During spray application the entire coating material is brought to a spray form in which it is easily inhaled. Whatever be the method used to apply an organic solvent based coating, the solvent has to be evaporated and this gives rise to atmospheric pollution problems.

In the electrostatic spraying method [42] the paint is atomized by low pressure compressed air and given an electrical charge by a combination of centrifugal and electrostatic forces. This method takes advantage of the attraction existing between bodies carrying unlike electric charges. The process is economical in paint usage and can be applied to a wide range of metal articles capable of carrying electric
When compressed air is used, the articles to be finished are carried on a grounded conveyor and charged to about 90,000 V with a current of a few milliamperes. The atomized paint particles bear a positive charge and are attracted to the grounded articles which become coated with paint. With such a system about 75% of the atomized material is deposited as useful coating. There is a considerable increase in efficiency, unlike an efficiency of 20% in the compressed air spraying technique. Further, the ability of electrostatic process to deposit material on to the surface of an object which is completely hidden from the spraying device, enables intricately shaped objects to be coated conveniently. In all electrostatic coating processes, it is essential that the articles being coated should be conducting and the paints for electrostatic application must have an electrical resistivity characteristics between certain well defined limits. In practice, most normal industrial and decorative paints except water based paints and some of the very dense paints like red lead primers can be formulated to suit electrostatic spraying process.

In order to comply with air pollution regulations, metal finishers may probably have to switch from low solids high solvents coating compositions to some other acceptable ones complying with legal requirements. Generally speaking water borne coatings [43] high solids coatings [44] and powder coatings [45] are the main choices for overcoming
the pollution problem although each one of them has its own limitations, depending on the particular product and application technique under consideration. Water based coatings have been developed for a variety of industrial applications and electrodeposition from water borne systems is now well established and has got several advantages. High solids coatings are to be regarded as merely a stop gap arrangement pending the successful development of suitable water borne coating systems, free of organic solvents. The greatest attraction of the latter is that the technology of application does not differ radically from the conventional solvent based coatings and hence existing application and curing equipments for solvent based systems can be adapted for use with water borne systems. Applying coating in the form of powder has got two advantages - organic solvents are entirely eliminated and the overspray can be conveniently collected, reclaimed/reused and at worst suitably disposed of. Different methods like fluidized bed technique, electrostatic spraying and electrostatic fluidized bed technique can be used for the powder application. High thickness can be built up by adopting this technology.

In the radiation curing technique also solvents can be completely eliminated [46,47]. High energy radiation often referred to as ionizing radiation like x-rays and electrons are useful in polymerization applications, their
energies exceed by much the bond energies of organic molecules. In addition to permitting a higher throughput of articles at greater energy efficiencies, radiation curing can be of help in reducing atmospheric pollution and fire hazards in the conventional paint industries. It can be combined very favourably with polymer deposition for modernising the industrial finishers' needs.

Of all the modern paint application techniques described above, electrodeposition from aqueous systems has revolutionised the coating industry because of the innumerable advantages of the process.