CHAPTER II
ELECTRODEPOSITION OF RESINS AND PIGMENTED RESINS

Introduction

Electrodeposition of resins and paints on to metal substrates from water borne systems has been developed because of its several advantages over other methods of paint application [48-50]. This is one example of direct industrial application of electrophoresis [51]. In this process an electronically conducting substrate is dipped into an aqueous solution of water-borne paint and a voltage applied. Fig.2 shows a schematic representation of the process of electrodeposition. The current flow through the system causes electrochemical reactions at the phase boundary of substrate-bath leading to the electrocoagulation of the resin. Two types of coating systems have been developed - anodic systems and cathodic systems [52-54].

The use of anodic electrodeposition as a method of coating articles has been known for many years. Rubber was the first material to be coated for the purpose of giving protection. The rubber emulsion or latex mix which contain accelerators and other ingredients on deposition gives a homogeneous coating on the anode and serves the usual functions of the coating. Sheppard and Eberlin [55] had done elaborate work on rubber deposition and were able to get
Fig. 2. Process of electrodeposition of resin
good coatings of rubber. Since then much work has been done in the field of electrodeposition and several water soluble resins suitable for electrodeposition has been formulated. A number of resins - both anodic and cathodic [56,57] have been synthesized capable of giving electrocoatings having much of the desired properties like hardness, impact resistance, flexibility, toughness, corrosion protection and chemical resistance.

Though the main purpose of the development of electrodeposition process from water borne resin systems was the elimination of fire and toxic hazards due to the use of organic solvents it later turned out to be a unique method of coating metallic substrates mainly because of the high corrosion resistance the coating imparted to metals especially steels. The overall advantages of the electrodeposition process over other paint application techniques [58] are:

1) uniform coverage of the coating over the substrate;
2) ability to coat an article of any shape and size;
3) elimination of fire and toxic hazards;
4) easy for automation;
5) less cost

Some of the aspects of the technology like formulation, process control and mechanism are dealt with in detail by several authors [59-62].
The main task in the development of the electrophoretic coating systems is the preparation of water soluble resins suitable for electrodeposition.

**Water reducible resins**

A water soluble polymer which is one that can be dissolved/dispersed in water with or without the assistance of cosolvents and neutralizing agents forms colloidal solutions [63]. The solvent-borne film forming polymers are too hydrophobic to form solutions in water. Water soluble versions of these solvent borne polymer types can be produced by introducing specific functional groups along the polymer backbone. These functional groups are hydrophilic or can be modified to produce hydrophilic groups. The resins which can be brought to water soluble system include alkyds, polyesters, acrylics and epoxies [64-67]. As a general rule free or basic functional groups are incorporated along the polymer backbone. These functional groups are capable of being neutralized by acids or bases to produce a water soluble system.

Water soluble resins have been developed both for conventional application techniques and for electrodeposition technology [68]. For conventional application like spraying and brushing the system contains less water and the technique of curing is either by air drying or stoving. In the case of electrodeposition, solids content in the bath is quite
small and water is used up to 80% and drying is done mainly by stoving though air drying technique also can be used depending on the coating system.

For getting stable water borne systems additives are also made use of. Especially when the system is not water soluble (without salt formation) additives like emulsifiers (cationic or anionic), protective colloids, thickeners, surfactants and coalescing agents are added as per the requirements of the particular system used.

**Water soluble resins used for electrodeposition**

Some of the resins used extensively for electrodeposition purposes are mentioned below [69].

**Maleinized drying oils**: Drying oils like linseed oil, dehydrated castor oil and tung oil can be maleinized and the adduct is deliberately made to contain residual carboxylic groups which can be neutralised by bases [70-72]. These water soluble systems give good electrocoatings when deposited on metallic substrates [73].

**Alkyd Resins**: Water soluble alkyd resins contain pendant acid groups which enables the water solubilisation. The acid groups are introduced along the polymer backbone which can be done in different ways. Generally water soluble alkyds are prepared from fatty acids rather than vegetable oils.
This overcomes the need for an alcoholysis or acidolysis stage to produce a product that can readily react with the remaining acids and polyols. Polyols containing primary hydroxyl groups such as trimethylol propane and trimethylol ethane are preferred to polyols such as glycerol as they are without secondary hydroxyl groups which do not react with anhydrides so readily \[74,75\].

Polyesters: Water soluble polyesters or oil free alkyds are based on components commonly used in alkyds. The processing techniques are also similar. The polyesters do not contain any fatty acid. They rely on the use of long carbon chain dibasic acids and suitable combinations of polyols to give them the required degree of flexibility \[76\].

Epoxy resins: Water soluble modified epoxy resins are being used in commercial quantities as binders in electrodeposition primers especially in automobile industries. Epoxy resins are well known as a coating material for their corrosion protective property \[77,78\]. They are widely used both for anodic electrodeposition and cathodic deposition. One of the earliest methods of preparing a water soluble epoxy resin was to react epoxy resins with maleinized oils

\[
\text{(epoxy resin)} \quad \text{(maleinized fatty acid)} \quad \text{(epoxy ester)}
\]

\[
\begin{align*}
\text{\begin{tabular}{c}
\text{CH-CH} \\
\text{0}
\end{tabular}} & \quad \text{R-C-OH} & \quad \text{\begin{tabular}{c}
\text{CH-CH} \\
\text{0}
\end{tabular}} \quad \text{OH} \\
\text{0} & & \text{0} \\
\end{align*}
\]
Epoxy esters when reacted with excess maleic anhydride or acid will give the maleic half ester which can be solubilised by base and used for electrodeposition.

\[
\begin{align*}
\text{epoxy ester} & \quad \text{(maleic anhydride)} \\
\text{CH}_2\text{-CH-CH}_2\text{-O-\text{C-R}} & \quad \text{CH}-\text{C} \quad \text{CH}_2\text{-CH-CH}_2\text{-O-\text{C-R}} \\
\text{OH} & \quad \text{OH} \\
& \quad 0 = \text{C-CH=CH-C-O} \\
\end{align*}
\]

These epoxy esters are used for anodic electrodeposition.

For cathodic electrodeposition cationic polymers are prepared by different methods. A typical example is by (1) amine modification.

\[
\begin{align*}
\text{(Epoxy resin)} & \quad \text{(Secondary amine)} \\
\text{R}_1\text{OH} & \quad \text{R}_2\text{OH} \\
\text{CH}-\text{CH}_2\text{-N} & \quad \text{H-N} \\
\text{OH} & \quad \text{R}_1\text{-OH} \\
& \quad \text{R}_2\text{-OH} \\
\end{align*}
\]

(Epoxy amine adduct)
(2) Quaternary ammonium salt formation

\[
\begin{align*}
-\text{O-CH}_2\text{-CH-CH}_2\text{O} + & \quad R_3N + \quad R_1\text{C} \quad \longrightarrow \\
(\text{epoxy resin}) & & (\text{amine}) & & (\text{fatty acid})
\end{align*}
\]

Apart from the reactions mentioned above epoxy resins are capable of undergoing a variety of reactions and can produce water soluble polymers which can be used for electro-coating.

Epoxy-polyamide resins have also been electrodeposited [79,80] from aqueous systems which give excellent properties. But there are some limitations. As they are two pack systems, the shelf life is very short.

Acrylics: Water soluble acrylics can be prepared by employing conventional acrylic polymerization techniques. Thermo-plastic and thermosetting acrylics are available and both cationic and anionic polymers can be produced because of the availability of a wide variety of ethylenically unsaturated monomers. Anionic water soluble acrylics can be produced because of the availability of a wide variety of
ethyleneically unsaturated monomers. Anionic water soluble acrylics can be produced by copolymerizing functional monomers such as maleic anhydride, methacrylic acid or acrylic acid with other monomer combinations. This gives pendant carboxylic groups which can be neutralised with bases.

Thermoplastic acrylic resins dry by evaporation as there is no crosslinking reaction. When water resistance is not a critical factor, these coatings can be used. Water soluble thermosetting acrylics are commonly produced by making a polymer which is solubilized by neutralizing the carboxylic groups by bases like amines.

Amino resin: Water soluble amino resins can be prepared but their very high reactivity and poor stability make them generally unsuitable for use singly in surface coatings.

Other water soluble polymers that are used for electrodeposition are the polybutadiene copolymers.

Apart from the systems mentioned above modified resins and combinations of resins can be prepared and coatings from these applied for incorporating specific properties to the coatings [81]. For example water soluble alkyds can be modified with acrylics and can be electrodeposited easily. Such a coating will have definite advantages like improved initial drying properties, water resistance, resistance to yellowing etc. Another example is the silicone modified
polyester or alkyd which has got improved properties of heat resistance and exterior durability. Alkyd-amino-epoxy combination can be electrodeposited and such a coating has got improved corrosion protection and drying properties [82].

**Electrodeposition of pigment**ed resins

Apart from the resin components the bath for electro-painting contains pigments, extenders and other additives which are necessary to impart the desired properties of the coating. Almost all the pigments used for solvent based coatings can be used for electrocoating also with the exception of those which are water soluble. A detailed account of pigmentation of finishes for electrodeposition is given by Tasker and Taylor [83]. The colloidal particles are adsorbed over the pigment particles and this facilitates the movement of these pigment particles towards the anode or cathode as the case may be. There is a critical pigment volume concentration beyond which the adhesion of the coating will not be good. Since mostly electrocoatings are applied for primer coating this becomes a very important factor.

In electrodeposition of pigment**ed resins complications will arise as this will be made up of the dissolved component ionised by electrolytic dissociation and an aqueous dispersion of a colloidal macromolecular material with pigments and extenders of varying particle size and crystalline
structure and the results of the application of an electric potential will also be very complicated [84]. The application of a direct current involves the carrying of the current by the migration of the ions and electrically charged colloidal particles.

**Mechanism of electrodeposition**

Several authors have investigated the mechanism of coating formation by electrodeposition [85-97].

Resinous material behaves as polyelectrolyte. Some of the counter ions are essentially free thus contributing to the conductivity of the system. Because of the absence of the supporting electrolyte the ionic conductivity of the system is directly related to the properties of the polyelectrolyte. Specific conductivities of the electrodeposition bath are in the order of $0.5 - 2.0 \times 10^{-3}$ mho at room temperature. This will double by raising the temperature to about 70°C. The molar conductivities of the bath varies from 10 to 50 mho at a two to three fold viscosity thus reaching the same order of magnitude as aqueous solution of strong electrolytes (100-150 mho).

The stability of the colloidal system depends among other things on the net charge of the particles. This can be neutralised by the passage of current. In the anodic system carboxyl groups are present and hydrogen ions are
more efficient for flocculation of the system containing carboxyl groups due to the basic character of these groups. In the cathodic system nitronium or sulphonium groups are neutralised by hydroxyl groups.

Electrophoresis of colloidal particles can be understood according to Helmholtz as an equilibrium between frictional forces and electrical forces. The velocity of migration, \( v \), is given by

\[
v = \frac{\zeta \mathcal{E}}{6 \pi \eta}
\]

where \( \varepsilon \) is the dielectric constant for the liquid concerned, \( \zeta \) Zeta potential, \( \mathcal{E} \) potential gradient, and \( \eta \) the coefficient of viscosity.

The macroions must be discharged in the course of the electrocoating process. This can be done directly via electron transfer or indirectly via neutralization by counter ions, e.g., protons. The initial current density is a determining factor in producing satisfactory coating. The mechanism of deposition is described as commencing with a deposit which is permeable to ionic migration, thus giving little voltage rise at constant current followed by electrosorption, dehydration, compacting and local heating which bring about a rapid increase in the resistance of the deposit. The process continues until there is practically no further passage of current.
1. Anodic electrodeposition

Using a clear solution of resin solubilised by a base for anodic deposition, the deposition will be affected by type of metal used for anode, current density, temperature, agitation, solid content and pH. The first effect of the application of the DC current is a destabilisation of the aqueous dispersion of the medium in the region adjacent to the anode and this destabilisation is brought about by protons or metallic cations at the anode. It is suggested that the anionic substances present in a paint and dischargeable at the anode can be divided into a number of types as follows.

1) simple inorganic anions from extraneous electrolysis,
2) organic anions arising from surfactants present in the aqueous phase which are not adsorbed onto the surface of emulsion droplets or pigment particles,
3) anions arising from unreacted products,
4) complex polybasic anions due to water soluble resins which may show a wide variation in molecular weight,
5) emulsion droplets and pigment particles carrying adsorbed layers of ionised anionic surfactants, and
6) emulsion particles carrying ionisable anionic groupings as part of a polymer chain.

The current in the bath is produced by the migration of ions and of electrically charged colloidal particles.
The velocity with which the particles move is a function of the dielectric constant and the viscosity of the suspending liquid, the applied field strength and the zetapotential at the interface. The migration velocities depend on the strength of the electric field, pH of the bath, electrical conductivity of the bath, dielectric constant of dispersing medium, radius and charge of particles, surface potential of particles and viscosity and temperature of the bath.

During anodic deposition several reactions are possible like direct discharge of the carboxylate groups, electrolytic decomposition of water, oxidation of binder, metal dissolution of the anode etc.

\[ R^-\text{COO} \rightarrow R^-\text{COO} + e \]
\[ H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e \]
\[ R^-\text{C-H} + H_2O \rightarrow R^-\text{C-OH} + 2H^+ + 2e \]
\[ Me \rightarrow Me^{2+} + 2e \]
\[ R^-\text{COO}^- + H^+ \rightarrow R^-\text{COOH} \]
\[ 2R^-\text{COO}^- + Me^{2+} \rightarrow R^-\text{COO-Me} \stackrel{00C-R}{\rightarrow} \]

All these reactions may take place at different rates depending on the process conditions. They take place in a thin diffusion layer next to the anode. Generally the most important reaction is the decomposition of water and metal dissolution may be important with soluble metals ([98]). Resins are
coagulated from the solutions or dispersions mainly by converting the highly soluble carboxylate groups into the much less hydrophilic carboxylic acid groups. The bases which are used for dissolving the binder remain in the electrodeposition bath. The pH rise is avoided by adding compensation material. Coagulation of the binders may also be effected by multicharged metal ions.

Electrodeposition is normally carried out either at constant current density or at constant voltage. When current is applied, electrochemical reaction starts. The concentration of the ions at the interface is given by Sand's equation

\[ C_{x=0} = C_b + \frac{2j}{nF} \sqrt{\frac{t}{\pi D}} \]

where \( C_{x=0} \) is concentration at the interface; \( C_b \) bulk concentration; \( j \) current density; \( t \) time; \( F \) Faraday's constant and \( D \) diffusion coefficient.

From this equation it is possible to calculate the interfacial concentration of \( H^+ \) ions and the pH at the electrode surface [99]. As an example with zinc phosphated steel, pH at the surface was calculated to be 2.2 whereas the bath pH was 8.9. If the film is an electronic insulator, it cannot transport the electrons which are required for the reactions to take place. Therefore, this charge transfer can take place only at the metal/film interface. The ions formed
in the reaction then carry current through the film. They react chemically with the carboxylic ions arriving from the bath giving rise to the formation of new layers of film, thus increasing the film thickness. The transport of the ions through the film is carried by the presence of a high electrical field.

Anode potential represents the sum of the voltage drops across the metal/film interface, across the film thickness and across the film-paint interface. At constant applied voltage non-ohmic behaviour should be expected at higher fields. Non-ohmic conduction in polymer film was already mentioned by different authors. It was assumed that this behaviour is caused by space charge region. The fields during the electrodeposition of polymers are high enough to cause the dissociation of deposited free acids and metallic soaps.

The mechanism of coating by electrodeposition is related to the ability of polyelectrolytes to change their water solubility depending on the pH value. The colloidal resin particles are transported by several processes to the substrate. In the bulk of the solution convective flow generally predominates. Since there is no supporting electrolyte the ionic conductivity of the system is directly related to the properties of the polyelectrolyte. Macro ions should be discharged in the course of electrodeposition process which can be by electron transfer or by neutralization by
counter ions. The film builds up resistance. It is an ionic conductor of high resistivity due to the low concentration of free protons. Protons are injected through the electrochemical reaction at the metal interface and they are transported via migration and diffusion through the film. The primary electrochemical reaction is the electrolysis of water. The formation of water insoluble precipitates is due to the decrease of the pH in the layer surrounding the electrode and the interaction of the binder with the hydrogen ions formed. Side reactions also occur such as various oxidation reactions of the binder [100].

Under ideal conditions, smooth, coherent, well adhering film without pores will be deposited onto the substrate. In practice some difficulties arise in achieving this result. In the diffusion layer a high degree of supersaturation of the gas is established resulting from an accumulation of organic components and the higher viscosity which retards the rate of nucleation for the bubble formation appreciably. The formation of an imperfect film is mainly because of the electrical heating of the film.

Electrodeposition can be carried out from both solubilized systems and nonsolubilized systems [101]. Water insoluble organic resins, chemically modified to contain groups such as carboxylic acid upon neutralization with bases are converted to water soluble emulsions. The suspended
colloidal particles are actually aggregates of polymer molecules. They are charged by the ionization of some of the carboxyl groups of the molecules. Neutralization of the resin also leads to a degree of solvation of the colloidal particles and the high degree of compatibility between the colloidal particle and the water vehicle. This produces the lyophilic dispersion type. The colloidal particles in this case may be regarded as a soft polymer and they may be expected upon coagulation to coalesce easily into films. The nonsolubilized systems are basically in the class of aqueous lyophobic dispersions. There is no interaction between colloid particles and water molecule. Stable colloid systems are achieved without resorting to the introduction of ionizable moieties such as carboxylic acid groups. Stability results from adsorption of ions or ionizable species and emulsifying agents from the fluid. This in turn leads to a stable ionic atmosphere or double layer surrounding the colloidal particle. The zeta potential is a quantitative measure of the difference in potential between the diffuse, mobile layer and surrounding bulk liquid. With solubilized systems the principal mechanism of deposition is acid coagulation due to decrease in pH. The weight of deposit formed is generally proportional to the number of coulombs of electricity passed but the coulombic yield does vary inversely with the degree of neutralization.
Beck [102] studied the mechanism of electrodeposition of paints using rotating disc electrode. He showed that for anionic electrodeposition resins there is a critical rotation speed which agrees with the theory of an acid boundary layer. With increase in speed of rotation the thickness of the diffusion layer and the concentration of the protons at the anode surface decreases. At the critical rotation speed the concentration of protons at the anode surface drops below the critical concentration which is necessary for resin coagulation and deposition process fails to occur.

2. Cathodic electrodeposition

Resins for cathodic deposition should be polymers which are soluble or readily dispersable in acidic or slightly alkaline pH range of the paint bath but which coagulate in the very alkaline diffusion layer at the cathode. Suitable polymers are either polycations or neutral polymers kept in solution by cationic emulsifiers. The main reaction leading to cathodic deposition is the electrochemical decomposition of water as in anodic deposition. Cationic amine resins neutralised with acid, are discharged by an acid-base reaction and loss their solubility and deposition takes place by virtue of the reduced solubility of the amine base compared with the amine salt. There is no other possibility for coagulation except by the formation of OH⁻ ions in the vicinity of the cathode [103] and hence there is no contamination of the coating.
Cathodic deposition requires a bath solution containing either resinous cations or a dispersed polymer stabilized with a cationic surfactant. The soluble resinous cations are derived from resins containing basic groups which have been rendered water soluble by neutralization with acid. These may be amino or quaternary ammonium compounds or sulfonium or phosphonium compounds. Coagulation of the resin at the cathode results from the alkaline conditions at the surface [104]. Reaction at the cathode surface are:

- electrolysis of water, producing hydroxyl ions and hydrogen gas

\[ 2H_2O \rightarrow 2H^+ + 2OH^- \]

\[ 2H^+ + 2e \rightarrow 2[H] \rightarrow H_2 \text{ (gas)} \]

- neutralization of charged cations (or cationic surfactant) by hydroxyl ions

\[ R-N^+-R' + OH^- \rightarrow R-N-R' + H_2O \]

The range of resins employed in cationic depositions is more restricted than that used in the anionic process. Self cross linking properties can be built on to 'backbones' of epoxy/amine, epoxy/acrylic and epoxy/isocyanate resins, but cross linking agents may be included in the bath solution. A critical examination of binders suitable for cationic deposition and the mechanism of film formation by cathodic process has been done by Verdino [105].
The cathodic coatings are claimed to be superior to anodic coatings mainly because of the fact that there is no dissolution of the substrate material which ultimately causes the damage as far as anodic coatings are concerned. However, cathodic coatings are not completely free from the metal ions, though it is to a less extent [106]. Actually it has been proved that some anionic systems work better than their cationic counterpart especially in salt spray and detergent resistance whereas in resistance to degradation in weatherometer tests cathodic coatings are found superior.

3. Potentiodynamic electrodeposition of resins

Potentiodynamic investigations like linear sweep voltammetry and cyclic voltammetry are widely accepted methods [107-111] for the study of mechanism of electrochemical reactions. The standard theory of potential sweep methods involves the potential scan rate as the most prominent parameter and is based on a diffusion and/or reaction controlled Faradaic conversion of the depolariser.

Electrodeposition of resins is a special type of electrochemical reaction in which the electrophoresis of resin molecules, decomposition of water and accumulation of protons/hydroxyl ions at the electrode and subsequent coagulation of polymer occur to produce a coating on the substrate which is an insulating film. The behaviour to
be expected for such a system may have some resemblance to the one observed during electropolymerisation reported in recent times [112-114]. Experimental results on the potentiodynamic electrodeposition of paint has been discussed by Bonora et al [115]. Cyclic current voltage techniques have also been used for the investigation of the passivating behaviour of the iron electrode in the electrodeposition process [116], the measurement of current voltage characteristics of the deposited wet film [117] and for the examination of the delamination process of organic coatings [118].

Potentiodynamic electrodeposition has been described [119,120] as a strong tool to study the whole electrodeposition process from the early stage upto the end of thickness of growth. A schematic representation of the potentiodynamic current voltage curve reported by Beck and Guder is shown in Fig.3. Initially, the current rises roughly linearly with time, thereafter it goes through a maximum, decreases to a minimum, rises again through a lower and flat maximum and approaches a limiting current density. On voltage scan reversal, the current collapses rapidly to merge into an ohmic resistance line at lower voltages.

In the early stages of the voltage scan curve both resistance limits the current and the slope of the curve, 

$$R_B = \frac{1}{A} \frac{\Delta E}{\Delta i}$$

where A is the area of the electrode, will be
Fig. 3. Schematic representation of cyclic current-voltage characteristic for potentiodynamic electrodeposition of paint.
indicative of the bath resistance. Current flow leads to water decomposition as the main electrode process. In an anodic electrodeposition process, protons accumulate in front of the electrode, after a time $T$, the critical hydrogen ion concentration at the phase boundary is attained and coagulation of the polymer occurs. Assuming the current maximum to correspond to the transition time $T$

$$T = \frac{E_p}{v_s}$$

where $E_p$ is the peak voltage and $v_s$ is the voltage scan rate. Based on the above assumption and theoretical considerations an equation for peak voltage as a function of scan rate has been derived [119] as

$$E_p^{3/2} = [\frac{3}{4} F C^* (\pi D)^{1/2} R_D A] v_s^{1/2}$$

where $C^*$ is the critical hydrogen ion concentration to effect coagulation, $F$ is Faraday constant and $D$ is diffusion coefficient.

Hence $\log E_p = \frac{2}{3} \log K + \frac{1}{3} \log v_s$

where $K$ is a constant.

A double logarithmic plot of $E_p$ versus $v_s$ will, therefore, give a straight line.

After the maximum, the current density decays steeply in spite of further increase in voltage due to the formation of the polymer film on the electrode. If the coagulation
of the polymer corresponds to formation of an adherent film, there should be a steep fall in current after the maximum. But the presence of a second maximum suggests that additional factors like reorganisation and conditioning of the film are operative in this part of the curve. This is followed by a limiting current density region where the current is small due to the presence of a weakly conducting polymer film.

On reversal of the voltage sweep direction, the current decays strongly due to the relaxation of the space charge layer in the film. This is followed by a region of negligible current. Redissolution of the resin is practically absent in this region, the situation compares well with the residual current, finally attained in the course of electrodeposition at constant voltage.

Characterisation of resin and electrodeposition bath

The resin which is the film forming material is normally characterised before proceeding to the paint formulation. IR and NMR studies are carried out for elucidating the structure [121,122]. Molecular weight of the resin can be determined by gel permeation chromatography. The main properties of the liquid paint evaluated are the viscosity, specific gravity, pigment volume concentration and non-volatile material [123]. The particle size of the binder material as well as the pigment materials has got considerable
influence on the film quality especially in the case of electrodeposition process and this can be determined by different methods including scanning electron microscopy.

For water borne systems used for electrodeposition purpose the conductivity of the bath is quite significant as this will affect the initial current density and thus the deposit characteristics [124]. Very high conductivity is not conducive to the deposition of compact films. Hence optimum conductivity at which good quality coatings are produced with each pigment used is to be standardised.

The main properties [60] of the bath studied apart from conductivity are the current-time behaviour, coulombic efficiency, throwing power and pigment migration efficiency.

Deposition of the resin/paint can be carried out at constant voltage or constant current. When high voltage is applied the current shoots up to the maximum initially and within seconds starts to fall due to the resistance build up at the metal/solution interface. A typical current-time curve is shown in Fig.4. The current-time behaviour is indicative of the nature of the film. If current fall with respect to time is smooth and reaches to the minimum nearing zero then it can be said that the deposit is uniform and nonporous. If on the other hand the current fall is not smooth and the current does not come to minimum values, then it can automatically be taken that the bath characteristics are not conducive to getting satisfactory coatings.
Fig. 4. Schematic representation of current-time curves obtained during electrodeposition of resins at constant voltage.
The deviation can occur because of several factors, e.g., higher conductivity of the bath, excess pigment volume concentration, higher or lower pH values etc. This behaviour is same in the case of both the anodic and cathodic systems.

Throwing power of the bath gives a good idea of the bath characteristics. If the throwing power is not optimum, the coverage of the coating will be poor especially on irregularly shaped articles. Throwing power depends on the conductivity, pH etc. of the bath. There are a number of methods to determine the throwing power, the main methods being the Tawn and Berry method, Ford method, pipe test etc.

Coulombic efficiency of the electrodeposition bath expresses the number of milligrams of the resin/paint deposited per coulomb of electricity passed. Since an insulating film is formed on the surface on electrodeposition, determination of this parameter indicates the efficiency of the electrodeposition system. Coulombic efficiency gives an idea of the side reactions taking place during deposition of resin.

The pigment migration efficiency is another property of the bath which is determined to find out the amount of pigment that is deposited along with the resin.

\[
\text{Pigment migration efficiency} = \frac{\text{Pigment binder ratio of the coating}}{\text{Pigment binder ratio of the bath}} \times 100
\]
The pigment binder ratio of the coating is normally higher than the pigment binder ratio of the bath and for each system this is to be standardised. A correlation can be made for each system by which the pigment to be added to a particular resin bath can be decided for getting a desired pigment binder ratio or pigment volume concentration for the paint coating.

**Evaluation of properties of coatings**

The evaluation of resin and paint film is done by subjecting the coatings/films to physical, chemical and electrochemical tests. The important physical properties which are normally assessed for finding out the suitability of the coating for practical applications are the hardness, flexibility, impact to loads, bond strength or adhesion of the film to the substrate material, abrasion resistance, tensile strength and reflectivity [125]. In addition to these physical properties the performance of the coated system in corrosive and chemical environments are also made.

1. Hardness

As far as organic coatings are concerned hardness is generally referred to as the resistance of the coating to indentation or scratching. So normally the scratch hardness of the coating applied to the specified surface is determined. There are different instruments available for
this purpose, the principle being to move a sharp diamond tip over the coating under different loads. The maximum load the coating withstands without making any deep scratch (indicator alarm given when the needle touches the basis metal) is noted. Another method of finding out the hardness of organic coatings is by the pencil method. Lead pencil (graphite) of varying hardness is used for this. This is a qualitative test, but is being used widely in industry.

2. Flexibility

Paint and varnish films must have sufficient elasticity so that they will not split or crack following upon shrinkage of the film or movement of the substrate due to weather or service conditions. The flexibility of films may be evaluated by examination of unsupported film or bending of coated panels. Bending tests over a range of mandrels are most widely employed. Good adhesion tends to give better apparent flexibility than does poor adhesion. Elongation can be measured as an independent property by using free films. The flexibility largely determines the ability of the film to resist cracking, chipping and forming. A number of external factors affect flexibility. They are mainly humidity, temperature, strain rate etc. Paint films tend to lose flexibility during service because of the loss of slightly volatile plasticizing components and chemical changes.
Mandrels, both cylindrical and conical are used quite often in evaluating the flexibility of coatings. In the cylindrical mandrel test different mandrels of varying diameters are used. The test specimen which are cold rolled carbon steel coated with the material to be tested are bent 180° using the different mandrels until cracks are visible. In the conical mandrel the relation between diameter of the mandrel and elongation of the film on it is given by

\[
\text{percent elongation} = 100 \frac{t}{2r + t}
\]

where \( t \) is thickness of panel and \( r \) is radius of mandrel.

In the conical mandrel method the coated panel is bent over the tapered mandrel which provides bending of different degrees to the coated specimen. The crack from the smallest end is marked and this distance noted. Elongation can be calculated from the reference already prepared or the distance can be directly indicated.

3. Impact resistance

A number of tests based on falling weight exist for finding out the impact resistance of the coatings. They provide a means of adjusting the height of fall of a standard weight, usually hemispherical at the base, on to a specimen placed at the base of the instrument. For any given weight and height of fall the resultant distortion of or
damage to the paint film will depend on the character of the anvil and the ease with which the substrate is deformed and the brittleness or extensibility of the film and its adhesion to the surface. The paint is required to be undamaged under a blow delivered by a defined weight falling through a fixed height. The maximum height from which the load can impinge without damage to the coating is noted and the impact resistance is expressed as kg cm\(^{-1}\) which can be used for comparative assessment of the coatings.

4. Bond Strength (adhesion)

The bond strength of an organic coating to the metal depends both on the adhesive strength as well as the cohesive strength of the coating material. The adhesive force of the coating to the metal surface depends on many factors like wettability of the coating material, free energy of the metal surface etc. The adhesion also depends on the surface condition of the metal substrates. Several methods are available to assess the bond strength of the coating over metal. If the film strength is poorer, cohesive failure occurs, the real adhesive force being much more than the value obtained. The adhesive tape test, knife removal method, peel tests and inertia tests are some of the tests which give reasonably reliable values and depending on the range of accuracy needed the method can be chosen. One of the more reliable methods for getting quantitative bond strength values is the Sandwich pull off test using a tensometer.
which gives the force used for the removal of the coating from the substrate. This method can clearly indicate whether the failure is due to lack of adhesion or cohesion of the coating.

In the pull of method the coating is applied over the concerned metal discs after cleaning. The disc is sandwiched between two cylindrical test pieces (doublets). For this purpose an adhesive with high bond strength (higher than the expected value for the test pieces) is used so that failure occurs only at the paint substrate interface or in the body of the paint film. The doublets are cured using special jigs to ensure correct alignment. For finding out the bond strength the doublets are pulled apart by subjecting them to progressively increasing stress at a constant rate in a tensometer until failure takes place. The maximum load at which the doublets are removed gives the bond strength of the coating to the substrate.

5. Abrasion resistance

Abrasion resistance is the ability of a material to withstand mechanical action such as rubbing, scraping or erosion that tends progressively to remove materials from its surface. It is not an isolated property in the coating but is related to other physical properties like wear resistance, cohesive strength, hardness, tensile strength and toughness. Several methods have been evolved to determine
the abrasion resistance. Methods using abrasive blasts, rotating disks, rotating wheels, methods employing rectilinear motion are some of the methods employed for finding out the abrasion resistance. The Taber abraser which uses the rotating wheels give reasonably good results.

6. Tensile Strength

Tensile strength is the greatest longitudinal stress a substance can bear without tearing apart. Tensile strength and elongation are the basic parameters of mechanical properties. Tensile strength is directly proportional to the rate of strain. Elongation of some degree is required so that coatings can conform to dimensional changes of the substrate. The tensile strength is determined using electronic tension tester. The free film is mounted on the instrument and load applied until the film breaks.

7. Reflectivity

Reflectivity/gloss of the paint coating becomes important for finish coats especially for enamels. This property is determined by using glossmeter in which the reflectivity of the coating is compared with a standard reflecting surface.

8. Corrosion and chemical resistance

For assessing the corrosion resistance and resistance to chemical environments, immersion tests and salt spray
tests are undertaken. Immersion in different chemical solutions give an idea of the life of the coating in a particular environment and accelerated salt spray test which uses sodium chloride solutions or synthetic sea water gives the indication of the coating life in marine environments. Apart from these, exposure to atmosphere also is done to get on-the-spot evaluation.

9. Electrochemical tests

The electrochemical tests for evaluation include potential-time measurements, impedance spectroscopy and study of variation of capacitance and resistance of the film in the respective media. These tests give a quantitative assessment of the behaviour of the coating in different environments.

A. Potential-time measurements

The variation of corrosion potential with time of a corroding metal can frequently be related to its corrosion behaviour [126,127]. Change towards more negative potential indicate removal of surface oxide films and development of active corrosion while a shift towards more noble potential indicate the onset of film formation and hence the cessation of corrosion.
B. Impedance measurements

Organic coatings serve as barrier to reactants especially corrosive media. When the coated metal surface comes into contact with an aggressive medium both the coating and substrate undergo chemical and physical changes. Electrochemical impedance measurements of protective coatings on metallic substrate supply valuable information about the protective properties and the mechanism of action.

In the a.c. impedance technique an a.c. signal is applied to the electrode to be studied and the resulting a.c. current response is compared to the a.c. potential perturbations. The impedance $Z$ is defined as having a magnitude given as $|Z| = \frac{\Delta E}{\Delta T}$ and a phase angle $\theta$ which corresponds to the phase shift between the two signals [128]. It is readily seen that the a.c. impedance technique is particularly well suited to isolate the individual components in the electrical behaviour of couple systems. The evolution rate of the impedance spectrum of an initially intact paint film correlates with the performance of the paint coating under various accelerated tests [129,130].

The electrical behaviour of the system examined can be represented in each case by an analogous circuit consisting of a capacitor and a resistance in parallel (Fig.5). The value of the resistance, $R$, is given by the diameter
cp-capacitance characterizing the continuous part of the coatings
Rp-the resistance of the coating
cd-double layer capacitance of the metal electrolytic interface.
Rt-charge transfer resistance
zd-diffusion impedance
Rs-solution resistance

Fig. 5.

cp-capacitance characterizing the continuous part of the coatings
Rp-the resistance of the coating
cd-double layer capacitance of the metal electrolytic interface:
Rt-charge transfer resistance
zd-diffusion impedance
Rs-solution resistance
of the circle, and the capacitance, $C$, can be calculated from the equation

$$\frac{RC}{2 \pi f_{\text{max}}} = 1$$

where $f_{\text{max}}$ is the frequency associated with the highest point on the semicircle [131]. The value of $R$ during immersion in the medium decreases and can be interpreted as penetration of the electrolyte into the coating and an increase in its porosity [132].

The charge transfer resistant $R_t$ is the only electrochemical value which is closely linked to the corrosion rate of the metal support. The equivalence between corrosion rate calculated from $R_t$ and that measured with the weight loss was established by Piens and Verbist [133] in the case of iron protected by a conventional epoxy paint. Charge transfer and diffusion processes give different impedance responses and therefore it is often possible to use a.c. impedance measurements to determine when the corrosion has commenced and when a film has broken down. The method can also be used to calculate film thickness and water uptake [134].

Changes in the value of capacitance with time depends largely upon the amount of water absorbed by the paint. As the water filling the capillaries and perforations in the paint film supplies electrolyte to the corrosion process at the metal/paint interface it appears reasonable to assume
that greater the volume of water the more easily the corrosion process develops. Hence the value of capacitance should give an indication of the protection capability of the paint coating [135-137].

Impedance measurements have been used to investigate diffusion of water into coatings, corrosion beneath organic coatings and the effect of aging and pigment on the dielectric properties of the coating. Charge transfer and diffusion processes give different impedance responses and therefore, it is often possible to identify what type of reaction is dominant.

Electrochemical studies of bare metals have shown the complexity of electrode kinetics. The processes which take place at the interface constituted by the metal and the corrosive medium are numerous and are by nature very different - electrochemical reactions, chemical reactions, solvation, adsorption of the intermediates of reactions, transport of material by migration, diffusion and natural or forced convection. The presence of organic coating on the metal introduces additional electrical and electrochemical properties like the dielectric behaviour and ionic resistance of the coating, its barrier effect on diffusion of chemical species.

Measurements made under direct current bring into play all these processes. When a.c. is used only those processes which require sufficient time to take place during
the alternation of electric field come into play and the slower processes do not occur. In order to determine the precise significance of the electrochemical values the various processes occurring must be separated and this can be done by using different frequencies. The measurements of impedance of an electrode over a wide range of frequencies provide an analytical examination of the various processes brought into play by a direct current in the system under study. The ionic resistance of an in-tact film is high and obscures other components of the behaviour of the paint-substrate system. But when the ionic resistance is sufficiently low or has become so after aging of the paint film or immersion in an electrolyte the diffusion of chemical species though the coating and that of the paint/substrate interface appear in the impedance spectrum and the paint/substrate system can be characterized completely.

C. Resistance and Capacitance measurements

It has already been established that changes in electrical resistance of a paint film in a medium can be related to its corrosion protective behaviour. Both DC and AC methods are used for measuring electrical resistance [138-140]. The pores in the paint film give access to the corrosive medium to attack the basis metal and hence the comparative protective property can be assessed from the change in the resistance over the period of exposure. Capacitance of the
paint film can provide some information on the absorption of water by the film. The measurement of these dielectric properties can give more information on the behaviour of the paint film in different media.