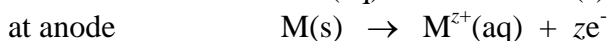


ELECTROPLATING

Electroplating is the application of a metal coating to a metallic or other conducting surface by an electrochemical process. The article to be plated (the work) is made the cathode (negative electrode) of an electrolysis cell through which a direct electric current is passed. The article is immersed in an aqueous solution (the bath) containing the required metal in an oxidised form, either as an aquated cation or as a complex ion. The anode is usually a bar of the metal being plated. During electrolysis metal is deposited on to the work and metal from the bar dissolves:



Faraday's laws of electrolysis govern the amount of metal deposited.

Articles are electroplated to (i) alter their appearance; (ii) to provide a protective coating; (iii) to give the article special surface properties; (iv) to give the article engineering or mechanical properties.

INTRODUCTION

Electrodeposition is the application of metallic coatings to metallic or other conductive surfaces by electrochemical processes.

Electroplating is both an art and a science. Although based on several technologies and sciences, including chemistry, physics, chemical and electrical engineering, metallurgy, and perhaps others, it retains in some ways the aspects of an art, in which experience is the only teacher. In fact, of course, all the sciences have elements of art which can be learned only by experience; all the reading of textbooks on chemistry will not produce a chemist. No text on electroplating will produce an expert electroplater; there is no substitute for experience and what is somewhat inelegantly termed know-how.

THE PURPOSES OF ELECTROPLATING

Some of the purposes for which articles are electroplated are:

- (1) Appearance
- (2) Protection
- (3) Special surface properties
- (4) Engineering or mechanical properties.

The distinctions between these aims are not, of course, clear-cut and there are many overlapping categories. A deposit applied purely for appearance must be, at least to some extent, protective as well. But the classification is convenient.

Some finishes are purely decorative. Many objects meant to be used indoors, in a dry environment and where danger of corrosion is slight, are nevertheless finished with lacquers, paints and electroplated coatings for purely aesthetic reasons. The very thin layer of gold applied to some articles of inexpensive jewellery has little or no protective value; it is there principally to attract a potential buyer.

There are many applications of electroplating, some of them of increasing importance at present, in which neither corrosion prevention or decorative appeal is the reason for using a

finish. Copper is an excellent conductor of electricity and is therefore basic to such items as printed circuits and communications equipment. It does, however, quickly form tarnish films that interfere with joining operations such as soldering and that also render contact resistances unacceptably high in relays and switches. To make soldering easier, coatings of tin or tin-lead alloys are often applied to copper, and for better contacts overplates of gold are frequently required. Other surface properties may call for modification; if light reflection is important, a silver or rhodium plate may be necessary. In wave guides for radar, high electrical conductivity is the most important criterion, and silver is the preferred coating. Good bearing properties may require coatings of tin, lead or indium. If a hard surface is required, chromium or nickel usually will serve. These few examples illustrate another use of metal finishing; to modify the surface properties, either physical or chemical, to render them suitable for the intended use.

Although the answer may be obvious, we may pause momentarily to consider this question: if these coating metals are necessary to provide the article with the desired properties, why go through the somewhat complicating process of electroplating? Why not simply manufacture the article out of the desired metal in the first place? Usually the answer is cost or availability, and, in some cases, the properties of the metals concerned. An all-platinum chemical reaction vessel of practical production size would be prohibitively expensive; but a steel vessel, clad with a relatively thin layer of platinum, serves the purpose at far lower cost. An all-nickel automobile bumper would render the car a luxury for the rich, aside from the fact that the required amount of nickel would probably be unobtainable. A tin can made entirely of tin would not only be more expensive than the good inside, but would also have no physical strength; tin is a very soft and weak metal. Chromium in massive form is almost impossible to work into useful shapes. In summary electroplating allows the use of relatively inexpensive metals like steel and zinc for the bulk of the article, while affording to the exterior the selected properties of the coating chosen.

THE ELECTROLYSIS CELL

The components of the cell

The physical embodiment of an electroplating process consists of four parts:

- 1 The external circuit, consisting of a source of direct current (dc), means of conveying this current to the plating tank, and associated instruments such as ammeters, voltmeters, and means of regulating the voltage and current at their appropriate values.
- 2 The negative electrodes or cathodes, which are the material to be plated, called the work, along with means of positioning the work in the plating solution so that contact is made with the current source.
- 3 The plating solution itself, almost always aqueous, called by platers the "bath";
- 4 The positive electrodes, the anodes, usually of the metal being plated but sometimes of a conducting material which serves merely to complete the circuit, called inert or insoluble anodes.

The plating solution, of course, is contained in a tank, which must be of a material appropriate to the solution it contains: often plain mild steel for alkaline solutions, and of steel lined with resistant material for acid solutions. Such linings may be of rubber, various plastics, or even glass or lead.

The typical plating tank will have three bare copper or aluminium conductors running down its length; these are called bus bars, and they are insulated from the tank itself by various means such as ceramic insulators. The two outside bars are connected to the positive side of the dc source, and on them are hung the anodes, usually by means of hooks. The central bus bar is connected to the negative side of the dc source and holds the work, usually held on racks which are similarly hung on the cathode bar by hooks. The racks themselves are so constructed as to hold one or many parts, depending on their size and shape, and are often custom-made for the particular work being processed. The racks usually are covered with insulating material except where they make contact with the work and the cathode bus bar. When the work consists of many small parts (screws, nuts, small electric connectors, and the like) which do not lend themselves to being hung individually on plating racks, they may be placed in bulk in a barrel, which takes the place of the cathode and is rotated in the plating bath so that all parts at some time come into contact with a cathode placed inside the barrel. The barrel has holes, too small to permit the parts to fall out but large enough to permit fairly good circulation of the solution and passage of the electrolytic current. Barrels are of many types; some are self-contained (oblique barrels) and hold the solution, the anode, and the cathode contact, thus dispensing with a plating tank altogether. Barrels meant to be inserted into a plating tank may be of many shapes and of many materials, and the cathode contacts may be so-called dangles, buttons or of other forms. Barrel plating is no different in principle from plating on racks, though it has its own problems of design and plate distribution.

Ingredients of a Plating Bath

Every plating bath contains ingredients which serve one or more of the following functions:

- 1 To provide a source of the metal or metals being deposited.
- 2 To form complexes with ions of the depositing metal
- 3 To provide conductivity.
- 4 To stabilise the solution e.g. against hydrolysis.
- 5 To act as a buffer to stabilise the pH.
- 6 To modify or regulate the physical form of the deposit.
- 7 To aid in dissolving the anodes.
- 8 To modify other properties, either of the solution or of the deposit, peculiar to the specific case.

There are two main purpose of forming complex ions of certain cations:

- 1 To stabilise the cation. Some metal cations are not stable in the simple aquated form, e.g. gold. They are much more stable when complexed to some ligand. The presence of the ligand lowers the concentration of the free (aquated) ion.
- 2 To hold the aquated form at suitably low concentration allowing control of the evenness of plating.

The cyanide ion, CN^- , is a common ligand forming complex ions such as $\text{Zn}(\text{CN})_4^{2-}$, $\text{Cu}(\text{CN})_4^{2-}$, $\text{Ag}(\text{CN})_2^-$ and $\text{Au}(\text{CN})_2^-$.

The Plating Metals

Most electroplating coatings fall into one of the following six categories:

- 1 Sacrificial coatings, used primarily for protection of the basis metal, usually iron and steel (sometimes call anodic coatings, meaning that electrochemically they are anodic to the substrate). Sacrificial denotes that the coatings "sacrifice" themselves in the act of protecting the basis metal.

- 2 Decorative protective coatings, used primarily for adding attractive appearance to some protective qualities.
- 3 Engineering coatings - a rather miscellaneous group whose members are used for specific properties imparted to the surface, such as solderability, wear resistance, reflectivity, conductivity, and many others. They are sometimes called functional coatings, though it would seem that protection is also a "function".
- 4 Minor metals - a small group of metals that are easily plated but have rather limited application.
5. "Unusual" metals - rarely electroplated, and when they are, they require special conditions, such as non-aqueous solutions.
- 6 Alloys - an almost unlimited number of alloys has been plated experimentally, since the possible combinations of the plateable metals, in various proportions, are innumerable. Only a few have attained commercial importance.

ELECTRICAL RELATIONSHIPS

Faraday's laws of electrolysis

Michael Faraday, perhaps the greatest experimental scientist in history, enunciated his laws of electrolysis in 1833, and these laws have remained unchallenged ever since. They are basic to both the understanding and the practical use of electrolytic processes. They may be stated as follows:

1. The amount of chemical change produced by an electrical current is proportional to the quantity of electricity that passes.
2. The amounts of different substances liberated by a given quantity of electricity are inversely proportional to their chemical equivalent weights.

Equivalent weight is an older term, but still used widely in analytical and electrochemistry. In redox chemistry it is the molar mass divided by the number of electrons in the balanced redox half-equation.

Mathematically Faraday's laws of electrolysis can be expressed as:

$$Q \propto zm/M$$

$$Q = It = zFn$$

where Q is the charged passed, I is the current passed, t is the time the current is passed, z is the change in oxidation state, m and M are the mass and molar mass respectively of oxidised or reduced species, F is the Faraday constant ($96\,485\text{ C mol}^{-1}$, the charge of one mole of electrons), and n is the amount of of substance oxidised or reduced.

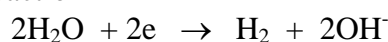
These laws correctly predict that:

- 1 by measuring the quantity of electricity passed, one has a measure of the amount of chemical change that will thereby be produced;
- 2 knowing the chemical equivalent weight of a substance, one can predict the amount of that substance that will be liberated by a given quantity of electricity.

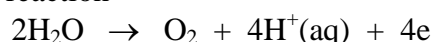
No true exceptions to these laws have ever been confirmed. Apparent exceptions can always be explained by the failure to take into account all the chemical reactions involved, or, occasionally, by the partially non-electrolytic nature of the reaction.

Current Efficiency

It has been stated that the total amount of chemical change at an electrode is exactly proportional to the quantity of electricity passing. Often, however, we are interested in only one of the several chemical changes taking place, and any current used up in causing other changes is considered "wasted". In the usual electroplating situation, our interest focuses on the quantity of metal deposited at the cathode or dissolved at the anode, and any hydrogen evolved at the cathode by the reaction



or oxygen at the anode by the reaction



represents a waste of electricity and a reduction in the efficiency of the process. Thus we speak of percentage current efficiency as the ratio of the desired chemical change to the total chemical change multiplied by 100:

$$\text{Current efficiency (CE)} = 100 \times \text{Act/Theo}$$

where CE is current efficiency in percent, Act is the weight actually deposited and Theo is the weight to be expected from Faraday's laws if there were no side reactions.

Cathode efficiency is current efficiency as applied to the cathode reaction, and anode efficiency is current efficiency as applied to the anode reaction.

Current Distribution

The current divided by the apparent area yields an average figure. Except for the simplest geometries of a cell, such as when the anode and cathode are concentric, the current is not uniform over the surface of an electrode. In fact, the manner in which the current distributes itself over an electrode surface in any practical case is quite complicated, usually far too much so to be simply calculated from geometry. Current will tend to concentrate at edges and points, and unless the resistance of the solution is extremely low (lower than in any practical case), it will flow more readily to parts near the opposite electrode than to more distant parts. Thus, except for the simplest parts subject to electroplating, the thickness of deposit, which depends on the current density, will not be uniform over the surface.

TESTING CORROSION

In order to determine whether a metal, a combination of metals, or a coating system is suitable for use in a given environment, it is necessary to test it in that environment. It is well to repeat here that corrosion is not an action but an interaction, which involves both the metal and its environment. It is pointless to test a panel in dilute sulfuric acid if the contemplated use involves exposure to seawater.

As nearly as possible, corrosion testing should be carried out in an environment that simulates that in which the part will be used. For most finished metal articles, this requirement is not at all easy to meet. Because corrosion is usually a fairly gradual process, the user or manufacturer cannot afford to wait for the results of a test carried out in strictly natural environments; by the time results are available, the purpose of the test - to predict the performance of the item - would be negated. Therefore many accelerated tests have been devised, with the aim of speeding up the process of corrosion while at the same time simulating its effects. But because the nature of the environment is so important to corrosion processes, it is difficult to speed up the process without changing it, and the best that can be hoped is that accelerated tests will be fairly accurate in predicting the actual service performance of an electroplated or otherwise finished metal article.

Natural environments are of many kinds and contain many types of corrosive chemicals. If a metal part is to be finished for a specific service, then it should be tested for corrosion resistance in as near a replication of that service environment as possible. Perhaps corrosion may be accelerated by heat; for example, tinplate is often tested in contact with the foods it will contain, but instead of the "room" temperature at which most canned foods are stored, higher temperatures are used in the test room so that any failures will be noted more quickly. Even such acceleration is not entirely free of doubt, since it is possible that the corrosion mechanism can change with temperature, and not all corrosion reactions are accelerated by heat.

Many electroplated items, however, are destined for service in various environments whose nature is not known at the time of manufacture. The best example of this type of service is provided by the bright work on automobiles; bumper bars, grilles, hubcaps, door handles, and other decorative trim. The product may be used in any one or a combination of several types of atmospheres, which differ greatly in their aggressiveness toward electroplated coatings and substrates.

Many industrial organisations and testing societies maintain outdoor exposure stations where metals and other materials can be exposed to the elements continuously, and note can be taken of their behaviour by inspecting them at suitable time intervals. This sort of testing is slightly accelerated, and for most purposes except long-range research not sufficiently so to obtain speedy results.

A closer approach to actual service conditions is obtained when specimens are mounted on "mobile" exposure. Thus panels may be placed on trucks driven normally on highways during a northern winter, subjected to deicing salts as well as the usual dirt and debris characteristic of such use, or mounted on tugboats plying say, New York Harbour. Such testing offers the advantage of severe exposure under real-life conditions; it suffers from the drawback that specimens may be mechanically damaged, lost or impossible to trace.

Truly accelerated laboratory tests - whose aim is to provide answers to the question "how well does the finishing system resist corrosion?" - have been developed and are in general use. However, how well such accelerated tests predict actual behaviour under service conditions is an unanswered question. Such tests include the following:

Neutral Salt Spray (Fog) Test. Widely used and specified, the test consists essentially of spraying the specimens with a mist of 5% or 20% sodium chloride solution in a closed cabinet, under strictly specified conditions of temperature and spray rate. Many standardising bodies, including ASTM, offer detailed directions for running the test: ASTM B 117.

Acetic Acid Salt Spray (Fog) Test. Similar to the above, with the mist solution acidified with acetic acid for faster action. ASTM B 287.

Copper-accelerated Acetic Acid Salt Spray (CASS) Test. Similar, but with the addition of copper salts to the mist solution; ASTM B 368.

Corrodkote Test. The specimen is coated with a slurry of kaolin containing copper nitrate, ferric chloride, and ammonium chloride. The slurry is allowed to dry and the coated

specimen is placed in a humidity chamber; it is removed, cleaned, and examined after stated intervals of time; ASTM B 380.

Electrochemical Corrosion Test (ECT). The specimen is made anodic in a specified electrolyte; under carefully controlled conditions corrosion is stated to occur within a few minutes.

Sulfur Dioxide Test. The specimen is suspended in a closed chamber in the presence of sulfur dioxide gas.

Humidity tests of various kinds. None of these tests has been shown to accurately predict service behaviour under all conditions. The neutral salt spray, though still specified, has lost favour for research purposes, for it often gives the wrong answer in comparing the relative merits of different coatings.

ENVIRONMENTAL IMPLICATIONS

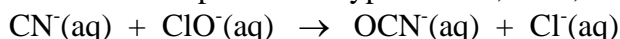
In most parts of the world the authorities set acceptance standards for the discharge of industrial effluent into sewers and water courses. It is usually necessary to obtain the approval of the appropriate authority in the form of a 'consent to discharge' before a discharge can be made or alterations are made in the concentration or volume of an existing discharge.

There are very few metal finishing plants from which the rinse waters can be discharged directly to the sewers as the contaminant concentrations are outside the limits set by local authorities. With the majority of installations, therefore, effluent treatment is necessary.

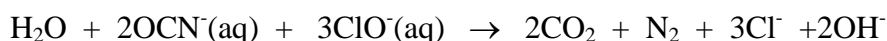
There are a number of methods which may be employed to reduce the level of contaminant in the effluent discharge and thus simplify subsequent effluent treatment. In the main these methods rely on good housekeeping with a liberal dose of common sense added for good measure.

In effluent treatment the usual practice is to separate the acidic discharges, together with those containing nickel or chromium from alkaline and cyanide discharges which may contain metals such as zinc, cadmium or copper. Cyanide baths must be kept alkaline as $pK_a(\text{HCN})$ is 9.21 and at that pH half of the cyanide would be present as volatile HCN!

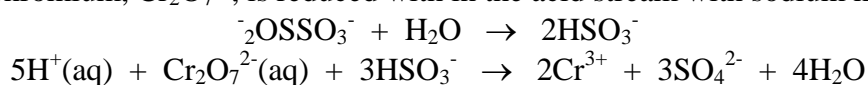
First cyanide is decomposed in the alkaline stream in a two stage process. It is treated with chlorine at $\text{pH} > 10$. Here chlorine is present as hypochlorite, ClO^- , and the reaction is:



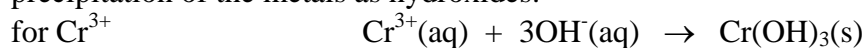
Then the pH is lowered to 8.5 and the cyanate is oxidised to harmless carbon dioxide and dinitrogen:



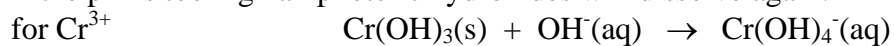
Hexavalent chromium, $\text{Cr}_2\text{O}_7^{2-}$, is reduced with in the acid stream with sodium metabisulfite:



The two streams are then combined and the pH adjusted to the optimum value for the precipitation of the metals as hydroxides:



If the pH is too high amphoteric hydroxides will dissolve again:



These are then separated out in the form of a sludge. Depending on the consent conditions the clarified effluent may then be discharged to waste or it may be necessary to re-adjust the pH to an acceptable value. It may also be necessary to filter the effluent before discharge.

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