Electroplating

Metal finishing

Metal finishing is the name given to a wide range of process carried out in order to modify the surface properties of a metal, e.g. by the deposition of a layer of another metal or a polymer, or by formation of an oxide film. The surface treatments which will impart corrosion resistance or particular physical or mechanical properties to the surface (e.g. electrical conductivity, heat or wear resistance, lubrication or solderability) and, hence, to make possible the use of cheaper substrate metals or plastics covered to give them essential metallic surface properties. It should be emphasized that not all surface finishing is carried out using electrochemical methods, but electroplating, anodizing and other conversion coating process, together with electrophoretic painting, represent a large portion of industry.

Metal finishing

Electroplating is a process of depositing a metallic coating of desired form over a surface(or substance) by the passage of electric current through a solution. A chemical solution which contains the ionic form of the metal, an anode (positively charged) which may consist of the metal being plated (a soluble anode) or an insoluble anode (usually carbon, platinum, titanium, lead, or steel), and finally, a cathode (negatively charged) where electrons are supplied to produce a film of non-ionic metal.

Electroplating is an important industrial process used to confer functional properties such as corrosion resistance, wear and abrasion resistance, tarnish resistance, heat resistance, electrical conductivity, bearing surface and solderability, and also to salvage worn-out components or mismachined parts. It is a very widely used and diverse technology. The coating may be a single metal, an alloy or, indeed, a metal-polymer or metal-ceramic composite.

The basic experimental set-up for electroplating

1. An electroplating bath containing a conducting salt and the metal to be plated in a soluble form, as well as perhaps a buffer and additives.
2. The electronically conducting cathode, i.e. the work piece to be plated.
3. The anode which may be soluble or insoluble.
4. An inert vessel to contain (1) to (3), typically, e.g. steel, rubber-lined steel, polypropylene or polyvinylchloride.
5. DC electrical power source, usually a regulated transformer/ rectifier.

Theory of electroplating

A metal salt in aqueous solution undergoes ionization to form ions. When a potential difference is applied to this salt solution by dipping two electrodes in the solution, the metal ion migrate to the salt is reformed by the anode metal passing into the solution in the form ions. For example, if the anode is made of coating metal, then the concentration of the electrolytic bath solution will remain unaltered during electrolysis, because metal ions deposited on cathode from the bath are continuously replenished by the reaction of free anions with the anode metal.

For example, when current of electricity is passed through $ZnSO_4$ solution, it will ionise into Zn^{2+} ions and SO_4^{2-} ions. Zinc ions will go to the cathode and will be deposited there. SO_4^{2-} ions will go to the anode, which is zinc metal or coating metal and will react with it to form zinc sulphate.

$$ZnSO_4 \to Zn^{2+} + SO_4^{2-}$$

Similarly, when copper sulphate is used as an electrolyte and copper is used as anode or coating material, the $CuSO_4$ will ionise as,

$$CuSO_4 \to Cu^{2+} + SO_4^{2-}$$

On passing electric current, Cu^{2+} ions will go to the cathode and get deposited there,

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

The free sulphate ions will migrate to the anode and dissolve an equivalent amount of copper to form $CuSO_4$.

$$Cu + SO_4^{2-} \longrightarrow CuSO_4 + 2e^-$$

The copper sulphate thus formed is dissolved in the electrolyte. In this way there is a continuous deposition of metal on the cathode.

A general procedure of electroplating

1. Cleaning with organic solvents and/or aqueous alkali. In some situations the aqueous cleaning is assisted by making the surface cathodic at 60-80^{0}C; this has the effect of increasing the pH locally at the surface and catalysing the hydrolysis of fats while the evolved hydrogen also removes organics by electroflotation.
2. Where the surface is covered by oxides as a result of corrosion, it is cleaned by immersion in acid; again electrochemical enhancement is possible by making the surface anodic.
3. Rinsing with water.
4. Electroplating.
5. Rinsing and drying.
6. Quality control prior to packing and despatch.

Process of electroplating

Electroplating is carried out in an electrolytic cell. The article to be electroplated is first cleaned with organic solvents to remove oils, grease etc and then treated with dilute HCl and H_2SO_4 to remove oxide scales etc. The cleaned article is then made cathode of the electrolytic cell and is hung on racks placed on cathode bar.

The anode is either coating material or an electrode of inert material like graphite. The electrolyte, which is a soluble salt solution of coating metal is taken in the cell. The anode and cathode are dipped in the electrolytic solution and a direct current of electricity is passed. Plating bath is heated with steam and when cooling is required, it is cooled with water in pipes or coils placed inside the cell or tank outside it. For heating the bath, the immersion electric heaters have also been used. Under the influence of electric current, coating ions migrate to the electrode and get deposited there. Thus a thin coating of the metal is produced on the cathode.

In order to produce brighter and smooth deposits, low temperature, high current density and low metal ion concentration etc are the favourable conditions.

Anodes in electroplating

The anode serves two purposes, first, it completes the electric circuit; and second, where it is a soluble anode, it enables replenishment of the metal content- removed during the plating process of the plating bath. There are two types of anodes used in electroplating they are soluble and insoluble anodes.

Soluble anodes

Soluble anodes help the plater to replenish the metal concentration of the bath automatically and involve minimum addition of chemicals.

These anodes preferred for two reasons:

1. metal replenishment in the form of salt is costlier than in the form of metal
2. If salt addition is restored to, the build of associated ions is unavoidable, and this is undesirable in the long run.

The disadvantages of soluble anodes are:

1. Tying up capital in the form of costly anodes
2. Slow but cumulative build of impurities-derived from the anodes in the plating solution
3. The need to ensure that the anode remains active during the periods of operation of the plating bath and does not form insoluble/passive films on its surface.
4. Passivation of anodes leads to imbalance in the metal content of the bath.
5. Formation of rough deposits is resulted if insoluble film loosen themselves from anodes and get deposited on cathode.

Insoluble anodes

Insoluble anodes confer the following advantages:

1. They may be firmly fitted in the tank or in the jig and demand practically attention
2. Since they are a one–time investment, the capital tied up in the electroplating shop is minimal and there are no recurring expenditures.
3. Since they maintain their dimensions intact, interelectrode distance is not altered. This is of particular benefit where the plater is engaged in internal plating of jobs.

The disadvantages of insoluble anodes are:

1. They do not supply the metal that is being plated out; therefore, the plater has to monitor the solution periodically and make suitable additions in the form of chemicals or resort to periodic additions based on, say, ampere-hours of working of the bath.
2. 2.The palter has to be conscious of the possible changes in pH of the bath. This is particularly the case in un buffered baths and in baths that are not highly acidic or alkaline.
3. The oxygen evolution at the anodes is likely to oxidise organic compounds in the bath and cyanide present. In either case, the concentrations of these compounds are lowered and require checks.

Current density

It is the current per unit area of plated surface. In electroplating the deposit thickness depends on the total weight of metal and the area which the deposit is applied; hence the current density is important. The current density is expressed in A/m^2 or A/dm^2 or in $A/inch^2$ or $A/ft^{2.}$

Limiting Current density

The current density is increase slowly in stages, and measure the cathode potential at each stage. The cathode potential increases steadily at first with increases in current density and a stage reached when the potential rises rapidly at a particular current density.

If current efficiency for metal deposition is measured, at various current density values, the current efficiency remains constant (at about 100%) till the point of rapid potential rise and decreases thereafter. This may be understood that, as the current density increased, the rate at which the ions are removed from the cathode vicinity increases. This is replaced by the diffusion of ions from the bulk.

When the current density is increased further, some other ion, usually H^+, is discharged together with the metal ions. This results in a rise in the cathode potential. Since fraction of the current is spent to produce hydrogen, the current efficiency for metal deposition is less than 100%. The current density up to which the current efficiency for metal deposition continues to be 100% is called limiting current density.

Preparation of the work surface (Pre- treatment)

Removal of heavy grease and oil

The plate is soaked in kerosene and swabbed with waste cotton.the residual kerosene is removed by washing the surface with soda ash or caustic soda. Alternatively, the job may be soaked in. For steel/magnesium alloys, sodium hydroxide, sodium carbonate, trisodium phosphate and surfactant are used. Following the dip, the casting is washed in water, dipped in sulphuric acid, washed again, and dried.

Descaling

It is a process, is done by mechanical methods such as polishing, tumbling, and blasting with sand, grit, or vapor.this is followed by immersing the work in an acid. This process is also called pickling. A number of acids and acidic salts are employed. The type of acid or salt, itsconcentration, and the operating temperature depend on the nature of the material. On occasion, heat scales are not removed readily by pickling. In such cases the scale is first loosened and is the dissolved in dilute acids, as detailed below.

For loosening scale:

potassium permanganate,	75g
sodium hydroxide,	90g
water,	1L
temperature,	80 to 100^{0}C

For dissolving scale:

hydrochloric acid/ sulphuric acid: 500 mL
water 1L
temperature: room temperature

Bright dipping

In this process the job is immersed in a solution of mixture of acids for a time ranging from 5s to 5min, to provide a bright surface free of stains. It is possible that smoothening of the dipped surface may also result, depending on the type of the solution used and the initial nature of the surface. In this process any stains formed soon after pickling are also removed. Otherwise, this dipping may be applied to the object after polishing the surface.

This step is purely optional and is left to the convenience of the plater.

Compositions for bright dipping for zinc and its alloys:

Chromic acid	300g
Sulphuric acid	3ml
water	1L
temperature	25^{0}C

Polishing and buffing

In polishing, the metal on the surface of the job is removed in stages by passing it through a variety of abrasives: coarse, medium, fine, and so on. The purpose of this operation is to smooth the surface of the job. Generally, the more rigid wheels are used for coarser polishing operations demanding fast metal removal. The more flexible wheels are used for fine polishing and on irregular surfaces.

In the buffing operation, very little material is removed and the surface finish is improved. The type of finish can be a satin finish to produce satin, brushed, or butler finishes; cut-down buffing, to effect initial smoothness; cut and color buffing, to obtain smoothness and some brightness; and color buffing, where mirror brightness is produced. The wheels are of muslin of different makes, sewn, pocketed, folded, and so on, and are more flexible than polishing wheels. Abrasives are combined with glue and converted to a greaseless compound in bar form. This is applied to the buffing wheel, and the surface to be finished is held against this wheel.

Preplating operations

If the job has been mechanically polished and buffed, the surface carries residues of fats and waxes of the buffing compounds, and also the abrasives, from these compounds. Further, if they have been exposed to the plating shop atmosphere-even it is for a short duration-the surface picks up airborne dust and dirt, and also products due to corrosion of the material such as oxides, sulfides, and so on, in the atmosphere. Thus the contaminants on the job as received by the plating shop are complex in nature. These contaminants should be removed, and this is achieved by cleaning in three stages: degreasing with organic solvents, alkaline cleaning, and acid dip.

Degreasing with organic solvents

Organic liquids such as trichloroethylene and perchloroethylene-a shade better in certain aspects and somewhat cheaper than trichloroethylene-are used to remove most of the greasy material on the surface of the job. They are applied by swabbing with cotton carrying the solvent or by dipping/soaking the job in the solvent or by condensation of the vapors of the solvent in a closed vessel.

Alkali cleaning

Solvent degreasing removes most of the soils and grease, but minute residues are left behind. These residues are removed by alkali cleaning. The type of cleaner and mode of cleaning depends on the substrate and nature of the soil to be removed. To hasten the rate of cleaning, higher concentration of alkali, heating the solution, increasing the duration of cleaning, and using current all help the electroplater.

The mode applying the different types of cleaners.

Hand cleaning

In this, cleaning is done by applying the cleaner over the job by brush or swab or cloth. Operator should apply the cleaning compound with all the safety precautions necessary for chemicals handled.

Soak cleaning

The job is dipped in hot alkaline solution, kept agitated. For effective cleaning, the concentration of the alkali and temperature should be as high as been indicated by tests.

Ultrasonic cleaning

High-frequency waves(20,000Hz above) are called ultrasonic waves. Its use in an alkaline cleaner enhances the efficiency of the cleaner, particularly for cleaning blind holes, crevices, and inaccessible areas. The equipment is costly, but its cost is justified while cleaning special components such as electronic parts and other precision components.

Electrocleaning

In this, the job is made the cathode or anode or alternatively the cathode and anode in an alkaline medium. In view of the scrubbing action of the gases (hydrogen at the cathode and oxygen at the anode), the electrocleaner is more efficient than soak cleaner and minimizes considerably the chemical attack on the substrate. Cathodic cleaning is generally done for nonferrous metals and nickel and its alloys. For ferrous articles, cathodic cleaning is followed by anodic cleaning. This combination avoids the possibility of hydrogen embrittlement of steels or metallic impurities.

Compositions for alkali cleaning for ferrous metals/alloys

Soak cleaner:

Sodium hydroxide,	12g/L
Sodium carbonate,	11g/L
Sodium tripolyphosphate,	12g/L
Sodium resinate,	3g/L
Sodium metasilicate,	18g/L
Alkyl benzene/naphthalene sulphonate,	3g/L
Ethoxylated doctyl phenol,	1g/L
Temperature,	90 - 95^{0}C
Duration,	1 - 5min

Electrolytic cleaner:

Sodium hydroxide,	31g/L
Sodium metasilicate,	20g/L
Sodium tripolyphosphate,	5g/L
Sodium carbonate,	3g/L
Sodium lauryl sulphate,	1g/L
Temperature,	80^{0}C
Current density:	50 – 100 A/ft^2
Duration:	2min cathodically, followed by 30s to 1 min anodically

Acid dipping

Soon after alkali cleaning and rinsing in water, the job is given a dip in dilute acid solution.This step serves two purposes: (i)Thin film of oxide or other compounds or tarnish films are removed. These are formed due to exposure to the atmosphere after cleaning. These films should be removed prior to electroplating.acid dip does that. (ii) Residual alkali adhering to the surface of the job-in spite of rinsing-is removed by acid dip. This avoids carryover of compounds of metal cleaner to metal cleaner to the plating bath or to any other solution.

The type of solution used and its composition depends on the nature of the material handled. Compositions for acid dipping for Al-Mg alloys

Nitric acid,	500 mL
Water,	500 mL
Temperature,	Room temperature
Duration	15s

Water wash and drying

After the acid dipping the work piece is washed with excess amount of deionised water and dried.

The plating bath

The plating bath is normally a complex mixture of soluble species of the metal being plated, electrolytes and various additives to ensure that the electroplate has the desired properties and quality.

The metal ion

The metal to be plated is present in solution either as the simple hydrated ion or as a complex but normally in high concentration, typically 1-3moldm^{-3}. This high concentration is essential because, while it is necessary to use a reasonable current density, the quality of the plate suffers badly if the deposition occurs under conditions where the electrode reaction is even partially mass-transfer-controlled.a non-complexing medium is frequently used for rapid plating on objects of simple shape while complexing media are employed when a high throwing power is important.

Electrolytes

Various electrolytes are also added in high concentration to give the bath maximum conductivity. They may also have the role of controlling the pH and buffering the solution particularly if hydrogen or oxygen is evolved at the cathode or anode respectively, since these reactions will tend to change the pH. An increase in pH may lead to deposition of metal hydroxides. This is a particularly difficult problem when the metal depositing is a good H_2 evolution catalyst and also easily hydrolyzed. Hence a watts bath contains boric acid. A pH above 2 may be essential to decrease H_2 evolution, with a consequently reduced tendency for H_2 embrittlement or hydride formation in certain metals.

Complexing agents

Complexing agents are used to make the deposition potential more negative when it is necessary to prevent a spontaneous chemical reaction between the cathode and the plating ion, e.g. plating copper onto iron or steel. These are also used to modify the Tafel slope for the metal ion reduction and, hence, to improve the throwing power of the bath. The most common complexing agents in electroplating are cyanide, hydroxide and, more recently, sulphamate ion. These also have a role at dissolving anodes; they can prevent passivation and therefore loss of current efficiency in the corrosion reaction and it is for this reason that a low concentration of chloride ion is a common constituent of many baths.

Organic additives

A wide range of organic molecules are added in relatively low concentration to the electroplating bath to modify the structure, morphology and properties of the cathode deposit. They are;

1. Brighteners

For a deposit to be bright, the microscopic roughness of the deposit must be low compared with the wavelength of the incident light so that it is reflected rather than scattered. Brighteners are commonly used in relatively high concentration and may result in substantial organic matter in the deposit. They usually cause the formation of an even, fine-grained deposit and, hence, may act by modification of the nucleation process. For nickel deposition from a watts bath, two types of brightener are recognized: (1) aromatic sulphones or sulphonates (2) molecules containing -CN, -NCS, or >C=O entities.

2. Levellers

These produce a level deposit on a more macroscopic scale and act by adsorption at points where otherwise there would be rapid deposition of metal. Thus, adsorption of additives occurs preferentially at dislocations because of a higher free energy of adsorption and peaks because the rate of their diffusion to such points is enhanced; the adsorbed additive will reduce the rate of electron transfer.

3. Structure modifiers

These additives change the structure of the deposit and may be even the preferred orientation or the type of lattice. Some are used to optimize particular deposit properties, and others to adjust the stress in the deposit. These are often called 'stress relievers'.

4. Wetting agents

These are added to accelerate the release of hydrogen gas bubbles from the surface. In their absence, the hydrogen which is often evolved in a parallel reaction to metal deposition can become occluded in the deposit causing, for hydrogen embrittlement.

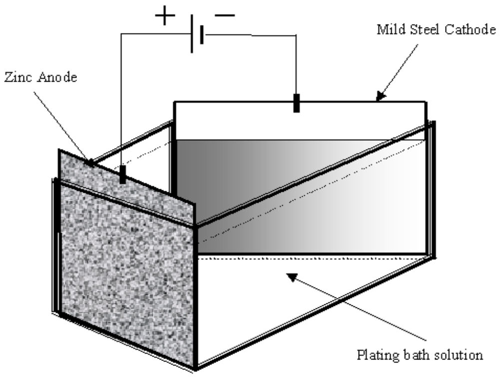
5. Buffers

Various buffers are added to controlling the pH of the solution particularly if hydrogen or oxygen is evolved at the cathode or anode respectively, since these reactions will tend to change the pH. An increase in pH may lead to deposition of metal hydroxides. This is a particularly difficult problem when the metal depositing is a good H_2 evolution catalyst and also easily hydrolyzed. Hence a watts bath contains boric acid.

Hull cell experiments

Any factor that produces a change in the appearance of the electrodeposit over a range of current densities can be assessed by a Hull cell test. The test is simple and quick in execution. It is used to control the concentrations of addition agents, to study the influence of impurities, to asses the efficacy of the purification treatment carried out on the bath, and to determine the influence of any parameter on the appearance of the deposit.

The Hull cell is made of an insulating material such as perspex or PVC. Its shape and dimensions are as given in figure. To carry out the test, the solution is placed in the cell and an anode of 60×65 mm size is positioned as shown. A polished and cleaned cathode-cold-rolled steel or thin-gauge brass/copper 100×75 mm in size is placed along the slant side of the cell and current is passed. At the end of the test, the Hull cell panel is removed, washed, dried, and inspected visually.



Portions corresponding to a specific type of deposit-bright/satinish, free of trees, free of the influence of metallic or organic contamination, and so on- are marked out and their distance from the nearer end of the cathode is noted. The current density at a point is calculated from the graph or by using the formula

$$I = c(5.10 - 5.24\ \log L)$$

Where I is the current density in Adm^{-2} at any point on the cathode, c is the cell current used for the test, and L is the distance in centimeters of the point on the cathode at which the current density is desired. The formula applicable over a distance of 0.7 to 8.2 cm on the panel.

Cathode current efficiency

It is defined as the percentage of the total current usefully employed for the cathodic deposition of the metal.

$$\text{Cathode current efficiency} = \frac{\text{wt. of metal actually deposited}}{\begin{array}{c}\text{wt. of metal calculated from the}\\ \text{quantity of electricity passed}\end{array}} \times 100$$

Anode current efficiency

It indicates the proportion of the electricity passing through a solution, utilized for dissolution of the anode.

$$\text{Anode current efficiency} = \frac{\text{wt. of metal dissolved}}{\begin{array}{c}\text{wt. of metal calculated theoritically}\\ \text{from ampere} - \text{hours}\end{array}} \times 100$$

Weight of deposit

The weight of the deposit calculated by using Faraday's laws

$$W = \frac{It}{96{,}500} \times \frac{A}{z}$$

Where I is current density, t is deposition time, A is the atomic weight, Z is the charge of the cation.

Thickness of deposit:

Thickness of metal deposited by electroplating depends upon the current density of the deposited metal. The thickness of the deposit can be calculated by using the formula

$$T = \frac{W}{a \times d}$$

Where W is the weight of the deposit, a is the of plated area, d is the density of the metal.

Covering power

It is a property of a plating bath is a measure of the ability of the solution to deposit metal in low-current-density areas such as recesses. It depends on the bath composition,nature of cathode surface and surface finishing. The electroplating for decorative process, the covering power of a bath is important. If it is low or poor, the products may have areas on which there is no electrodeposit and the substrate or the undercoat is exposed.

Throwing power

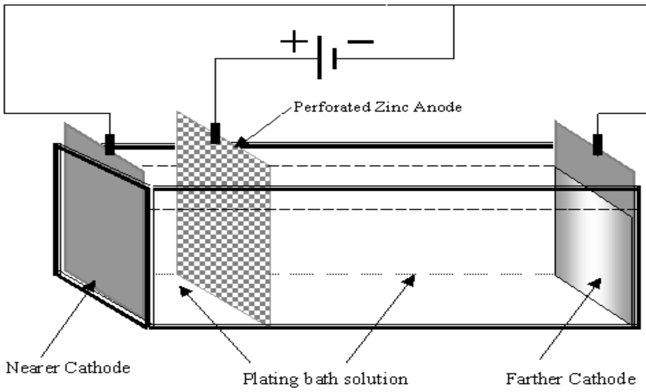
It is a qualitative term used in electroplating to describe the ability of the system to produce a uniformly thick deposit on the substrate surface. The Throwing power is considered good when the current distribution is uniform even on an irregularly shaped substrate.

Throwing power measurements cannot be utilized for quality control of plating baths, but are useful for evaluating new plating formulations or addition agents. The Haring-Blum cell is used for determining the throwing power of plating baths. The cell consists of a box of PVC/perspex or similar insulating material of dimensions 15×5 cm. The solution is used to a depth of 5 cm. Sheet metal cathodes are fitted at both ends of the box and are connected by a rod. A perforated or wire gauge anode is placed between the cathodes. The anode distance can be adjusted to such values as 2.5, 5.0 and 10.0 cm from one of the cathodes.

The cathodes are weighed initially. Electrodeposition is carried out for a known time. At the end of the test, the cathodes are weighed again and from this, the throwing power is arrived at by using the equation.

$$Throwing\ power(\%) = \frac{K - M}{K + M - 2} \times 100$$

Where K is the ratio of the distance from the anode of the farther and nearer cathodes, respectively, and M is the ratio of the metal obtained on the nearer and farther cathodes.



The parameters affecting electroplating:

Current density

When low current density is used, metal deposited slowly and thus produced are coarse grained deposits. If increase the current density, the deposits obtained are fine grained. But we cannot increase the current density beyond the limiting density. Because, there are two possibilities: (1) The secondary reactions such as hydrogen discharge; this leads to a rise in hydroxyl ions in the solution and formation of metal hydroxides or basic salts of metals. The deposit may become fine grained, but is likely to be burned, spongy or dark in appearance. The hydrogen alters the physical look of the deposit by causing either pits or streaks. (2) The cathode layer is depleted fast of its metal ion concentration, while the bulk solution continues to have its original metal content. Because of the rapid discharge of ions to form metal atoms, there is a likelihood of the nuclei growing outward toward the bulk of the solution with high metal content. Under these conditions, nodule formation or treeing of deposits occurs.

Temperature

There are three factors involved in the influence of temperature: (i) The supply of ions to the cathode is hastened so that the negative effects due to an inadequate supply of ions are mostly averted. (ii) Rate of growth of nuclei is increased, leading to coarse-grained deposits. (iii) The hydrogen discharge and the accompanying consequences are favored, leading to bad-quality deposits. Therefore, the outcome of raising the bath temperature is a result of the three forgoing factors. At the average temperatures employed in most plating baths, a positive result is so common that good deposits are obtained in practice.

Metal concentration

The important thing in a bath is the concentration of metal salt from which the desired metal is being plated out over the substrate. Generally, a higher current density can be employed in high-metal-bearing baths. Here the fact that the hydrogen over voltage is increased by an increase in current density is an additional advantage. To get the best out of a particular bath, is employing the highest possible current density, cathode rod movement, agitation of solution, or stirring of the bath are desirable so that supply of the cathode is commensurate with their discharge.

*p*H in electroplating

The control of pH of a plating bath is necessary in order to operate the bath with optimum efficiency and to maintain the desired physical properties of the deposits. **Eg;** If nickel or iron plating is carried outside the recommended pH range, the deposit may become pitted, cracked or curled. Similarly, zinc may become spongy or porous. Besides, too low a pH (away from the optimum) may lead to hydrogen evolution and a consequent decrease in metal deposition efficiency. This in turn may lead to an accumulation of hydroxyl ions in the vicinity of the cathode and consequent precipitation of basic salts, which may get included in the electrodeposit, thereby altering deposit properties. Therefore, the bath pH may have to be adjusted periodically.

Additional agent

When the addition agent is present in excess, the nuclei carry a large amount of the addition agent and the deposit turns out to be brittle. This explains the need to control the concentration of the grain refining agent added to the bath. But in the absence of additional agents, coarse grained, treed, nodular, or burned deposits result.

Type of bath

Good deposits are obtained from solutions containing complex ions rather than simple metal ions. Zinc, cadmium, copper, or silver from cyanide baths is an example. Similarly, a lead deposit from silicofluoride or fluoborate baths is fine grained, while from nitrate or acetate solution it is coarse grained. Likewise, nickel from a nickel ammonium sulfate bath is smoother than from a single nickel sulfate bath. In all these cases and in chromium deposition, the presence of a colloidal substance or in soluble complex serves the role of the addition agent in that it favors the formation of fresh nuclei and prevents the growth of the nuclei already formed, leading to the production of smooth deposits.

Testing of deposits

Thickness

1. Drop test

A dropping or separating funnel is taken and a tube ending in a small-bore tip is attached to it. The reagent is placed in the funnel and the tip is arranged to be 9 ±1 cm away from the surface of the test sample. The test sample itself is kept inclined at 45^0 to the horizontal. The stripping reagent is allowed to drop on to the clean plated surface at a rate of 100 ±5 drops/min. the time is required to strip the deposit to the recorded and thickness is recorded.

2. Jet test

A jet off stripping solution is allowed to flow as a stream under a nearly constant solution head of 25cm on to the clean test sample arranged at 45^0 to the horizontal. The time required for stripping at a given temperature of the solution is noted and from the calibration graph supplied with the apparatus, the deposit thickness is read off.

3. Coulometric test

In this method the test sample made the anode in a cell with an appropriate solution. A prescribed current is passed across the deposit and the solution. The deposit dissolves in a proportion to the current flowing. At the end point, the cell voltage changes and the interval between starting the electrolysis and the time at which the voltage changes is recorded. From the area A (cm^2) stripped, the density, d (g/cm^3) of the deposit, the current passed I(amps), and the time of dissolution t(sec), the deposit thickness T(micrometer) is calculated from the formula.

$$T = \frac{Ite \times 10{,}000}{dA}$$

Where ***e*** is the electrochemical equivalent of the metal dissolved, in grams/coulomb.

Adhesion

1. Bend test

The size of the test sample should be amenable for bending. The specimen is fitted in a bench vice mandrel and bent forward and backward through 90^0. Copper, nickel and nickel-chromium deposits can be tested thus. One should note that deposits which evidence cracking due to brittleness are not treated as being of bad quality.

2. Burnishing test

The copper ion is rubbed over edge of the plated surface (of 6 cm^2 area), for 15sec with a pressure adequate to burnish the deposit. The method is applicable to thin and medium coatings of copper, nickel, nickel-chromium, zinc, cadmium, lead, tin, lead-tin, silver and gold.

3. Grinding test

In this, the plated job is applied to a grinding wheel such that the edge is ground in the direction of the substrate to the coating, tending to separate the coating. Instead of a grinding wheel, a hack saw may be employed. Thin or soft deposits cannot be tested thus and are particularly suited to hard deposits such as chromium, nickel, and nickel-chromium.

4. Heat test

The plated part is heated to a specific temperature in an air oven and then quenched in water at ambient temperature. When bonding is poor, blisters are formed. The method is employed for copper, nickel, nickel- chromium, chromium, gold, silver, lead, lead-tin and zinc.

Corrosion resistance

1. Neutral salt spray test

Mist of 5% or 20% of the sodium chloride solution is sprayed over the specimens at 35^0C. The pH of the condensed solution should be between 6.5 and 7.2 at 25^0C. A 5% solution is preferred more often, since the use of a 20% solution leads to problems such as clogging of the nozzles. This spray is not used at present, as it does not indicate correctly the relative corrosion resistance of the coatings.

2. Acetic acid salt spray test

This is similar to preceding test, with the difference that the pH of the spraying solution is adjusted with acetic acid to 3.2 ± 0.1 at 25^0C. The temperature of testing is 35^0C. This is a more severe test than the neutral salt spray test.

3. Corrodekote test

A specially made slurry is brushed completely over the test sample, allowed to dry in an hour's time, and then exposed to an atmosphere with 90 to 100% humidity but with no condensation at 38^0C. At the end of 24h the specimens are examined for corrosion, such as in the case of a zinc alloy substrate, but in the case of a steel substrate, the job is washed in running water and then inspected.Dissolve 2.5g of $Cu(NO_3)_2$ in 500mL of distilled water (R-1) ,Dissolve 2.5g of $FeCl_3$ in 500mL of distilled water (R-2) ,Dissolve 50g of NH_4Cl_3 in 500mL of distilled water (R-3) . Slurry is prepared by mixing 7mL of R-1,33mL of R-2, 10mL of R-3 in a beaker then add 30g of kaolin mix for 2 minutes.

4. Sulfur dioxide test

The test sample is suspended in a closed chamber with a water container at the bottom. Sulfur dioxide is passed through the water at ambient temperature for 10 to 15 min so that the concentration of Sulfur dioxide 1 to 2% by volume is present in the atmosphere. The humidity should be at least 95% . Test specimens may be exposed for a period of 24h. This test is more rapid than the salt spray tests and exposes cracks and pores in the chromium deposits in less than 3h. The method is suitable for plated coatings on Cu/Zn alloys and not used at present for Ni/Cr systems since sulfur dioxide is very aggressive to Ni, forming voluminous corrosion products which interfere with the test.

Porosity

1. Ferroxyl test

Good-quality paper is dipped into a solution of 50g/L of sodium chloride + 50g/L gelatine and dried, and then cut into convenient-size pieces. The test sample is degreased with organic solvent, and the test paper is placed on the sample and wetted with 50g/L sodium chloride solution. After 10min the paper is taken and dipped in 10g/L potassium ferricynide solution. The pores are indicated by blue spots, corresponding to their position in the coating. The method can be used only on steel substrates. Limitations of this method are (i) big pores are shown up in preference to small ones, (ii) less than 50% of the existing pores are detected.

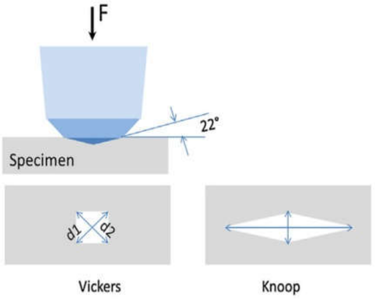
2. Hot water test

The clean test sample, preferably immediately after the last rinse after plating and any post plating treatment, is kept immersed in clean tap water at 80 to 85^0C with aeration for 3 to 6h and later dried by allowing the water to evaporate, and observed. Pores are seen as corrosion spots. The method is applicable to tin, nickel, and other deposits on steel or any ferrous basis, and is useful to assess plated coatings on industrial chemical equipment.

Hardness

To distinguish the hardness of electrodeposits from those of massive metals or alloys the terminology "microhardness" is used. The method used is the penetration method. A diamond indenter, pyramidal in shape, called a Vickers and Knoop indenter, are employed. The test consists of pressing the indenter with a known load against the deposit for 30 to 60s, releasing it.

Measurement is done on both the diagonals in the case of Vickers tester and on the long diagonal in the case of the Knoop tester, using a microscope



By taking the values of the load *L* in kilograms and the diagonal in millimeters, the micro hardness is calculated as follows:

$$H_V = \frac{1.854L}{d^2} \quad or \quad H_K = \frac{L}{0.070d^2}$$

Where H_V is the Vickers number and H_K is the Knoop number, all expressed in Kg/mm^2 .

The modern developments in electroplating

1. Electrodeposition of alloys having a controlled composition as cheaper alternatives to single metal coatings
2. Composition of metals with either polymers or ceramics to provide unique wear-resistant or tribomet coatings, e.g. Ni-PTFE, Co-carbides.
3. Increasing consideration of toxic plating baths; in particular cyanide solutions for gold and cadmium have partly been replaced by non-cyanide liquors.
4. Electroless plating of an increasingly wide range of single metals, alloys and composites, e.g. Ni-PTFE
5. Continued development of non-aqueous baths, particularly for aluminium and titanium.

Applications of electroplating

1. Electroplating is used for decoration or better appearance
2. Plating for protection
3. Plating for special surfaces

4. Electroplating for engineering effect
5. Electroplating on non-metallics
6. Electroforming

Electroplating of copper

Cyanide baths

Cathode	Steel
Anode	Copper,steel
Cooper cyanide	40g/L
Sodium cyanide	50g/L
Sodium carbonate	30g/L
Rochelle salt	60g/L
pH	10.2-10.5
temperature	40-60^{0}C
Current density	20-40A/ft^{2}

Acid Bath

Cathode	Steel
Anode	Copper,steel
Cooper sulfate	200g/L
Sulfuric acid	50ml
Sodium carbonate	2%
pH	1.2-1.7
temperature	35-50^{0}C
Current density	20-50A/ft^{2}

Electroplating of zinc

Alkaline baths

Cathode	Steel
Anode	Zinc,steel
Zinc	35g/L
Sodium cyanide	15g/L
Sodium hydroxide	23g/L
Sodium sulfide	1g/L
pH	>13.0
temperature	25^{0}C
Current density	15-

Acid baths

Cathode	Steel
Anode	Zinc,rubber-lined steel
Zinc sulfate	240g/L
Ammonium chloride	15g/L
Ammonium sulfate	30g/L
Licorice	1g/L
pH	3-4
temperature	25^{0}C
Current density	20A/ft^{2}

Electroplating of nickel

This is widely plated metal in the plating industry, for both decorative and protective applications. The bath compositions is as follows

Cathode	Steel
Anode	nickel, steel
Nickel sulfate	240g/L
Nickel chloride	45g/L
Boric acid	30g/L
Sodium lauryl sulfate	1g/L
pH	4.0-5.0
Temperature	25-65^{0}C
Current density	10-60A/ft^{2}

Electroplating of Gold

Gold deposits are used for many industrial applications, as in the electrical industry, electronics, telecommunications, and aerospace, primarily because of the tarnish and corrosion resistance, good electrical conductivity and ability to reflect infrared radiation.

Cathode	Steel
Anode	Pt, stainless steel or gold
Potassium gold cyanide	1.5-3.0g/L
Potassium cyanide	7.5g/L
Potassium carbonate	20g/L
Dipotassium monohydrogen phosphate	1g/L
pH	11-13
Temperature	60-70^{0}C
Current density	1-5A/ft^{2}

Electroplating of Zinc-Nickel alloy

Acid sulfate bath

Cathode	Steel
Anode	zinc, steel
Zinc sulfate	140g/L
Nickel sulfate	100g/L
Boric acid	30g/L
Trisodium citrate	1g/L
pH	4.0
Temperature	30^{0}C
Current density	1- 4A/dm^{2}

Alkaline bath

Cathode	Steel
Anode	zinc, steel
Zinc sulfate	10-50g/L
Nickel sulfate	10-50g/L
Sodium hydroxide	50-180g/L
Ethylenediamine	10ml
Triethanolamine	0-90ml
pH	>12.0
Temperature	30-40^{0}C
Current density	1- 4A/dm^{2}

Electroplating of Zn-Fe alloy

Acid sulfate bath

Cathode	Steel
Anode	zinc, steel
Zinc sulfate	110-130g/L
Ferrous sulfate	9.5-14.2g/L
Ammonium sulfate	80-100g/L
Sodium citrate	30-45g/L
Citric acid	8-12g/L
Ascorbic acid	0.1-0.2g/L
pH	2.2-3.5
Temperature	30^{0}C
Current density	2.5A/dm^2

Alkaline bath

Cathode	Steel
Anode	zinc, steel
Zinc sulfate	0.09M
Ferrous sulfate	0.01M
Sodium hydroxide	80M
Sodium sulfate	30M
Ascorbic acid	0.01M
Triethanolamine	0.1M
pH	14
Temperature	50^{0}C

Electroplating of Zn-Co alloy

Acid bath

Cathode	Steel
Anode	zinc
Zinc Chloride	80-90g/L
Potassium Chloride	150-200g/L
Boric acid	20-30g/L
Cobalt Chloride	1-20g/L
pH	5-6
Temperature	25-40^{0}C

Alkaline bath

Cathode	Steel
Anode	zinc
Zinc Oxide	80-90g/L
Sodium hydroxide	80-150g/L
Cobalt(additive)	1-2g/L
Gelatin	3g/L
pH	5-6
Temperature	25-40^{0}C
Current density	0.1-4.0A/dm^2