

UNIT-I

DYNAMIC ELECTROCHEMISTRY

Electrochemistry is the branch of science which deals with the relationship between Chemical energy and electrical energy and the interconversion of one form into another.
i.e Chemical reactions produced by passing electric current through an electrolyte or production of electric current through a chemical reaction.

Types of conductors

Conductors: Conductors are substances which allow electricity to pass through them. Examples: All metals, graphite, fused salts, solution of electrolytes.

Non-conductors (Insulators): Substances which do not allow the passage of electric current through them are called non-conductors.

Examples: wood, plastics, rubber, most non metals.

Types of conductors

- (i) **Metallic conductor:** Metallic conductors allow electricity to pass through them without undergoing any chemical change. The flow of electric current is due to the flow of electrons in the metal.
- (ii) **Electrolytic conductors :** These are substances which allow electricity to pass through them in their molten states or in their aqueous solutions. Conduction occurs due to the movement of ions.

Differences between metallic conduction and electrolytic conduction

Metallic conduction	Electrolytic conduction
Conduction occurs due to the movement of electrons.	Conduction occurs due to the movement of ions in a solution.
Does not involve any transfer of matter.	Involves transfer of electrolyte in the form of ions.
Conduction decreases with increase in temperature.	Conduction increases with increase in temperature.
No change in the chemical properties of the conductor.	Chemical changes occur at the two electrodes.

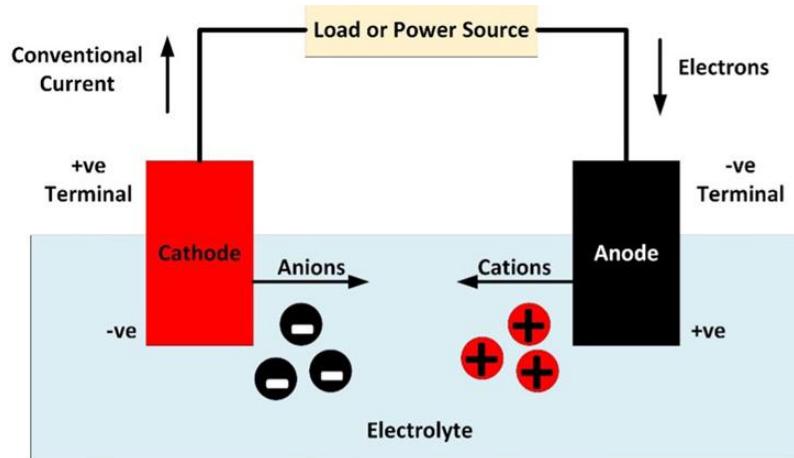
Types of electrolytic conductors

- **Strong electrolytes:** Completely dissociate into ions in solution. Examples: HCl, NaOH, NaCl, KCl.
- **Weak electrolytes:** Which dissociate only to some extent in solution.
- **Non – electrolytes:** Do not ionize in solution.

Cell Terminology

- i. **Current :** Flow of electrons through a conductor.
- ii. **Electrode :** Electrode is a material (rod, bar, strip) which conducts electrons.
- iii. **Anode :** Electrode at which oxidation occurs.
- iv. **Cathode :** Electrode at which reduction occurs.

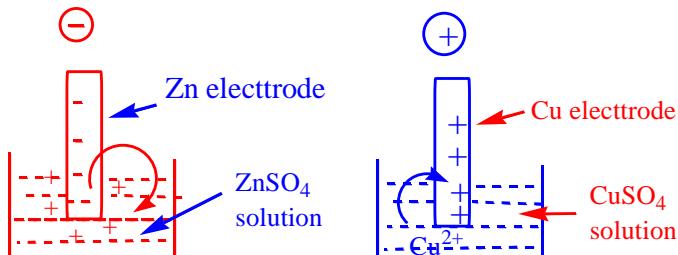
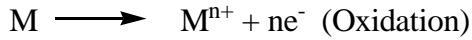
- v. **Electrolyte** : Water soluble substance forming ions in solution and conducts electric current.
- vi. **Anode compartment**: Compartment of the cell in which the oxidation half reaction occurs. Contains the anode.
- vii. **Cathode compartment**: Compartment of the cell in which the reduction half reaction occurs. Contains the cathode.
- viii. **Half – cell**: Part of the cell, which contains an electrode dipped in an electrolyte. If oxidation occurs in this half, then it is called the oxidation half cell. If reduction occurs at the cell, it is called the reduction half cell.
- ix. **Cell**: Device consisting of two half cells. The two half cells are connected by a conductor.



1.1 ELECTRODE POTENTIAL

When a metal (M) is placed in a solution of its own salt (M^{n+}) one of the two processes are possible.

- (i) +ve metal ions may pass into solution
- (ii) +ve metal ions from solution may deposit on the metal



- ✓ When the Zn electrode is dipped in ZnSO₄ solution, gives Zn²⁺ ions and electrons.
- ✓ When Cu electrode is dipped in CuSO₄ solution, Cu²⁺ ions from solution deposit on the metal.

Due to the separation of charges between the electrode and the solution, an electric potential is set up between the metal and its solution. A layer of + or - ve ions formed on the metal is known as **Helmholtz electrical double layer**. At equilibrium, the potential difference becomes a constant value (**Electrode potential of the metal**).

- The tendency of the electrode to lose electrons is **Oxidation potential**.
- Tendency of an electrode to gain electrons is **reduction potential**.

Single electrode potential (E):

Tendency of a metallic electrode to lose or gain electrons when it is in contact with a solution of its own ions.

Standard electrode potential (E^0):

Tendency of a metallic electrode to lose or gain electrons when it is in contact with a solution of its own ions of 1 M Concentration at 25°C .

1.2 ELECTROCHEMICAL SERIES (or) EMF SERIES

The potential of an electrode at a given temperature depends upon the concentration of the ions in the surrounding solution.

If the concentration of the ions is unity and the temperature is 25°C , the potential of the electrode is termed the standard electrode potential. The standard electrode potential of a number of electrodes at 25°C are given in the following table.

The potential of the standard hydrogen electrode (SHE) is used as the reference electrode.

Definition:

When the various metals are arranged in the order of their increasing values of standard reduction potential on the hydrogen scale, the arrangement is called the electrochemical series.

Electrochemical series

Electrode	Electrode reaction	E^0 (V)	Nature
Li^+/Li	$\text{Li}^+ + \text{e} \rightleftharpoons \text{Li}$	-3.01	Anodic Pt- Reference :
Mg^{2+}/Mg	$\text{Mg}^{2+} + 2\text{e} \rightleftharpoons \text{Mg}$	-2.37	
Pb^{2+}/Pb	$\text{Pb}^{2+} + 2\text{e} \rightleftharpoons \text{Pb}$	-1.12	
Zn^{2+}/Zn	$\text{Zn}^{2+} + 2\text{e} \rightleftharpoons \text{Zn}$	-0.76	
Fe^{2+}/Fe	$\text{Fe}^{2+} + 2\text{e} \rightleftharpoons \text{Fe}$	-0.44	
Sn^{2+}/Sn	$\text{Sn}^{2+} + 2\text{e} \rightleftharpoons \text{Sn}$	-0.136	
H^+/H_2	$2\text{H}^+ + 2\text{e} \rightleftharpoons \text{H}_2$	0.00	
Cu^{2+}/Cu	$\text{Cu}^{2+} + 2\text{e} \rightleftharpoons \text{Cu}$	+0.34	
Ag^+/Ag	$\text{Ag}^+ + \text{e} \rightleftharpoons \text{Ag}$	+0.80	
Au^+/Au	$\text{Au}^+ + \text{e} \rightleftharpoons \text{Au}$	+1.50	
$\frac{1}{2}\text{F}_2/\text{F}^-$	$\frac{1}{2}\text{F}_2 + \text{e} \rightleftharpoons \text{F}^-$	+2.87	Cathodic

SIGNIFICANCE OF EMF SERIES (OR) APPLICATION OF ELECTROCHEMICAL SERIES (OR) APPLICATIONS OF NERNST EQUATION

a) Calculation of standard emf of the cell

E^0 can be calculated if the standard electrode potential values are known.

$$E_{\text{cell}} = E_{\text{right}}^0 - E_{\text{left}}^0$$

b) Relative ease of oxidation or reduction

Higher (+ve) value of standard reduction potential, greater is the tendency for reduction. Metals at the top of the table have low reduction potential and have a lesser tendency of getting reduced. Hence, they are more easily oxidized.

Fluorine has higher +ve value of standard reduction potential (+2.87 V) and shows higher tendency for reduction.

Lithium has highest – ve value (-3.02 V) and shows higher tendency towards reduction.

c) Displacement of one element by the other

Metals which lie higher in the series can displace those which lie below them in the series.

Copper will displace silver from its solution.

Iron will displace copper from its solution.

d) Determination of equilibrium constant (K) for a reaction

$$-\Delta G^0 = RT \ln K = 2.303RT \log K$$

$$\log K = \frac{-\Delta G^0}{2.303RT} = \frac{nFE^0}{2.303RT} \quad [\because -\Delta G^0 = nFE^0]$$

From the value of E^0 , the equilibrium constant for the reaction can be obtained.

e) Hydrogen displacement behavior

Metals with – ve reduction potential (metals placed above H_2) in emf series will displace hydrogen from acid solutions.

Zinc will displace H_2 from dilute acids whereas silver cannot.

f) Predicting the spontaneity of redox reactions

If E^0 of a cell is +ve the reaction is spontaneous ($\Delta G = -ve$)

If E^0 of a cell is -- ve the reaction is non-spontaneous. ($\Delta G = +ve$)

1.3 CORROSION

The branch of engineering that deals with the study of corrosion and its prevention safely is known as corrosion engineering.

Definition:

Corrosion is defined as the gradual deterioration of a metal or alloy by the chemical or electrochemical reaction with the environment.

Examples:

- (i) Rusting of iron.
- (ii) Blackening of silver particles in the atmosphere.
- (iii) Fogging of nickel.



Causes of corrosion

Metals occur in nature either in (i) native state (or) free State (ii) in combined state

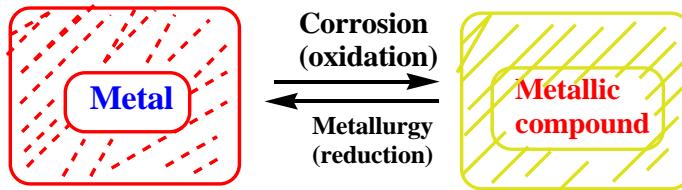
i. Native state

Metal those occurring in nature in native (or) free (or) uncombined state (or) non-reactive with the environment. They are noble metals. They do not undergo corrosion. Example: Au, Pt, Ag

ii. Combined state

Except noble metals, all the other metals are reactive and react with the environment and form compounds such as oxides, sulfides, chlorides and carbonates by reaction with the environment. They exist in nature in the form of their stable compounds (ores). Example: Fe_2O_3 , ZnO , PbS , CaCO_3

How and why corrosion occurs



- ✓ Corrosion is a natural process that converts a refined metal into a more chemically stable oxide.
- ✓ When the metals are used in various environments, such as corrosive gases, moisture, the metal surface tends to decay, which is the reason for corrosion.
- ✓ Due to corrosion, some of the useful properties of metals such as electrical conductivity, ductility, and malleability are lost.

Consequences of corrosion

- ✓ The economic and social consequences of corrosion include
- ✓ Poor appearance.
- ✓ Plant shut down due to failure.
- ✓ Replacement of corroded equipment.
- ✓ Preventive maintenance like painting and coating.
- ✓ Necessity for over design to allow for corrosion.
- ✓ Loss of efficiency of equipment.
- ✓ Contamination or loss of product.
- ✓ Safety (i.e., fire hazard or explosion or release of toxic product).
- ✓ Collapse of construction due to sudden failure.
- ✓ Health (Pollution due to a corrosion product or due to the escaping chemical from corroded equipment).

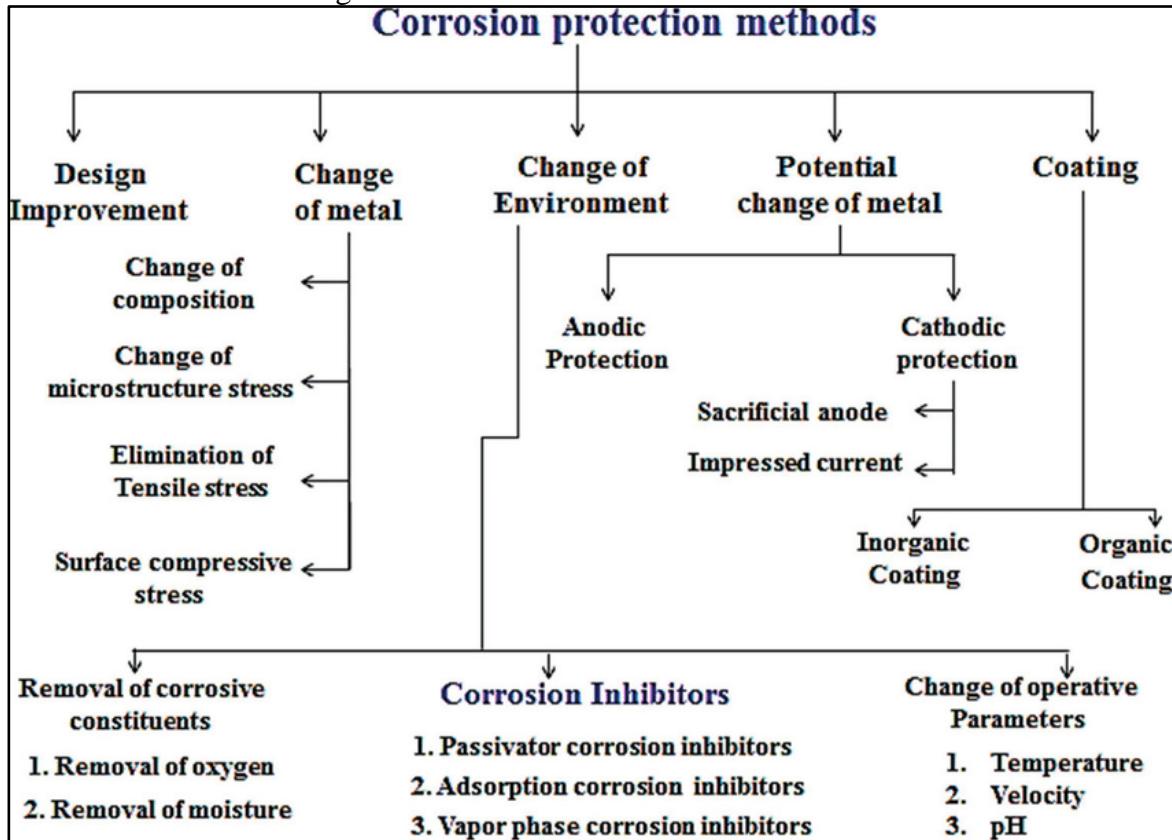
Prevention of Corrosion

- Preventing corrosion is of utmost importance in order to avoid huge losses. The majority of the structures that we see and use are made out of metals. This includes bridges, automobiles, machinery, household goods like window grills, doors, railway lines, etc.
- While this is a concerning issue, several treatments are used to slow or prevent corrosion damage to metallic objects.
- This is especially done to those materials that are frequently exposed to the weather, saltwater, acids, or other hostile environments.

Some of the popular methods to prevent corrosion include,

- Electroplating
- Galvanization
- Anodization
- Passivation
- Biofilm Coatings

- Anti-Corrosion Protective Coatings
- Painting and Greasing
- Use of Corrosion Inhibitor or Drying Agents
- Periodic Cleaning of Metal Surface



1.4 SURFACE PREPARATION

- Generally metal surfaces are covered with impurities like rust, scale, oil and grease.
- Presence of these impurities will produce porous and discontinuous coatings.
- In order to obtain uniform, smooth, cohesive and adherent coating, these impurities must be removed, by treating the surface to be coated.

(i) **Solvent cleaning (degreasing)**: Organic solvents such as toluene, xylene, acetone, CCl_4 are used to remove oils, greases, and fatty substances on the metal surface.

(ii) **Alkali cleaning**: Useful for the removal of old paint coating from metal surfaces. Solutions of NaOH , Na_2HPO_4 , with some detergents, emulsifying and wetting agents are used. After alkali treatment, the surface is rinsed with water and then with 0.1% chromic acid.

(iii) **Acid cleaning (Pickling)**: Applicable for the removal of oxide coatings and other corrosion products.

Acids like HCl , H_2SO_4 , HNO_3 , H_3PO_4 are used.

(iv) **Mechanical cleaning**: Oxide scales, rust are removed by grinding, wire brushing and polishing.

(v) **Flame cleaning:** High velocity hot flame is blown over the metal surface to remove moisture and loosely adhering particles.

(vi) **Sand blasting:** The operation of forcibly propelling a stream of abrasive material against a surface under 25 – 100 atm. Used for removing oxide scales.

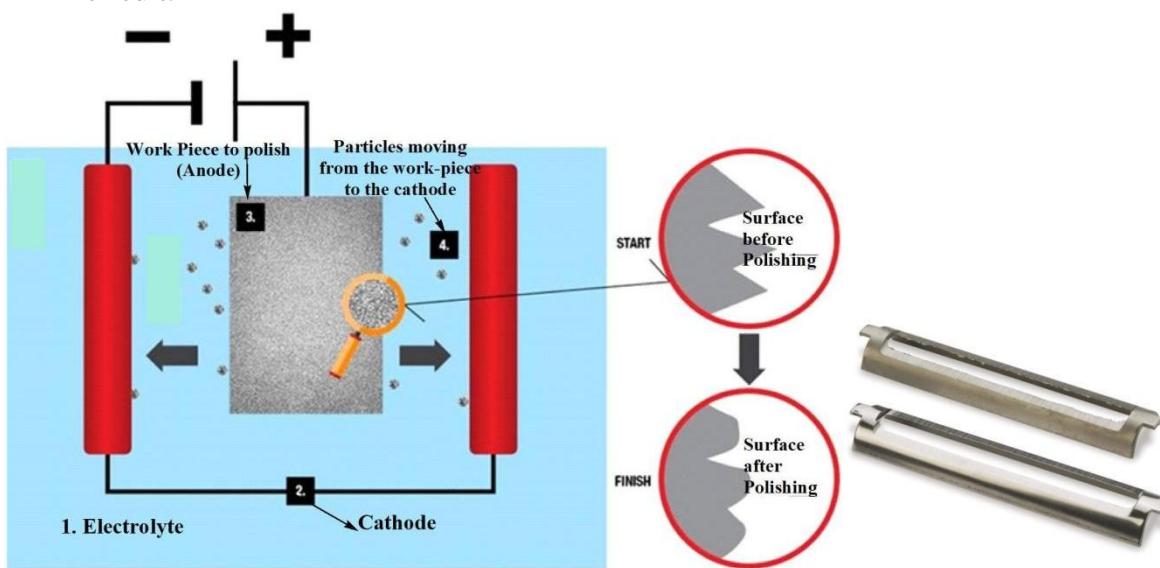
1.5 ELECTROPOLISHING

Definition

Electropolishing is an electrochemical process in which the atoms of a workpiece submerged in an electrolyte are converted to ions and are removed from the surface as a result of a passage of an electric current.

Principle

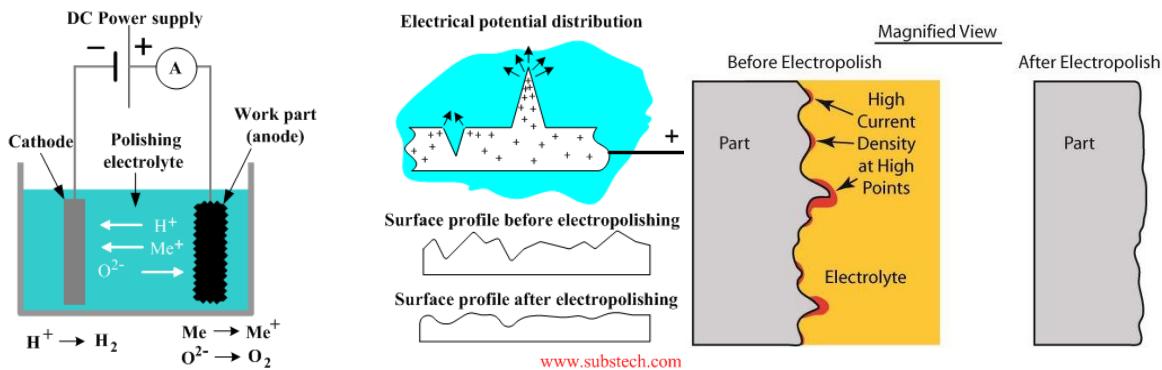
- In an electropolishing cell (see the figure below) the work piece is anode. It is connected to the positive terminal of the direct current power supply. The negative terminal is connected to a cathode plate commonly made of stainless steel, copper or lead. The anode and the cathode are immersed into an electrolyte solution.
- Electropolishing is similar to Electrochemical machining where the workpiece material is removed due to the conversion of the atoms into ions, formation of an insoluble precipitate and its transfer from the surface. The DC power supply, the anodically connected work piece, the electrolyte and the cathode form an electric circuit.



- According to Faraday's law the amount of the removed material is directly proportional to the amount of electric charge, passed through the circuit. The amount of electric charge $Q=I*t$ (I – electric current, t – time).
- The amount of the metal removed from the workpiece surface in an electropolishing process varies from 0.001 to 0.0025 (2.5-64 μm).
- The important feature of the electropolishing process is its ability to dissolve asperities (peaks) on the work surface much faster than the material in "micro-valleys". Such selective dissolution is a result of different values of the electrical potential of the peaks and valleys. The positive charge of the anodically connected work piece is concentrated in the peaks where the current density is higher than

average which causes a selective dissolution of the peaks and smoothing the surface.

Electropolishing



Benefits of electropolishing:

- Bright appearance.
- Absence of abrasive scratches.
- Improved fatigue strength.
- Defects free surface.
- Lower coefficient of friction due to smoother surface (reduced micro- asperities).
- Better corrosion resistance.
- Allows processing fragile and delicate parts.

Disadvantages of electropolishing:

- Rough surface defects cannot be removed;
- Electropolishing multiphase alloys may cause roughening due to selective dissolution of different phases.

1.6 ELECTROPLATING OR ELECTRODEPOSITION OF COPPER

- Electroplating is a coating technique. It is the most important and most frequently applied industrial method of producing metallic coating.
- ***"Electroplating is the process in which the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution containing the soluble salt of the coating metal."***
- The base metal to be plated is made cathode of an electrolytic cell, whereas the anode is either made of the coating metal itself or an inert material of good electrical conductivity (like graphite).

Objectives of Electroplating

1. On Metals

1. To increase the resistance to corrosion of the coated metal.
2. To improve the hardness and physical appearance of the article.
3. To increase the decorative and commercial values of the article.
4. To increase resistance to chemical attack.
5. To improve the properties of the surface of the article.

2. On Non-Metals

1. To increase strength.

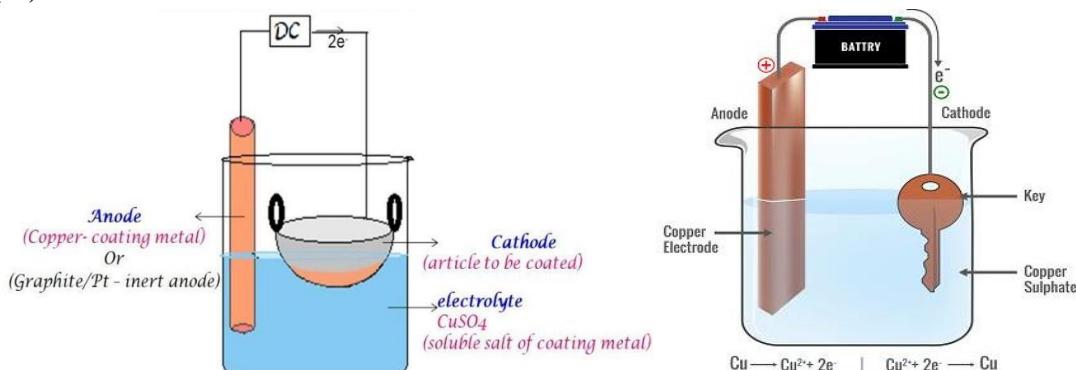
- To preserve and decorate the surfaces of non-metals like plastics, wood, glass, etc.
- For making the surface conductivity by utilization of light weight, non-metallic materials.

Procedure for Electroplating of Copper

- The article to be copper plated is first treated with organic solvent like carbon tetrachloride, acetone, tetrachloroethylene to remove oils, greases etc.
- Then it is made free from surface scales, oxides, etc. by treating it with dil. HCl or H_2SO_4 (acid pickling).
- The cleaned article is then made as the cathode of the electrolytic cell.
- The anode is a copper plate or rod.
- The electrolyte is a copper sulphate solution.
- When direct current is passed, coating metal ions (Cu^{2+}) migrate to the cathode and get deposited there. Thus, a thin layer of coating metal (copper) is obtained on the article made as the cathode.
- In order to get strong, adherent and smooth deposits, certain types of additives (glue, gelatine, boric acid) are added to the electrolytic bath.
- In order to improve brightness of the deposit brightening agents are added in the electrolytic bath.

The favorable conditions for a good electro deposit of copper are

- Optimum temperature – 40°C
- Optimum current density – $30\text{-}40 \text{ mA cm}^{-2}$.
- Low metal ion concentrations.



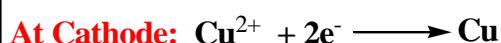
Theory of Electroplating of Copper

If the anode is made of coating metal (Cu) itself in the electrolytic cell, during electrolysis, the concentration of electrolytic bath remains unaltered, since the metal ions deposited from the bath on cathode are replenished continuously by the reaction of free anions with the anode.

- If CuSO_4 solution is used as an electrolyte, it ionizes as



- On passing current, Cu^{2+} ions moving to the cathode (the key to be placed) and get deposited there.



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



- The copper sulphate thus formed dissolves in the electrolyte. Thus, there is a continuous replenishment of electrolytic salt during electrolysis.

Uses of Copper plating

- It serves as an undercoat for chrome plating.
- It is used for smoothing out the irregularities on the surface.
- It is used as a protective coating for steel articles.
- It is coated at the bottom of stainless steel (copper bottom) in cooking utensils to effect better heat transfer.

1.6. 1 FACTORS INFLUENCING ELECTROPLATING

Polarization

- ✓ During electrolysis, the electrical energy supplied by the external source is converted into chemical energy.
- ✓ When the current is passed through an electrolytic bath, the electrolyzed products deposit on the surface of the electrodes. Hence, the passage of current gradually decreases and falls almost to zero.
- ✓ This is due to back e.m.f. which drives the current in the opposite direction to which imposed current flows from the battery.
- ✓ This phenomenon of *setting up of the back e.m.f. during electrolysis is called “Polarization” and the current developed is called polarization current.*
- ✓ The polarized voltaic cell is called a secondary cell. Due to polarization, the rate of diffusion of reactants/products onto the surface of the electrodes decreases.
- ✓ The more adherent and non-porous the film formed, the more it contributes to the increase of polarization at an electrode. These are of considerable importance in determining the rate of corrosion of a metal.

Decomposition potential

- ✓ This happens when applied e.m.f. is just sufficient to overcome the back e.m.f. *The minimum voltage required to bring about the electrolysis without any interruption is called “Decomposition potential”.*
- ✓ The decomposition potential depends on the nature of the solution and electrode material.
- ✓ If the metal has higher solution pressure, the electrode tries to send the ions back into the solution more easily. Therefore it is more difficult to deposit that metal i.e., it has a higher decomposition potential.
- ✓ For example, the solution pressure of Zn is more than that of Cu. It is found that Zn has higher decomposition potential (2.55V) than that of Cu (1.5V).
- ✓ If the applied e.m.f. is less than 2.55V and more than 1.5V between the Cu electrodes, only Cu will be deposited on the cathode while Zn remains in the solution.
- ✓ Thus if the difference in decomposition potentials is large, metals may be separated.

Hence, knowledge of decomposition potential is important in electro refining, electro metallurgy, etc.

Over Voltage

- ✓ It was observed that during electrolysis back emf arises and a minimum voltage is to be applied for continuous electrolysis.
- ✓ When this emf is compared with the decomposition potential, it is found that the value is higher than the required emf value. This difference between the observed voltage and the theoretical voltage is known as over voltage.
- ✓ Over voltage depends on the nature of the electrode, physical state of the substances deposited, current density and temperature. It is due to surface phenomenon.
- ✓ It depends on how ions are discharged and the rate at which they are discharged. Hydrogen overvoltage is of particular significance in many electrolytic reactions and especially in electroplating and corrosion.

Composition of the electrolytic bath:

- ✓ The metal salt used for the preparation of the electrolytic bath must be highly soluble, good conductor and should not undergo any chemical transformation like hydrolysis, reduction etc. in the bath during electrolysis.
- ✓ To get very adherent and thin coating films, low metal ion concentrations are preferred.
- ✓ Electrolytes give conductivity to the bath and high concentration of the electrolyte ensures max conductivity
- ✓ Conductivity of electrolyte effects “Throwing Power” (ability of the bath to give even deposit) of the bath

Concentration of the electrolyte is another important factor:

- ✓ Low concentration of metal ions will give uniform coherent deposition.
- ✓ To maintain low conc. of metal ions, complexing agents are added to the electrolyte.

Additives:

- ✓ These are the substances added to the bath to improve the nature of the deposit, they are complexing agents, brighteners, levelers, wetting agents, structure modifiers, and pigments.
- ✓ *Complexing agents* are added to maintain low metal ion concentration in solution, to improve throwing power of the plating bath, to increase the solubility of the sparingly soluble salts and to avoid the passivity of anode. The most commonly used complexing agents are hydroxide, cyanide and sulfate ions.
- ✓ *Brighteners* are the chemical substances added to get bright and lustrous deposit, for example: sodium formate, coumarin, thiourea, cobalt sulphonate, etc., are added as brighteners in Ni plating. The concentration of these brighteners must be maintained in the optimum range, otherwise results in a fine grained deposit.
- ✓ *Levelers* are the substances that help to form a uniform deposit on the surface by preferential adsorption at the places where rapid deposition of the metal takes place. Many brighteners also behave as levelers.
- ✓ *Structure modifiers*: These are also called stress relievers. These substances alter the structure of the electro deposit and thereby modify the properties of the electric deposit.
- ✓ *Wetting agents* are used to remove the adsorbed hydrogen from the cathode, otherwise it may lead to pitting.

Thickness of the deposition should be optimized to get a strong and adherent deposition:

- ✓ For corrosion protection multiple coatings are given to get impervious coating without any discontinuity.
- ✓ For decorative purposes, a thin coating is given.

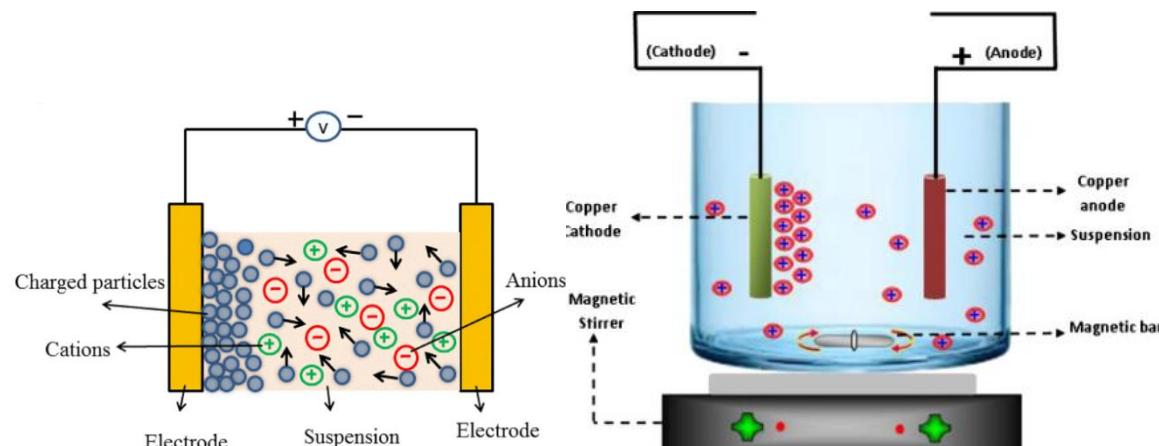
Current density

- ✓ Current density is the current per unit area of the article being plated (amps cm^{-2}).
- ✓ The C.D should be maintained at optimal level to get uniform and adherent deposition.
- ✓ If current density is high, it results in loose and brittle deposits. If current density is low, it takes a long time for electroplating, since the rate of electro deposition is low. Hence optimum current density should be employed.

1.7 ELECTROPHORETIC DEPOSITION (EPD)

“Electrophoretic deposition (EPD) is a technique where charged particles in a stable colloidal suspension are moved through the liquid due to electric field and deposited on an oppositely charged conductive substrate, forming the intended material or device”.

- The EPD technique, first extensively utilized in ceramic coatings, has recently become the center of attention in the industrial sector, owing to the outstanding versatility of its utilization with different materials and their combinations.
- The other merits of this kind of technique, a colloidal process, includes the ease of control over the thickness and surface morphology of the deposited layer, straightforward apparatus, short preparation time, and cost effectiveness.
- Electrophoretic deposition (EPD) is a method of **coating a conductive part with particles suspended in a fluid dispersion under the influence of an electric field applied between the work part and the counter electrode**.
- The counter electrode is an electrode used in a three electrode electrochemical cell for voltammetric analysis or other reactions in which an electric current is expected to flow.



- Electrophoretic deposition utilizes electrically charged particles moving between two electrodes (an anode and a cathode) immersed in a liquid media. The fluids of electrophoretic dispersions are dielectric (insulating material or a very poor conductor of electric current) in nature.
- In electrophoretic process, the coating is formed by a deposition of relatively large powder particles which may be polymeric, ceramic or metallic.

The following characteristic features define electrophoretic deposition:

- There is a stable dispersion of particles in a solvent (a colloid).
- The particles gain a surface charge as a result of an electrostatic interaction with the molecules of the solvent.
- The particles are capable to move in the suspension towards the work part under the influence of a voltage imposed between the work part and the counter electrode (the phenomenon called electrophoresis).
- A rigid deposition composed of condensed particles is built up on the work part surface
- The deposited coating is adhered to the surface of the work part.

Process:

- When a voltage is applied between the electrodes the charged particles start to migrate towards the electrode with the opposite electric polarity.
- The particles are deposited first of all at the surface areas with the highest electric potential.
- The formed coating decreases the potential of such areas and equalizes the potential distribution over the part surface.
- As a result a uniform and even film forms over the whole part surface including the surface of cavities, edges and corners.
- The coating thickness is determined by the voltage value which is typically 25-400 V. After a coating of a certain thickness is built the deposition process stops.
- The industrial applications of electrophoretic deposition are referred to as e-coating, electrocoating, electrophoretic painting or electrophoretic coating.

The deposition process includes the following stages:

- Hanging the work parts
- Alkaline cleaning
- Rinsing
- Acid cleaning
- Immersion in adhesion promoter (wetting agent)
- Electrophoretic deposition
- Rinsing and dispersion recovery
- Rinsing in de-ionized water
- Dehydration oven
- Curing

Advantages of Electrophoretic deposition

- ✓ The coatings have excellent scratch resistance and corrosion resistance. Acrylic and polyurethane coatings are also resistant against ultra-violet light.
- ✓ Relatively high speed of coating.
- ✓ Relatively high purity.
- ✓ Uniform coating thickness without porosity.
- ✓ Applicability to a wide range of materials (metals, ceramics, polymers).

Uses of Electrophoretic deposition

- ✓ This process is industrially used for applying coatings to metal fabricated products.

- ✓ The most popular applications of electrophoretic deposition are coating of automotive parts with epoxy, acrylic and polyurethane films.
- ✓ It has been widely used to coat automobile bodies and parts, tractors and heavy equipment, electrical switchgear, appliances, metal furniture, beverage containers, fasteners, and many other industrial products.
- ✓ In the fabrication of solid oxide fuel cells EPD techniques are widely employed for the fabrication of porous ZrO₂ anodes from powder precursors onto conductive substrates.

1.8 ELECTROCHEMICAL MACHINING

It is the process of removing metal by electrochemical process.

Definition

Electrochemical machining is the process of selective dissolution of the anodically connected workpiece material submerged in an electrolyte together with a cathodically connected tool.

Principle

Electrochemical machining is the process of conversion of the atoms into ions and their removal from the surface as a result of a passage of an electric current.

Reactions

The electrochemical reactions occurring in the electrochemical machining process are as follows:

At the anode

The Fe atoms are converted into ions



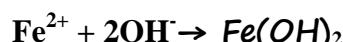
The electrons lost by the Fe atoms travel to the cathode through the DC power supply.

At the cathode

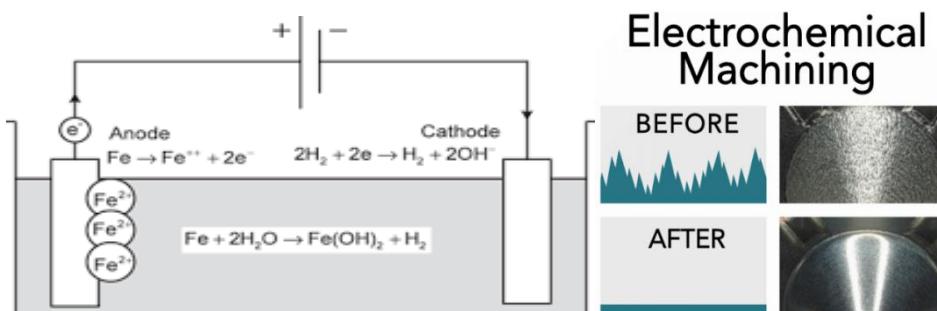
The electrons react with water molecules forming gaseous Hydrogen and hydroxyl ions.



The cations and the anions react in the aqueous solution and form insoluble ferrous hydroxide:



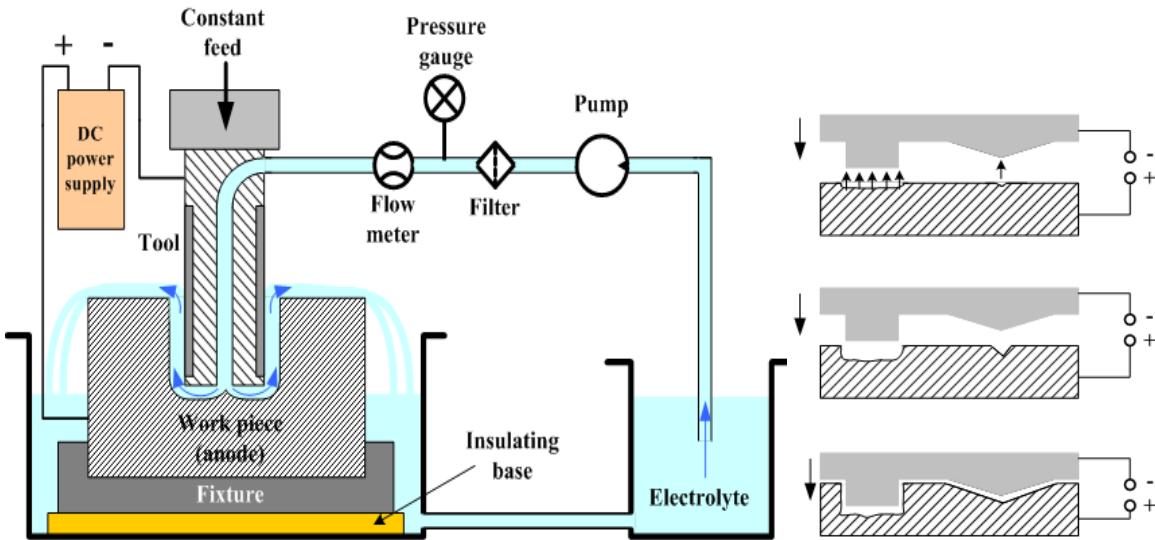
The insoluble hydroxide is taken away by the flowing electrolyte and then it precipitates at the tank bottom forming the sludge.



The work piece is mounted in a fixture electrically isolated from the tank and other machine parts.

- The workpiece is connected to the positive terminal (anode) of the Power Supply.
- The tool is connected to the negative terminal (cathode).

- The electrolyte is continuously flowing through a hole in the tool to the gap between the workpiece and the tool surfaces.
- The tool is moving towards the work piece at a constant speed of about 0.05"/min (1.25 mm/min).
- The gap between the tool and the workpiece is kept constant.
- Stable behavior of the process is a result of a control of the power supply voltage.
- The final shape of the workpiece formed as a result of the electrochemical machining process is similar to the shape of the tool.



Electrolytes used in electrochemical machining

- Sodium chloride (**NaCl**) at the concentration of 20% - for ferrous alloys (e.g. Steels and cast irons and cobalt alloys).
- Hydrochloric acid (**HCl**) - for Nickel alloys.
- A mixture of 10% hydrofluoric acid (**HF**), 10% hydrochloric acid (**HCl**), 10% nitric acid (**HNO₃**) - for Titanium alloys.
- Hard and brittle materials are ground by the method.

Advantages of electrochemical machining:

- The rate of machining does not depend on the hardness of the workpiece material.
- The tool does not wear. Soft materials (e.g., copper) may be used for tool fabrication.
- No stresses are produced on the workpiece surface.
- High surface quality may be achieved.
- High accuracy of the machining operation.

Disadvantages of electrochemical machining:

- Higher cost.
- Electrolyte may cause corrosion of the equipment.
- Large production floor is required.
- Only electrically conductive materials may be machined.
- Not environmentally friendly.

Applications of electrochemical machining

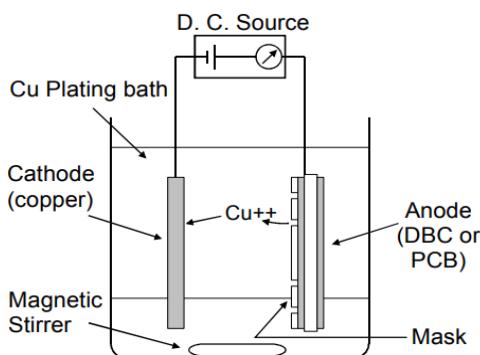
- Turbine blades and rifle barrels are fabricated by electrochemical machining.
- Used to produce holes and cavities which cannot be obtained by conventional machining methods.
- Fabrication of thin walled parts.

1.9 ELECTROCHEMICAL ETCHING

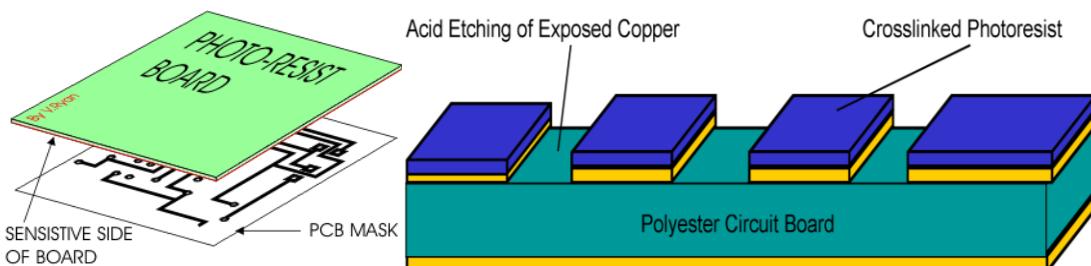
Principle

All metals have a natural tendency to lose or gain electrons depending on their electrode potential values. By measuring the electrode potential, the degree of electrochemical etching may be measured. Thus micro structural elements of different electrochemical potential are attacked at different rates. It may be considered as forced corrosion.

Electroetching is a metal etching process that involves the use of a solution of an electrolyte, an anode, and a cathode. The metal piece to be etched is connected to the positive pole of a source of direct electric current.

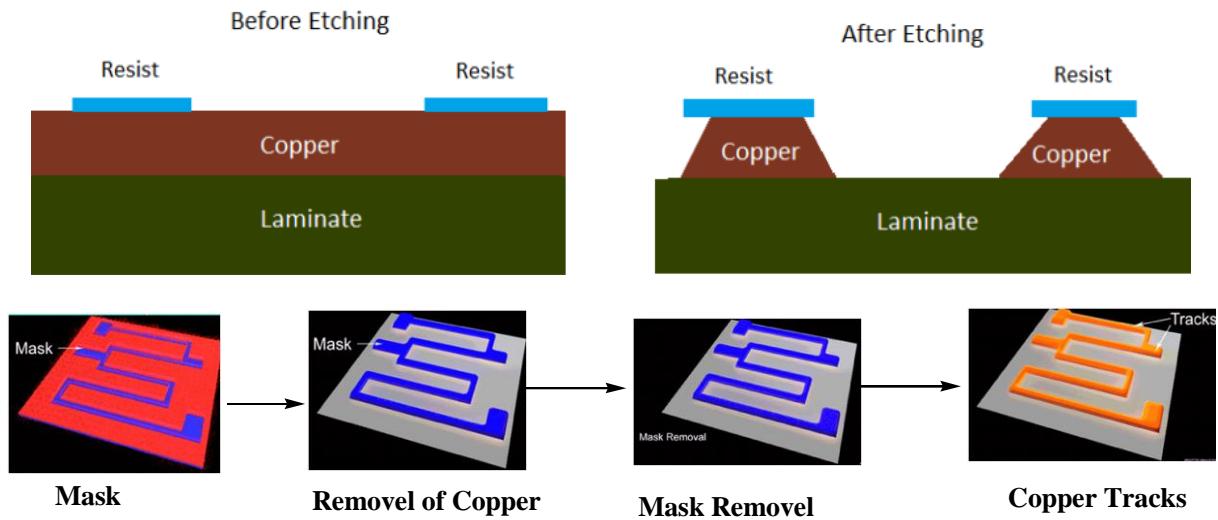
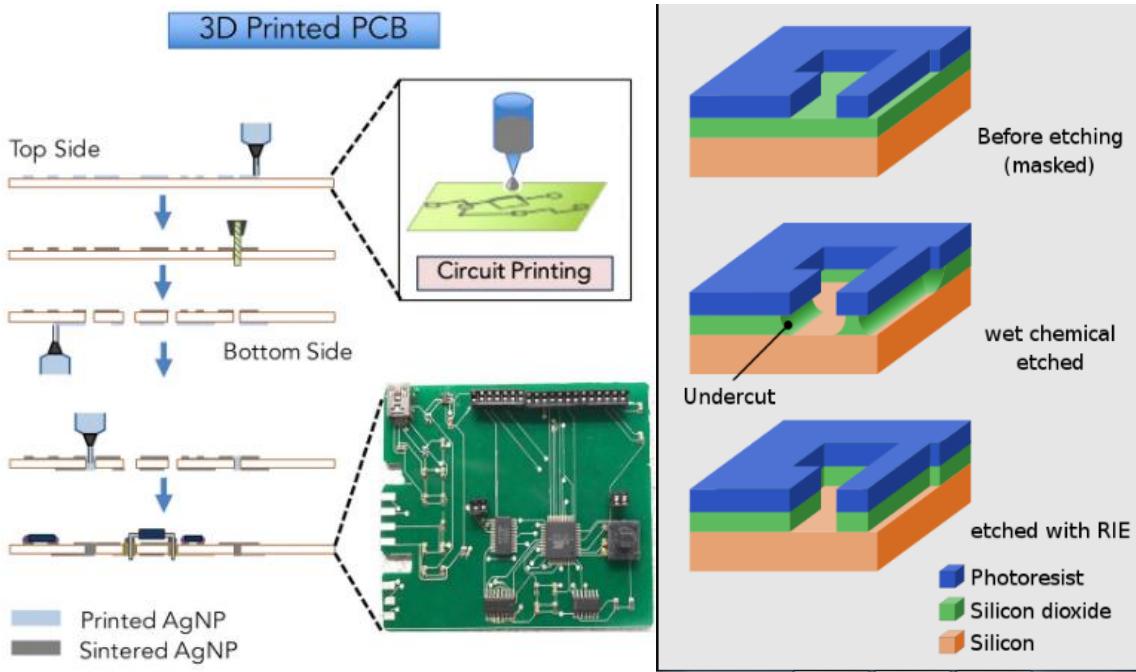


Schematic of the electroplating cell used for etching the copper on substrates



Electrochemical etching of copper from PCB

- The substrate being etched acts as the anode.
- The cathode is made of copper or any copper coated board.
- The plating bath contains an etchant solution like acids, bases, neutral solutions, mixture of solutions, molten salts etc.
- Currently used printed circuit board etching solvents are iron (Ferric Chloride), cupric chloride (Cupric Chloride), alkaline ammonia (Alkaline Ammonia), sulfuric acid hydrogen peroxide (Sulfuric Acid + Hydrogen Peroxide).
- The polished PCB substrates were cut into squares. The substrates were then ultrasonically cleaned with a degreasing detergent and alcohol.



- They are air dried and heated to remove the moisture.
- Photoresist material is sprayed on the substrate which acts as a mask for the remaining part to develop a patterned substrate.
- The coated substrates were air dried and heated to 80-85°C and exposed to UV radiation for 30 mins.
- After exposure, the substrates were immersed in a developer solution to produce the desired PCB pattern.
- On completion of the etching process, the specimen should be rinsed in clean water to remove chemicals and stop any reactions from proceeding further. After that the specimens are water rinsed, rinsed in alcohol and dried in warm air.