CLEANER TECHNOLOGY IN ELECTROPLATING INDUSTRY

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METAL PLATING

- Metal Plating is a surface covering in which a metal is deposited on a conductive surface. Plating has been done for hundreds of years; it is also critical for modern technology

METAL PLATED ITEMS

ELECTROPLATING

- Electroplating is the process of coating one metal over another by using electricity.It involves the formation of an electrolytic cell consisting of the cathode (the object to be plated) and the anode (the metal used for plating), immersed in an electrolytic solution.The object to be electroplated is also called a substrate.When direct current is applied to the aqueous solution, the metal at the anode begins to dissolve, and the free metal ions reach the cathode to form a thin layer of coating on the object.

ELECTROLESS PLATING

- Electroless plating, also known as chemical or auto-catalytic plating, is a non-galvanic plating method that involves several simultaneous reactions in an aqueous solution, which occur without the use of external electrical power.The application of anti-oxidation chemicals completes the process, rendering the component resistant to corrosion and friction

Electroless nickel plating

- It is an auto-catalytic chemical technique used to deposit a layer of nickel-phosphorus or nickel-boron alloy on a solid workpiece, such as metal or plastic. The process relies on the presence of a reducing agent, for example hydrated sodium hypophosphite ($NaPO_2H_2 \cdot H_2O$) which reacts with the metal ions to deposit metal.

Galvanization

- Galvanisation or galvanization (or galvanizing as it is most commonly called) is the process of applying a protective zinc coating to iron or steel, to prevent rusting. The most common method is hot dip galvanizing, in which steel sections are submerged in a bath of molten zinc.

Advantages of Metal Plating

- Nickel plating can reduce the build-up of friction in certain materials such as electrical connectors.
- Plating with silver can enhance electrical conductivity, making it a highly-effective process for the manufacturing of electronics and electrical components.
- Plating with palladium can absorb excess oxygen that commonly results during the manufacturing of catalytic converters for automobile

- A zinc-nickel alloy can prevent the formation of sharp protrusions known as whiskers that can occur during certain types of manufacturing operations.
- Electroless nickel plating is commonly used in magnetic applications such as the manufacturing of computer hard drives.
- Copper plating is an ideal solution for providing an undercoating that facilitates adhesion with additional coatings.
- Palladium plating is becoming an increasingly popular choice in manufacturing processes where extreme thickness is required.
- Plating processes such as gold or zinc-nickel are capable of withstanding extremely high temperatures.

PROCESS OF METAL PLATING

- Most metal finishing operations have three basic stage-

1. Pre-treatment
2. Plating
3. Post plating

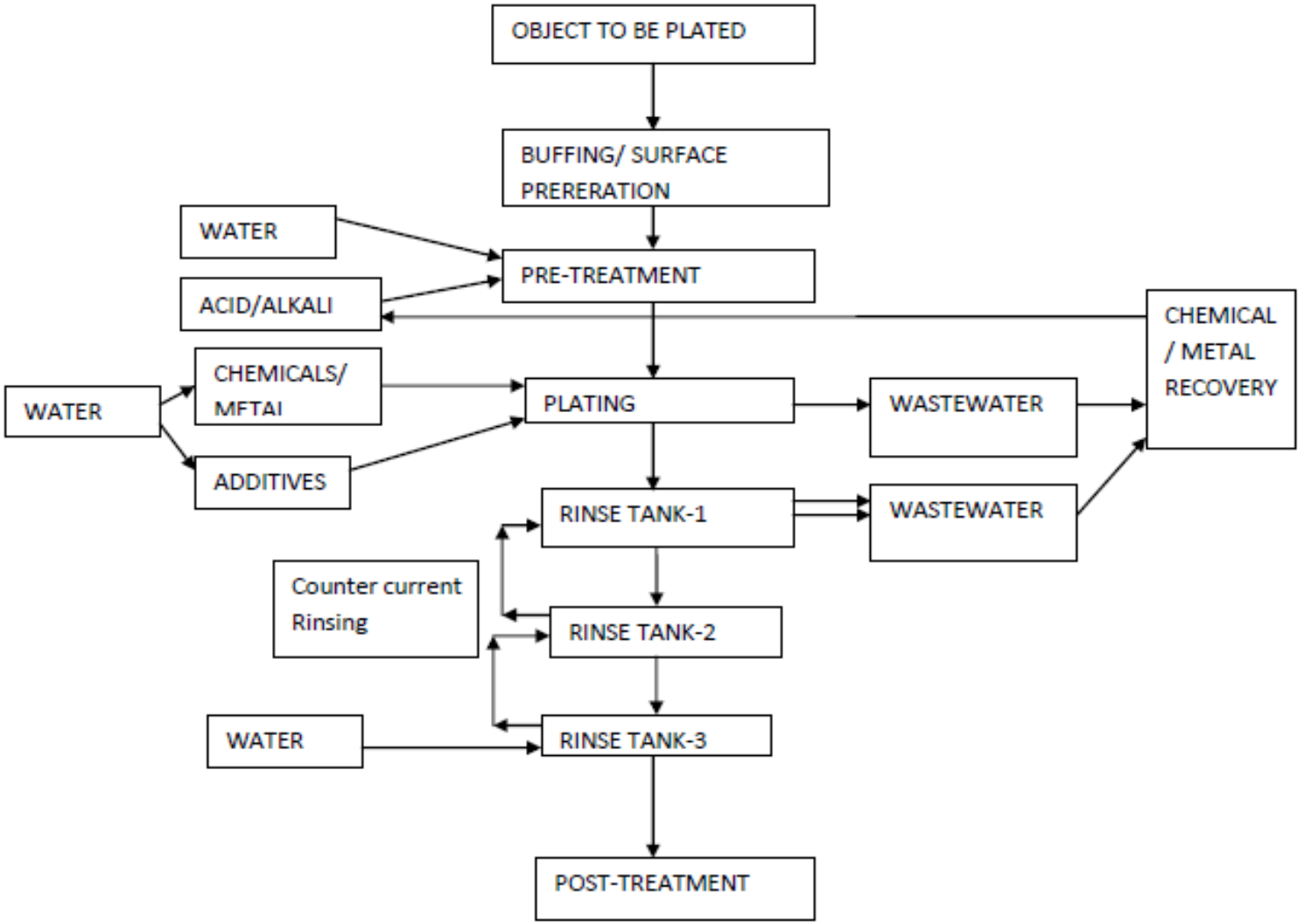
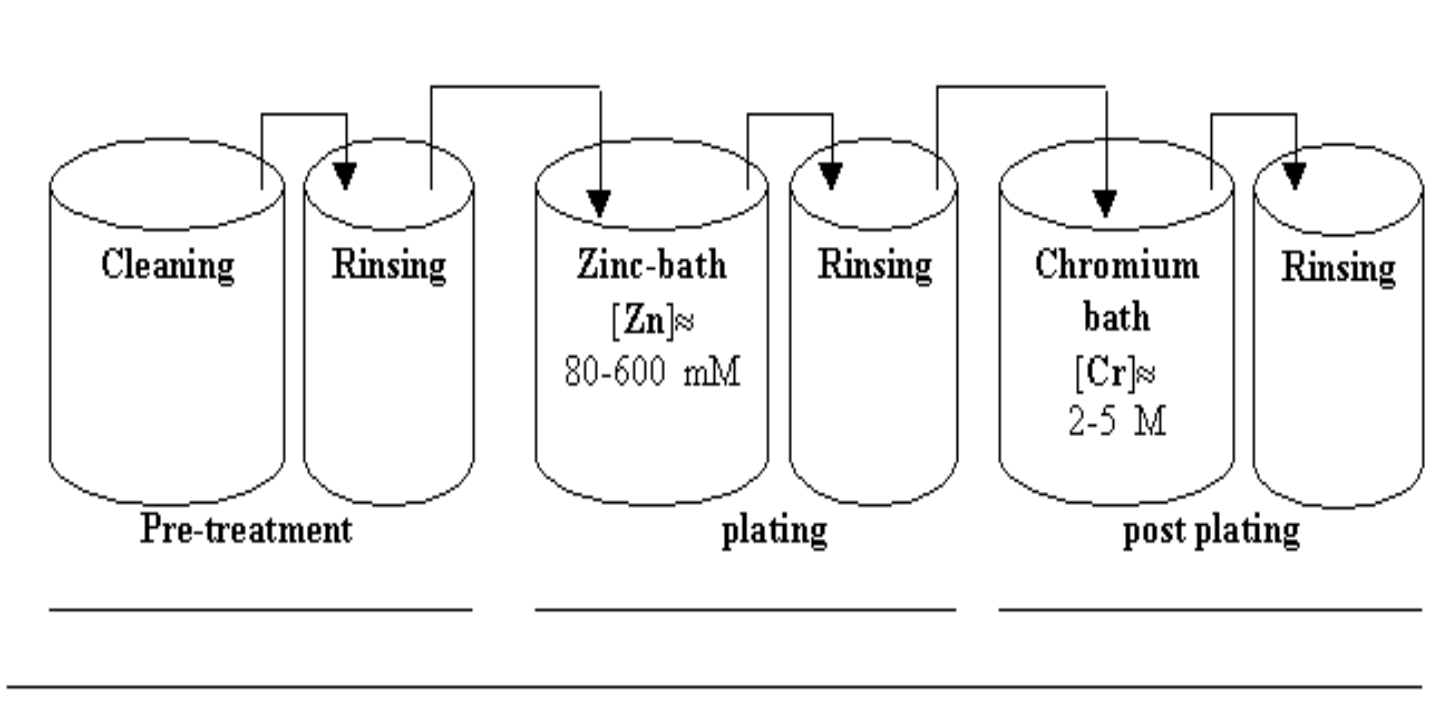


Figure 4.1 TYPICAL FLOW CHART OF ELECTROPLATING PROCESS


Cleaning
Rinsing
Zinc-bath
[Zn]≈
80-600 mM
Rinsing
Chromium
bath
[Cr]≈
2-5 M
Rinsing
Pre-treatment
plating
post plating

Steps for Electroplating

- 1.Surface Cleaning
- 2. Sand Blasting
- 3. Electroplating
- 4. Removal of Chemical Residue
- 5. Chemical Rinsing
- 6. Rinse in hot water.

1. SURFACE CLEANING

- Cleaning should enhance the surface of the part to be cleaned. If not used properly, however, it can impair the surface. You may remove a soil and, in the process of doing this, oxidize or make the surface partially or completely inert. In this sense, you have soiled the surface with a new contaminant! But applied correctly, cleaning can enhance the acceptance of the subsequently applied coating.(remove oil and grease also)

- For making proper bond between coating and metal.

- Suspended parts in vat of boiling chemical solvents. Hot vapor comes in contact with cold metal and condenses, dripping down into vat along with any contaminants, leaving the parts clean and dry.

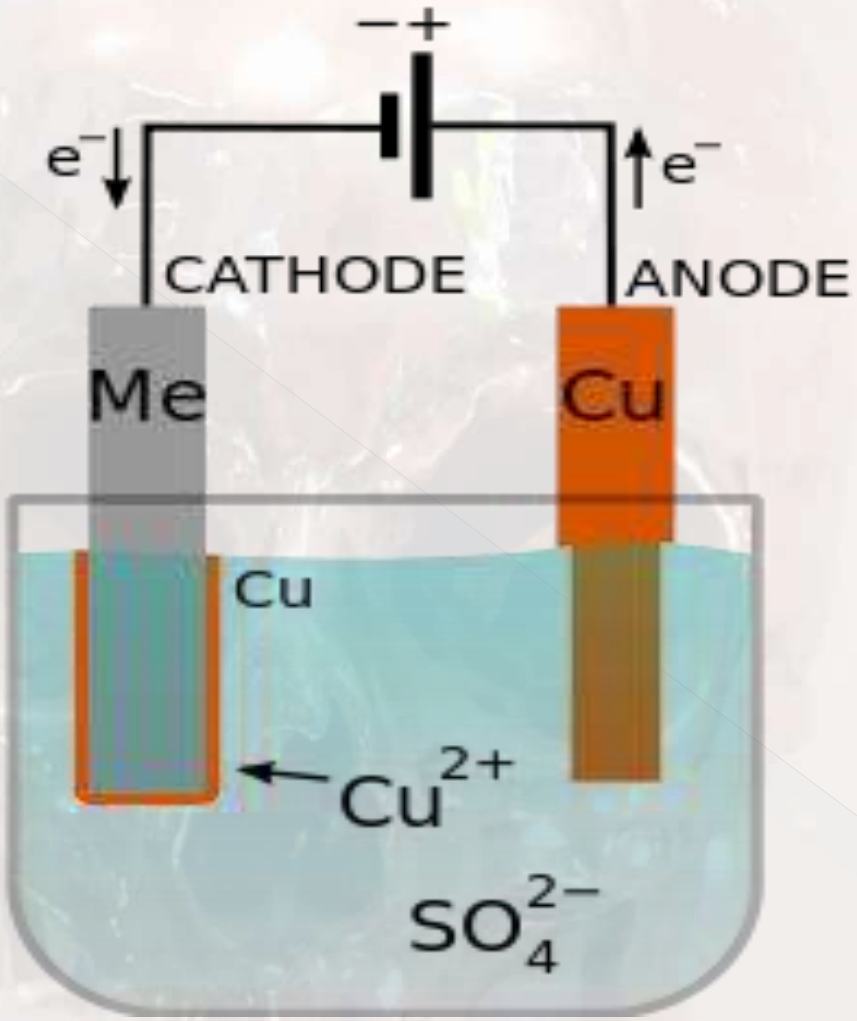
2.SAND BLASTING.

- Sand blasting with aluminum oxide will roughen up the surface so that the plating metal adheres better.

3. Electroplating

- Electroplating tank is filled with water and chemicals to help conduct electricity. The sides of the tank are lined with bags or balls of the plating metal. The support frame holding the part is connected to a negative terminal of the electrical source. The metal that is to be plated is connected to the positive terminal. A DC current of up to 6 volts dissolves the plating metal which travels through the water, attaching to the negatively charged piece to be plated. The process can take just a few minutes for thin plating to several hours for thick plating.

- The process used in electroplating is called **electrodeposition**. It is analogous to a galvanic cell acting in reverse. The part to be plated is the cathode of the circuit. In one technique, the anode is made of the metal to be plated on the part. Both components are immersed in a solution called an electrolyte containing one or more dissolved metal salts as well as other ions that permit the flow of electricity. A power supply supplies a direct current to the anode, oxidizing the metal atoms that it comprises and allowing them to dissolve in the solution. At the cathode, the dissolved metal ions in the electrolyte solution are reduced at the interface between the solution and the cathode, such that they "plate out" onto the cathode. The rate at which the anode is dissolved is equal to the rate at which the cathode is plated, vis-a-vis the current through the circuit. In this manner, the ions in the electrolyte bath are continuously replenished by the anode


−+
e⁻
e⁻
CATHODE
ANODE
Me
Cu
Cu
Cu2+
SO42−

4. REMOVAL OF CHEMICAL RESIDUE.

- Rinsing In Water After Electroplating Process To Remove Chemical Residue
- A composition for removal of chemical residues from metal or dielectric surfaces or for chemical mechanical polishing of a copper surface is an aqueous solution with a pH between about 3.5 and about 7.
- These residuals can hinder the next processes.

5. CHEMICAL RINSING

- Chemical Rinsing to make parts more rust resistant.

- To make metal even more resistant , it immerse in series of compound (containing chemicals),this triggers a chemical reaction in the plating and enhancing its properties to withstand corrosion .
- Chemical rinsing change the colour of metal also.
- It also use to enhance aesthetic values.

Electroplating

6. RINSE IN HOT WATER

- To settle down all the reactions in plating, the final step of rinse in hot water carried out.

- There is also removal of various unwanted materials that can harm the plating in future.

METAL PLATING AND ENVIRONMENT CONCERN

Table No 4.1: Different steps for pre treatment and their environmental concerns

Steps	OPERATION	CHEMICALS/ TOOLS	FUNCTIONS	ENVIRONMENTAL CONCERNS*
1) Surface preparation	Buffing	Scrapper	Smoothens the surface by scrapping	Powder formed from buffing. If not controlled the dust may enter the respiratory tract and cause breathing problems.
2) Pre-treatment a)	Acid activation	(i) Mild acids like citric, phosphoric acid used for aluminum, zinc castings and other sensitive alloys. (ii)Strong acids- hydrochloric, sulfuric and nitric (steels and stainless steels)	Removes oxides, any deposits/ scales.	Uncontrolled vapour, gases emitted by acids can cause damage to the eyes, nose, throat and lungs.
b)	Cleaning of surface of object	By use of Solvents (chlorinated hydrocarbons such as tetra chloro-ethylene)	Removal of grease, oil, dirt, scales from the surface of the items.	Inhalation of tetra-chloro-ethylene may affect different organs of human like Liver, kidney etc. Long-term inhalation exposure cause reproductive problems, such as spontaneous abortions.
c)	Electrocleaning	Alkali and direct	Removal of impurities on	It causes irritation on skin. Overdose can

2	Bronze	Copper cyanide, sodium cyanide, Na_2SnO_2 and sodium hydroxide	1.) Yellow bronze may also be used as for finishing, where it is a suitable imitation for gold used in bathroom fittings, furniture hardware etc	Cyanide vapours	High concentrations may cause unconsciousness, abnormal heart rhythm, coma and even may lead to death
				Volatile organic Carbons (VOC) emission	No detrimental effect on health
3	Cadmium	Cadmium Cyanide, Sodium Cyanide, Sodium Carbonate and sodium Hydroxide	1.) Cadmium electroplating is widely used in aircraft industry due to the excellent corrosi on resistant 2.) It can be dyed to many colors, has good lubricity and solder ability, and works well either as a final finish or as a paint base.	Cadmium vapours	Irritation of respiratory system, sore and dry throat, chest pain and breathing problems. A long term exposure effect includes kidney damage and is a suspected carcinogen.
				Cyanide vapours and VOC emission	Long term exposure to low levels of cyanide may affect the nervous system

4	Chromium	Chromic acid, sulphuric acid, sodium fluoride	1.) Thin layer of chromium, (below 1 µm thickness) is used on automotive parts (interior and exterior), plumbing fixtures, metal furniture, hand tools, bicycles. 2.) For wear-resistance, they are used in Hydraulic cylinders and rods, industrial rolls, diesel engine cylinders, automotive engine valve stems and piston rings, plastic molds, metal forming tools, cutting tools	Hexavalent chromium vapours,	Hexavalent chromium causes lung cancer in humans. These can cause damage cornea of the eye and can affect nose and throat, with frequent nosebleeds. After many years of exposure, burns in the nostrils are especially slow to heal and may develop into open, oozing sores (ulcers)

5	Copper	(i) Copper cyanide, sodium cyanide, sodium hydroxide and sodium carbonate	1) The process is used primarily in printed wire board manufacturing and electroforming operations	Cyanide vapours	Cyanide vapours emitted may causes headache, nausea, dizziness and difficulty in breathing.
		1) Copper pyrophosphate, Pot assium Pyrophosphate and Ammonium Hydroxide		VOC emission	No detrimental effect
		2) Copper sulphate and Sulphuric acid		Acid mist	It can cause serious damage to the eyes, nose, throat and lungs
		3) Copper Fluoroborate , Fluoroboric Acid, Boric Acid and hydrofluoric (HF) acid		Hydrogen Flouride (HF) vapours	Chronic exposure of HF can discolour, damage tooth enamel

6	Gold	(i) Potassium gold cyanide, potassium cyanide, potassium hydroxide and Potassium dichromate	1.) Gold plating of silver is used in the manufacture of artificial jewelry. 2.) Gold plating is often used in printed circuit boards.	Potassium cyanide vapours	Highly toxic in nature and can prove to be life threatening
		(ii) Gold potassium cyanide, potassium chloride and Potassium Phosphite			
		(iii) Gold potassium cyanide, potassium chloride and Citric Acids			
7	Nickel	(i) Nickel sulphate, Nickel chloride, Boric acid and Sulphuric acid	1. It is commonly used in coating of many engineering applications that protects the		Nickel compounds can cause skin allergy and cause a chronic skin condition called

	(ii) Nickel Sulphamate, Nickel chloride and Boric acid	material from corrosion. Applications include oil field valves, rotors, drive shafts, paper handling equipment, fuel rails and optical surfaces for diamond turning etc 2. It is also used in door knobs, kitchen utensils, bathroom fixtures, electrical/mechanical tools and office equipment. 3.) It is also commonly used as a coating in electronics (printed circuit board manufacturing)	Nickel sulphate fumes, Acid mist Hydrogen fluoride vapours	"nickel itch" Nickel fumes have been proven to cause nasal and sinus cancers. Hydrogen chloride vapours can discolor the teeth, and both sulfuric and hydrochloric vapours can also cause erosion of the enamel in exposed teeth Hydrogen fluoride vapours cause digestive disorders, including nausea, vomiting, abdominal cramps and diarrhea

13	Zinc	(i) Zinc chloride, Potassium chloride, Ammonium chloride, Boric acid	1.) Commonly used on nuts, bolts, metal brackets etc.	Chlorine gas, ammonia vapours	Unpleasant ammonia odour.
		(ii) Zinc cyanide, Sodium cyanide, Sodium hydroxide, Sodium carbonate	2.) It also makes an excellent undercoat for powder coating or paint.	Alkali mist	Persistent vapour exposure can damage the nostrils of the nose.
		(iii) Zinc oxide, Sodium hydroxide			

Waste generated from metal plating industry

- Electroplating industry has been generating a huge amount of waste in the forms of wastewater, spent solvent, spent process solutions and sludge

The industry of Electroplating generates wastes in different forms which are solid, liquid and gaseous (Chapter-1) and has been declared under 17 major polluting industries in India by CPCB.

Solid waste generated from the process

- Solid waste includes residues such as cleaning powder; buffing compounds generated during the pre-treatment process and spent anodes during the plating process
- when any recovery system is used the solid waste is generated as spent resins when an Ion exchange method is used for recovery.

Liquid wastes.

- The majority of the waste generated in electroplating process is in liquid form.
- They pollute the environment more as compared to solids and gases and consequences of uncontrolled affect the health seriously

Characterization of solid and liquid wastes by CPCB.

- 1. Acid Residues
- 2. Alkali Residues
- 3. Rinse water from pre-treatment and plating operations.
- 4. Spent bath containing sulphide, cyanide and toxic metals
- 5. Sludge from bath containing organic solvents
- 6. Phosphate Sludge.
- 7. Etching residues.
- 8. Plating metal sludge
- 9. Chemical Sludge from wastewater treatment.

Characterization of gaseous wastes by CPCB.

- 1. Vapours from Chlorinated solvents during pre-treatment
- 2. Volatile organic Compounds (VOCs)
- 3. Acid/ Alkali Mist
- 4. Vapours of Metals (such as Platinum, Hexavalent Chromium, Rhodium, Cadmium etc)
- 5. Vapours of chemicals (e.g. Nickel sulfamate fumes, Potassium cyanide fumes etc)
- 6. Cyanide vapours from plating bath.
- 7. Hydrogen fluoride and Ammonia vapours.

Minimization of wastes in electroplating industry.

Minimizing the resource use

a) Purchase of excess of raw material remains unused and thus enhances the cost ofprocess.

b) In case of excess of raw material there is a tendency to overuse the surplus raw material. This will lead to higher generation of waste.

Modifying the process

- **The use of sensors**
- Water level sensors are present to indicate level of water in tanks instead of human intervention will definitely improve the efficiency of the process. By modifying the process, the efficiency of process can be increased and waste generation can be minimized.

Use of suitable plating baths

The simple way of calculating amount of electrolyte using basic principle of chemistry can help in deciding the size of bath. Thus, smaller size of bath (optimal range) will reduce the waste generation.

Modifying the product.

Use isopropyl alchohal in place oftetrachloroethylene use of non cyanide alternatives over cyanide solutions produces less hazardous waste.

Minimization of drag out losses

When plated parts are withdrawn from a plating process unit, they retain some part of the plating bath solution, termed as “drag-out".The drag out that cause loss of material should be minimized to save both chemicals and water used for rinsing

Wastes treatment process

Evaporation process for chemical recovery.

- As more and more plates are rinsed, the concentration of chemicals in the rinse tanks increases due to drag out of plated objects.
- After some rounds of rinsing, the concentration of chemicals in rinse tanks rises to such an extent that it appears to be equivalent to that of plating bath.
- In order to make water in rinse tank suitable forrecycling process of evaporation is used. The concentrated chemicals can be recycled in plating bath via pump.

Concept behind the evaporation process.

- Every chemical solution is made up of at least one or more solvent, and one or more dissolved materials known as solute.
- There is huge difference in vapour pressure of solvent and solute.
- Due to high vapour pressure solvent gets evaporated and remaining solute gets deposited.

Ion exchange method

- Whenever an ion is removed out of an aqueous solution and is replaced by another ionic species, this is what we generally refer to as “ion exchange”.
- There are synthetic materials available that have been specially designed to enable ion exchange operations athigh performance levels
- “Ion exchangers” can be used in processes of environmental protection such as purification, decontamination, recycling or even for the design of new environment-friendly production processes

Concept behind the ion exchange method.

- To each of the monomer units of the polymer, “functional groups” are attached.
- These functional groups can interact with water soluble species, especially with ions.
- Ions are either positively (cations) or negatively (anions) charged.Since, the functional groups are also charged; the interaction between ions and functional groups is exhibited by electrostatic forces
- Positively charged functional groups (For example, a quarternary amine) interact with anions and negatively charged functional group (For example, a sulfonic -, phosphonic - or carboxylic acid group) will interact with cations