Metal finishing.

It is a process carried to modify the surface property of conducting and non conducting materials by depositing a layer of metal on its surface.
ex:- electroplating, electroless plating

=> Objectives of metal finishing / technological importance of metal plating.
* objectives of this to impact ch - such as
1) improving resistance against corrosion of plated metal.
2) improving resistance against chemical attack.
3) improving hardness of metal.
4) improving electrical property
5) improving decorative appearence of the metal.
6) reducing frictional loss.

Electroplating.
Its a process of depositing metal or alloys or composite on the surface of anoth other metal by means of electrolysis. The aim of electroplating is to alter the properties and characteristic of surface, to improve the appearence, to withstand corrosion; enhance ag resistance, good electrical conductivity.

=> Factors affecting the nature and electrodeposit.

There are several factors which affects the nature of electrodeposit. They are :-

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1) Metal ion concentration.
2) Complexing agent
3) Current density
4) Organic additives
5) pH
6) temp
7) ~~throwing~~ throughing power.

1) Metal ion concentration.

The metal ion concentrating in plating soln should be maintained b/w 1 to 3 mole/dm. Higher concentration increases the mass transfer leading to poor deposit, lower conc leads to discontinious deposit.

2) Complexing agent.

They are added to plating soln to convert metal ion into complex ion to get fine grained deposit.

Complexing agents are employed to

a) prevent the reocn of cathode metal with metal ion.

b) improving throughing power of the plating bar

c) enhance the solubility of ~~slity~~ slightly soluble metal solids.

The most common complexing agents used in the plating are Cyanide, hydroxide, sulphate ions.

3) Current density.

Current density is the applied current per unit area of cathodic surface expressed in Ampere/m^2.

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- At lower current density, less no of ions are reducing in surface. The atoms finds most favourable position for deposit. At higher current density large no of ions are reduced on the surface the atoms formed moves very fast leading to rough and powdery deposit.
- Evolution of H^+ ions takes place on electrodes due to fast depletion of H^+ ions.

4) Organic additives.

- Wide range of organic compounds are added in relatively at lower concentration to modify structural, morphology and properties of deposit.
- Added agents are classified into several groups based on their action.

a) Brightness:

- They are added to plating solⁿ to obtain dry deposit on the surface.
- Brightness on the surface increases which the roughness of deposit is less compared to wavelength of incident light.
- Brightness increases crystallinity and orientation of deposit so that light falling on it is reflected rather than scattered.
- Brightness are used in relatively compared to other agents.
- usually used brighteners are thiourea and Cumarin (Flavouring agent in ice-cream)

b) Levellers.

- These compounds produce a levelled deposit on a mole macroscopic scale.
- They act by adsorption at points where there would be rapid deposition of the metal. The adsorbed additives reduce the rate of deposition and

rate of moments of electrons by acting as warrior.
- Usually used levellers are Sodium, Alkylsulphonates.

c) Structure modifiers
- The electrode deposit produced on the surface experience internal stress due to misfitting of the atom. The high stress results in breaking of deposit.
- The structure modifiers modify the structure of the deposit reducing the internal stress usually used modifiers are saccharine.

d) Wetting agents.
- During electroplating in somecases there is simultaneous deposition of metal and Hydrogen, the strongly adhered Hydrogen bubbles out as H^+ ion gas breaking the deposit that creates pit in the deposite.
- The wetting agents absorb Hydrogen and eliminate pit. Usually used wetting agent is Sodium sulphate

e) pH
- For a good deposition, the pH of grating soln must be properly maintained.
- At low pH evolution of H^+ ions occurs at cathode resulting burnt deposit.
- At high pH metal ion precipitate as hydroxides on the surface.
- Hence optimum pH range must be maintained i.e b/w 4 to 8.

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6) temp :-

A good and fine grained deposit is obtained at slightly higher temperature because at high temp of metal solubility of metal salts increases leading to high conductivity of solution at the increasing temperature corrosion of equipments, evolution of Hydrogen at cathode and decomposition of Organic compounds takes place. Therefore, plating is carried out generally at moderate temp of 30-60°C.

7) throwing power.

- The ability of plating soln to produce uniform deposition on an irregular object is measured by its throwing power.
- The cell contains two cathodes & a plating soln whose throwing power is to be determined therefore two cathodes are replaced in a cell at different distance C_1 and C_2 where $C_1 > C_2$ from anode placed at center, electroplating is carried out.
- Weight of the metal deposited on cathodes are determined W_1 = weight of deposit on C_1.
  W_2 = weight of deposit on C_2.

Throwing power is calculated by appling the equation

$$TP = \frac{x-y}{x+y-2} \times 100.$$

where $x = \frac{C_1}{C_2}$ $y = \frac{W_1}{W_2}$

=> Electroplatting of gold :-

It is the process of depositing gold on copper i.e Cu and Ag (silver) are passing current through plating solution is called electroplatting of gold.

Electroplatting is carried out by the following steps :-

(1) Pretreatment : (Surface coating) :

The surface is cleaned with organic solvent to remove oil and greece followed by cleaning with dilute H_2SO_4 to remove scale. Finally, polish using Silicon carbide (SiC), wash with water and air dry.

2) Plating process :-

High purity gold platting is carried out on pretreated surface in cyanide bar with following composition.

(i) Plating soln : Gold cyanide (8 to 10 g/lt)
(ii) Buffer : Pottassium dinitrogen phosphate (to maint. pH = 11)
(iii) Temperature : 30 to 60°C
(iv) Current density : 3.5 A/m².
(v) Anode is the stainless stell, cathode is the article on which coating is to be done by passing D.C at desired temp (30°c to 60°c).

Metal ion from the platling solution difuses and get deposited over cathode.

Cathodic reaction :-

$$Au[(CN)_4]^- + 2e^- \longrightarrow [Au(CN)_2] + 2CN^-$$

$$[Au(CN)_2] + 2e^- \longrightarrow Au + 2CN^-$$

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Applications:-

1) Manufacturing of electrical switch, connector pins.
2) Providing corrosion resistance to copper.
   PCB [printed circuit Board]
3) Manufacturing of gold plated jewellary.

Electroplating of Chromium:-

The process of depositing chromium on surface of substance like stainess steel

(i) Pretreatment on surface coating.

The surface is subjected to cleaning with organic solvents to remove oil and greece followed by cleaning with dilute H_2SO_4 to remove scales, finally washed with water and air drive.

(ii) Plating process:-

Chromium plating is done on pre treated surface with following composition and condition

1) plating soln - chromium oxide $(CrO_3) + H_2SO_4$.
2) temperature - 40-60°C.
3) Current density - 100-200 A/m²
4) Anode metal - pb (lead) alloy coated lead oxide (PbO_2).

   Cathode - article on which coating is to be done on passing current at fixed temp.

5) Chromium ions in the soln which is at Cr^{+6} reduces to Cr^{+3} to form complex in soln in presence of Sulphate ions. $(SO_4)^{2-}$

   Finally Cr^{+3} reduces to Cr (metallic chromium) and deposits on cathode surface.

6) High concentration of Cr^{+3} in the soln leads to reduction in throwing power and plating rate.
7) The good depositing concentration Cr^{+3} is maintained to limited quantity. The PbO_2 oxidises the

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a part of Cr^{6+} to Cr, thus reduces the quantity of Cr^{6+} and maintains concentration (concentration of Cr^{6+} increases in sol^n when Cr^{0} metal is used as anode)

→ Following reactions takes place.

1) Anodic reaction

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$$

2) Cathodic reaction

$$Cr(VI) \xrightarrow{SO_4^{2-}} Cr(III) \rightarrow Cr.$$

Applications :-

* Coating on heavy duty machines, tools, automotive parts to prevent corrosion.
*

⇒ Electroless plating.

The process of deposition of metal from its salt sol^n on catalytically active surface using suitable reducing agent.

Advantages :-

* no electric current is required.
* it has a good throwing power.
* semiconductors and non semiconductor can be coated.
* deposition is more and compact and highly adhearant.
* coating has unique chemical, mechanical, magnetic properties.

Difference b/w electroplating and electroless - plating :-

	Description	Electroless plating	Electroplating
1)	Driving force	Catalytic redox rexn	Power supply
2)	Anodic rexn	Reducing agent → oxidized product +e⁻	$M \rightarrow M^{n+} + e^-$
3)	Site for cathode rexn.	surface is catalytically prepared.	surface is drastically prepared
4)	Site Application	- both conductors and non conductors.	only for conductors
5)	Nature of deposit	Metal with reducing agent and oxidised product.	Pure metal.

⇒ Electrolessplating of Nickel.

Controlled deposition of layer of Nickel on the surface of material is carried out in following steps

(i) Pretreatment (or) surface coating.

The metallic surface is washed with organic solvents or alkaline soln to remove greece on materials.

Stainless steel is activated by dipping dilute H_2SO_4.

Non metallic objects are activated by dipping in (Tin chloride) $SnCl_2$ followed by palladium chloride to get thin layer of Palladium.

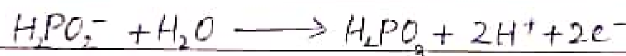
(ii) Plating process.

It is carried out by placing the surface activated article in following composition.

1) Plating soln - NiCl (20gm/lt)
2) Reducing agent - Sodium hypo phoshate (20gm/lt)
3) Complexing agent - Sodium succinate (15 gm/lt)
4) Buffer - Sodium acetate (10gm/lt), maintain pH upto 11
5) Temp - 346K (73°C)

Both oxidation and reduction takes place on the same surface, the reducing agent reduces the Nickel ion from the surface to Ni atom and deposits on the activated surface. Due to oxidation of hypophosphate H^+ ions releases into soln. The pH decreases the plating quality gets affected in acid, therefore buffer is used to get good quality coating.
The following rexn occurs during the plating process i.e.,

Oxidation



$$H_2PO_2^- + H_2O \longrightarrow H_2PO_3 + 2H^+ + 2e^-$$

Reduction

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

⇒ Applications :-
1) Coating of inner surface of perfumed bottles inorder to avoid corrosion.

⇒ Electrolessplating of Cu on PCB (Printed Circuit board)

Electrolessplating of Cu on PCB is carried out in following steps:-
1) Pretreatment of surface / surface coating / surface activation.

The surface of substrate is clear to free from greece by immersing in chemical agent.

Then the surface is activated by dipping in Tin chloride followed by palladium chloride to get a thin layer of palladium.

2) Plating process

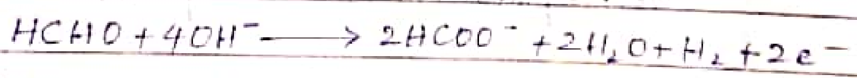
Plating of Cu is carried out by placing the activated substrate surface to following composition

a) Plating soln - $CuSO_4$ (12 gm/lt)
b) Reducing agent - Formaldehyde (8gm/lt)
c) Buffer - Sodium hydroxide (15 gm/lt) + Rochell salt (14 gm/lt) at pH 11.
d) Complexing agent - EDTA (20 gm/lt)
e) Temp - room temp

The reaction progress at room temp; reducing agent formaldehyde reduces Cu^{+2} ions from the salt soln to metallic Cu used as basic medium in presence of palladium (Pd) as catalyst. Complexing agent produce good plating. The plating soln is analysed at every four hours to maintain uniform or optimum concentration and the ratio of reagents.

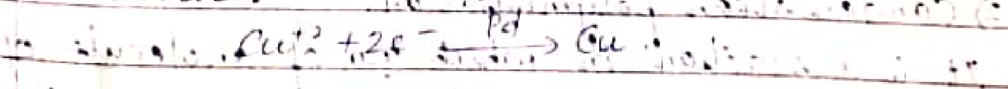
The following rxn's takes place.

Oxidation



$$HCHO + 4OH^- \longrightarrow 2HCOO^- + 2H_2O + H_2 + 2e^-$$

Reduction



$$Cu^{+2} + 2e^- \xrightarrow{Pd} Cu$$

Applications

* It is used in PCB (printed Circuit Board) double sided and multilayer holes, in which having drilling holes.