

PARIVESH

***WASTE MINIMISATION AND ECO-
FRIENDLY ELECTROPLATING PROCESSES***

***CENTRAL POLLUTION CONTROL BOARD
DELHI***



केन्द्रीय प्रदूषण नियंत्रण बोर्ड

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EDITORIAL

Electroplating has a long history in India. Like many industrial activities, it gained momentum after the Independence. Modern day electroplating started in early sixties in Mumbai with 'dull Nickel', with 'bright Nickel' following soon after. Since then, the industry has grown steadily and currently there are more than 600 automatic plants in the country. During the period 1970-85, the import restriction regulation in force led to higher growth of this industry. The sector employs about 1,30,000 people in approximately 12,000 organized units. They are spread across the entire country with significant concentration in several states like Punjab, Haryana, U.P., Maharashtra, Tamil Nadu and West Bengal.

Electroplating is considered a major polluting industry because of the discharge of toxic materials and heavy metals through wastewater (effluents), air emissions and solid wastes into the recipient environment. Considering this, CPCB decided to bring out newsletter on electroplating industries, which would be useful to the electroplating units, regulatory agencies, consultants and others interested in pollution control.

This issue of newsletter *Parivesh* provides an overview of electroplating processes, environmental effects, treatment options, waste minimization and eco-friendly electroplating processes.

The information contained in this issue has been collated and compiled by my colleagues, Dr. A. B. Akolkar, Additional Director, Shri. U. N. Singh, Senior Environmental Engineer, Shri. R.C. Saxena, Senior Environmental Engineer and Ms. Pavithra L.J., Assistant Environmental Engineer under the overall guidance of Dr. B. Sengupta, Member Secretary.

(J. M. Mauskar)

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Section 1

Introduction

1.1 Introduction

Electroplating is one of the varieties of several techniques of Metal Finishing. It is a technique of deposition of a fine layer of one metal on another through electrolytic process to impart various properties and attributes, such as corrosion protection, enhanced surface hardness, lustre, colour, aesthetics, value addition etc. Electroplating operations form part of large scale manufacturing plants (e.g. automobile, cycle, engineering and numerous other industries) or performed as job-work by small and tiny units. They are spread across the entire country with significant concentration in several states like Punjab, Haryana, part of U.P., Maharashtra, Karnataka, Andhra Pradesh, Tamil Nadu and West Bengal. Electroplating is considered a major polluting industry because it discharges toxic materials and heavy metals through wastewater (effluents), air emissions and solid wastes into the recipient environment.

1.2 Types and Location of Units

The Industry is widely spread out across the country. While there are primarily two varieties- (i) Primary User and Original Equipment (OE) manufacturer, who do electroplating as one of their overall manufacturing activity and (ii) Job work units, who do only plating for a large variety of components for both domestic and export purpose. Certain states have large number of units concentrated in some towns / cities, such as:

Andhra Pradesh – Hyderabad

Delhi

Gujarat- Ahmedabad

Haryana- Faridabad

Karnataka- Bangalore

Maharashtra - Mumbai, Pune, Nashik

Punjab - Ludhiana

Tamil Nadu - Chennai, Madurai

Uttar Pradesh - NOIDA

It is difficult to find out the distribution of production between the organized and small scale / tiny / unorganised sector. However, judging by the consumption of chemicals and additives, it is estimated that about 18,000 tons are consumed by organized sector, while tiny and unorganised sector consumes about 10,000 tons. Therefore, approximately 36 % of the industry is contributed by the unorganised sector.

Section 2 Processes & Chemicals Used

2.1 Plating Process

The basic electroplating system consists of:

- 1) A plating bath filled with water containing a small amount of acid or alkali added to improve its conductivity. Thus baths used for plating are either acid bath or alkaline bath.
- 2) An anode (positive electrode) - either the plating metal or an inert electrode; this is expended as the process goes on and replenished periodically
- 3) A cathode (negative electrode) - the item to be plated; these can be either hung inside the bath or placed in a barrel, which is rotated slowly to make the plating material deposited evenly

Usually, the bath is contained in metal container, lined with acid/alkali resistant membrane e.g. pvc sheet to make it insulated from electric circuit.

The application of direct electric current across the bath solution causes the migration of

- ◆ Positively charged particles (anions) towards the negative electrode (cathode) and
- ◆ Negatively charged particles (cations) towards the positive electrodes (anode)

The processes are often exothermic and this leads to elevated bath temperature compared to the ambient temperature. The process efficiency depends to some degree on the

- ◆ Concentration of acid and alkali in the solution
- ◆ Temperature and
- ◆ Voltage applied across the electrodes

The item to be coated is immersed in the bath solution as the cathode and the coating substance (the anode). However, if an inert electrode is used, the coating substance would be the metal salts in liquid form added to the solution. The metal salts subsequently dissociate into anions and cations, which then deposit onto the items to be plated.

Apart from the bath chemicals and anode material, other chemical agents are used, such as:

- ◆ Brightener
- ◆ Wetter
- ◆ Booster
- ◆ Purifier

These chemical agents help to provide desired attributes, such as bright surface finish, improved and even metal deposition, depolarization, faster reaction etc. etc. The chemicals vary according to the process variants and finishing requirements for a particular metal plating.

By and large, most metal finishing operations typically involve 3 to 4 principal work steps or process operations, which may occur singly or in combination. These are:

- ◆ Surface preparation

- ◆ Pre-treatment
- ◆ Plating and
- ◆ Post-treatment

2.2 Process Details

2.2.1 Surface Preparation / Pre-treatment

The purpose is to prepare and clean the items for plating. The activities involved are as shown in **Table 2.1** below

Table 2.1: Surface Preparation & Pre-treatment

Main Activity	Step	Operation	Function
Surface Preparation	1	Buffing	Smoothing of surface deficiencies by scrapping
Pre-treatment	2	Cleaning	Removal of oil, grease, dirt, scales from the surface of the items using solvents (often chlorinated hydrocarbons)
	3	Rinsing	Removal of adherent solvent/alkali/acid using water flow

2.2.2 Plating

In the plating process, the items to be plated are placed as the cathode in an electrolytic bath containing metal salts. A Direct Current is passed (at low voltage) through the electrolyte, wherein metal ions are plated onto the cathode. The ions in solution are replenished by :

- ◆ The dissolution of metal from the anode (the plating substance) or
- ◆ Increasing the metal salt concentration of the solution (when using an inert electrode) or both

After plating, the plated items are rinsed with water. After rinsing the items are dried either normal air drying or hot air drying or in an oven. The operations of plating, transfer from plating to rinsing tanks (in which bath solution *drag-out* occurs) and rinsing can either be manual or mechanized (automatic)

2.2.3 Post-treatment

Most Electroplating operations are completed by the plating operation, if the items do not require post-treatment (as in the case of Double Nickel Chrome Plating). The purpose of the post-treatment is:

- ◆ to enhance the physical appearance of the item
- ◆ to improve the corrosion resistance of the item
- ◆ for decorative purposes

There are a varied number of post-treatments:

- ◆ conversion coatings
- ◆ chromating
- ◆ phosphating
- ◆ passivating
- ◆ metal colouring and
- ◆ sealing

A brief description of these are given in the following paragraphs:

(a) **Conversion Coating:** Conversion coating is provided to prevent corrosion and to limit the growth of salts, which may form due to corrosion. Many heavy metals, such as Chromium, Vanadium, Molybdenum and Tungsten in their high valence states have the ability to prevent such corrosion. The most commonly used conversion coating is hexavalent chromium using soluble chromate salt such as Potassium di-chromate, called chromate conversion coating or chromating.

(b) **Phosphating:** This is a process of coating a metal surface (usually galvanized iron & steel, aluminium etc.) with a layer of insoluble metal phosphates by treating it with an acidic phosphate containing solution. Zinc, iron and manganese phosphate coatings are common of which Zinc Phosphate is the most commonly used salt. Phosphating is done as an excellent base for receiving paints, oils and cold-forming lubricants

(c) **Sealing :**Anodic coatings are usually porous and are sealed and are sealed to improve colour durability and resistance to staining and corrosion. Sealing is done by immersion in hot water during which amorphous alumina surface of the anodic coating is converted to crystalline alpha alumina hydrate, which increases the volume and closes the pores.

(d) **Metal Colouring:** In this process a colour is formed on the surface of metals. This is quite an old process, which is not much used at present. However, Aluminium colouring is in vogue.

2.3 Process Chemicals

A wide variety of chemicals and substances are used, depending upon the surface properties of the objects to be electroplated, plating and finishing requirement as well as the technology / facility offered by the platers. It is very difficult to provide full details of all those used; because there are more than one commonly used process for certain metals. Hence a general description will be covered in this section.

2.3.1 Brass Plating: In brass plating, generally a cyanide bath is used, which comprises, $\text{Cu}(\text{CN})_2$, NaCN , $\text{Zn}(\text{CN})_2$ and Na_2CO_3 . The anode is non-consuming conductor.

2.3.2 Bronze Plating: Bronze being a combination of Copper and Tin, the bath salts comprise $\text{Cu}(\text{CN})_2$, NaCN , Na_2SnO_2 and NaOH . Bath is therefore cyanide alkaline. Anode is non-consuming conductor like in brass plating.

2.3.3 Cadmium Plating: Cadmium plating also uses an alkaline cyanide bath comprising bath salts like $\text{Cd}(\text{CN})_2$, NaCN , Na_2CO_3 and NaOH .

2.3.4 Chromium Plating: There are variations of Chromium plating - ordinary chrome, hard chrome and bright chrome. Generally, chromic acid bath is used comprising bath salts like H_2CrO_4 , H_2SO_4 and NaF . NaF is used to improve the conductivity of the electrolyte.

2.3.5 Copper Plating: Three types of bath are used - (i) Cyanide Copper bath, (ii) Copper pyrophosphate bath and (iii) Acid Copper bath. As the name suggests, the bath in the third is acidic, while the first two are alkaline. Bath constituents for Cyanide Copper bath are : $\text{Cu}(\text{CN})_2$, NaCN , Na_2CO_3 and NaOH . For Copper pyrophosphate, $\text{Cu}_2\text{P}_2\text{O}_7$, NH_4OH and $\text{K}_4\text{P}_2\text{O}_7$ are used. In acid copper process, a mix of CuSO_4 and H_2SO_4 is used.

2.3.6 Gold Plating: Four processes are available - (i) Alkaline Cyanide [using $\text{KAu}(\text{CN})_2$, KCN , KOH and $\text{K}_2\text{C}_2\text{O}_7$], (ii) Neutral Gold bath [using $\text{KAu}(\text{CN})_2$, KCl and K_2HPO_3], Acid Cyanide [using $\text{KAu}(\text{CN})_2$, KCl and Citric Acid] . It may be noted that the main constituent in all three processes is Potassium Gold Cyanide. The fourth is Flash Gold process using AuCl_3 and HCl .

2.3.7 Nickel Plating: Three processes are commonly used - (i) Watts Nickel bath [using a mix of NiSO_4 , NiCl_2 , H_2SO_4 and H_3BO_3], (ii) Nickel Sulphamate Bath [using $\text{Ni}(\text{NH}_2\text{SO}_3)_2$, HNH_2SO_3], (iii) Wood's Nickel Bath [using NiCl_2 and HCl]. None of the processes use Cyanide.

2.3.8 Palladium: Being a precious metal, usage is somewhat restricted. Only one process using acid bath is commonly used. Bath constituents are: PdCl_2 , NH_4Cl and HCl . Sometimes Palladium-Nickel plating is used in which Palladium and Nickel is deposited in one bath. In this process, bath constituents are: $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$, Nickel Sulphamate and NH_4OH .

2.3.9 Platinum : Two processes are available : (i) Alkaline Platinum and (ii) Acid Platinum. In the former, H_2PtCl_6 , $(\text{NH}_4)_3\text{PO}_4$ and NH_4OH . In acid Platinum, bath constituents are: $\text{H}_2\text{Pt}(\text{NO}_2)_2\text{SO}_4$ and H_2SO_4 .

2.3.10 Rhodium: Only one process using acid bath comprising Rhodium Sulphate and Sulphuric acid is used.

2.3.11 Silver : Two processes are available, both using Silver Cyanide. Silver Cyanide bath comprises $\text{KAg}(\text{CN})_2$, KCN and K_2CO_3 . Acid bath uses $\text{KAg}(\text{CN})_2$, Na_2HPO_4 and H_3PO_4 .

2.3.12 Tin: There are three processes - (i) Alkaline, (ii) Acidic and (iii) Fluoroborate.. In alkaline Tin process, principal chemical used are Sodium Stannate and Caustic Soda; Tin Sulphate uses Stannous Sulphate and Sulphuric Acid. In Tin Fluoroborate process, Chemicals used are : $\text{Sn}(\text{BF}_4)_2$, HBF_4 , H_3BO_3 and HF .

2.3.13 Zinc: There are three processes available (i) Acid Cyanide, (ii) Alkaline Cyanide and (iii) Alkaline Cyanide Free. Acid Cyanide uses a bath comprising ZnCl_2 , KCl , NH_4Cl and H_3BO_3 . In Alkaline Cyanide, bath constituents are : ZnCN , NaCN , NaOH and Na_2CO_3 . In the Alkaline Cyanide Free (ACF) process, bath chemicals are rather simpler, ZnO and NaOH . The latter is gaining popularity as a Cyanide free process.

2.3.14 Anodising: Anodising is mainly used as a pre-cleaning operation but sometimes used as a metal finishing operation. In anodising, the object is made Anode, so that impurities and other metals are removed. Sulphuric acid is mainly used as electrolyte in the bath.

2.3.15 Phosphating: Phosphating is carried out mostly as post treatment of plating. However, it is often used as undercoat to receive paint on metal. Bath constituents are Zinc-Calcium Phosphate and Na_3PO_4 .

2.3.16 Chromating: This is also a post treatment to plating. Bath constituents are Na_2CrO_4 and Na_2CO_3 .

2.3.17 Etching: This is used as a pre-treatment to plating and generally uses acidic bath – Ferric Chloride etchant (Ferric Chloride and HCl), Acid etchant (mix of CuCl_2 , HCl and H_2O_2). In Ammoniacal etchant, a mix of Ammonium Chloride, Ammonium Hydroxide and Sodium Hypochlorite) is used.

Section 3

Environmental Effects of Electroplating Wastes & Chemicals

3.1 General

The Chemicals used in various electroplating operations are numerous. These chemicals can be classified generally as (i) Acids and Alkalis for cleaning purpose, (ii) inorganic Chemicals, particularly heavy metals, which take part in reactions pertaining to plating and (iii) organic chemicals which help in achieving certain properties or to enhance the process of plating. Often, some of these chemicals are unknown to both users and traders, as they are traded as proprietary items manufactured by Chemical companies.

The environmental effects are caused by several routes – (I) by directly reacting with air, water and soil, resulting in degeneration or disintegration, (ii) by accumulating as persistent chemicals (geo-accumulation (iii) by entering environmental pathways and transcending from non-living to living beings, causing *toxicity* to living organisms and (iv) entering into food chain – finally affecting humans and cattle. Some are carcinogenic, while others are mutagenic. Central and most important in this matter are health effects on workers, who are exposed routinely and persistently. Over a period of time such exposures, even at a low level, have been known to cause diseases and various infirmities. Moreover, the pollutants can enter the environment through air (particulates, gases and vapours), water (both in soluble and suspended form) and soil (as sludge, and leachate reaching groundwater).

The toxicity of these metals has also been documented throughout history: Greek and Roman physicians diagnosed symptoms of acute lead poisoning long before toxicology became a science. Today, much more is known about the health effects of heavy metals. Exposure to heavy metals has been linked with developmental retardation, various cancers, kidney damage, and even death in some instances of exposure to very high concentrations. Exposure to high levels of mercury, gold, and lead has also been associated with the development of autoimmunity, in which the immune system starts to attack its own cells, mistaking them for foreign invaders. Autoimmunity can lead to the development of diseases of the joints and kidneys, such as rheumatoid arthritis, or diseases of the circulatory or central nervous systems.

Once emitted, metals can reside in the environment for hundreds of years or more. Evidence of human exploitation of heavy metals has been found in the ice cores in Greenland and sea water in the Antarctic.

3.2 Cyanides

Cyanide is extremely toxic to humans. Acute (short-term) inhalation exposure to 100 milligrams per cubic meter (mg/m^3) or more of hydrogen cyanide will cause death in humans.. Acute exposure to lower concentrations (6 to $49 \text{ mg}/\text{m}^3$) of hydrogen cyanide will cause a variety of effects in humans, such as weakness, headache, nausea, increased

rate of respiration, and eye and skin irritation. Tests involving acute exposure of rats and mice have shown hydrogen cyanide to have extreme acute toxicity from inhalation exposure.

The most toxic form of cyanide is free cyanide, which includes the cyanide anion itself and hydrogen cyanide, HCN, either in a gaseous or aqueous state. At a pH of 9.3 - 9.5, CN and HCN are in equilibrium, with equal amounts of each present. At a pH of 11, over 99% of the cyanide remains in solution as CN, while at pH 7, over 99% of the cyanide will exist as HCN. Although HCN is highly soluble in water, its solubility decreases with increased temperature and under highly saline conditions.

3.3 Chromium

Chromium is naturally found in rocks, animals, plants, soil and in volcanic dust and gases. It is one of the high priority persistent, bio-accumulative and toxic (PBT) chemicals that do not readily break down in the environment, are not easily metabolized, may accumulate in human or ecological food chains through consumption or uptake and may be hazardous to human health or environment. A PBT chemical, once released to the environment, may present increasing long term toxic effects to human health and the environment, even if the release was of a small amount.

Chromium is present in the environment in several different forms. The most common forms are Chromium (0), trivalent (III) and hexavalent (VI). Chromium occurs naturally in the environment and is an essential nutrient required by the human body. Chromium enters the environment mostly in the Chromium (III) and (VI) forms as a result of natural processes and human activities. It cycles between the soil, the atmosphere, surface and ground waters. Electroplating is one of the several industrial activities (like stainless steel welding, chemical manufacturing, tanning, textile processing & dyeing and coal ash from power plants), that discharge both Cr(III) and Cr(VI) into water and soil. Chromium (III) is considered safe and is an essential nutrient. Hexavalent

3.4 Cadmium

Cadmium is a natural element in the earth's crust. It is usually found as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulfur (cadmium sulfate, cadmium sulfide). All soils and rocks, including coal and mineral fertilizers, contain some cadmium.

Cadmium enters air from mining, industry, and burning coal and household wastes. As far as Electroplating industry is concerned, it enters water and soil from waste disposal. Some cadmium dissolves in water Cadmium may enter the environment from spills or leaks at hazardous waste sites. It binds strongly to soil particles. Cadmium particles in air can travel long distances before falling to the ground or water. It does not break down in the environment, but can change forms. Along environmental pathways and food chain in particular, fish, plants, and animals take up cadmium from the environment. Once ingested, Cadmium stays in the body a very long time and can build up from many years of exposure to low levels.

In the Electroplating work place, Cadmium may enter the human body through breathing (if Cadmium dust is in the indoor air), eating contaminated foods containing it; and most importantly, drinking contaminated water. The contamination of drinking water contributes to by far the greatest potential of environmental hazard, apart from Cadmium bearing sludge disposal.

3.5 Lead

Aside from smoke, lead is probably the oldest human-made atmospheric and occupational toxin, dating back at least 8,000 years to the first lead-smelting furnaces. Today, lead poisoning remains the single most significant preventable disease associated with an environmental and occupational toxin.

3.6 Copper

Copper is very common in the environment. It occurs naturally in rock, soil, water, sediment, and air, as well as in plants and animals.

Considerable data indicate that copper does not biomagnify in the food chain. The typical ratio of the concentration of copper in plants to that in soil is estimated at 0.25 (or 25%). Most plants contain less than 10 ppm copper on a dry-weight basis, and concentrations in animal foods are 2 to 4 ppm, with dairy products containing less than 1 ppm.

3.7 Zinc

Zinc is part of nature. Most rocks and many minerals contain zinc in varying amounts and zinc exists naturally in air, water and soil. The average natural level of zinc in the earth's crust is 70 mg/kg (dry weight), ranging between 10 and 300 mg/kg.

Harmful effects from too much zinc generally begin at levels from 10 to 15 times higher than the recommended dietary allowances of 5, 12, and 15 milligrams per day (mg/day) for infants, women and men, respectively. Eating large amounts of zinc can cause stomach cramps, nausea, and vomiting. Taken over an extended period of time in high amounts, zinc can cause anemia, damage the pancreas, and lower levels of high-density lipoprotein cholesterol (the good form of cholesterol). Breathing dust or fumes containing large amounts of zinc can cause a short-term disease called metal fume fever. This disease is an immune response affecting the lungs and body temperature. It is not known if there are long-term health effects from breathing high levels of zinc. It is also not known if high levels of zinc affect human reproduction or cause birth defects. However, infertility, low birth weight, and skin irritation have been observed in laboratory animals such as rats, guinea pigs, mice, and rabbits given high doses of zinc. The Environmental Protection Agency (EPA) has stated that adequate information to evaluate the carcinogenicity of zinc is not available. However, no studies exist that indicate that zinc causes cancer in humans.

3.8 Nickel

Nickel is a metal found in the earth's crust. The average worldwide concentration in soil is 8 parts per million (ppm).

About 10% of women and 2% of men in the population *are highly sensitive* to nickel. A portion of these sensitive people can develop a skin rash called nickel dermatitis if they are exposed to nickel through direct contact. This is the most common type of reaction to nickel exposure.

Exposure to readily water soluble nickel salts occurs mainly during the electrolytic refining of nickel (producing industries) and in electroplating (using industries). Depending upon the processes used, exposures are usually to hydrated nickel (II) sulfate or nickel chloride in solution.

3.9 Tetrachloroethylene (TCE) or Perchloroethylene

Tetrachloroethylene is widely used for metal degreasing (Vapour cleaning) and dry cleaning operations. The main effects of tetrachloroethylene in humans are neurological, liver, and kidney effects following acute (short-term) and chronic (long-term) inhalation exposure. Adverse reproductive effects, such as spontaneous abortions, have been reported from occupational exposure to tetrachloroethylene;

3.10 Trichloroethylene

Trichloroethylene used in degreasing operations is the chief source of atmospheric presence of this chemical.

Acute (short-term) and chronic (long-term) inhalation exposure to trichloroethylene can affect the human central nervous system (CNS), with symptoms such as dizziness, headaches, confusion, euphoria, facial numbness, and weakness. Liver, kidney, immunological, endocrine, and developmental effects have also been reported in humans. A recent analysis of available epidemiological studies reports trichloroethylene exposure to be associated with several types of cancers in humans, especially kidney, liver, cervix, and lymphatic system. Animal studies have reported increases in lung, liver, kidney, and testicular tumors and lymphoma. The Agency is currently reassessing the cancer classification of trichloroethylene.

Section 4

Recovery of Metals

4.1 General

During electroplating operations, metal salts are used partly by electro-deposition of metals and partly by rinsing and washing. While the first part goes into plating, the second part is lost and actually poses a problem in wastewater treatment. Even in plating baths, solutions often need to be discarded because of presence and build-up of impurities that either hinder the efficiency of plating process or cause deterioration in quality of plating. Either way, the baths are to be discarded before fresh bath is made. This is indeed a waste both in monetary terms and environmental considerations. Bath regeneration is therefore done to counter discarding it entirely.

Various methods are used for regeneration of baths and contents of pre-treatment, rinse and wash tanks. These methods are briefly described below with their specific advantages and constraints of use. Of these methods, metal recovery through ion-exchange presents highest potential and serves the dual purpose of resource (metal) recovery and waste minimisation (by re-use of water of regenerated bath solutions). Hence this process would be discussed in more detail.

4.2 Filtration & Centrifugation

Filtration with or without centrifugation is one of the widely used and effective methods for prolonging and improving the life of bath. Although it does not directly recover metals, it enhances the use of metal salts thus controlling and reducing the wastage of metal salts.

Activated carbon filter is widely used to remove dissolved organic impurities (example: Nickel Baths) in addition to its action in removing solids. Such filters are used continuously or intermittently during plating.

4.3 Evaporation

4.3.1 General

Evaporation losses are considerable in hot baths; such water losses can be compensated by recycling cascade rinsing (last tank of cascade). In theory, if the effluent rate equals the evaporation rate, a complete recovery of bath chemicals can be achieved. Even if complete recovery is not achieved, substantial recovery can easily be obtained.

4.3.2 Simple Measures

As the simplest example, the direct recovery of plating baths is realised with a static dragout tank. Rinse water from this tank is used for the replenishment of volume losses of the process bath due to the evaporation. Periodic water transfer from dragout into the process tank is made manually or better by a small pump. Practical recovery ratio realised

by this method is not usually higher than 50 – 60 %. Many platers in the small scale sector in India employ this technique.

As an improvement to above, in case of cold bath, the dragouts and contents of first static rinse tanks can be concentrated by forced evaporation. However, application will depend on the trade-off between energy and operating cost versus cost of recovered chemicals (such as metal salts). Clearly, this technique is used in case of expensive chemicals. A more desirable method would be to use condenser, which would enable to recirculate the condensate (water) to rinse tanks and chemicals to bath.

4.3.3 Advanced Techniques – Tin, Copper, Zinc etc.

Efficiency of direct recovery can be significantly improved by the introduction of several drag-out/rinse tanks arranged in series. Such a technique has been developed in Poland and applied in Poland and several countries with encouraging results. Air lift pumps (made of PVC) are used for rinse water transfer from tank to tank and from the first rinse tank to the plating tank. The return rates and opening and closing of valves are automated (controlled by electronic level controller and conductometric probes). Depending upon the plating line output, the evaporation losses of the bath and the space available in the shop, 4 dragout tanks in a series can be introduced. The tanks can work in closed loop system with zero discharge. This technique has been successfully used for Nickel, Tin and Copper plating baths and other hot baths recovery with an efficiency of 85 – 95%. It has also been used for recovery of cold baths such as Zinc, wherein a small evaporator is used. Such a system for Zinc barrel plating line has been quite successful. Recovery ratio of Zn plating bath was 98% (about 300kg Zn per year). Average water consumption for rinsing was reduced from 200 l/sq.m. to 18 l/sq.m., i.e., achieving a rinse-water reduction of 91%. Other savings included:

1. Reduction of Energy cost in plating shop
2. Reduction of consumption of anode and plating salts
3. Reduction in cost of waste water treatment
4. Reduction of sludge volume

4.4 Electrolytic Recovery & its Economics

4.4.1 General

This technique is now well developed and used in both large and small scale electroplating units. One major constraint of this method is that complete recovery of the metal from dilute solutions cannot be achieved. As the metal salt concentration reduces, due to the metal extraction, the voltage must be increased in order to continue with the cathodic deposition. Voltage enhancement is ultimately limited by secondary reactions. Hence in practice, electrolytic recovery is used in conjunction with other methods. For example, electrolytic recovery of Copper from pickling baths has been successfully used.

Electro-dialysis is one of the techniques in this group. In this technique, rinse water is pumped through a stack of ion-selective membranes that allow metal ions (for example in Nickel recovery, Nickel, Sodium and other cations) to pass through when an electrical

current is applied. Nickel passes into an acid solution, which must then be neutralised for re-use. Over 99% of Nickel can be recovered and treating relatively large volumes (of rinse water) is possible. However, since Nickel passes into an acid solution, it needs to be neutralised for re-use. Moreover, membrane life and serviceability can be a concern with Electro-dialysis systems.

7.4.2 Nickel Recovery / Recycling by Ion-exchange

Nickel baths are followed by several counter current flowing water rinse tanks to prevent carry over and contamination of subsequent chrome plating baths. Typically, Nickel bath solutions of around 0.1 litre per sq. m. of plated area is lost as dragout to the rinse tanks. There are two options to deal with the waste water – (a) Treat the waste water by alkaline precipitation and dispose of the waste water and put the sludge in secure landfill; (b) Recover Nickel and recycle to Nickel plating bath (recovery rate >97%) and treat the balance 3% or so. A plater would choose the more economical between the two desired alternatives. There are conventional ion exchange units as well as advanced ion-exchange units.

In a conventional unit, the rinse water is pumped to ion-exchange column containing strong acidic cation exchange resin characterised by high capacity, good chemical resistance and stability. The resins exchange hydrogen ions and Nickel ions are retained on resin which gets saturated with Nickel Salts after sometime. Then passing of Nickel solutions are stopped and resin regenerated with 55 pure Sulphuric or Hydrochloric acid. The regenerated solution contains Nickel ions in the form of NiSO₄ or NiCl₂. All brightener and products of its breakdown are also removed leaving regenerated solution free from organic contamination. The solution can now be returned to plating tanks – semi-bright Nickel and/or tri-Nickel.

The comparative economic comparison of a small plant is given in **Table 4.1**.

**Table 4.1: Economic Comparison of Waste Treatment vs. Nickel Recovery
(Basis: 2.5 kg of NiSO₄ per day)**

Component	Waste Disposal cost		Operating Cost (Rs) of	
	Rs. per day		Recovery System	
Nickel Salt @ 165 per kg	2.5 kg	Rs. 412.50	-	-
Sulphuric Acid Rs. 6 per kg	-	-	3 kg	18
Electricity @ 4 per kWh	3	12	3	12
Labour	LS	50	LS	50
Chemical for Sludge handling	LS	2	-	-
Total per day		476.5		80
Total per year @ 300 working days/yr		1,42,950		24,000
Net Saving per yr				1,18,950

Clearly, recovery/recycling presents a very encouraging case in favour of its adoption, even in small plants. However, the capital investment and cost of replacement of resin must also be considered for net gain.

For a good quality control on plating and consequently on the bath constituents, the following are to be considered.

1. Contaminants that have accumulated in the rinse tanks should be removed before the Ni solution is recycled to the plating baths; If not, the recycled contaminants would build-up in the bath and cause an adverse effect on the plating quality and bath life. Carbon filters are used for this purpose.
2. Brighteners are usually Sodium salts of organic compounds and they are consumed / degraded in the plating process or lost to dragout. Dragout actually provides an important outlet for degraded brighteners and Sodium. Recycling presents following problems
 - degraded brighteners increase the load on Carbon filters
 - some decanting of the tank may be required to control Sodium levels
 - Brightener control is difficult when a portion is recycled
 - recycling to semi-bright tanks require absence of brighteners of the bright baths
3. recovered solution should be sufficiently concentrated – a Ni-concentration of 35 – 40 g/l is acceptable for direct recycling
4. Recycled mix of Ni salts (Sulphate and Chloride in a particular ratio) should be same as original mix ratio
5. pH of the recycled solution should be in correct range
6. In some Ni-plating baths, the Ni concentration builds up beyond the required limits. This occurs due to the the difference of the current efficiencies of the cathode and anode. The anode efficiency does in fact approach 100% butr the cathode efficiency usually falls in the range 90-96%; this causes more Ni anode dissolution into the bath solution than what is being plated and the Ni concentration and pH in the bath will increase. This problem can be controlled with the use of specially designed insoluble anodes.

In the advanced recovery system using ion-exchange process, some of these problems have been tackled to provide better efficiency and performance. This type of system uses two short packed resin columns (i.e., cation and acid sorption) with fully automated operation. Economic comparison is shown on **Table 4.2**.

Table 4.2: Economic comparison of Advanced Ion-exchange Nickel Recovery vs. Waste Treatment (Basis: 2.5 to 3.0 kg /hr dragout operation)

Component	Waste Disposal cost		Operating Cost (Rs) of Recovery System	
	Rs. per day	Rs		
Nickel Salt Sulphate + chloride @165 per kg	20,000 kg	3,300,000	200 kg	Rs.33,000

32% Hydrochloric Acid @ Rs 4,000/tonne	-	-	2,000kg	Rs. 8,000
93% Sulphuric Acid Rs. 6,000 per tonne	-	-	9,000 kg	Rs.54,000
100% Caustic Soda @Rs.15,000 per tonne	6.3 tonne	Rs.94,500	7.5 tonne	Rs.112,500
10% sludge + handling @ Rs.500 per tonne	75 tonne	Rs. 37,500	0.75 tonne	Rs. 375
Plant water @ Rs.15 per cu.m.	45,000 cu.m.	Rs. 6,75,000	-	-
D.M. Water @ Rs.25 per cu.m.	-	-	5,400 cu.m.	Rs.1,35,000
Total per year		41,07,000		3,42,875
Net Saving per year				37,64,125

The operating advantages are;

- Very dilute rinse feed solution (<0.5 to 1.0 g/l as Nickel) resulting in high concentration purified product (>35 – 40 g/l as Nickel)
- Organic brighteners are rejected allowing direct recycle to semi-bright baths
- Prevents Sodium build-up in plating bath
- Regeneration of resin with a mixture of Sulphuric and Hydrochloric acid produces a mix of Nickel Sulphate and Chloride that matches bath chemistry
- Excess regenerant acids from the initial product of the first resin bed are sorbed out in the second resin bed resulting in the final Nickel products having a pH suitable for direct recycle.

4.4.3 Chrome Recovery / Recycling by Ion-exchange

In decorative plating, only about 15% of Chromic Acid added to the bath actually gets plated on the objects. The balance is lost as dragout to rinses and fume scrubbers. Clearly this indicates a huge waste of metal, which is also very hazardous. Moreover, decorative as well as hard chrome plating baths become contaminated over a period of time due to dissolution of metals from the plated components and other operational factors. These dissolved cationic contaminants (trivalent Cr, Fe, Ni, Cu, Zn etc.) lower the throwing power of the bath and lower current densities. This results in slower plating operation, consuming more energy. Plating quality is also adversely affected. All these factors together (i.e., defects in surface coating, material loss and costs of treatment and disposal to comply with pollution control regulations) lead to purification and recycling of Chromic Acid.

Conventional ion-exchange based recovery system comprises cation and anion exchange columns. The first column, containing cation exchange resin, removes trivalent Cr, Ni, Fe, Cu etc. The effluent, then containing only hexavalent Cr is passed through anion exchange resin. This removes hexavalent Cr, leaving the effluent free from all metal ions. When the resins get saturated, they are regenerated and recovered Chromic Acid is recycled to baths. The economic comparison is shown in **Table 4.3**

The cost of a typical locally manufactured plant (of 2.5 kg Chromic Acid recovery costs about Rs. 1,00,000 with a resin volume of 50 litres. The cost of resin is Rs. 600 per litre with minimum life of 1 year (average life is between 2 to 3 years). The depreciation available on the investment is 100 %. Therefore pay back period is about a year.

**Table 4.3: Economic Comparison of Waste Treatment vs. Chrome Recovery
(Basis: 2.5 kg of Chromic Acid from static Rinse Water per day)**

Component	Waste Disposal cost		Operating Cost (Rs) of Recovery System	
	Rs. per day			
Chromic Acid @110 per kg	2.5 kg	275	-	-
Sodium Metabisulphite @ Rs.12 per kg	7.5 kg	90	-	-
Caustic Soda @ Rs.14 per kg	4 kg	56	4 kg	56
Saving on Sulphuric Acid @ Rs. 3 per kg	2 kg	6	3 kg	12
Electricity @ 4 per kWh	3	12	10	40
Labour	LS	50	LS	50
Chemical for Sludge handling	LS	2	-	-
Saving on plant water (after recycling)	LS	5		
Total per day		496		158
Total per year @ 300 working days/yr		1,48,800		47,400
Net Saving per yr				1,01,400

Despite such encouraging results, conventional ion exchange recovery systems have one problem. Direct recycle of the dragout solution to the plating bath will also recycle the metal contaminants and lead to build-up of contaminants as recycling goes on. An effective recycling system has to incorporate both recovery and purification. However, dragout solution after purification could be too dilute for direct recycle to the chrome bath. A good arrangement would be to use an atmospheric evaporator for the purified recycled solution. The availability of two or three counter flowing rinse tanks in the plating line could ensure a high degree of recovery with such a system (over 90 – 96% of dragout losses) with the possibility of also reducing rinse water requirements by 70 – 80% .

The economic comparison of larger capacity plants is given in **Table 4.4**.

**Table 4.4: Economic Comparison of Chrome Bath Recovery with Treatment
(based on 3,785 litres bath volume; 240 g/l chrome; 15 g/l metals)**

Item	Advanced Ion-	On-site Treatment	Off-site
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	exch. System		Treatment
Bath replacement	-	Rs.1,50,500	Rs.1,50,500
Chemicals	Rs.23,177	Rs.74,605	-
Solids Disposal	-	Rs57,663	-
Liquid Disposal	-	-	Rs.3,44,000
Total Costs	Rs.29,154	Rs2,82.768	Rs.4,94,500

Typical recovery efficiencies of various techniques and methods, including simple static recovery rinse used by most of the small scale platers, are summarised in **Table 4.5**. However, it may be noted that the recovery efficiencies reported here are only general indicators. Proprietary processes and techniques using same method can achieve higher efficiencies. Also, adoption of a particular technique depends not only on metal and/or chemical recovery efficiency but also on effect on plating quality, overall economy and availability of operational skill. Whatever the variant, metal recovery means (i) a straight forward pollution abatement at source, (ii) a cleaner production process and (iii) substantial saving of water.

4.5 Reverse Osmosis

Reverse Osmosis is one of the membrane filtration techniques, in which the pore size of the membrane varies from 1 to 15 Angstrom and the liquid is filtered through a semi-permeable membrane, which allows only water molecules since the pressure is more than the osmotic pressure. Application of this process is based on the fact that since the RO membrane normally rejects compounds and ions above a molecular weight of 150, most of the ions will be rejected. When rinse water is subjected to RO, water (with some copounds) will come out as permeate and the rest of the chemicals will remain in the concentrate or rejects. The concentrate can be recycled to bath. This is possible when rinses from various processes are segregated. If they are mixed, the concentrate will contain a variety of chemicals and obviously, it will need to be evaporated (with solar energy) and sludge disposed as hazardous sludge. The major limiting factor for use of RO system is the presence of Iron and free chlorine, which the membranes are not able to withstand, causing fouling of membrane. If sufficient pre-treatment precedes RO, then it is a viable alternative to conventional system.

The process has been in use in BHEL, Trichy since the last four years for Chromium plating rinse-water with a capacity of 50 litre per hour (permeate). The savings achieved by lower consumption of water and chemicals pay for the plant in about two years. More facilities like this are successfully being built in Madurai Electroplaters' park in Madurai, and other parts of Tamil Nadu

Table 4.5: SELECTED METAL RECOVERY TECHNIQUES & METHODS FOR TYPES OF PLATING

Methods / Techniques	Cyanide Silver Plating	Cyanide Copper Plating	Acid Copper Plating	Nickel Plating	Chrome Plating (Decorative)	Thick Chromium Plating	Cyanide Zinc Plating	Acid Zinc Plating	Cadmium Plating (Cyanide)	Chromic Passivation	Copper Pickling	Acid Pickling
Ion Exchange			y	y	y	y				y	y	Y
Electrolysis	y		y				y	y	y		Y	
Electro-Dialysis					y	y		y				Y
Evaporation	y			y	y		y		y			
Static Recovery Rinse		y	y	y	y ⁽¹⁾	y	y		y		y	y
Typical Recovery Efficiency	> 99%	98%	80 - 98%	98%	y ⁽¹⁾ -70-98% y- 98%	95%	70%	80%	70%	98%	98%	80%

Source: UNEP, : “Environmental Aspects of the Metal Finishing Industry, A Technical Guide”, Paris, 1993

Section 5

Waste Minimisation & Treatment for Prevention and Control of Pollution

5.1 General

Electroplating generates all three forms of waste – liquid, gaseous and solid. Of these, liquid wastes are predominant. Such liquid wastes include : (i) spent chemicals and solutions such as acids, alkalies, cleaning agents, bath chemicals comprising plating chemicals as well as additives such as brighteners, levellers etc. and rinse waters, which may contain some or all of these depending upon sources, method of plating and housekeeping practices.

Gaseous wastes include solvents and vapours from hot pre-treatment and process baths. They include acid alkali mist, Volatile Organic Compounds (VOCs). In some cases, mists and VOCs may contain metals in addition to process chemicals. According to one estimate, approximately 30% of the solvents and degreasing agents used can be released as VOCs when baths are not regenerated.

Solid wastes include, sludges generated from wastewater treatment, sludges from cleaning and bath tanks and various residues like, cleaning powder, buffing compounds, spent anodes and various scraps. Unused chemicals, spent resins from ion-exchange / metal recovery systems also contribute to solid waste. Much of the solid waste contain hazardous and toxic substances.

Waste minimisation therefore occupies the most important position in the control of pollution from electroplating and overall protection of the recipient environment – water, air and land (soil).

5.2 Waste Minimisation & Process Modification

Waste minimisation in an Electroplating unit may include any one, combination or all of the following:

1. Minimisation of Wastewater Generation

This is the single most significant step towards waste minimisation. The results of the in-depth study points to an immediate need towards this objective. While the large and organised units practice full or partial wastewater minimisation, small scale and tiny units do not do anything at all. Numerous studies reported in literature also point out to several approaches, which can be briefly stated as;

- Introduction of rinse water recirculation with automatic benefit of chemical recovery and reuse
- Static rinse water recovery
- Avoiding and controlling spillage – single largest cause of high wastewater generation in the unorganised sector. By using troughs between tanks and using well defined linear configuration in place of barrels and avoiding haphazard rinsing and washing will ensure very significant reduction in quantum of wastewater generated.
- Introduction of cascade and/or counter- current rinsing
- Use of fogging and spraying on objects (rack plating)

- Introduction of metal recovery by electrolytic method (ion-exchange and its advanced application leading to high recovery ratio of water (upto 80%).

Analyses of cost saving by metal recovery using ion-exchange process indicate that for a small scale plant @ 2.5 kg Chromic acid per day and 2.5 kg Nickel Sulphate per day, gross saving would be Rs. 1.01 lakh and 1.20 lakh per year. For large plants @ 2.5 kg Nickel Sulphate per hour, the saving by advanced ion-exchange would be Rs.37.64 lakhs per year.

2. Minimisation of Gaseous Emission

Except a few states (e.g., Karnataka and Maharashtra), State Pollution Control Boards do not generally require electroplating units to provide any measure for elimination or control of gaseous emission. As discussed earlier, gaseous emission takes place as vapours from hot baths, normal evaporation from cold baths do not constitute significant source of such emission and VOCs from organic cleaning baths.

Use of collecting hoods and scrubbers can significantly control or eliminate vapours from baths. Collecting arrangements have improved substantially but older plants either have no collecting hoods or only side suction arrangement, which are not effective at all. Completely covered baths are ideal solution but they are useful in completely automated plants as used in Europe and parts of North America. However use of top suction hoods with properly designed scrubber system certainly controls much of the gaseous emission. As far as emission of VOCs are concerned, ideal solution is not to use those with high environmental concerns even if they are used, the best practice is to keep the tanks fully covered at all times and using vapour arresting devices.

3. Minimisation of Solid Waste

Major part of solid waste (that too, hazardous) is sludge from waste water treatment plant. Therefore, if measures are taken to minimise waste water generation by adopting methods stated in sub-para 1 above, waste water sludge generation is minimised. Other constituents of solid waste are: (i) spent anodes, (ii) tank sludges, (iii) spent carbon filters and (iv) empty containers of chemicals etc.. The last-named one is usually sold to scrap dealers. Tank sludges and spent carbon filters may contain hazardous metal salts. While the quantity depends on production, disposal practices should conform to regulatory requirements pertaining to hazardous substances. Therefore using non-hazardous chemicals will lead to minimisation of hazard in solid waste from process chemicals. Use of Cyanide free process (e.g. Alkaline Cyanide Free Zinc plating), use of trivalent Chromium in place of hexavalent Chromium are examples of such hazard minimisation.

4. Minimisation of Noise Emission

Plating activity by itself does not produce significant noise, except barrel plating of small objects. Major source of noise is operation of air blowers used for blowing air in plating (for Nickel Plating) and in pre-cleaning operations. Such noise is minimised by putting the air blower in a separate room with noise muffling arrangements. In many plants and factories, it was observed that high ambient noise level in plating areas is caused by activities other than electroplating such as machining, stamping, metal forming, forging, etc. etc. Noise reduction in such activities is however, outside the purview of this study.

5.3 Best available Technology (BAT)

The Best Available Technique (BAT) means the most effective and advanced stage in the development of activities and their methods of operation, which indicate the practical suitability of particular techniques for providing in principle the basis for minimum emission values designed to prevent and, where it is not practicable, generally to reduce emissions and the impact on the environment as a whole.

Specific BAT approach

Ideas to implement some specific BAT measures are summarized herewith under the heading of:

- pre-treatment activity
- plating activity

5.3.1 Specific CP Approach in Pre-Treatment

Table 5.2: BAT approaches in pre-treatment

Application in Pretreatment	Method	Benefit
Pre-cleaning of small size Work pieces	Use a centrifuge to remove all dirt prior to degreasing <u>or</u> to impose cleanliness requirement onto the client (medium tech)	- Reduce lengthy pre-treatment - Reduce electricity consumption in surface preparation
Removal of accumulated oil and grease	Use centrifuge (medium tech)	- Reduce infiltration of impurities (undesirable salts and organics including oil and grease) in degreaser tank - Prolong life span of degreaser bath
Ultra-filtration of alkaline Degreaser bath for inlet water	Self-explanatory (high tech)	As above
Ultrasonic degreasing	Self-explanatory (high tech)	As above

For visualisation of some of the applications, see same illustration in Drawings 1, 2 and 3 at end of this Section.

5.3.2 Specific BAT Approach in Plating

Table 5.3 summarises BAT approach in plating.

Table 5.3: BAT approaches in plating lines

Application in Plating	Method	Benefit
Water flow meter and Conductivity meter	- Introduce on-line flow meter in water intake pipe - Introduce on-line conductivity meter in process tank	Water savings from correct adjustment of : - water flow into last rinse tank - plating chemical replenishment
Reverse osmosis (RO) on last Rinse water for inlet water	RO is not recommended for use in systems where : - pH is 12-14 or pH is 0-2 - organics in influent water > 5 g/l	Reduce infiltration of impurities (undesirable salts and organics) into rinsing tanks
Zinc plating	Place evaporator next to the plating bath. The inlet pipe and back-filling pipe is installed in the process tank	Reduce consumption of zinc

Nickel, chrome, copper and tin plating	Recover heavy metals from used rinsing water for reuse in plating baths by means of electrolysis cell or ion exchanger (and evaporation unit, if required)	<ul style="list-style-type: none"> - Saving of raw materials - Reduce amount of sludge - Reduce concentrations of heavy metals in wastewater - Recover heavy metals for re-use or secondary raw materials to be sold off
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5.4 Potential initiatives and cost estimates

The below tabulation gives an idea of the different cost range relating to the various initiatives. It is to be noted that the costs are broad estimates only.

Table 5.4: Potential solutions and cost estimates

Applicability	Initiatives / Actions	Cost Range in Rs
Low-tech measures	• Cleaning + maintenance	Negligible
	• Drip guard (polypropylene plastic material) between tanks	Negligible
	• Replace leaky tanks and repair leaky pipes	Negligible
	• Sheltered storage for chemical drums with secondary containment but without drainage	Negligible
	• Insulation of hot process tanks and piping	Negligible
	• Put air blower in separate enclosure	Rs. 10,000 – Rs. 50,000
Medium-tech measures	• Water flow meter and conductivity meter *	Rs. 5,000
	• Multiple counter flow rinsing / sequence	Rs. 10,000 – 50,000
	• Barrel rotation * (at top position) *	Rs. 15,000 – 25,000
	• Spray rinsing *	Rs. 10,000 – 35,000
	• Centrifuge (pre-treatment)	Rs. 70,000 – 1,00,000
High-tech measures	• Introduce / improve vapour collection hoods And scrubber system	Rs. 50,000 - 1,50,000
	• Reverse osmosis or ion exchanger	Rs. 50,000 – 3,00,000
	• Ultra filtration / Ultrasonic (pre-treatment)	Rs.1,00,000
	• Back filling to plating baths - Evaporator bath and activated carbon filter - Electrolysis cell	Rs.15,000 – 50,000 Rs. 30,000 – 1,00,000

* Includes construction and installation of electrical contacts for operation mechanisms

Note : In view of the availability of different designs and systems, the details of costs can vary. The industry is encouraged to acquire the latest cost information from the equipment supplier if any cleaner production initiative in the above is taken up.

5.5 Waste Treatment Options

5.5.1 General

An electroplating unit generates various streams of liquid waste, which require different treatment techniques. Such separate treatment (often pre-treatment) avoids the possibility of mixing incompatible wastes, which makes treatment difficult, expensive and less reliable. Often such mixing can be a hazard to personnel or formation of complexes that are difficult to treat, such as mixing of Nickel plating wastewater with Cyanide bearing wastewater leading to formation of Nickel Cyanide. Therefore, segregation of wastewater streams is of paramount importance. During the in-depth study, it has been noted that in majority of small-scale and tiny units, this is just not done, indicating an urgent need to introduce this basic requirement.

As a general rule, waste streams and characteristics must be carefully evaluated before selecting a treatment scheme. It was found during the study that units in large and medium scale have opted for treatment schemes that cater for their particular wastes, although there is a commonality of treatment methods and/or processes used. In some circumstances, (e.g., in Bangalore), it is found to be economical, practical and much better managed to have a centralized waste treatment facility operated by a separate entity. In fact it is a welcome development that in many states, industrial estates and parks are coming up to shift existing units and accommodate in a properly organised group of electroplating units with a CETP (example Faridabad in Haryana; Madurai in Tamil Nadu, Anand Parbat area in Delhi etc.)

5.5.2 Principles of Treatment

For most heavy metals, precipitation as insoluble hydroxy or sulphite compounds is achieved by addition of simple reagents followed by pH adjustment and sedimentation. In the case of hexavalent Chromium, it is necessary to first chemically reduce the metal to trivalent state and then form insoluble precipitates. However for certain very hazardous heavy metals such as Cadmium, a totally separate system may be advantageous, including separate disposal procedures.

Where the wastewater contain cyanides, removal of cyanides is achieved by oxidation to harmless residues, followed by a precipitation step to remove accompanying soluble metal ions.

It is important to distinguish between treatment of rinse water (high flow and low concentration) and discarded strong process solutions (cleaners, acid dips, plating solutions etc.) of low volume and only occasional discharge but of high concentration. Clearly, a batch treatment system would cope with two types of wastewater rather than a continuous flow system which is likely to be upset by shock loads. The guiding principle is to store such strong wastes and release them gradually into treatment system. Thus flow equalisation is an important operation to integrate into the treatment system.

5.5.3 Treatment Processes

5.5.3.1 Treatment of Hexavalent Chromium bearing wastewater.

Hexavalent chromium compounds come from processes such as polishing and brightening, pickling, passivation, chrome plating and plastic metallisation. Reduction of Cr(VI) to the more easily precipitated trivalent state (rather non-toxic) can be achieved in many ways.

Sulphur compounds are commonly employed for the reduction of hexavalent chromates. Advantages include short reaction times, the simple observation of the reactions by measuring redox potential and a low yield of sludge after neutralisation with Sodium hydroxide. The sulphur compound include (i) Sulphur-di-oxide gas, dissolved in solution, (ii) metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) or normal sulphite (Na_2SO_3). These compounds, in acid solution (pH range 2 to 3), dissociate and the bisulphite anion (HSO_3^-) reduces the Cr to the trivalent state.

Stoichiometrically, for the reduction of 1 g of Cr (VI), 0.92 g of S is required. From this, the quantities of the appropriate reagents can be computed, assuming the reaction quickly goes to completion. Iron salts can also be used because they are sometimes cheaply available. The theoretical requirement is 3.22 g Fe (II) and 6.60 g H_2SO_4 Or 4.91 g of HCl for reduction of 1 g of Cr (VI). **Table 5.4** shows the yield of hydroxide precipitation and of dissolved Sulphur salt (contributing to raised TDS) indicating the burden on the environment in other forms. The high amount of sludge produced is one of the discouraging factors against use of Fe salts and not normally used in India.

Table 5.4: Precipitation of Hydroxides and Neutral salts from reduction of Cr (VI)

Reducing Agent	Yield of Na_2SO_4 From neutralization (kg)	Precipitated hydroxides as dry matter (kg)
Sulphur di-oxide	4.1	1.98
Sodium bi-sulphite	8.2	1.98
Ferrous Sulphate	16.4	8.34

Source: UNEP: "Environmental Aspects of the Metal Finishing Industry, A Technical Guide", Paris, 1993

5.5.3.2 Treatment of Cyanide bearing wastewater

The Chemistry of Cyanide detoxification is relatively complicated and in most cases, degradation needs more than one reaction step.

Degradation with Chlorine

Cyanides can be oxidized by chlorine; both chlorine gas and Sodium hypochlorite can be used. Except in very large plants, where use of Chlorine gas is more economical, most plants use Sodium Hypochlorite. In case of use of Chlorine gas, the hydrochloride generated together with hypochlorite requires further neutralisation chemicals. This technique is suitable if the Cyanide concentration ranges between 0.1 and 1.0 g/l. A disadvantage of using chlorine gas is the high production of salts from the subsequent neutralisation.

When Sodium Hypochlorite is used, there is a two step process. In the first step, cyanides are oxidised by hypochlorite to cyanogen chloride, which is an extremely toxic gas. The second step, which takes place almost simultaneously, involves hydrolysis of cyanogen chloride to cyanate. The latter is highly soluble in water but care should be taken to ensure that the temperature does not exceed 40⁰ C, so that degassing does not take place. Hazards are best minimized by ensuring as rapid a hydrolysis as possible. This is achieved at a high pH of around 11.5 with a detention time of upto 1 hour to guarantee complete reaction. Good mixing is essential. In some countries the retention time may be set by regulation. In most cases found during the in-depth study, further oxidation from Cyanate to Nitrogen and Carbon is not carried out and the effluent is sent to an equalisation tank for neutralisation. Where further oxidation is required, it is carried out by using Sodium Hypochlorite again at a pH of 8.0 to 8.5. It is very important to have correct and reliable pH control to prevent toxic gas formation under acidic conditions.

Degradation with Active or Activated Oxygen

Oxidation of Cyanides directly using oxygen leads to a great benefit that no salts are produced and no neutralisation of solution is required. This can be done by using (i) Hydrogen Peroxide, (ii) Persulphuric Acid and (iii) catalytic oxidation.

Theoretically, 1.3 kg H₂O₂ is sufficient per kg of cyanide. However, in practice, (a) excess H₂O₂ is required to ensure complete reaction and (b) this process is not recommended with low initial cyanide concentration i.e., less than 500 mg/l.. Addition of catalysts or Formic acid accelerates the reaction, enabling the method suitable for use in the concentration range of 100 to 1000mg/l.

Persulphuric acid is often used as Oxygen delivering substance. It hydrolyses to H₂O₂ and sulphuric acid in aqueous solution. Direct ozonation is another available method. Concentrated peroxides and persulphates are hazardous substances and should be dealt with accordingly.

Electrolytic Process

When the cyanide waste is concentrated, an economical solution for degradation is electrolysis in presence of chlorides. Cyanides can be oxidised by electrolytic splitting of oxygen from hydroxides.

Precipitation of Cyanides

Iron ions form highly stable complexes with cyanides. A precipitation of divalent or trivalent hexacyanoferrates is possible as a detoxification step within the final wastewater treatment. But the resulting sediment is not fit for disposal to a landfill site, because acids or photolytic reactions may, under certain circumstances, release cyanides from the residue. Such sediments can be subjected to thermal destruction.

Comparison of Methods

The popular detoxification method for cyanides in small metal finishing plants is still oxidation by chlorine. Advantages are the speed of reaction, easier process control, low costs and a relatively long experience in handling.

For concentrated wastes, precipitation as hexacyanoferrates is suitable but must be followed by thermal degradation.

Peroxy- compounds have the general disadvantage of long retention times. These processes are useful only where small quantities of cyanide bearing wastewaters are to be treated. The content of salts in the effluent is low.

In summary, if cyanides are destroyed in a continuous flow stream, hypochlorite treatment may be the best choice because of its simple handling and other advantages as mentioned before. If concentrated or small volumes are to be treated, techniques should be chosen which yield a minimum of waste even if performance and maintenance is more complex.

5.5.3.3 Neutralisation and Precipitation

This principal operation in the wastewater treatment is intended to convert dissolved metals to insoluble hydroxides and removed from the effluent. The operation is preceded by flow equalisation as an essential step. The precipitation chemicals used are Sodium Hydroxide, Lime and Soda. Magnesium hydroxide is sometimes used but the reaction is slower and pH range is limited. Alkaline wastewaters are neutralized by sulphuric acid but it has a constraint for sulphate limits, if set as effluent standard. Smaller facilities use Sodium Hydroxide solution (450 g/l). However, if the wastewater contains fluorides, Lime solution should be used. Lime solution is cheaper and used by larger units. A lime solution preparation unit is required in the latter case.

The maintenance of correct pH is essential for efficient precipitation of metal hydroxides. **Fig 5.4** shows the pH ranges for precipitation of several metal hydroxides. For most cases, pH would be in the range of 8.5 to 11. Unnecessary high pH may interfere with the formation of a good settleable sludge. Therefore, the best practice is to maintain a pH slightly above minimum pH value. Further adjustment may be required in case of specific effluent standard.

5.6 Housekeeping Guidelines

Although good housekeeping is a matter of attitude, particularly the attitude of management and shared by the workforce, it is more of a necessity than an option in an industry like electroplating. Many of the chemicals used are hazardous and toxic, there is good potential of accidents to occur and the industry poses threats of adverse impacts on the natural environment. These factors lead to a great need for good housekeeping. in order to ensure health and safety of all working personnel as well as the public at large. The housekeeping can be subdivided into three main topics: (a) storage and handling of chemicals (b) housekeeping in production shop floor i.e., pre-cleaning and plating operations and (c) housekeeping of rejects and wastes. In order for housekeeping to be effective and routinely carried out, the following are essential:

- Management accepting its lead role in providing safe working conditions and procedures.
- Participation by the workforce in ensuring safety at work
- Clear allocation of responsibilities for safety and health services
- Safety training and instruction, on induction and on-going
- Reporting, investigation and analysis of accidents and working conditions
- Dissemination of information on hazards and risks
- Co-operation with labour and safety instructions and reviews

In the following paragraphs, brief guidelines are given for better housekeeping;

5.6.1 Storage and Handling of Process Chemicals

Process chemicals consist generally of (a) acids, (b) alkalies (c) cleaning agents (d) metal salts for preparation of bath solutions (e) additives and (f) anodes. The basic guidelines are:

1. Acids and alkalies should be stored separately
2. Containment bunds should be provided on floor to contain accidental leakage or spills
3. Volatile organic compounds should be stored in gas tight containers and kept under lockable covered sheds
4. Only authorized personnel shall have access to these materials. These personnel should be made aware of material characteristics through training; Material Safety Data Sheets (MSDS) should be displayed at a prominent location.
5. Training to provide aid during accidents and spills should be given to designated personnel, whose names and contact details should be displayed at prominent locations
6. Wherever possible, solution preparation should be done in lined tanks/containers and transferred to process baths by pumps only.

5.6.2 Housekeeping in Production Shop Floor

This aspect is by far the most important activity in the day-to-day running of an electroplating plant. Good housekeeping will ensure smooth production, encouragement to personnel and developing a positive attitude among all. These can be generally summarised as:

1. Avoid clutter and untidy working condition. Introduce floor marking to designate areas for material storage, movement of personnel and handling equipment such as pallet trucks and worker stations, control panels and so on.
2. Ensure that floor should always be dry, non-slippery and clean
3. Provide curbing and channels to accommodate valve gland leaks and overflows, condensates and drainage and lead them to designated holding and/or equalisation tanks for treatment and/or recovery
4. No rinse-water or drag-outs should spill on the floor – the most important item totally ignored in small and tiny units across the country
5. A holding pit should be provided to arrest accidental spills or leakages on shop floor, sloped towards it.

6. Floor should be kept clean and free of obstacles for unhindered movement of personnel.
7. While filling or topping up tanks/ baths, care should be taken to prevent overflows- use following techniques:
 - Fit hoses with spring loaded nozzles
 - Use metering pumps to accurately transfer required quantities, where feasible
 - Where water is added directly from piping, use float level controls
 - Install backflow- preventers, where water is discharged below solution surface
 - Supervise regularly and keep records of all such operations, indicating overflows, losses, spills etc, whatever occurs.
8. Regularly check all alarms, control devices and meters/recorders as per manufacturer's advice
9. Check all metal protection such as tank lining, painting on railings, piping, chains and hoists and electrical/piping racks against signs of corrosion. A timely intervention saves lot of expensive repairs, shutdowns and avoidable accidents.

5.6.3 Housekeeping of Rejects and Wastes

Rejects and Wastes generated in Electroplating wastes include the following:

- Process waters of various kinds
- Spent process solutions and electrolytes
- Surplus chemicals
- Empty containers, packing materials
- Scraps of various kinds
- Sludges and filter cakes

Process Water, Spent Process Solutions and Surplus Chemicals

The detailed considerations for the first three have been discussed in **Section 4** and **Sub-sections 5.1** through **5.3.1**. However, general guidelines can be summarised as under:

1. All process wastewater should be segregated according to their characteristics
2. Wherever feasible, recovery of metals and other chemicals should be recovered care being taken to ensure undesirable salt content do not rise in recycled solutions
3. Flow equalisation tanks must be provided before treatment of various streams and in each unit operations
4. For very small wastewater flow, it is advisable to haul wastewater to a common treatment facility
5. Tanks, piping, valves, filters shall be of corrosion resistant materials and leakproof. Arrangement should be provided to arrest leakages by channels and curbing and brought to holding tanks/equalisation tanks for further treatment/disposal.
6. Surplus chemicals not meant for use or return to vendor, should be diluted and discharged slowly into appropriate stream of wastewater; they should not be

disposed of by discarding them into general waste bins or *washing them down the drain unless specifically permitted by regulatory authorities*

7. Hazardous chemicals and wastes shall be disposed through licensed contractor

Empty Containers, Packing Materials etc.

Since many chemicals used in electroplating are toxic, there is good chance that virtually anything coming in contact with operations can be contaminated. Good housekeeping will ensure that this will not be the case and if contamination occurs, they should be de-contaminated or disposed properly. The following may be noted:

1. Tools and equipments should be kept only in designated area and not left elsewhere
2. Separate waste bins for different kinds of waste should be used with clear labelling and workers trained to use them
3. If empty containers are used as waste bins, it should be first thoroughly cleaned and all previous markings obliterated and /or painted over
4. Containers of toxic and hazardous chemicals should not be used for other storage; they should be disposed as per manufacturer's instructions
5. All materials that are contaminated with chemicals can be considered to be toxic as safety measure and treated accordingly.

Sludges and Filter Cakes

Disposal of sludges is now one of the major environmental concerns for the electroplating industry. Because of heavy metal content, sludges from wastewater treatment plants are considered hazardous. Many countries including India have regulations concerning handling, storage and disposal of such hazardous materials.

Based on the findings of the in-depth study, it was noted that in many areas irrespective of the state, centralised sludge disposal facility has not been built by the State Pollution Control Boards. In such cases, the industry has been asked to organise safe storage for a specified period. The following guidelines may be useful in this regard:

1. Sludges should be compressed and dewatered to reduce volume as much as practicable
2. They then should be poured in PE bags, sealed and labelled or tagged with date, quantity and description of content
3. These bags should be kept in a watertight compartment, preferably concrete chambers with lockable covers
4. Manual handling and/or carrying as headload by manual labour should be strictly prohibited
5. Most units simply store them on roof tops or in "godowns" with leaky tin roofs; such practice allows sufficient wetting and eventual run-off of such sludges entering soil and groundwater. This practice is against the spirit of environmental protection.
6. Formation of leachate must be avoided at all times to prevent remobilisation of toxic and hazardous substances in the sludge.
7. Pre-treatment and chemical stabilisation of the sludge by the generator himself may be done, particularly by large units.
8. Only properly designed, constructed and certified/authorized landfill sites should be used for final disposal.

Section 6

ECO FRIENDLY ELECTROPLATING PROCESS

A process is eco friendly if it offers no deterioration to the environment in which it operates as a consequence of process reactants, process products, process waste or the process itself

Solvent cleaners

Solvents are used for pre-treating the work pieces before plating. The removal of oils and grease from metal surfaces prior to the application of coatings has been achieved by a combination of alkaline degreasing and organic solvent dissolution. Eg., Acetone, ether, benzene, toluene, CCl₄, trichloroethylene etc.

The main disadvantages are the solvents are toxic and flammable. Effects on Ozone layer of the upper atmosphere

The preferred solvents are Perchloroethylene, Methylene chloride. Ultrasonic cleaning with alkali and acidic substances can also be done.

Brass Plating

Brass plating is one of the most common alloy plating processes in use today. Brass can be plated in many applications and in varying thicknesses. Another property of brass plating is its ability to provide good adhesion to steel and rubber. Brass is, therefore, commonly used in the manufacture of steel wire cord for use in tires. Other applications of brass plating include a variety of decorative and engineering finishes

Alternative Non-cyanide Bath Solutions for Brass Plating

Various non-cyanide brass solutions have been developed in the past, however, cyanide brass solutions are still the most prevalent solutions used by metal finishers today

Brass Pyrophosphate: Among the non-cyanide brass plating baths, pyrophosphate appears to be one of the most promising. However, field reports have stated that additives are necessary to operate this application properly. Otherwise, problems develop with unalloyed zinc getting contained in the deposit. Metal finishers have used the additive histidine in a pyrophosphate solution successfully. The deposits have shown similar qualities to the traditional copper zinc alloy deposits.

Brass Pyrophosphate-Tartare: Tests have been completed on an alkaline pyrophosphate-tartare bath containing histidines as an alternative to brass cyanide solutions. Tests on these solutions have found that their alloy composition was almost constant over a wide range of current densities. Moreover, bright brass deposits having a uniform composition and color were obtained over almost the entire cathode area.

Cadmium Plating

Cadmium is extremely toxic and need to be tightly regulated. Because of its regulatory status and the high cost of cadmium plating, many platers are substituting cadmium with zinc where possible. Metal finishers have found some problems with finding substitute bath solutions or low-cyanide cadmium solutions for many applications.

Common Uses: Cadmium exhibits superior corrosion resistance (especially in marine environments), lubricity, and other specific engineering properties. Cadmium also is easily welded. Often, cadmium-plated material is chromated to increase corrosion resistance. The largest segment of the cadmium plating market is the military.

Alternative Non-cyanide Process Solutions for Cadmium Plating

Cadmium plating solutions that do not use cyanide are commercially available. These include cadmium acid and cadmium alkaline plating solutions. Some of the alternatives have improved performance when compared to cadmium. These benefits include:

- Zinc substitutes exhibit improved corrosion resistance
- Zinc-nickel alloys have better wear resistance
- Zinc-cobalt deposits show good resistance to atmospheres containing sodium dioxide

Some of the limitations of cadmium alternatives include:

- Increased electrical contact resistance for zinc coatings
- Reduced lubricity
- Decreased throwing power
- Decreased corrosion resistance in marine environments

Cadmium Neutral or Acid Sulfate/Cadmium Acid Fluoroborate

Three non-cyanide, cadmium-based alternatives are available: neutral sulfate, acid fluoroborate, or acid sulfate. However, these cadmium-based alternatives do not have the throwing power of cadmium cyanide processes. The only substitute that is capable of high cathode efficiency is acid fluoroborate, but only at high current densities

Zinc Alloys

Numerous zinc alloy processes are commercially available including zinc-nickel, zinc-cobalt, zinc-tin, and zinc-iron. The use of zinc alloys has grown because of their potential to replace cadmium, particularly in countries such as Japan where the use of cadmium has been strictly curtailed or prohibited. Zinc alloys were introduced in the Japanese and German automotive industry for use in fuel lines and rails, fasteners, air conditioning components, cooling system pumps, coils, and couplings. Other industries that use zinc alloys as a substitute for cadmium include electrical power transmitting equipment, lock components, marine, and aerospace industries. Metal finishers also have substituted zinc-nickel coatings for cadmium on fasteners for electrical transmission structures and on television coaxial cable connectors.

Zinc-Iron Acid or Alkaline: The primary advantage of zinc-iron is its ability to develop a deep uniform black conversion coating. Additionally, the alloy is easily welded and machined and is used easily on strip steel. This coating has been used successfully as a base coat prior to painting.

Zinc-Nickel Acid: Zinc-nickel acid solutions provide bright coatings that exhibit high throwing power. Good corrosion properties are maintained after parts- forming operations and heat treating because acid zinc-nickel delivers a higher nickel content than the alkaline zinc bath, which tends to increase corrosion.

Tin-Zinc Alloy A tin-zinc alloy has been developed. It contains 75 percent tin and 25 percent zinc and can be used in either rack or barrel plating

Zinc Chloride: Performance results demonstrated that while the zinc chloride finish was similar to the cadmium finish, the cadmium-plated parts, however, exhibited superior corrosion resistance

Copper Plating

Copper plating is widely used as an underplate in multi-plate systems and as stop-offs for carburizing as well as in electroforming and the production of printed circuit boards. Although relatively corrosion resistant, copper tarnishes and stains rapidly when exposed to the atmosphere. Copper plating can change the appearance, dimensions, or electrical conductivity of a metal part. Jewelry manufacturing, aerospace, and electronics often use copper plating . For plating copper, certain non-cyanide alkaline baths of proprietary composition have been developed. Four widely known alternatives to copper cyanide plating are copper acid sulfate, copper acid fluoroborate, copper alkaline, and copper pyrophosphate.

Alternatives	Finish Appearance	Ductility	Plating Uniformity
Copper Alkaline	(+) Good appearance	(+) Good	(+) Better throwing than cyanide
Copper Acid Sulfate or Fluoroborate	(+) Good appearance (+) Excellent leveling	(+) Good to excellent	(-) Less macrothrowing power than alkaline (+) More microthrowing power than alkaline
Copper Pyrophosphate	(+) Good, fine grained, and semi-bright	(+) Good	(+) Good throwing power

Copper Strike Alternatives

Copper Pyrophosphate: Dilute copper pyrophosphate has been viewed as a feasible replacement for the cyanide strike because the solution does not degrade substrates. The main disadvantage of this chemistry is that it usually takes three times longer to plate than traditional cyanide solutions.

High-pH Nickel: High-pH nickel plating solutions have been available for a long time as a substitute for cyanide copper strike on zincated surfaces and zinc die castings. To obtain optimum results with high-pH nickel, the plater must balance the ratio between nickel sulfate and sodium sulfate.

Gold Plating

Until recently, gold plating was used primarily for decorative purposes in jewellery and flatware. Currently, gold is widely used in the electronics industry because of its good electrical contact properties as well as corrosion and oxidation resistance. Typical applications for gold plating include printed circuit boards, contacts, connectors, transistor bases, and integrated circuit components. Gold plating also is widely used in the chemical industry for reactors and heat exchangers

Traditionally, gold has been plated from potassium gold cyanide solutions, although many different types of gold and gold alloys are available.

The four general groups of gold plating solutions are alkaline gold cyanide, neutral gold cyanide, acid gold cyanide, and non-cyanide solutions (generally sulfite-based). Alkaline cyanide baths have been used for the past century. Because of the complexing action of cyanide, however, obtaining consistent co-deposit of gold alloys is difficult unless the process is operated at high current densities. As a result, platers have limited the use of alkaline cyanide baths to flash deposits.

Alternative Solution	Advantages	Disadvantages
Gold Sulfite	<ul style="list-style-type: none"> •Excellent throwing power •Can plate on complex parts •Performs as well as gold cyanide solutions 	<ul style="list-style-type: none"> •Solutions are less stable, therefore, require more monitoring and conditioning
Cobalt-Hardened (No Free Cyanide) Gold	<ul style="list-style-type: none"> •Works well on slide wear applications 	<ul style="list-style-type: none"> •Deposits are brittle and thermal shock can cause cracking

Nickel

Nickel is used indirectly but significantly in pale colored gold plating processes. Nickel is regarded as the best bleaching agent for gold and is used extensively. used as brightening and hardening agent in gold plating.

Nickel free gold are now available and these contain metals such as palladium, silver, copper and zinc.

Cu55-Sn45 is considered as the best replacement for nickel undercoat

Silver

The largest use of silver plate is in the flatware and hollowware trade. The second

largest use is in the electronics industry where large amounts of silver are plated onto conductors, wave guides, and similar items because of silver's unsurpassed electrical conductivity. In most of these applications, silver is plated over copper and copper alloys. The aerospace industry uses silver as a plate over steel in aircraft engine manufacturing.

Commercial silver electroplating has been practiced since the middle of the nineteenth century. The plating bath contains silver in the form of potassium silver cyanides and free potassium cyanide. Platers also can use sodium cyanide, but they generally prefer the potassium form.

Alternative Solutions for Silver Cyanide

Given the large amounts of cyanide used in silver plating, finding suitable alternatives could greatly reduce cyanide levels in wastewater. Several attempts have been made to introduce non-cyanide alternatives. Most of these solutions are based on ammonium, halide, and aminothio complexes containing silver and a variety of conductivity salts and brightening agents. In almost all cases, the non-cyanide solutions have had problems especially in producing thick, bright deposits. Many of the alternatives that have been tested are unsuitable because of photosensitivity.

Zinc Plating

Zinc plating is versatile and used for many different applications. Because zinc is relatively inexpensive and readily applied in barrel, tank, or continuous plating, platers prefer it for coating iron and steel parts when protection from either atmospheric or indoor corrosion is the primary objective.

Zinc is deposited electrolytically from three different solutions: a cyanide bath, an acid chloride bath, and an alkaline non-cyanide (or zincate) bath. Zinc is also used in the galvanizing process. Workpieces usually are chromated after plating. The conventional zinc coating is dull gray in color with a matte finish. Another common zinc coating is bright zinc with a bleached chromate conversion coating or a clear lacquer coating, which is sometimes used as a decorative finish.

Alternatives to Cyanide Zinc Baths

Alternatives	Corrosion Protection	<u>Finish Appearance</u>
Zinc Alkaline	(+) Good, greater protection in difficult-to-rinse areas	(+) Good brightness
Zinc Acid Chloride	(+) Good, but less protection in difficult-to-rinse areas	(+) Excellent brightness and leveling

Alkaline zinc baths also form carbonate similar to cyanide solutions. Symptoms of this include yellows in blue bright chromate, a drop in brightness, and poor coverage. If carbonate levels become too high, platers should consider one of the following options:

- Decant the bath and rebuild to specifications
- Freeze out the carbonate
- Mix the bath with a compatible barrel plating bath to equalize carbonate.

Zinc Acid Chloride: Chloride zinc baths have been available since the 1960s. The original baths used chelates or ammonium chloride. Today, however, most baths use either potassium or ammonium chloride. The advantages of the chloride systems include brilliant deposits, high cathode efficiency, good leveling properties, low energy consumption, and easily treated non-toxic electrolyte. The disadvantages are poor throwing power, higher initial equipment investment, and higher brightener costs compared to the alkaline processes.

\Alternatives to Cyanide Stripping

Several non-cyanide alkaline immersion stripping baths are available to remove copper or nickel from various substrates. These baths typically use either the ammonium ion or an amine to provide complexing. Persulfate or chlorite anions can be used as well as proprietary formulations. The use of non-cyanide strippers eliminates cyanide from the spent stripper solution. In general, these non-cyanide strippers are less toxic than their cyanide-based counterparts and are more susceptible to biological and chemical degradation, resulting in simpler and less expensive treatment and disposal costs.

Chromium Plating:

Electroplating processes and aluminum finishing use chromium plating heavily. The most common hexavalent chromium-bearing solutions include decorative and hard chromium, aluminum conversion coating, bright dipping of copper and copper alloys, chromic acid anodizing, aluminum deox/desmut, chromate conversion coatings on cadmium and zinc, and copper stripping with chromic acid. Because of hexavalent chromium's high toxicity and cost for treatment and disposal, the industry has focused on reducing or eliminating its use. Hexavalent chromium is a known carcinogen and a designated hazardous air pollutant. Approximately 80 percent of the available power supplied to hexavalent chromium processes generates hydrogen gas. Evolution of the gas produces a mist of fine water particles with entrained hexavalent chromium. This mist is regulated under the Occupational Safety and Health Administration (OSHA). Protection of employee health and safety as well as the environment requires a high level of emissions control.

Trivalent Chromium

Use of trivalent chrome eliminates misting problems and the added reduction step in wastewater treatment. Adherence, throw, and coverage also are improved. Higher rack densities also can be achieved because bath concentration is much lower, dragout is less, and the amount of sludge produced by wastewater treatment is reduced substantially. However, plating thickness is limited to 0.1 mil; coatings thicker than this usually have problems with cracking and palling. Therefore, this technique usually is not suitable for hard chromium coatings, which can require finish thicknesses of 20 mils or more. Although the color tones of trivalent chromium coatings are different from those of hexavalent chromium, additives to the trivalent chromium bath often can ameliorate the difference. One of the main barriers for

increased use of this solution is customer acceptance. Primarily, customer concern is related to the color of the deposit.

Alternatives to Chrome Plating

Electroless Nickel Phosphorous: The use of electroless nickel finishes from conventional hypophosphite solutions has been investigated as an alternative. The use of electroless nickel as an alternative is limited by its somewhat poorer physical properties including lessened hardness and abrasion resistance. The corrosion and wear properties depend on the phosphorous content, which can vary from 1 to 12 percent.

Nickel-Tungsten Electroplating: Two nickel tungsten-based alloy electroplating processes are available as potential alternatives to chrome plating: nickel-tungsten boron (Ni-W-B) and a nickel-tungsten silicon carbide composite (Ni-W-SiC). The two processes are similar in that they are both electrolytic and they deposit a coating of nickel and tungsten with minor percentages of either boron or silicon carbide to enhance the coating's properties.

Tin-Cobalt Alloy: Tin-cobalt alloys provide a finish that is similar in appearance to chromium. The tin-cobalt appearance ranges in color from a bright, chromium appearance to a warm, silvery gray color. Color is controlled by varying the percent of tin in the alloy. To achieve the appearance of a chromium plate, the optimal tin-cobalt ratio in solution is 50:50. This ratio results in a plate that is 80 percent tin and 20 percent cobalt. Reducing the cobalt content of the plate below 17 percent results in a matte gray appearance.

Tin-Nickel Acid or Near Neutral: Tin-nickel alloy plating can be used as a replacement for decorative chromium plating for both indoor and outdoor applications because of its faint rose pink cast. This alloy is resistant to corrosion and tarnish and has good contact and wear resistance. Other advantages of this coating include excellent frictional resistance and ability to retain an oil film on its surface. Tin-nickel alloy plating solutions have a high throwing power, which enables the solution to function where plating chromium in deep recesses is a problem.

Chemical and Electrochemical Conversion: Chemical and electrochemical conversion treatments are designed to deposit a coating on metal surfaces that perform corrosion protection and/or decorative functions and, in some cases, to prepare for painting. Processes include anodizing, chromating, passivation, phosphating, metallic coating, and electropolishing

Anodizing: Anodizing differs from electroplating in two ways. First, the work piece is the anode rather than the cathode as in electroplating. Second, rather than adding another layer of metal to the substrate, anodizing converts the surface of the metal to form an oxide that is integral to the substrate.

Types of anodizing: Industry uses three principal types of anodizing: chromic acid anodizing (called Type I anodizing), sulfuric acid anodizing (called Type II anodizing), and hard coat anodizing, a combination of sulfuric acids with an organic acid such as oxalic acids (called Type III anodizing). Because of the structure, the

anodized surface can be dyed easily. These dyes are organic or organometallic and often contain chrome in the trivalent state. Whether the pieces are dyed or not, they need to be sealed. Sealing can be performed with hot water, nickel acetate, or sodium dichromate, depending on the required properties.

Alternative to chromic acid anodizing: Because of federal and state mandates being imposed on operations using hexavalent chrome, researchers have investigated the feasibility of substituting Type I anodizing with Type II sulfuric acid anodizing. Conversion from chromic acid to sulfuric acid anodizing is not a simple chemical substitution according to suppliers. The conversion requires a complete changeover of anodizing equipment and partial modifications to downstream waste treatment facilities. Replacement of the anodizing tank often is required because of the differences in acidity between sulfuric acid and chromic acid. Sulfuric acid anodizing processes also have different voltage and amperage requirements, necessitating replacement of the rectifier. The operating temperature of the electrolytic bath also is different for the two processes.

Chromating

Platers often use chromate coatings to minimize rust formation and to guarantee paint adhesion after anodizing aluminum parts. These coatings also are used over zinc and cadmium to simulate the appearance of bright nickel and chromium. Other applications include use as a coating over zinc or cadmium-plated parts to prevent the formation of white rust. Depending on the color, chromating takes place in a solution of chromic acid and additives. Although these baths contain hexavalent chrome, they are not electrolytic baths and, **therefore, do not generate the same level of mist/fumes of chrome electroplating or anodizing. Unfortunately, like chromium plating, chromating involves highly carcinogenic and toxic materials. If inhaled, chromate mists can eventually cause lung cancer.**

Alternatives of Chromating

Cobalt/molybdenum: conversion coating process uses an undisclosed proprietary formulation identified generally as cobalt- and molybdenum-based. The cobalt and molybdenum ions are much less hazardous than chromium and behave similarly. The coating does not have the ability to inhibit pitting corrosion as effectively as chromium, therefore, a second step is required to meet military specifications. The second step is an organic emulsion seal that enhances corrosion resistance and paint adhesion characteristics.

Passivation using molybdate and phosphate

Platers can use MolyPhos for passivation of electroplated zinc instead of chromate.

Zirconate conversion coating

Zirconium carbonate	55 grams/l
Nitric acid	10ml/l
PH	1.7

METHANE SULFONATE BATHS

Advantages:

- High solubility
- High conductivity
- Low toxicity
- Bio degradability

Pb/Sn solder bath,copper Ni,Sn,Zn,Ag, electroless nickel and copper.

Replacement of toxic Processes

- Cyanide by non cyanide plating processes
- Using trivalent chromium for plating and passivation
- Replacement of cadmium with zinc
- Use of hard electroless nickel for hard chrome
- Use of aqueous solvents based cleaners
- Resist use of nickel undercoat to gold plated artificial jewellery

Electroplating and surface finishing industry is always an industry, which has attracted environmental concerns from both within the industry and from external regulatory bodies due to discharge of large quantity of heavy metals from this category of industry and the bioaccumulation property of heavy metals. Hence it is the duty of the platers to protect the environment by adopting suitable eco friendly plating processes.

Section 7

Existing Wastewater Discharge Standards in India & Other Countries

7.1 Existing Standard in India

The standards for discharge of industrial wastewater are promulgated under the Environment Protection Act of 1984. These standards are generally based on concentration of specified pollutants, while some standards are load based. In case of wastewater from Electroplating operations, the existing standard is concentration based and is given in **Table 7.1**.

Table 7.1: Existing Wastewater Discharge Standard for Electroplating Industry

S.No.	Parameters	Concentration not to exceed, mg/l (except pH & temperature)
1	PH	6.0 to 9.0
2	Temperature	Shall not exceed 5 ⁰ c above the ambient temperature of the receiving body
3	Oil & Grease	10
4	Suspended Solids	100
5	Cyanides (as CN)	0.2
6	Ammoniacal Nitrogen (as N)	50
7	Total Residual Chlorine (as Cl)	1.0
8	Cadmium (as Cd)	2.0
9	Nickel (as Ni)	3.0
10	Zinc (as Zn)	5.0
11	Hexavalent Chromium (as Cr)	0.1
12	Total Chromium (as Cr)	2.0
13	Copper (as Cu)	3.0
14	Lead (as Pb)	0.1
15	Iron (as Fe)	3.0
16	Total Metal	10.0

Source: EPA Notification {S.O. No.393(E) dated 16th April, 1987}

These standards have generally been adopted by the State Pollution Control Boards and used to issue consent orders and for monitoring of quality of wastewater discharge. The Karnataka State Pollution Control Board also applies Air (Prevention & Control of Pollution) Act for Electroplating Units and requires the industries to use gas & fume collection and treatment from baths.

CPCB is reviewing the existing standards for electroplating industries, which has been published under CPCB COIND series. The new proposed standards shall include Aluminium, Tin, Fluorides, Phosphates, etc., and air emission standards in work zone area.

7.2 Discharge Standards in European Countries

7.2.1 General

Within the European Community, a number of directives apply to metal finishing industries. Directives are legally binding on member states but the individual member states may select their own legal and administrative means of implementation. The discharge standards in selected Countries are depicted in Table 7.2.

Table 7.2: Typical Discharge Values in Selected Countries

S. No.	Parameter	Sweden	France
1	Cadmium	0.1	0.2
2	Chromium (total)	1.0	2.0
3	Chromium (hexavalent)	0.1	0.1
4	Cyanide (free)	0.1	0.1
5	Cyanide (total)	1.0	1.2
6	Copper	1.0	2.0
7	Lead	1.0	0.2
8	Zinc	2.0	5.0
9	Nickel	1.0	5.0
10	Tin	1.0	2.0
11	Silver	1.0	-
12	Iron	2.0	5.0
13	Aluminium	2.0	5.0
14	Fluorides	-	15
15	Oil	-	5
16	Suspended Matter	10.0	15.0
17	COD	-	150
18	pH range	-	6.5 – 9.0

Source: UNEP, environmental Aspects of the Metal Finishing Industry, Tech report Series No. 1, 1993

7.3 Discharge Standards in USA

Under the provisions of the Clean Water Act, every facility discharging into a Publicly Owned Treatment Works or waterway must apply for a permit, which specifies what pollutants may be discharged and a schedule for compliance, monitoring and reporting must be established. The applicable regulation is 40 CFR 413. This regulation stipulates limits for specified pollutants e.g., metals, Cyanides and Total Toxic Organics (TTO). The limits for units engaged in electroplating of common and precious metals are in **Table 7.3**.

Table 7.3: US Pollutant Limits for Common Metals Facilities
(mg/l, maximum concentration for any one day)

S. No	Pollutant	Common Metals		Precious Metals	
		Limit for plants discharging less than 38,000	Limit for plants discharging = or more than 38,000	Limit for plants discharging	Limit for plants discharging

		litres / day	litres / day	less than 38,000 litres / day	= or more than 38,000 litres
1	CN	Available, 5.0	Total, 1.9	Available, 5.0	Total, 1.9
2	Pb	0.6	0.6	0.6	0.6
3	Cd	1.2	1.2	1.2	1.2
4	Cu	-	4.5	-	4.5
5	Ni	-	4.1	-	4.1
6	Cr	-	7.0	-	7.0
7	Zn	-	4.2	-	4.2
8	Total Metals	-	10.5	-	10.5
9	TTO	4.57	2.13	4.57	2.13
10	Ag	-	-	-	1.2

Note : - indicates limits not specified.

A comparison between Common and Precious metals standards shows that only Silver is introduced as an additional parameter. There are separate standards for Anodizing, Coating, Milling and Etching sub categories.

7.4 World Bank Standard

The World Bank issues guidelines for development projects assisted by them. In its Pollution Prevention and Abatement Handbook, issued in July 1998 the guidelines related to the Electroplating Industry recommend various specific measures.

Table 7.4: World Bank Discharge Standard of Effluent from Electroplating Industry

S. No.	Parameter	Maximum Value (mg/l, except pH)
1	PH	7 – 10
2	TSS	25
3	Oil & Grease	10
4	Arsenic	0.1
5	Cadmium	0.1
6	Chromium (hexavalent)	0.1
7	Chromium (total)	0.5
8	Copper	0.5
9	Lead	0.2
10	Mercury	0.01
11	Nickel	0.5
12	Silver	0.5
13	Zinc	2
14	Total Metals	10
15	Cyanides (free)	0.2
16	Fluorides	20
17	Trichloroethane	0.05
18	Trichloroethylene	0.05
19	Phosphorus	5

Source : World Bank, Pollution Prevention Handbook, July 1998