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Presentation paper*:
Environmental considerations in the Metal finishing Industry
of Asia and the Pacific Region

prepared to be presented at
Workshop/Seminar on Environmental Considerations for the Chemical, Metallurgical
and Engineering Industries in the Asia and Pacific Region.

United Nations Industrial Development Organization
Vienna



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Environmental Considerations in the Metal Finishing Industry
of Asia and the Pacific Region

The demand for natural resources and environmental amenities in the Pacific Region is bound to increase sharply for three reasons. First, the population which was 273 million in 1982 is expected to increase to 380 million in the year 2000.

Second, the expected annual growth rate of economic activity is at about 5 percent. This growth rate is likely to continue, doubling the demand on natural resources, ceteris paribus, every 15 years or so. Third, the process of production inevitably becomes more capital and technology intensive.

Consequently, pressure on the natural resources will continue to increase.

Prof. Dr. Emil SALIM, State Minister For Population and Environment, Indonesia, 30th October, 1987 /1/.



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CHAPTER I

I. INTRODUCTION

Metals surface treatment is a significant source of pollution, especially when compared to other manufacturing operations. Due to the toxicity of the many chemicals involved, and sometimes also due to the toxicity of the metals themselves, any release of by-product may cause serious damage to the environment.

Metal finishing involves a vast number of operations in which metals are cleaned, prepared, treated and coated. Intermediate operations too, are often performed in order to make surfaces receptive to a final coating. The coatings themselves are of various composition and consistency. A long history of widespread traditional plating techniques are exposed in this report.

It is well known that different Asian and Pacific Region countries encounter different environmental problems. The financing of cleaning up historic dump sites and more recent and persistent chemical spills has become an unacceptable burden on the public programs in industrialized countries. As environmental issues have become more complex, pollution control strategies have become more systematic and integrated. Preventive approaches rather than curative approaches have become more widely valued and appreciated. More responsibility for environmental control now tends to be taken on by the company, and practical contributions are expected of all operational and managerial personnel.

Japan^{/2/} has already begun a strong environmental policy through the Japanese Federation of Economical Organizations, "Keidanren". This agency has introduced legislation concerning its general environmental policy. It is the first general strategic maneuver made by Japanese industry to ameliorate environmental problems. The results of these environmental policies will be introduced at the UN Conference for Environment and Development in Brasil, in June of 1992. It should be noted that Keindaren is the first Economic Organization in the world which has taken this initiative. The principal points of Keidanren's strategie are as follows^{/2/}:

- 1- a general company's policy;
- 2- an interactive system;
- 3- the considering of the industrial effects on the environment;

- 4- the advancement of technical development;
- 5- a technological-transfer
- 6- emergency measures
- 7- public relations and education programs
- 8- community interrelation
- 9- overseas operation and exchange
- 10- contributions to environmental policy
- 11- taking direct action in care of the greenhouse effect

Keindaren has obligated industrial companies not only to abide by the national and local standards but also to have a R & D program in their directive and to use recycleable materials. In addition, these companies must publish environmental literature about their own products for their clients.

Gaishi Hiraiwa (President of Keidanren) noted that some companies were not in agreement with this project because of its restrictive policies. Nevertheless, Keidanren convinced these companies about the importance of this project^{/2/}.

11 MITIGATING THE IMPACT OF INDUSTRY ON THE ENVIRONMENT IN DEVELOPING COUNTRIES: ALTERNATIVE APPROACHES

International agencies responsible for promoting environmental quality in developing as well as some developed countries, currently propound the following philosophy of environmental management:

- a. adopt cleaner, waste minimizing technologies;
- b. recycle when above is impossible,
- c. when recycling is impossible, treat residues, effluent, and gaseous emissions;
- d. if all else fails, dispose of wastes in an environmentally sound manner.

Unfortunately, this philosophy is 'first world' centred. It assumes :

- that financial and human resources needed for acquisition, operation, maintenance, and repair of technology are accessible;
- that a regulatory systems is present which is equipped to enforce comprehensive laws and regulations designed to effectively control the environmental impact of industrial production;
- and that an industrial culture is present which places great importance on regulatory compliance.

The reality within many developing countries is quite different. A legal and regulatory structure may be in place but its resources are rarely adequate.

The accessibility of technology or the lack thereof also presents severe problems. Most developing countries are experiencing severe foreign exchange problems, and may only access advanced technology through bilateral or multilateral aid. This aid, if given is allocated in return for the acquisition of capital goods in which the technology is embodied. Unfortunately, the funds are rarely allocated for the essential parts required for repair and maintenance, or for often radical upgrading of knowledge and skills of plant operators.

As opposed to the traditional or popular culture, the industrial culture of developing countries remains less influenced by environmental concerns, whereas the industrial culture of other developing countries has found that in which environmental considerations weigh ever more heavily on the shoulders of company managers and directors. This is probably the result of a combination of expediency and perception: Direct costs are lower without pollution control equipment, and industrial output appears to have a greater foreign exchange earning potential than does clean river water or city air.

This is a brief and necessarily simplified statement of the position which is held by many bilateral and multilateral aid agencies which represent developing countries. It is, nevertheless, a sufficiently accurate description of the circumstances found in these countries, and suggests that the pre-eminence of adopting technologies which are still considered advanced in the Developed Countries, must remain a very long, long-term goal. In the meantime, there remains the problem of how to improve environmental management within the individual countries concerned. The 'alternative' approach toward improved environmental management is Good Housekeeping. It is supported by training, and alternative technologies (including waste minimization and maximization of recycling) should become an integral but long term target rather than first priority.

The term 'good housekeeping' when applied to an industrial process refers to a wide variety of steps:

- It ensures that individual inputs follow the process specifications;
- It assures that regular and proper maintenance is carried out;
- It ensures that the physical parameters of the process (temperature, pressure, levels of moisture or oxygen, for example) are followed according to the process specifications;
- And it ensures that a simple monitoring system is in place to enforce that these requirements are met continuously.

Training is essential to "Keeping a Good House". A well trained work force will operate a plant according to the design specifications, regardless of the vintage of the technology. It is also in the interest of the managers and owners to ensure that their plant is operated properly, because an efficient plant is more profitable.

The 'good housekeeping' approach toward environmental improvement has many commendable advantages:

- a. it can be implemented within the existing resource base of the company without any delay (except for training, when required);
- b. the company's benefits are immediate and visible, in terms of lower costs, less rejection of off-specification product and reduced waste disposal costs (where these are levied);
- c. the environmental benefits arise without need of an extensive, efficiently implemented and enforced legal and regulatory infrastructure, in terms of lower levels of wastes, effluent, and gaseous emissions;
- d. a national campaign to encourage better Housekeeping can be achieved with a very small input of resources.

1.2 SURFACE FINISHING

The term 'surface finishing' is imprecise, covering many operations, including:

- surface cleaning,
- surface preparation,
- surface coating,
- and other intermediate operations.

Surface finishing may have significant effects on human health and safety, and on the environment because:

- many chemicals used are toxic;
- some of the treated metals are toxic;
- work is usually carried out in a confined atmosphere;
- water is used extensively in all involved processes in the metal finishing industry.

The surface finishing industry is quite diverse, varying from large plants to small companies, with most of the output coming from the large plants. In many instances, as in that of the metal smelting and forming industry, surface treatment is simply one stage in a series of many. In other instances, as in the plating industry, the plating of metal or plastic articles is the only activity of the firm.

Because most firms in the industry are small, cash flow is typically a limiting factor for any expenditure decision, and profitability is low. Decisions to invest are difficult to justify, whether investments are for a new or established plant, or health and safety or pollution control measures.

Approaches for pollution control and for health and safety regulations include:

- improving Housekeeping in the plant;
- retrofitting processes;
- replacing chemicals of concern;
- using different processes;
- recovering and recycling post-process resources.

While discussing Pollution Control & Pollution Prevention, special attention should be given to:

- industrial processes, specifications;
- the emissions, effluent, and wastes produced;
- the health and safety, and environmental problems that the wastes present;
- waste minimization;
- new technologies;
- resource recovery;
- economic and other non-regulatory incentives to improve environmental, and health and safety management in the surface finishing industry.

The industry of surface finishing is a particularly appropriate choice of topic for this seminar from the point of view of industry in developing countries for a number of reasons:

1. The environmental impact of emissions, residues, and effluents from the industry is and will be highly significant if not mitigated.
2. It demonstrates the potential benefits of "good housekeeping" and of minor process modifications arguably better than any other industry.
3. The high proportion of small companies in the industry in developed countries means that the difficulties of introducing advanced waste minimization technologies is the greater, and that the benefit of an alternative, in-house approach to improved cost efficiency and waste reduction is more readily adopted.

2.0 INTRODUCTION

2.0.1 SURFACE FINISHING

* Surface finishing consists of various chemical and physical processes which change the surface (decorative), increase its corrosion resistance, or produce surface characteristics essential for subsequent operations (functional)^{*/3/}.

This report focuses on metal finishing. The Good Housekeeping approach as described above is, applicable however to other industries, although the process details obviously differ from industry to industry. The seminar will be of most use to UNIDO personnel if the the surface finishing industry is regarded only as a case study.

The types of processes we consider are:

Mechanical processes	sandblasting grinding barrel finishing polishing and buffing
Chemical processes	solvent cleaning alkaline cleaning acid pickling, etching, bright dipping salt bath cleaning quenching`cyaniding` chemical conversion coating `electroless` and immersion plating
Physical processes	plastic and paint coatings hot dip coating
Electrolytic processes	electrocleaning electropolishing anodising electroplating

These processes are outlined below, with more emphasis given to those which present more severe environmental, or health and safety problems.

21 DESCRIPTION OF THE INDUSTRY

21.0 Mechanical Processes

21.1 Sandblasting.

Metal parts are frequently cleaned and given a smoother surface finish by sandblasting. Aluminium oxide and silicon carbide, rather than sand, are usually used as abrasives in dry blasting the workpiece. In wet blasting, a slurry consisting of the abrasive, wetting agents, rust inhibitors and anti-settling agents. The abrasive must be disposed of as solid waste when significant impurities accumulate. Following sandblasting the rinse waters may contain some abrasive, metal scale and oil.

21.2 Grinding.

Grinding operations require the use of lubricating oils, wetting agents, rust inhibitors and other additives applied to an abrasive wheel or belt. An oily sludge containing ground metal is collected for disposal. Although grinding crates no waste water, it may add oil, grit, and metals to solid or liquid waste streams.

21.3 Barrel Finishing.

Barrel finishing, or tumbling, is used to clean, deburr and polish metal, ceramic and plastic substrate. The workpieces are loaded into a rotating barrel with abrasives and one or more additives such as alkaline cleaners, anti-rust agents, acids or oils. A variation of the rotating operation is vibratory finishing, during which the load may simply be oscillated or may undergo both actions simultaneously. The parts are subsequently rinsed; oils, chemical additives, grit, common metals, and cyanide may enter the effluent stream. The process solution is generally discharged after of each production run.

21.4 Polishing and Buffing.

Polishing and buffing involves the application of an abrasive material to a rotating wheel which contacts the workpiece. Greases, oils, soaps and other compounds are used in the process. Along with fine metallic grit, these compounds enter wastewater or solid waste during area cleanup. Fine metal and abrasive dust is also released in to the atmosphere of the work area and into the outside environment unless containment equipment is installed.

TABLE 1: OF MECHANICAL PROCESSES IN THE METAL FINISHING INDUSTRY INCLUDING CHEMICALS USED AND ENVIRONMENTAL IMPLICATIONS

DESCRIPTION MATERIALS USED, WASTE SOURCES, EMISSIONS, COMMENTS

GRINDING

cutting by means of grinding materials

materials to be finished: mostly Fe, Al^{/14/}
grinding material: diamond, sand, flint, quartz garnet, pumice, emery, corundum, aloxite, Siand W-carbide, boron compounds, Si-coumpounds as additives for special cutting purposes^{/4, 6, 14/}
cementing substances: ceramics, minerals, organic stuff (resins, rubber, polyvinyles)^{/14/}
remark: rubber only to be used with low grinding temperatures^{/14/}

ENVIRONMENTAL IMPACT:

emissions into air: vapors from heat reactions;
emissions into air, water or ground: dusts of polish, binder, metals, metal oxides (especially Al, Fe, Cr), grinding material (as mentioned), toxic Si-compounds, cotton lintners, fibres, greases, oils, waxes, cooling agents with contaminations of abraded particles^{/6, 10, 11, 14/}

DESCRIPTION MATERIALS USED, WASTE SOURCES, EMISSIONS, COMMENTS

POLISHING BRIGHTENING

mechanical polishing

materials to be finished: metals
polishing materials: waxes, greases, oils, diatomite, Vienna or French chalk, oxides of Si, Al, Fe^{/14, 15/}
remark: polishing temperature 500 to 1000 °C at the metal surface^{/11/}

ENVIRONMENTAL IMPACT:

emissions into air, water or ground: carbonates, silicates, borates, phosphates, chromates, soaps, surfactants, sequestering agents, rust inhibitors, tartrates, ammonium salts, anti-tarnishing agents^{/6/}

2.2.0 Chemical Processes

2.2.1 Solvent-Cleaning.

Solvent cleaning is a widely used process which removes heavy surface oil and grease. A solvent is placed in a boiling chamber. Escaping vapours rise above the liquid and condense on overhead cooling coil. The condensed liquid is returned with two cleaning mediums, i.e., a liquid phase and a vapour phase. In some cases, parts are not immersed in the liquid because the condensed vapour is sufficient for cleaning. Some cleaning may be done simply by immersing the workpiece in cold solvents

Common solvents used in liquid and vapour cleaning are chlorinated hydro-carbons such as 1,1,1-trichloroethane, trichlorethylene, perchlorethylene and methyl liquid cleaners. Pure solvent may be separated from the oil and from the oily sludge build-up by distillation then reused. Smaller amounts of solvent, when spent, are often simply discarded into the sewage system. Irritating and hazardous solvent fumes may escape into the plant and outside atmosphere.

2.2.2 Alkaline-Cleaning.

Alkaline spray and soak cleaning are major sources of contaminated wastewater because of the frequency with which these operations are used in the finishing sequence. Many unit operations require a cleaning stage immediately before or after the operation or both.

The cleaning agents are water-soluble combinations of alkalis and chemical additives, which are specific to the nature of the surface to be cleaned and to the soil to be removed. There are no less than 700-surface cleaning agents commercially available. As well, many additives are proprietary, making it difficult to categorize the ingredients of the cleaning agents.

The cleaning solutions vary in alkalinity and accumulate saponified greases (soaps), emulsified greases, small amounts of base metals, complexed metal and solids. Baths are discharged when spent, and generate substantial quantities of sludge when treated. One or more rinses always follow cleaning and small amounts of cleaning agent end up in the wastewater.

Attention should be given to open tanks that may release polluting mists and fumes.

2.2.3 Acid-Pickling/Etching/Bright-Dipping.

Acid pickling removes any alkaline residue left from cleaning and any scale and rust. The most common acids used are hydrochloric, sulphuric, nitric, chromic and phosphoric.

Acid solutions may have concentrations of up to 50-percent and, for some applications, the acid may be heated. Usually the workpiece is immersed briefly in the acid bath but recently some spray operations have been introduced. In spite of the use of chemical inhibitors, a significant amount of metal from the workpieces and the plating racks is dissolved causing these acid baths to have a short life and to be di-

scharged frequently is necessary. Rinse waters containing dragout from pickling baths contribute metals, acids, oils, wetting agents, detergent and additives to plant effluent waters. Open acid tanks emit noxious and hazardous chemical fumes which require collection and treatment.

Etching baths are a combination of acids that dissolve the surface of a metal or plastic workpiece in a controlled manner, often in order to produce a specific design configuration and condition. This surface treatment is also required in preparation for finishes such as the electroless plating of nickel or copper on printed circuit boards, or for improving coating adhesion, particularly on plastics. Many acids, including chromic acid, are used in etching baths and contribute to waste production when discharged. Waste consists mainly of the dissolved materials (plastics or metals), spent acids, and the rinse water associated with the etching process.

A related treatment is the stripping of defective electrodeposits by immersing the workpiece in an acid bath similar to an etching bath. In some cases, electrolytic stripping is used to accelerate the metal removal process.

Bright dipping is a process used to remove oxides and to prepare the surface of copper, copper alloys, aluminium and stainless steel for other finishes. The waste produced is similar to that of pickling and etching, consisting of a variety of spent acids, base metal and rinses.

2.2.4 Salt-Bath-Pot-Cleaning.

Molten baths of sodium hydroxide, sodium cyanide and other chemical additives are used to remove rust and scale from metal. Sludge is produced and batch discharges of the salt bath occur regularly. Rinse waters contain removed metal, cyanides and burned oil residues.

2.2.5 Quenching/Cyaniding.

Quenching baths are either:

1. pure oil.
2. oil with chemical additives.
3. water-oil emulsions.
4. brine solutions, or
5. water based solutions, depending on the cooling characteristics desired.

Brine quenches may contain sodium chloride, calcium chloride, sodium hydroxide, sodium carbonate, hydrochloric or sulphuric acid. Water and water-based quenching and rinsing solutions may contain dissolved salts, soaps, alcohols, oils, emulsifiers and slime. Molten cyanide baths are used in heat treating and carbonitriding. These baths are usually composed of sodium and other inert salts.

Rinse water and quenching bath discharges contribute to liquid effluents. Spent baths include some reactive chemicals as well as any metal scale, oxide and oil from the workpieces. This waste may also form a sludge requiring periodic disposal.

2.2.6 Chemical Conversion Coating.

Chromiting, by means of a chemical reaction, produces a thin chromete coating on zinc, cadmium, aluminium, copper or brass that provides corrosion protection. Chrom coatings may also alter colour and luster and act as a base for paints. The contents of chroming baths are usually chromic acid, dichromate, and active organic or inorganic compounds. In these acidic baths, both hexavalent and trivalent chromium are used and may enter the waste stream either through rinse water or discharge of spent solutions.

Phosphating is a related process which provides steel or iron with a superior bonding surface for paints, waxes, oils and lubricants and also improves metal forming capabilities. Phosphates of zinc, iron, manganese and calcium in phosphoric acid make up the bath. Other metal salts and additives may be present. Phosphate coatings are usually "sealed" by a mild chromic acid rinse.

Colouring baths, used to blacken phosphate conversion coatings, may contain copper, nickel, lead, iron, zinc or arsenic in a variety of solutions, the ingredients of which are invariable proprietary. This chemical process produces a metal oxide that is highly resistant to heat and fading.

The waste produced from all chemical conversion coating operations is contained in rinse waters and bath discharges of process baths.

2.2.7 Electroless and immersion plating.

Electroless, or autocatalytic is used to apply nickel, cobalt, palladium, platinum, copper, gold, silver and alloys of these metals onto another metal or plastic. The metal being deposited acts as the catalyst while it is being reduced from its ionic state in solution to form a deposit. Because the deposit is its

own catalyst, the thickness of the coating continues to increase at an even rate. Autocatalytic plating is commonly used in plating nickel or copper on plastics, such as for printed circuits boards, or in providing a metal base on plastic to prepare it for electroplating. Plastic and other nonconductors must be etched prior to electroless plating.

Immersion plating applies a metallic coating without the use of an electric current. The metal in solution is deposited upon on the work-piece by displacing the basis metal.

Some autocatalytic and immersion plating baths are listed in Table 3. The wastes generated immersion and autocatalytic plating consist of rinsewater and process bath discharges. Immersion process baths contain metal salts, chromates, dissolved base metal, alkalis, and cyanide or ammonia complexing agents. Autocatalytic baths contain the coating metal, sodium hypophosphite, formaldehyde or other reducing agents and various complexing and chelating agents.

TABLE 2: OF CHEMICAL PROCESSES IN THE METAL FINISHING INDUSTRY INCLUDING CHEMICALS USED AND ENVIRONMENTAL IMPLICATIONS

DESCRIPTION MATERIALS USED, WASTE SOURCES, EMISSIONS, COMMENTS

PRECLEANING, STRIPPING

chemical elimination of rust, tinder, and oxide layers

baths for iron and steel: HCl, H₂SO₄, H₃PO₄, alkaline derusting salts (caustic soda, gluconates, heptonates, NaCN^{/6/})

-stainless steel: HNO₃, HF^{/6/}

-copper and alloys: HNO₃, H₂SO₄, accelerators, CrO₃, NaCN, Na₂Cr₄^{/6/}

-aluminium and alloys: H₂SO₄, HNO₃, HF, caustic soda^{/6/}

-magnesium and alloys: H₂SO₄, HNO₃^{/6/}

ENVIRONMENTAL IMPACT:

emissions into air, water or ground: sulphates, nitrates, dichromates, fluorides of Fe, Cu, Al, Ni, Mg^{/14/}

FINAL CLEANING

Degreasing:
-chemical

materials to be finished: metals

organic cleaner: tri- and perchloroethylene, ethylene, gasoline, kerosene, solvent naphtha, ethanol, emulsifying agents, amines, surfactants, dichloromethane, diethyl ether, glacial acetic acid, carbon tetrachloride^{/5, 6, 14, 15, 16/}

inorganic, alkaline cleanser: NaOH, KOH, NaCN, Na₂CO₃, silicates, alkaline phosphates, phyrophosphates, carbonates, detergents, surfactants, soaps, Na-hexametaphosphate, borax^{/6, 14, 15, 16/}

removed substances: mineral oil, paraffin, waxes, colophonium

remark: substitution of cyanide cleaning by KH-tartrate is possible

ENVIRONMENTAL IMPACT:

emissions into water or ground: bath materials, removed substances

TABLE 2: (Cont'd)

DESCRIPTION MATERIALS USED, WASTE SOURCES, EMISSIONS, COMMENTS

FINAL CLEANING (Cont'd)

-electrolytic (supporting chemical degreasing)
 ENVIRONMENTAL IMPACT:
emissions into air: H₂, O₂, (decomposition of H₂O)^{14/}

-neutralisation neutralisation baths: acids, alkaline solutions^{14/}
neutralisation and pickling baths: alkaline cyanides, KH-tartrate^{14/}
 ENVIRONMENTAL IMPACT:
emissions into water or ground: bath materials

SURFACE ACTIVATION

-pickling bath for -iron and steel: HCl, H₂SO₄, H₃PO₄, alkaline derusting salts (caustic soda, gluconates, heptonates, NaCN^{6/}
-stainless steel: HNO₃, HF^{6/}
-copper and alloys: HNO₃, H₂SO₄, accelerators, CrO₃, NaCN, Na₂CrO₄^{6/}
-aluminium and alloys: H₂SO₄, HNO₃, HF caustic soda^{6/}
-magnesium and alloys: H₂SO₄, HNO₃^{6/}
liquid and solid emissions: sulphates, nitrates, dichromates, fluorides of Fe, Zn, Cu, Al, Ni, Mg^{6, 14, 15/}
 ENVIRONMENTAL IMPACT:
emissions into air: acid mists and vapours^{16/}

-blasting (see above under PRE-CLEANING)

2.3 Physical Processes

2.3.1 Plastic and Paint Coatings.

Plastic powder coatings are increasingly being used in a number of applications because of the ease of transporting the dry powder, and because the absence of harmful solvents and odours. The plastic is electrostatically charged and sprayed onto the oppositely charged workpiece. The coating is then thermally fused in an oven and excess powder is recycled. The workpiece is initially prepared by one of the surface preparation and cleaning processes and is usually phosphated.

Industrial paint is applied in spraying booths or by dip coating. Mechanical surface finishing, cleaning or chemical conversion coating prepare the surface.

TABLE 3: ELECTROLESS AND IMMERSION PLATING BATHS

ELECTROLESS PLATING (Autocatalytic)

Nickel	nickel chloride nickel sulphate sodium hypophosphite sodium hydroxyacetate acetic acid lactic acid molybdic acid propionic acid
Copper	copper sulfate sodium potassium tartrate sodium hydroxide sodium carbonate formaldehyde versene-T
Gold	potassium gold cyanide potassium cyanide potassium hydroxide potassium borohydride
Silver	silver cyanide sodium cyanid sodium hydroxide dimethylamine borane thiourea

IMMERSION PLATING

Tin	on aluminium: sodium stannate
	on copper : tin chloride sodium cyanide sodium hydroxide
	on steel : stannous sulfate sulphuric acid tin chloride
	on zinc : tin chloride

Electrocoating is an electrolytic process used to deposit an organic material, such as paint. A direct current sent through an alkaline bath causes the pigment particles to migrate towards the cathodic workpiece.

The waste water from coating operations contains scrubbing and rinse waters, any solvents, pigments, resins, common metals, additives present in the coating, and built up impurities and solids. Waste plastic or paint form a sludge which is disposed of separately. Volatile solvent fumes are hazardous to both health and environment and must be contained.

2.3.2 Hot Dip Coating.

Metal may be physically coated by being dipped in a molten metal bath. An alloy of the two metals is formed at the contacting surface and binds the metal coating to the substrate. Precleaning and a flux dip are often required to prepare the metal surface for dipping. Quenching follows hot dip coating. Aluminium, lead and tin are sometimes applied in this process for decorative and protective functions. However, hot zinc coating, also called galvanizing, has many industrial applications and is the most commonly used. A major use is the galvanizing of steel strip to impart corrosion resistance.

No waste is generated during the actual hot dip coating operation but rinse waters from precleaning and quenching may contribute common metals to effluent with problems and quantities similar to electroplating operations.

2.4 Electrolytic processes

2.4.1 Electrocleaning.

Electrocleaning removes the final traces of soil, and chemically activates the metal surface for plating. The alkaline bath, similar to that used for soak alkaline cleaning, is composed of caustics, wetting agents, buffering agents, dispersants and other chemicals. As a 3- to 12-volt direct current is applied, the cathodic workpiece repels negatively-charged colloidal soil particles and hydrogen gas is produced, creating a scouring action. The current may be reversed, causing the workpiece to become anodic and oxygen gas to be produced. The positively-charged workpiece will now repel metal ions and metal smut. Whether a direct, reverse or periodically reversing current is applied depends upon the base metal and the soil to be removed. Nickel and nickel alloys must be cleaned cathodically, for example.

The alkaline bath must be discharged when an excessive soil load has accumulated. A rinse always follows electrocleaning and the effluent contains alkaline cleaners plus soil and metal residues.

2.4.2 Electropolishing

Electropolishing produces an excellent, smooth, pit-free surface, particularly on stainless steels. The workpiece is the anode. Ferrous alloy and copper workpieces use phosphoric or sulphuric acid or both as the electrolyte, the acid proportions are variant upon on the type of metal. Electropolish processing varies in duration from two to seven minutes.

Rinsing is necessary and adds acids, metals, soil and oil to the effluent. Batch discharge of the process acids is required periodically, resulting in a large volumen of sludge.

2.4.3 Anodizing.

In anodizing, the workpiece acts as the anode and a thin oxide coating is formed on the surface. Most anodizing is performed on aluminium, although other metals, such as magnesium, are also treated. Anodic coatings protect against corrosion and abrasion and produce a base for many colouring and decorative effects. Variation in coating thickness and weight is controled by bath temperature, type, time and voltage.

Sulphuric acid at a 12 to 25 percent concentration is an inexpensive and easily controlled 'all purpose' electrolyte for anodizing. Coating thickness may range from 2.5 to 30 μm . Chromic acid anodic coatings are opaque and are often used as a base for paints, particularly in military applications. A bath of 3 to 10% chromic acid applied for about 30 minutes can form an oxide coating of up to 10 μm thick. Other acids may impart desired porosity, hardness or other surface characteristics. A seal, such as nickel acetate, is required after anodizing.

Wastewater is generated from both process and sealing bath discharges, and from associated rinse waters containing base metal, chromates, and colouring organics and dyes.

2.4.4 Electroplating

Electroplating is the electro-deposition of a thin metallic coating upon the surface of an object to provide corrosion protection or a decorative finish, or to otherwise affect the appearance and properties of the surface. Metal ions are supplied by the dissolution

of metal anodes or the addition of metal salts to the solution. The positive metal ions migrate toward the cathodic workpiece and adhere to its surface. The workpieces are usually suspended on a rack or loaded into perforated barrels.

Hundreds of electroplating solutions may be used depending on the metals involved, results desired, and costs. Recent environmental concerns have created even more plating bath variations which omit or reduce such constituents as chrome, cyanide and organic additives. As with most surface finishing processes, air emissions may contain hazardous substances that also require collection or treatment or both. The more common electroplated metals and their electrolyte solutions are listed in Table 4.

Nickel plating is an important process in the metal finishing industry because it is so widely used for household articles, appliances, automobiles, furniture, sporting equipment and so on. Nickel adds decorative and protective qualities and is part of the standard combination coating of copper-nickel-chromium on zinc steel and brass, die castings.

Nickel is electroplated from baths containing nickel sulphate, nickel chloride and boric acid. This bath has been the basis of nickel-plating operations since 1916. The emergence of brighteners and semi-brighteners removed the need for buffing decorative finishes and have gained wide use. Cobalt plating, also known as black nickel plating, was developed when nickel anodes were not readily available. It does not offer any advantages over nickel and is more expensive.

Hard chrome plate is an industrial finish applied primarily to resist wear or to restore worn parts. Decorative chrome plate is a thin top-coat, usually over nickel plate. A dissolved chromium salt, hexavalent form, is always the source of chrome in plating baths because soluble chrome anodes are not practical. In the future, hexavalent chrome may be replaced by the less toxic trivalent form. However, this does not produce the same finish.

The copper cyanide process has the broadest application and is often used in conjunction with nickel and chrome plate. On active metals such as zinc and steel a copper cyanide strike is necessary. Acidic copper baths, such as the copper sulphate bath, have a cost advantage over cyanide baths and are more acceptable environmentally but they cannot replace the cyanide baths for many applications. The copper pyrophosphate bath is important to the electronics industry for plating through-holes in printed circuit boards. This bath is non-toxic although it does contain phosphates.

TABLE 4: ELECTROPLATING BATHS

NICKEL

Bright:	nickel sulphate nickel chloride boric acid sulphonic acids sulphonamides	Semi-bright:	nickel sulphate nickel chloride boric acid
Acid:	nickel sulphate nickel chloride boric acid	Black:	nickel chloride ammonium chloride sodium thiocyanate sodium chlorid

CHROMIUM

Acidic:	trivalent chromium chloride chromic acid sulphuric acid fluorsilic acid
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COPPER

Cyanide:	copper cyanide complex sodium cyanide potassium cyanide sodium hydroxide potassium hydroxide	Pyrophosphate:	copper pyrophosphate potassium hydroxide ammonia
Sulphate:	copper sulphate sulphuric acid		

ZINC

Cyanide:	zinc cyanide sodium cyanide sodium hydroxide	Sulphate:	zinc sulphate aluminium sulphate sodium acetate glucose or licorice
Chloride:	zinc chloride hydrochloric acid ammonium chloride potassium chloride		

BRASS

copper cyanide zinc cyanide sodium cyanide	sodium carbonate ammonia
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TABLE 4: ELECTROPLATING BATHS (CONTD)

TIN

<p>Alkaline: nickel sulphate potassium stannate potassium hydroxide sodium hydroxide</p>	<p>Chloride: stannous chloride nickel chloride ammonium fluoride ammonium bifluoride sodium fluoride hydrochloric acid</p>
<p>Acid: stannous sulphate stannous fluoborate sulphuric acid phenolsulphonic acid fluoboric acid</p>	

CADMIUM

<p>Cyanide: cadmium cyanide cadmium oxide sodium cyanide sodium hydroxide</p>	<p>Acid: cadmium fluoborate ammonium fluoborate boric acid fluoboric acid</p>
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GOLD

potassium cyanide
potassium gold cyanide

SILVER

<p>silver cyanide potassium/sodium cyanide potassium/sodium carbonate</p>	<p>potassium hydroxide potassium nitrate carbon disulphide</p>
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LEAD

<p>lead fluoborate fluoboric acid</p>	<p>boric acid hydroquinone</p>
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IRON

<p>ferrous sulphate ferrous chloride ferrous fluoborate calcium chloride</p>	<p>ammonium chloride sodium chloride boric acid</p>
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Cadmium is a moderately expensive metal compared to zinc. Although it offers superior corrosion resistance to alkalis and to marine atmospheres, its toxicity and cost discourage its use. A cyanide bath is commonly used to plate cadmium. Acid baths have been developed to avoid the waste problems involved but the operating conditions required and the deposit quality are not as suitable as with the cyanide bath.

Zinc electroplating is widely used where controlled thicknesses are required for corrosion protection and for decorative appeal. Conventional zinc cyanide baths create environmental problems and, as a result, acidic potassium baths and alkaline zinc baths are being used more widely. The zinc sulphate process is used by steel companies on strip plating lines.

Tin plate is used in the food industry for tin foil and tin cans, for food handling equipment, and in the electronics industry. Various plating baths are available, the choice being determined by the end use of the product.

TABLE 5: OF ELECTROLYTIC PROCESSES IN THE METAL FINISHING INDUSTRY INCLUDING CHEMICALS USED AND ENVIRONMENTAL IMPLICATIONS

<u>DESCRIPTION</u>	<u>MATERIALS USED, WASTE SOURCES, EMISSIONS, COMMENTS</u>
SURFACE PREPARATION	
electrolytic and chemical polishing and brightening	<u>materials to be finished:</u> metals <u>polishing baths:</u> perchloric, nitric, acetic, phosphoric, sulphuric, chromic acids, glycerine, aniline, arsenates ^{/3, 14, 15, 9/} <u>neutralisation:</u> alkaline baths ^{/9/}
PRECLEANING, STRIPPING	
electrolytic descaling	<u>baths:</u> H ₂ SO ₄ , HCl, H ₃ PO ₄ , NHO ₃ , HF, inhibitors (e. g. hexamethylenetetramine, thiourea, dibenzyl sulphoxide) ^{/6, 14/} . <u>remark:</u> recycling of baths (ion exchange or salt precipitation by intermediate cooling) ^{/6, 14/}
ENVIRONMENTAL IMPACT:	
<u>emissions into air:</u> H ₂ .	
<u>emissions into water or ground:</u> Metal salts ^{/6, 14/} .	
ELECTROCHEMICAL DEPOSITION	
electroplating:	<u>electrolytic solutions:</u> acids, alkalines, salts ^{/13/} <u>buffer:</u> NH ₄ OH/HCl, acetic acid/Na-acetate ^{/13/}

TABLE 5: OF ELECTROLYTIC PROCESSES IN THE METAL FINISHING INDUSTRY INCLUDING CHEMICALS USED AND ENVIRONMENTAL IMPLICATIONS (Cont'd)

DESCRIPTION MATERIALS USED. WASTE SOURCES. EMISSIONS. COMMENTS

ELECTROCHEMICAL DEPOSITION (Cont'd)

-copper plating	<p><u>baths:</u> $\text{CuSO}_4/\text{H}_2\text{SO}_4$, $\text{Cu}(\text{BF}_4)_2/\text{HBF}_4/\text{H}_3\text{BO}_3$, alkaline baths of CuSO_4, wetting agents: $\text{CuCN}/\text{NaCN}/\text{KCN}$ with alkali carbonates and hydroxides, Na-K-tartrate; hydroxides, sulphides, NaCNS (brightening agent); $\text{Cu}_2\text{P}_2\text{O}_7$, $\text{K}_4\text{P}_2\text{O}_7$, $(\text{NH}_4)_2$-oxalate, NH_4OH, KNO_3/13, 15, 16/ <u>polishers:</u> thiourea, gelatin, cellulose, organic sulfonic acids/13/ <u>bath filtration:</u> asbestos materials, charcoa/13/ <u>remark:</u> floating bodies, foam or liquid cover reduce cyanide volatilisation/13, 15/; replacement of cyanide by pyrophosphate baths are possible/13/ ENVIRONMENTAL IMPACT: <u>emissions into air, water or ground:</u> cyanides (vapour, waste water, sludge), H_2, Cu-, Fe-, Al-salts/13/</p>
-nickel plating	<p><u>baths:</u> NiSO_4, NiCl, H_3BO_3, Ni-citrate, organic wetting and polishing agents (e. g. cumarine, H_2O_2, emulsifier (inhibits reflecting surfaces)/13, 15, 16/ <u>surface hardening bath:</u> NiSO_4, NH_4Cl, NiCl_2, $(\text{NH}_4)_2\text{SO}_4$, H_3BO_3, Ni-acetate/13, 15/ ENVIRONMENTAL IMPACT: <u>emission into water or ground:</u> bath chemicals</p>
-chrome plating	<p><u>baths:</u> CrO_3, H_2SO_4, Cr_2O_3, HF, H_2SiF_6, Na_2SO_4, Cr_6^+ (as sulphate, chloride, fluoride, nitrate salt)/13, 15/ <u>catalyzer:</u> SrSO_4, K_2SiF_6/13/ <u>emissions into air:</u> chromic acid vapour, H_2, O_2/5, 13/</p>
-zinc plating; cadmium plating; silver plating and metallisation of plastics see /3/	

25 Waste Stream Generation and Characteristics

Surface finishers produce and discharge a variety of waste streams including process wastewaters, spent process solution, sludges and air emission. The metal finishing processes that generate these discharges and emission are shown in Table 6.

2.5.1 Wastewaters.

For proper plating to occur, the parts must be clean and free of contamination from previous processes. Therefore, considerable quantities of raw water (or demineralized) are used to rinse the parts. Depending on the process for which the rinsing takes place, the wastewater produced may be acidic or alkaline and may contain particular metals or combinations, solvents or cleaning solutions, and/or particulates (dirt).

TABLE 6: WASTE STREAM GENERATION AND CHARACTERISTICS

Processes	Wastewaters						Air
	Metal	Chromium	Cyanide	Oils	Solvents	Wastes	Emmissions
Deburring	X	X	X	X		X	X
Polishing	X			X		X	X
Solvent Cleaning	X			X	X	X	X
Alkaline Cleaning	X		X	X	X	X	X
Pickling	X	X					X
Etching	X	X					X
Bright dipping	X	X					X
Salt bath descaling	X		X	X		X	
Quenching	X		X	X		X	
Chromating	X	X					
Phosphating	X	X					X
Passivating	X	X					X
Plastic coating					X	X	X
Paint coating					X	X	X
Hot dip coating	X						X
Electroless plating	X	X	X				X
Anodizing	X	X					X
Electropolishing	X						X
Electroplating	X				X	X	X
Electrocleaning	X		X	X	X	X	X

Another source of wastewater contamination comes from floor drains. Often, due to poor housekeeping, plating solution is allowed to drip as the rack or barrel is passed from tank-to-tank, and this solution subsequently finds its way into the plant's sewer system.

2.5.2 Hazardous Wastes and Sludges.

Several waste streams, including spent process solutions and sludges, are considered 'hazardous'. Hazardous wastes are those which, due to their nature and quantity, are potentially hazardous to human health and/or the environment and which require special disposal techniques to eliminate or reduce the hazard. Any substance or mixture being discarded is considered hazardous if it is flammable, carcinogenic, toxic, corrosive, explosive or meets other criteria developed by a federal-provincial working group. Table-6 summarizes the types of wastes generated by surface finishers and Appendix I lists the hazardous wastes recognized in the Transportation of Dangerous Goods Act (TDGA)^{9/}. Spent process solutions include:

- a) acidic waste from pickling, etching, bright dipping and electro-polishing,
- b) alkaline cleaning baths and electrocleaning baths,
- c) solvent degreasing waste,
- d) salt bath descaling solution, and
- e) spent baths themselves when they can no longer be rehabilitated.

The acidic waste contains a high level of dissolved metals, oils and suspended. Acids contained in the spent liquors or wastewaters, if discharged to sewer, can corrode the sewer line and damage municipal treatment facilities. Alkaline discharges have similar undesirable characteristics and effects. The large number of different compounds and additives in cleaning solutions often make recovery of metals or chemicals from the spent solutions impractical.

Solvent waste contains soil and oily buildup. This waste can interfere with sewage pumps, pH sensors and other effluent treatment equipment. Solvents themselves are toxic and classified as hazardous (Appendix I). Oily waste is composed of free oil, emulsified oil, and grease. Many additives and organic priority pollutants are soluble in hydrocarbons and are found in the oily layer of cleaning waste. Oils affect the odour and taste of water and are harmful to aquatic life. A moderately sized surface finishing operation will generate about 5m³ of solvent and oily waste annually. Solvents and oils should be separated from aqueous waste and recovered by distillation (if feasible) or suitable disposed of.

Spent plating and coating solutions are generated during electropolishing, electroless plating, hot dip coating, anodizing and chemical conversion coating operations. These wastes, and the relating rinsewaters, may be acidic or alkaline and may contain hexavalent and trivalent chrome, cyanide and other toxic compounds.

A number of metal finishing operations leave sludges on the bottoms of plating bath tanks. Large amounts of sludge are also formed during cleaning, painting and effluent treatment. Sludge from effluent treatment is only one to five percent solids and can be dewatered to reduce its volume. Sludges usually contain hazardous materials which could upset the municipal treatment plant if discharged to sewer.

CHAPTER III

3. IMPROVING METAL FINISHING TECHNIQUES IN REGARD TO ENVIRONMENTAL PROTECTION

3. INTRODUCTION

In view of the many possible sources of pollutants, and their multiple origins, a systematic, organized approach to pollution control is required in the industry. The selection of process technologies that achieved an intrinsically low rate of waste generation is a vital part of such an approach. Additional treatment technology to reduce the effect of the remaining residues is a subsequent step. Recycling and recovery are usually included within these two areas of consideration.

Considerable economic advantages can be expected to accompany the the environmental benefit that flows from such a systematic approach to pollution control. The application of more advanced levels of technology can improve process control so as to achieve:

- efficient use of raw materials;
- decrease in rinsewater consumption;
- decrease in the consumption of reagents for effluent treatment;
- decrease in the size of effluent treatment facilities;

Many improvements will of course require an initial investment, such as new equipment (cost, setting up time, extra floor space), retraining of staff, possible higher energy consumption, and extra supervision. Nevertheless, the environment benefits can be substantial, and even from a purely economic point of view, the resulting improvements in through-put and product quality are often enough to justify investments in cleaner processes.

Every plating shop needs to evaluate its own situation, so as to be able to select the best package of measures. This evaluation should include: consumption of process chemicals, water and energy, assesment of the production methods in use from the standpoint of environmental impact, and the need and options for waste treatment and disposal.

For most establishments, a proper process control laboratory will help in:

- control of finishing processes within narrower and lower operating ranges. Lower operating ranges means savings in chemicals dragged out, reduced need for treatment, and less sludge for disposal;
- trouble shooting to reduce rejects caused by out-of-control situations;

- efficient operation of treatment baths, determination of dumping frequencies by test rather than habit, control of additives to processing baths;
- determining effectiveness of treatment.

3.1 MINIMIZING EFFLUENTS

Both the volume and strength of effluents are important in regard to the input on environment. As well as having a greatly diminished pollution potential, there is a concomitant saving in requiring a smaller effluent treatment plant. A number of effluent reduction options are discussed below.

3.1.1 Drainage and Dragout

Most of the contaminants in rinses come from the dragout of chemicals when work pieces (and the work carriers) are transferred from the treatment bath to the rinse tank. Volume of dragout depends on the drainage procedure, in particular:

- the speed of withdrawal;
- the shape of the work pieces;
- details of barrel perforations;
- the dripping time;
- the concentration of the bath chemicals;
- the viscosity of the bath;
- the temperature of the bath;
- the position of the work piece on the rack.

The reduction in dragout is a particularly useful first step to pollution reduction as substantial benefits can be achieved for almost no additional investment. The following suggestions should be helpful in minimizing dragout.

If barrels are used for the rinsing operation, they should be immersed twice in the rinse tank, with a complete rotation over the tank between immersion to improve drainage.

Barrels create more difficulties than racks because of entrapments in and on the barrel itself. Barrels containing simple parts that do not collect solutions should not normally be rotated during drainage, since rotation will hold the solution on the surface of the pieces. However, rotation of barrels for cup-shaped components is necessary to effect proper drainage.

A simple test for the effectiveness of any barrel-parts combination is to measure the amount of solution recovered after allowing the liquid to drain into a dry container for various combinations of operation. A more thorough test is to measure, by chemical analysis, the amount of chemicals carried over into a tank of clean water. (The volume of the tank needs to be known, of course, to permit the calculation). This method measures the total carry-over, not just the amount lost by dripage.

It is important to inspect barrels frequently to ensure that the holes remain clear. Barrel holes in polypropylene cylinders, for example, are subject to peening over when heavy parts are run.

With rack systems, the rack and the work pieces should be placed above the plating tank for dripping (see Fig. 1).

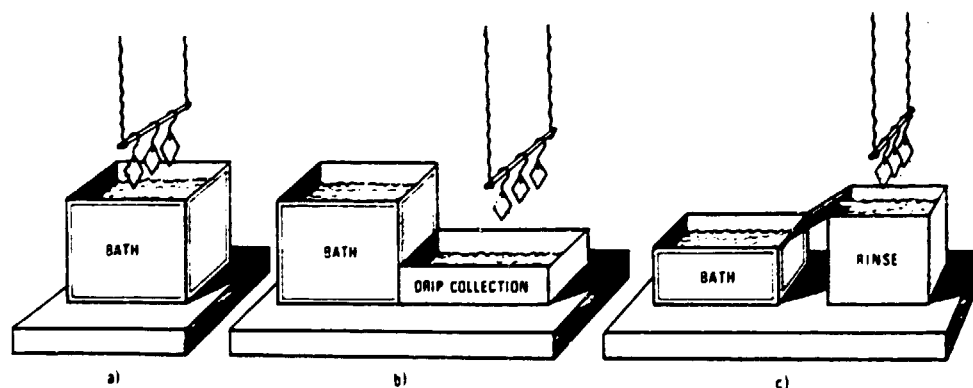


Figure 1 : Allowing sufficient dripping time for treated work pieces is the simplest and most cost-efficient method of pollution control: (a) over the treatment bath, (b) over a special drag-out recovery tank and, (c) after every rinsing over the rinsing bath. Baths which are close together reduce the opportunity for spillage. The use of drain-boards made of corrosion resistant material helps to return drips to the baths when parts are transferred between tanks.

In all cases, sufficient dripping time should be allowed. With chrome plating, for example, this time should at least be 20 seconds for each work piece.

By draining the work pieces carefully, about 70 % of the dragout problems can be eliminated. (For hot solutions, caution must be exercised to avoid the solution drying out onto the parts, as this makes rinsing subsequently more difficult).

Draining of work pieces can be further improved by additional equipment. Air stream dripping (see Fig. 2) reduces the required time significantly. Other techniques include the removal of solution drops by vibrations or ultrasonic treatment. In some cases the addition of surfactants to the bath may improve drainage, provided that these substances themselves do not create problems at subsequent operational steps, or constitute a pollution problem.

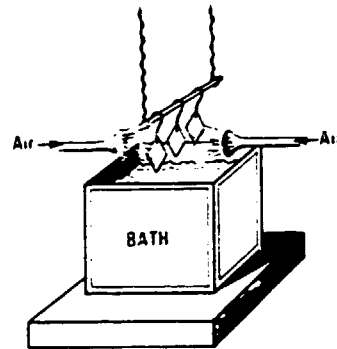


Figure 2 : Principle of improved dripping of the work pieces by air stream or fog spray treatment above the bath. When applying this technique, (care must be taken that) air velocity should not be excessive and drops are collected in the bath tank. Air must also be oil-free to avoid deterioration of the finish.

3.1.2 Reduction of Rinsewater Consumption

Traditionally, the metal finisher has used water generously for rinsing purposes, often without attempting to measure the amounts really required. This practice is now raising many questions because of the cost of treating the resulting large volumes of waste water. The high-price of water in urban areas is a contributing factor in many places.

Where water is still being used freely without any attempt at control, it is usually quite easy to reduce consumption by at least 50% and, in some instances, by as much as 90%. The consumption of rinsing water is governed by:

- the arrangement of the rinsing tanks;
- the length of time during which the work piece is being rinsed;
- the volume of rinse water that can be brought into contact with the work piece in a given time;
- the concentration of the solution adhering to the work piece;
- the temperature of the work piece and the water;
- the shape of the work piece, and the turbulence of the solution;
- the position of the work piece on the rack;
- the draining time required over the process tank prior to rinsing.

3.1.2.1 Minimizing Water consumption

The first step, both in new and existing plants, is to find out how much rinsing is required. This question has been the subject of much study, and theoretical calculations are available from handbooks (e.g. 17, 18). Most metal finishers, however, prefer to work out the actual requirements on their own as follows:

- a- run the process with those pieces which are the most difficult to rinse, e.g. to the form;
- b- run the procedure with the bath where the rinsing procedure is the most complex;
- c- determine the water flow rate for that bath. This can be done with a bucket and a stop watch or by measuring how long it takes to fill a tank to a given depth;
- d- gradually reduce the flow water until the rinse becomes inadequate because of contamination of subsequent baths or because stains are remaining on the work pieces;
- e- increase the flow to about 10% more than the level in step 4;
- f- install flow restrictions to keep the flow-rate constant, and permit only supervisors to make changes.

Automatic control of water flow can be achieved with a controller that measures conductivity in the rinse tank.

While rinse water minimization is an important goal, care must be taken that this does not increase the carry over of contaminants, which cause defects in the work, or rejection of contaminated baths. Chemical analysis should corroborate the visual inspection of rinsewaters.

3.1.2.1 Improvement of Rinsing Effectiveness

A significant improvement in water consumption can be obtained by optimizing the rinsing quality of the baths. Possibilities to improve the rinsing efficiency include:

- air agitation of the rinse water, or agitation by hydraulic, mechanical or ultrasonic methods (note that air agitation, while simple, is energy intensive, and requires a clean, oil-free air supply);
- agitation of work pieces during rinsing;
- raising the water temperature;
- introduction of fresh water at the bottom of rinse tanks, using a spreader, or better yet, an eductor;
- use of spray rinsing techniques.

A well equipped bath is shown in Fig. 3.

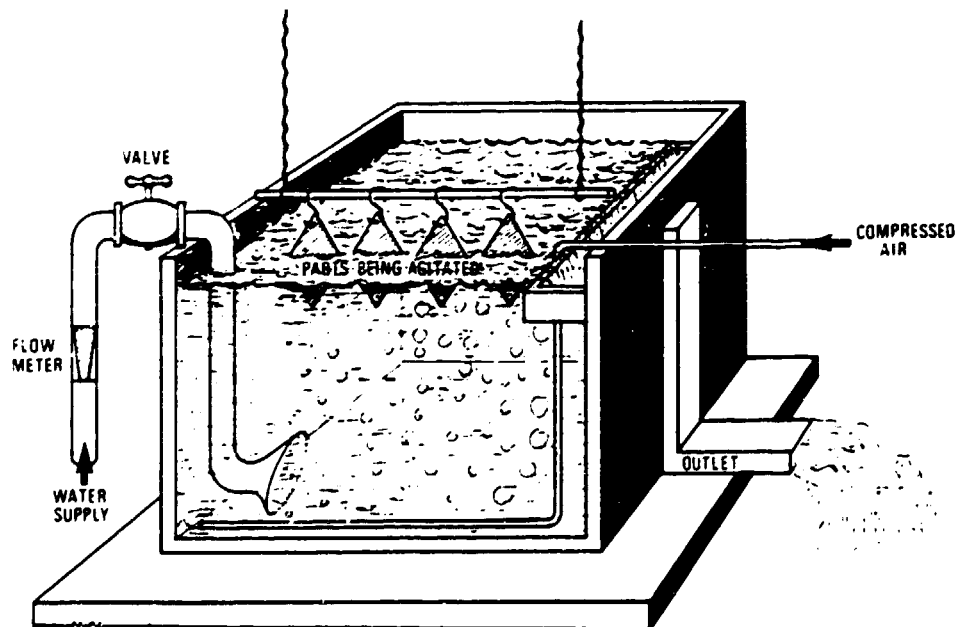


Fig. 3: Control of water flow and improvement of rinsing efficiency.

31.2.3 Flow Rinsing, Static Rinse Baths and Cascade Rinsing

The simplest rinsing procedure uses simple flow rinsing in a single rinse bath with a continuous high water flow to clean the work piece. Chemicals dragged out into the rinse tank are lost. Improvements in water consumption, chemical loss, and final treatment can be achieved by using one or more intermediate static rinse baths in sequence before the final continuous flow rinsing tank (see Fig. 4). The water in the static rinse baths is periodically replaced.

The highest efficiency is obtained by installing a counter-current rinse water cascade as shown in Fig. 4. For most tank designs, the best efficiency will be obtained with a bottom water supply and a top water run-off for each bath, as shown earlier in Fig. 3.

In existing plants where multiple cascade rinsing is not already in use, at least two counterflow tanks should be installed wherever possible. Their introduction will dramatically reduce water consumption (up to 90 %) while not changing the rinsing effect. A third tank would allow a further reduction. New installations should be equipped with multiple cascade rinsing from the start.

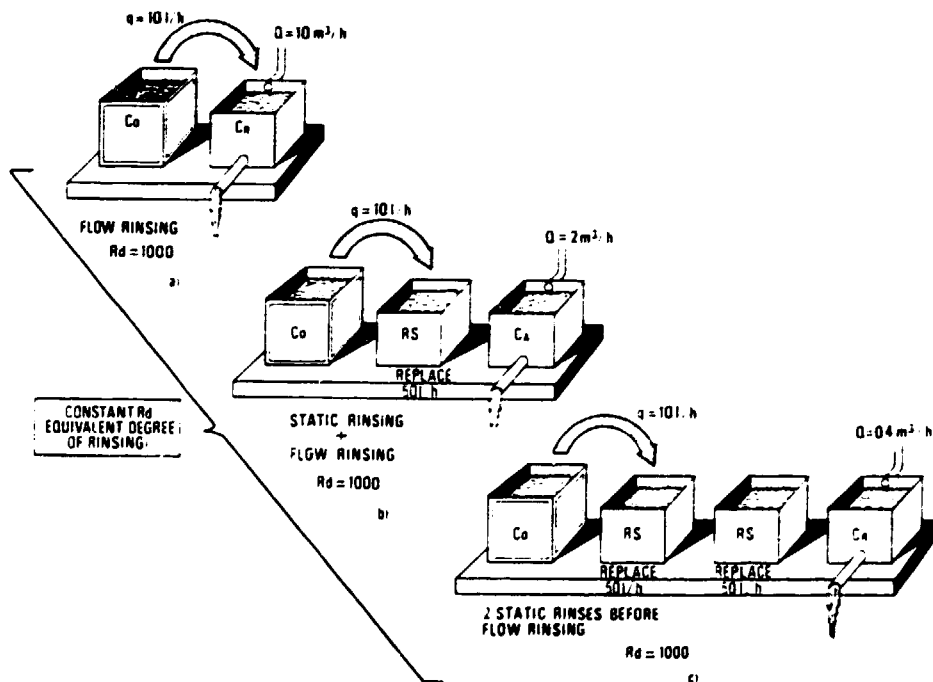


Figure 4 : Effect on rinse water consumption by use of intermediate static rinse baths to achieve an equivalent degree of rinsing.

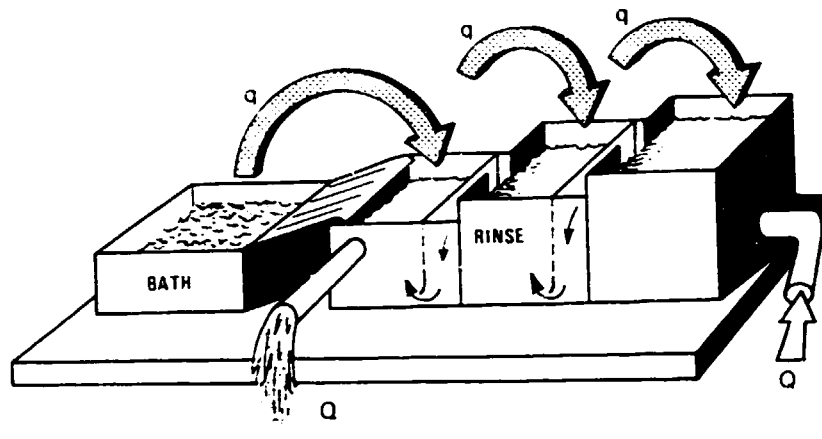


Figure 5: Schematic design of cascade rinsing.

Water consumption is reduced by using the countercurrent principle: the effluent of the downstream rinse bath serves as water supply: C_0 = concentration of the treatment bath, C_1, C_2, \dots, C_n = concentrations of the 1st, 2nd, ..., and last rinsing bath within the cascade; q = drag out ratio specified as volume per hour; Q = water flow rate.

3.1.2.4 Static Recovery Rinse

An alternative to flow rinsing arrangements is to use one or more static rinse tanks. With such a system the dragout accumulates in the rinse tanks, and therefore can be recovered. The solution contained in these tanks can be used to make up the plating bath losses caused by evaporation and dragout (see Fig. 6).

Under some circumstances the bath chemicals can be recovered almost completely.

The following are particular advantages of the static recovery rinse:

- lower costs due to recovery of the bath chemicals;
- decrease in labour for bath maintenance.

Disadvantages of this process are:

- the increase in plating operations by an increased number of rinse tanks;
- the increase in floor space requirement for these rinse tanks.

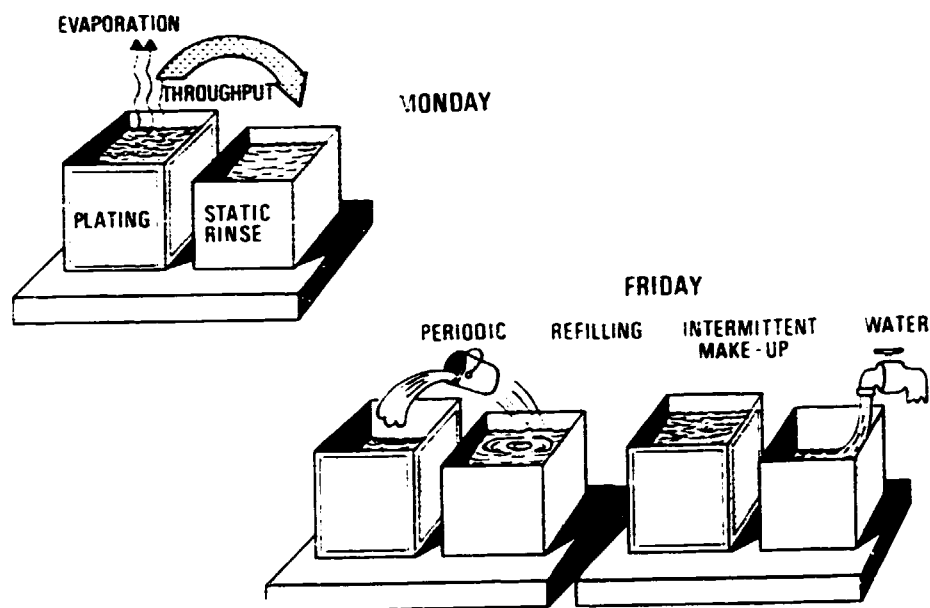


Figure 6: Schematic design of static recovery rinse.

3.1.2.5 ECO - Rinse

ECO (ie. "economical!") rinses are static rinses in which the workpieces are immersed in the rinse tank before and after treatment in the plating bath (Fig. 7). The term dragin-dragout may also be applied to this procedure. Dragout is lowered to 50% because the same quantity of liquid is transferred to the treatment bath (by the untreated workpieces) as to the subsequent rinse tank (by the treated pieces). The recovery of chemicals is optimized by the use of an ECO rinse followed by cascade rinsing. Effluents carried over compensates for the evaporation from the treatment bath.

In using this procedure, careful attention should be placed on observing that contaminants do not build up in the rinse tanks over time. Organic contaminants can be removed by passing the solution periodically through a carbon filter.

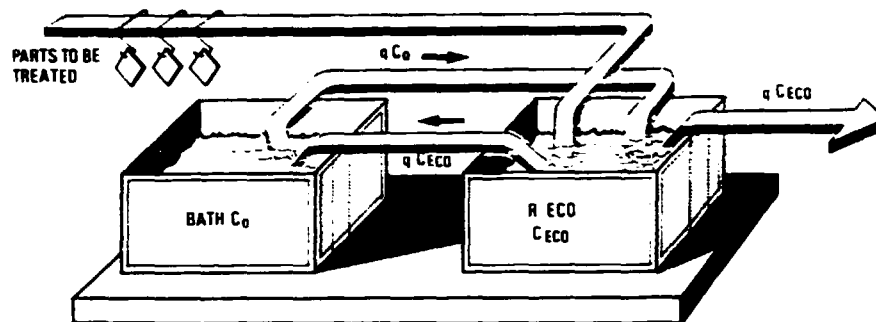


Figure 7 : ECO-Rinse operation. The work pieces are immersed before and after the treatment bath in a static rinse tank; a smaller quantity of chemicals is concentrated in the rinse water under steady state conditions because half of the dragout is transferred back into the treatment bath; q = dragout ratio, C_0 = bath concentration, C_{ECO} = ECO rinse concentration: $C_0 = 2 \times C_{ECO}$, i.e. $C_{ECO} = C_0/2$.

3.1.2.6 Spray Rinse

Spray or jet rinse offers some advantages, especially for zinc, copper or nickel plating in the barrel :

- a decrease in water consumption;
- the reduced cost of concentrating the solution prior to recycling into the plating bath.
- there is considerably less static recovery rinse: 99% of dragout can be recovered by spray rinse.

A number of different process configurations are possible. For example, dripping liquid from the work pieces can be directly returned to the treatment bath, spray effluent can be trapped by an extra tank, or the spray solution is drained into the following rinse tank. A further possibility is to use several successive sprays over a series of counter-current flow tanks. The water from each succeeding tank is used for the preceding spray rinse stage.

3.1.2.7 Reactive Rinse

Reactive rinsing is the use of rinsewater from one operation as the source for another. For example, rinsewater following chloride zinc plating may be used for the hydrochloric acid rinse preceding the zinc plating, utilizing the wetters in the zinc to promote drainage. Any rinsewater dragged back into the zinc contains zinc solution just carried out. Rinse waters in rack operations may be used in companion barrel plating operations, where lower rinse ratios may be acceptable. Another method of accomplishing similar goals is to simply dip a rack of barrels in the rinse immediately following a process before being immersed into the process itself, thereby dragging back what has been previously dragged out in the operation.

3.1.3 Regeneration of Baths

In order to keep solution strength constant, the chemicals lost to a process are periodically replaced. However, the accumulation of by-products (which may consist of precipitated, suspended or dissolved substances) will eventually result in a deterioration of the finishing quality. The replacement of baths yields a significant quantity of waste to be discarded and the process which maintains the baths in the best condition for as long as possible is the most desirable. Some regeneration methods are described in the following pages. Operators are advised to consult their suppliers for individual applications and the installation of suitable equipment.

A related consideration to the above is bath re-use for an application where less exacting requirements exist. The progressive re-use of cleaning solutions from the rear of a series of baths to the front of the sequence where the highest levels of contaminations exist is one application of this technique.

While bath regeneration and re-use are highly desirable from both economic and environmental points of view, it is unwise not to have some spare capacity in the general waste treatment system so as to cater for spent baths if the regeneration system should one day fail. The lack of such back-up could otherwise cause severe complications, and perhaps lead to the temptation of illegally dumping the bath contents.

3.1.3.1 Filtration and Centrifugation

Filtration or centrifugation (Fig. 8) are effective methods for improving the life of a treatment bath. An activated carbon filter can be used to remove dissolved organic impurities in addition to its action in removing solids. The removal of oils from alkaline cleaners by ultra-

filtration considerably prolongs the life of treatment baths, and reduces interference by oils with flocculation and settling steps during clarification. Separation of the grease film from degreasing baths is another example of the use of centrifugation or filtration (see Fig. 8). In addition, a number of newer technologies such as hydrocyclones, packed media filters, and electrolytically enhanced cross-flow membrane filters are being refined and should become more readily available in the future.

Filtration or centrifugation can be carried out during normal operation, either continuously or intermittently. The advantages of these techniques are:

- fast regeneration of the treatment bath with high efficiency;
- the working process does not have to be interrupted;
- resulting wastes are highly concentrated (and may thus be able to be recovered);
- disposal of residues may be easier than would be the case for concentrated liquid wastes.

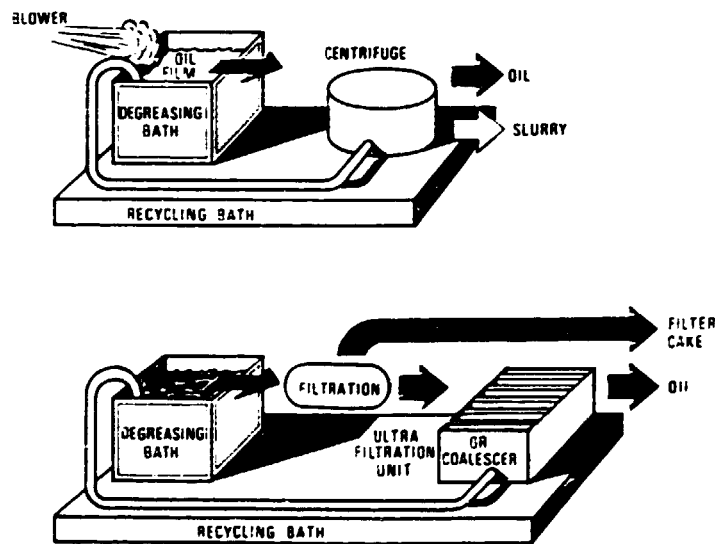


Figure 8: Filtration or centrifugation of suspended or sedimented particles from treatment baths.

Despite the advantages, the comparatively high investment and operating costs have tended to inhibit the use of these techniques. Nevertheless, there are circumstances where filtration or centrifugation offer interesting alternatives to other approaches.

Normal evaporation losses from hot treatment baths can often be compensated by the re-use of effluents from the rinsing cascade as illustrated in Fig. 9. If the effluent rate equals the evaporation rate, a complete recovery of bath chemicals can theoretically be obtained. If the rate is inferior, the rinse bath can still be concentrated by forced evaporation to achieve the required strength.

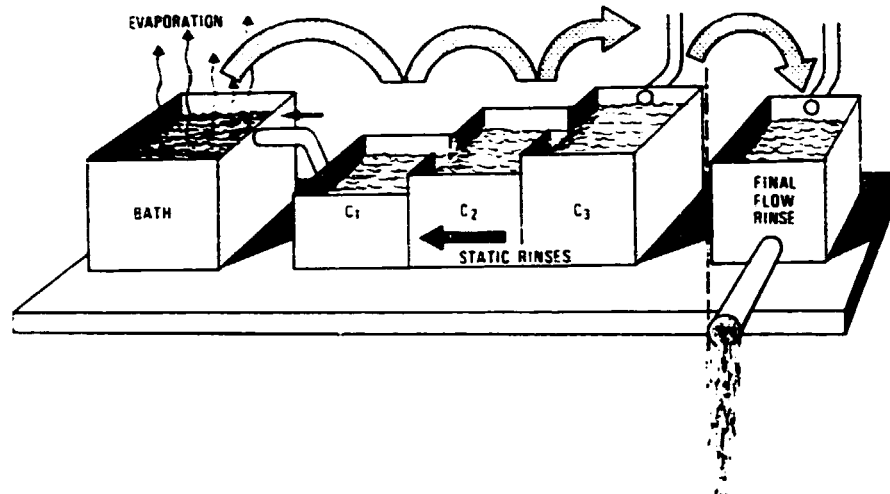


Figure 9: Use of rinse effluent to compensate for evaporation loss in a bath.

In the case of cold baths, recovery of the bath chemicals is still feasible (Fig. 10), but forced evaporation requires additional investment in equipment and high energy costs. If a condenser is used, both dragout chemicals and water can be recirculated (e. g. Fig. 10 (a) and (b)).

If there is a possibility that dissolved minerals in the feed water will build up and interfere with the treatment process, it is recommended to use de-ionized water for makeup. Other contaminants that build up may need to be removed by cation exchange or similar techniques from time to time.

Forced evaporation techniques could be considered for processes involving highly toxic or expensive chemicals. Given the installation and operating costs, as well as the requirement for technical and chemical know-how, they are best suited to larger plants. They may, nevertheless, be also considered for advanced new plants of smaller enterprises where a high level of technology is desired. In suitable climates, solar energy may be a useful source of heat for evaporation. For a more detailed description of the necessary equipment the reader is referred to literature reference /18/ or handbooks on this subject.

Fig. 10 (c) illustrates an evaporation technique with practically complete recycling of rinse water and bath chemicals. Due to possible corrosion problems accompanying evaporation of strong electrolyte solutions in 10 (c) it is in fact more common to carry this out on the more dilute rinse solutions.

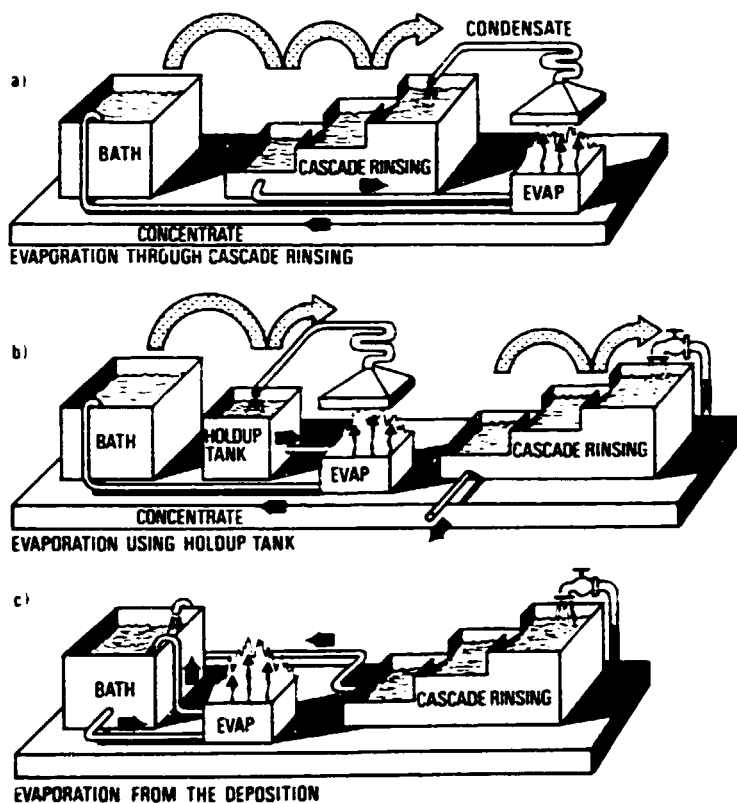


Figure 10 : Possibilities for the use of evaporation and condensation to avoid or minimize the loss of bath chemicals.

3.1.3.3 Freeze Separation

The freezing of solutions may be used to concentrate and separate dissolved impurities. It can, for example, regenerate copper cyanide by removing the carbonates.

Thermodynamic energy requirements for separation by freezing are less than energy required for evaporation (the theoretical values are 334kJ/kg instead of 2257 kJ/kg) It is this technique, therefore, that has a lower operating cost than evaporation. Investment costs may be acceptable for larger metal finishing plants.

21.3.4 Electrolytic Recovery

Electrolytic recovery of metals is a well developed technique. It can be recommended for smaller as well as larger finishing facilities, especially in cases where the cathodically deposited metal can be re-used for metal plating within the plant.

It is characteristic of this technique 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 the cathodic deposition. Voltage enhancement is ultimately limited by secondary reactions such as water decomposition. Electrolytic recovery can, only be one of several steps within a pollution control strategy. Nevertheless, the efficiency of traditional recovery methods is gradually being improved by the development of new electrochemical reactors incorporating, for example magnetic activation or porous electrodes. Such new techniques should gradually find their way into more common use in the coming years.

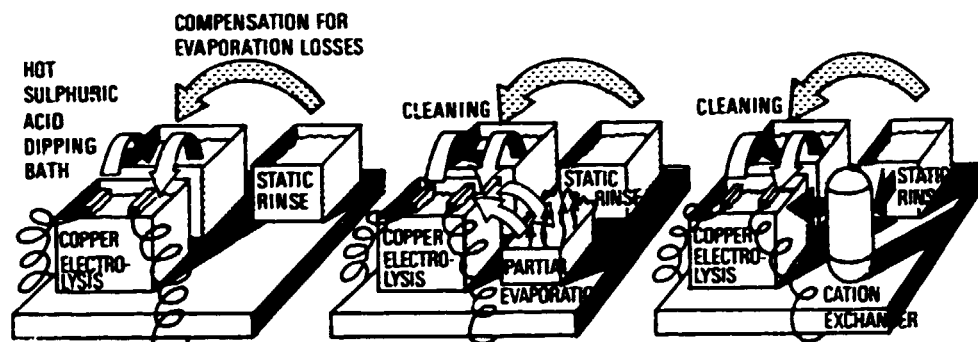


Figure II: Examples of electrolytic copper recovery from pickling baths combined with evaporation (hot bath or evaporator) or ion exchange techniques.

Fig. II shows how an electrolytic cell may be integrated into a treatment chain. Three examples of the implementation of electrolytic copper recovery from pickling are shown. It should be emphasized that electrolytic recovery combined with metal concentration by evaporation (hot treatment bath, use of an evaporator), or by a cation exchanger, improves the recycling efficiency considerably. Chrome (III) recovery from chromic acid baths is also possible by electrolysis.

3.1.4 Recovery from Dilute Solutions

The preceding techniques will be useful in minimizing the loss of chemicals to the effluent stream. Only rarely however can the loss be totally prevented. A further consideration is then to attempt to concentrate the remaining inevitable losses so as to facilitate the subsequent recycling or treatment. Methods described below can be helpful in extracting chemicals which are present in low concentrations. Accordingly, while they have useful particular applications, they are not all equally suited for all types of baths or effluents. Further expert advice should be sought in order to make the best choice.

For ion exchange processes, columns filled with special resins are employed to extract specific anions or cations (eg. nickel) from liquids which pass through the columns.

Ions exchangers are effective for recovering materials from dilute solutions, but investment and processing is rather expensive. Furthermore their maintenance is not simple.

Regeneration has to be undertaken from time to time when the resin is saturated with ions. Ion exchange systems with automatic regeneration are now commercially available. Alternatively, resin cartridges may be sent off to a commercial regeneration facility.

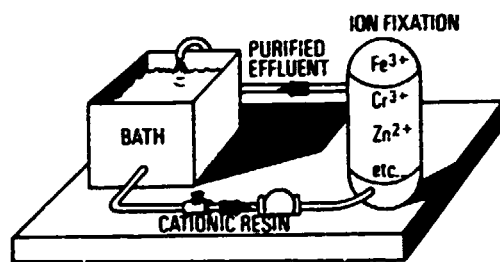


Figure 12 : Use of ion exchange : regeneration of a treatment bath by the removal of metal ions results in a significantly extended life time of the bath, reduce consumption of chemicals, and a enhanced level of product quality.

Fig. 12 shows installation of an ion exchanger. A more sophisticated system (Fig. 13) consists of three exchangers in sequence for the elimination of metal ions from a chromic acid bath. Here ion exchange is used for the regeneration of treatment baths to significantly enhance their service life.

In modern installations, ion exchangers are essential for the reduction of water consumption (rinse waters are used in a closed system without an effluent) and for the recycling of treatment chemicals. Recovery of other wastes by means of ion exchange will also become more significant in the future. For example it can be used to recover copper from process waters in the electronics industry.

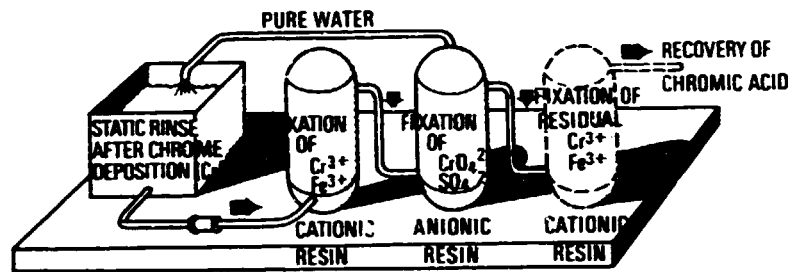


Figure 13 : Ion exchangers is sequence for the recycling of metal ions, of rinsing water, and of chromic acid.

3.1.4.1 Reverse Osmosis

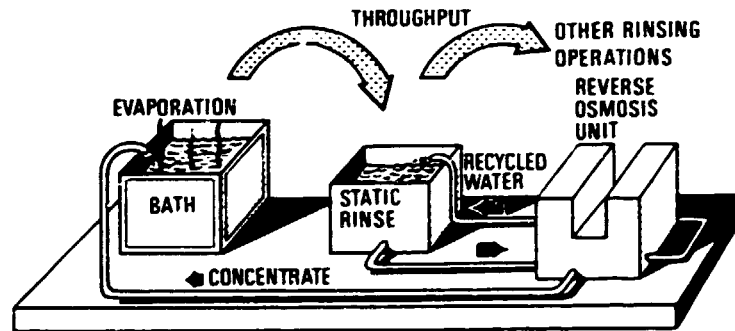


Figure 14 : Application of reverse osmosis : the dragged out chemicals are re-cycled to the treatment bath.

Reverse osmosis can be used to concentrate a solution by using high pressures to force solvent molecules through a semi-permeable membrane. The larger solute molecules cannot pass through the membrane and are left behind, becoming gradually more concentrated as the solvent is driven off. Eventually the concentrated wastewater is bled off

for further treatment, or for recovery. Equipment is rather specialized, requiring special membranes and high pressures of 20 to 30 bars. Accordingly, reverse osmosis is expensive, and the maintenance of the membrane needs a skilled operator. It is suitable for large plants with access to technical skills. Fig. 14 shows how a reverse osmosis unit can be integrated into a process line.

3.1.4.2 Ultrafiltration

Ultrafiltration employs larger membrane pores than reverse osmosis, and therefore can operate with lower applied pressures (from 1 to 8 bars). Ultrafiltration is useful for the separation of chemicals of larger molecular size, such as oils and dissolved organic substances. It can for instance be applied to remove emulsions or colloids from degreasing or amorphous phosphatation baths, or for the separation of smaller contaminating molecules from larger sized particles.

Due to the nature of materials likely to be recovered, it is more applicable as a pretreatment in waste-water treatment than as a method of recovery of useful chemicals.

Water treated by ultrafiltration is less pure than that obtained by reverse osmosis. Subsequent purification (e.g. by ion exchange) may be necessary. The specific advantage of ultrafiltration is to separate large molecular weight materials effectively from solutions.

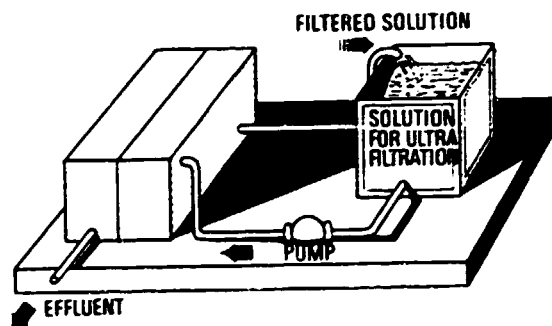


Figure 15 : Ultrafiltration system for the separation of colloids, and particles or dissolved substances with large molecular sizes (molecular weight between 1000 and 100,000).

3.1.4.3 Other Membrane Techniques

In electrodialysis, the diffusion of ions across a membrane is accelerated by an electric potential (Fig. 16). Generally this method is useful for the concentration and purification of chromic acid baths as well

as rinsewaters generally. It is useful in achieving recovery of bath materials, and is suitable for small as well as larger plants.

There are also other membrane exchange techniques under development. They promise to be suitable for the removal of heavy metals, but they are still in the experimental stage and are not yet routinely applied.

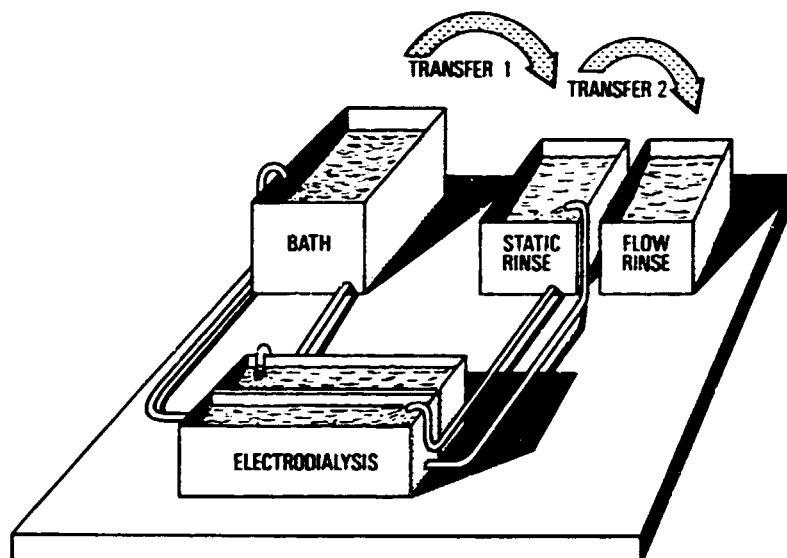


Figure 16: Typical placement of an electro dialysis step in a low pollution operation.

3.1.5 Combination of different Technologies

Some of the technologies discussed so far can be used in combination so as to achieve higher efficiencies than would be individually possible. The selection of such a combination depends on a careful analysis of the production process, the purification objectives, and the relative cost factors under the conditions prevailing at each plant.

In some cases combinations are not only options, they are necessary. In the case of decorative chromium treatment, for example, electro dialysis in connection with a static rinse requires a further concentration step (eg. evaporation) for the chromic acid solution from the electro dialyser before it can be usefully re-introduced into the plating bath.

Another example concerns the cascade rinse effluent from a cold plating process. This must again be concentrated before it can be re-used.

Not all opinions can be discussed here. Table A shows a number of combinations that can be easily used to achieve the efficiencies shown. Other combinations must be investigated on a case by case basis.

3.2 WASTEWATER TREATMENT

Several different waste streams will usually originate from a single metal finishing plant. The different composition and concentrations of these waste streams will require different treatment procedures, and in many cases it is advisable to treat them separately so as to achieve the highest removal efficiency. Separate treatment (or at least pre-treatment) also avoids the possibility that incompatible wastes will undergo undesirable reactions in the storage tanks. These types of reactions can be a hazard to personnel because they may generate toxic gases, or form compounds that are difficult to treat, eg. nickel cyanide.

In all cases the waste stream must be carefully evaluated before selecting a treatment scheme. Many enterprises have opted for treatment schemes that cater for their own wastes, but in some circumstances it may be economic and practical to arrange a centralized waste treatment facility for a group of enterprises close together.

It is also common in many cities for industries to discharge wastewaters to a public sewerage system. Public sewage treatment systems, however, usually rely on biological processes which cannot deal with heavy metal wastes. Accordingly many authorities only accept pre-treated effluents in their system. Such a system then provides dilution, but little further treatment.

Figure 17 depicts the basic elements of a typical wastewater treatment system for metal finishing operations. In the following sub-paragraphs, specific parts of the overall system will be discussed.

For most heavy metals, precipitation as insoluble hydroxy or sulphide compounds is achieved by the addition of simple reagents followed by pH adjustment and sedimentation. In the case of hexavalent chromium, it may be necessary to first chemically reduce the metal to a form where it will readily form insoluble precipitates.

Cyanide removal is achieved by oxidation to harmless residues. A precipitation step may still need to follow the oxidation stage in order to remove the accompanying soluble metal ions.

For particularly hazardous substances such as cadmium a totally separate treatment system may be advantageous, including separate dispo-

sal procedures. In all cases, to ensure that treatment will be effective there is a need to distinguish between treatment of rinsewaters (high flow and low concentration) and discarded strong process solutions (cleaners, acid dips, plating solutions) of low volume and only occasional discharge, but of high concentration. A batch treatment system can cope with the two types of wastewater, but a continuous flow system is likely to be overloaded by shock loads. Accordingly, a simple approach is to store any strong solutions and release them slowly into the treatment system. The flow equalisation stage is vital to ensure that the treatment process can function as designed.

	Cyanide copper plating	Acid copper plating	Nickel plating	Decorative chromium plating	Thick chromium plating	Cyanide zinc plating	Acid zinc plating	Cyanide cadmium plating	Chromic passivation	Copper pickling	Acid pickling
Dripping	x	x	x	x	x	x	x	x	x	x	x
Eco rinse		x	x	x	x	x	x	x	x	x	x
Static recovery rinse	x	x	x	x	x	x	x	x	x	x	x
Ion exchange		x	x	x	x				x	x	x
Electrolysis		x	x			x	x	x			x
Electrodialysis				x	x		x				x
Evaporation				x	x	x		x			
Pollution avoidance	98%	80%, 98%, 98%	70%, 98%, 98%	70%, 95%, 95%	70%, 80%, 98%	80%, 80%	70%, 80%, 98%	98%			98%

Adapted from "Disposal of Hazardous Waste-Metal Finishing Waste", NATO-CCMS, Study No. 121, 1981.

TABLE 7:

SPECIFIC COMBINATIONS OF POLLUTION REDUCING TECHNOLOGIES AND THEIR EFFICIENCY IN WITH REGARD TO VARIOUS METAL FINISHING PROCESSES

3.2.1 Detoxification of Hexavalent Chromium

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

WASTEWATER TREATMENT

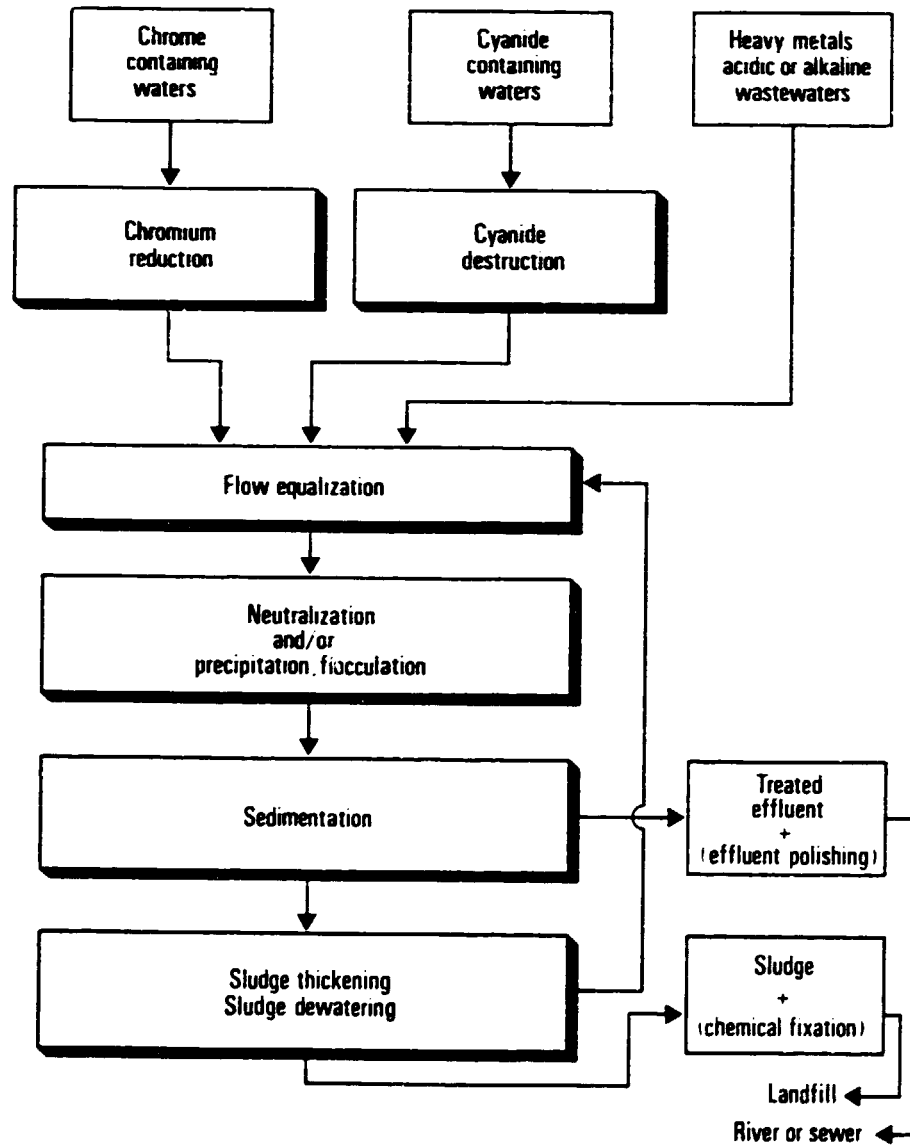


Figure 17 : Elementary block design of a wastewater treatment system for a typical metal finishing operation. In practice a number of additional treatment processes may be added to recover materials, and to enhance treatment effectiveness.

3.2.1.1 Chromate Reduction with Sulphur Compounds

Sulphur compounds are commonly employed for the reduction of hexavalent chromates. Advantages include short reaction times, the simple observation of the reactions by measuring the redox potential, and a low yield of sludge after neutralisation with sodium hydroxide. The sulphur compounds may conveniently be sulphur dioxide gas (SO_2) (the gas is dissolved in the solution), metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$), or normal sulphite (Na_2SO_3). All these substances react with hexavalent chromium in the same way: in acid solution (optimum pH range: 2 to 3) they are dissociated and the bisulphite anion (HSO_3^{-2}) reduces the chromium to the trivalent state.

Stoichiometrically, for the reduction of 1 g of hexavalent chromium 0.92 of S is required. From this the quantities of the appropriate reagent can be calculated, assuming the reaction goes quickly to completion.

Table 8 shows the yield of hydroxide precipitation and of sulphur salt after chromium reduction to indicate the burden on the deposition site or the environment.

In view of the deleterious effects of sulphur compounds on concrete sewers and drains, the effect of the reaction products may need some evaluation. The requirements of the relevant authorities should be ascertained before installing and operating the reduction plant.

3.2.1.2 Reduction with Divalent Iron Salts

Iron salts are often used because they are cheap, and readily available as by-products from other processes (removed from waste water, for example). The theoretical requirement is 3.22 g Fe (II) and 6.60 g H_2SO_4 (or 4.91 g HCl, respectively) for the reduction of 1 g of hexavalent chromium. The high volumes of sludge generated increases the cost of disposal compared to other methods (see Table 8).

Reducing Agent	Yield of Sodium Sulphate from Neutralization (kg)	Precipitated Hydroxides as Dry Matter (kg)
sulphur dioxide	4.1	1.98
sodium bisulphite	8.2	1.98
iron(II) sulphate	16.4	8.14

TABLE 8: Precipitation of hydroxides and neutral salts from hexavalent chromium reduction by sulphites or iron salts^{/19/}.

The cathodic reduction of hexavalent chromium is performed in acid solution. pH control is achieved through acid addition as required (the theoretical value equals that of the iron salt reaction). The electrolytic efficiency is 95%, the practical energy consumption around 1.2 kWh/kg CrO₃. However, the presence of iron or copper affects the efficiency of electrolytic reduction, and these metals may need to be removed first if they are present. The lowest concentration possible under practical conditions is 0.5 mg/l, but it is not recommended to run the process to this value, because at low concentrations the time requirements increase considerably. If the chromium concentration is not high (100 to 1000 mg/l), other reducing methods can also be used. Higher concentrations should be pre-treated electrolytically, followed by other reducing processes.

3.2.2 Detoxification of Cyanides

Processes for the detoxification of cyanide have been thoroughly researched, as cyanide is one of the most toxic agents used in the metal finishing industry. The chemistry of cyanide detoxification is relatively complicated and in most cases degradation needs more than one reaction step.

3.2.2.1 Degradation with Chlorine

Large detoxification facilities work economically with chlorine gas addition or electrolytic chlorine production. The use of (12% to 15%) sodium hypochlorite solutions is recommended for smaller plants. If chlorine gas is used, 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 is the high production of salts from the subsequent neutralisation.

In a first step, cyanides are oxidized by hypochlorite to cyanogen chloride, an extremely toxic gas. The second step, the hydrolysis of cyanogen chloride to cyanate, takes place virtually at the same time in the reaction vessel. Although cyanogen chloride is highly soluble in water, the temperature must not exceed 40 °C to avoid degassing of solutions.

Hazards are best minimized by ensuring as rapid a hydrolysis as possible. However, pH should not be too high if the further oxidation of cyanate to nitrogen and carbon dioxide is to be carried out. This third degradation step, not always required by the water authorities in industrialized countries, is again achieved by hypochlorite. A suitable pH for both reactions is around 8.5, and this should be very carefully maintained.

Alkaline, zinc or cadmium cyanides are destroyed rapidly. Under excess hypochlorite conditions, suitable pH and with solution turbulence, copper cyanides need about 30 minutes oxidation time. For safety reasons, three times the minimum reaction time should be allowed, i.e. 90 minutes. In some countries the times may be set by regulation. Complexed, other noble metal, iron or nickel cyanides however need much higher hypochlorite excess and longer times for an adequate reaction. These cyanides should preferably be first separated by ion exchange. Regeneration then yields alkaline cyanides which are readily degradable. Recycling of the metals from the cation exchanger is also possible, and is a particular advantage for the expensive noble metals. Wherever possible unnecessary complexing of metals with cyanide should be avoided in the plating process.

The oxidation of 1 kg of cyanide (CN⁻) to cyanate theoretically requires 2.86 kg of sodium hypochlorite, or 2.69 kg of chlorine gas. If chlorine (Cl₂) is used, neutralisation of the generated hydrochloride requires 3.08 kg of NaOH per kg NaCN.

For the oxidation of cyanates additional hypochlorite is required. In this case the theoretical amount for the complete degradation of cyanide to nitrogen and carbon dioxide is 7.12 kg sodium hypochlorite or 6.70 kg of chlorine gas (and 7.7 kg NaOH for neutralisation), per kg of cyanide.

Oxidation of cyanides has to be checked by chemical analyses in order to regulate the dosage of chemicals. Special electrodes for pH, cyanide or chloride are available. The addition of chemicals may be undertaken manually, or automatically by special equipment. There should be no free chlorine in the effluent in order to avoid the possibility of oxidizing chromium to the hexavalent state when effluent is mixed with other wastewaters.

3.2.2.2 Cyanide Degradation by Active or Activated Oxygen

If oxygen is used for the degradation of cyanides, no additional salts are produced, and no neutralisation of the treatment solution is necessary. There are several methods in use.

A suitable oxygen producing agent is hydrogen peroxide (H₂O₂). Theoretically 1.3 kg H₂O₂ is sufficient per kg of cyanide. In practice an excess of H₂O₂ is necessary to ensure a useful reaction rate. This process is not recommended with low initial cyanide concentrations (less than 500 mg/l). The reaction can be accelerated by addition of catalysts or formic acid, and may then be suitable for cyanide concentrations between 100 and 1000 mg/l. Persulphuric acid can also be used

as the oxygen delivering substance. It hydrolyses to H_2O_2 and sulphuric acid in aqueous solution. Direct ozonation is another possibility. Concentrated peroxide and persulphates are hazardous substances and must be handled with care.

The catalytic oxidation of cyanides by non-activated oxygen is also possible. Several carbon products have been tested as catalysts. Due to longer reaction times, these methods are recommended only for wastewaters containing low concentrations of cyanides, especially as after-treatment.

3.2.2.3 Other Cyanide Oxidation Processes

Electrolytic cyanide degradation can be carried out in the presence of chlorides. Cyanides can be oxidized by electrolytic splitting of oxygen from hydroxides. This technique works economically only with concentrated cyanide wastes.

3.2.2.4 Precipitation of Cyanides

Iron ions form highly stable complexes with cyanides. A precipitation of divalent or trivalent hexacyanoferrates is possible as detoxification step within the final wastewater treatment. But the resulting sediment is not suitable for a landfill waste deposit, because acids or photolytic reactions may under some circumstances release cyanides from the deposit. Disposal, therefore, should occur by other means such as thermal destruction.

3.2.2.5 Thermal Degradation of Cyanides

Thermal degradation of cyanide substances yields nitrogen or nitrates and carbon compounds (formates, carbonates), together with an inorganic residue from any associated metal cations. Burning at 1200 to 1400 °C, it destroys cyanides completely, yielding nitrogen and carbon dioxide as products.

Thermal processes are applicable only for concentrated wastes. The equipment required is capital intensive and skilled maintenance is necessary. Metallic combustion residues may still pose a disposal problem. As a rule such techniques have a use only for solid residues which cannot easily be brought into solution for treatment in aqueous media.

3.2.2.6 Comparison of Cyanide Degradation Techniques

The standard detoxification method for cyanides in small metal finishing plants is still oxidation by chlorine. Advantages are the reaction speed, the possibilities of analytical process control, low costs, and a

relatively long experience in handling. The precipitation of cyanides from concentrated wastewaters as hexacyanoferrates is suitable, if a thermal degradation step follows. Peroxy-compounds have the general disadvantage of requiring long reaction times. These processes are useful where only small quantities of cyanide waters are to be treated. The content of salts in the effluent is low.

If cyanides are destroyed in a continuous flow stream, hypochlorite treatment may be the best choice because of its simple handling requirements. 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.

3.2.3 Neutralisation and Precipitation

This step is the principal operation that converts dissolved metals to insoluble hydroxides and thus allows them to be removed from effluents. Neutralisation must in general be preceded by effective flow equalisation procedures to allow the system to operate effectively.

"Neutralization" of metal finishing waste waters is to be understood more as a traditional term than as a real neutralisation : it does not mean the adjustment to a pH of 7.0, but a precipitation of the metal hydroxides from alkaline media (see Fig. 18 for best ranges).

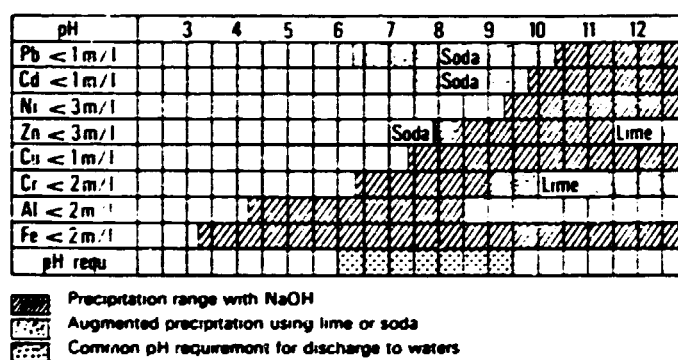


Figure 18 : For the precipitation of solid metal hydroxides the waste water has to be adjusted to specific pH ranges. (Fig. taken from /19/)

In earlier times the elimination of metal hydroxides during neutralisation of the waste water was seen as a secondary effect of neutralisation, but since metal discharges are now recognized as serious ecological risk, the precipitation subsequently became as important as neutralisation itself.

As precipitation agents, sodium hydroxide, lime, and soda are generally used. Magnesium hydroxide is also sometimes used as it produces a better sludge. However the reaction is slower and pH range is limited. Alkaline wastewaters are neutralized by technical sulphuric acid, subject to discharge limits for sulphates not being exceeded. Smaller facilities are advised to use sodium hydroxid solution (450 g/l), unless wastewaters contain fluorides. In larger factories, and in the presence of fluorides, lime solution treatment should be used - it is cheaper than applying NaOH and also removes the fluoride. In the other hand this treatment requires the installation of a lime milk preparation plant.

The correct pH for the precipitation of the metal hydroxides varies with the metal ions under consideration. In Fig. 18 pH ranges are given for the precipitation of several metal hydroxides. For most cases, the pH will be within a range of 8.5 to 11. Unnecessarily high pH may interfere with the formation of a good settleable sludge, and accordingly a pH only slightly above minimum is recommended. For mixed metals in-situ tests should be carried out to determine the best pH. For discharge of the final effluent precise requirements may differ from one regulatory authority to another. Further adjustment of the pH to near 7 may be necessary before discharge if discharged quantities are large or the receiving waters are sensitive to alkaline effluents.

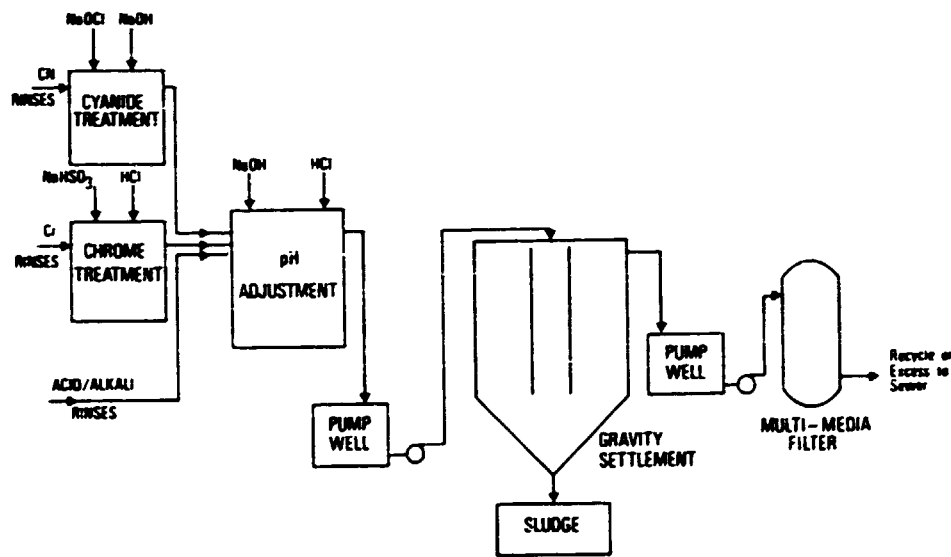


Figure 19: Common Configuration for Effluent Treatment involving Neutralisation^{1/} (Fig. from W.Regan, Australia).

Neutralisation itself is rapid. The process should be carried out in two stages. In the first (or "pre-reaction") tank either acid or alkali is added with vigorous agitation to a preset pH point controlled by pH point controlled by pH electrodes. The retention time in this first tank is approximately 10 minutes. In the second stage final pH adjustment occurs. More acid (or alkali) is added, still with vigorous agitation, and the pH is controlled to the optimum set-point for minimum solubility of the various metals present in the waste stream. Retention time in the second stage is 10 minutes as well. If alkalis other than sodium hydroxide are used, longer reaction times are necessary. A common configuration for effluent treatment involving neutralisation is shown in Fig. 19.

In special cases, for example, if the metal ions are complexed by EDTA or NTA and a precipitation under the conditions mentioned above is not possible, there are more effective processes like sulphide precipitation, high pH precipitation, solvent extraction, or starch xanthate extraction.

3.2.4 Sedimentation and Clarification

Following the precipitation stage, solids removal is normally achieved in gravity settlement systems such as is illustrated in Fig. 20. These are normally used as continuous flow devices, but where the waste volume is small a batch system may be used. Batch systems usually use two settlement tanks, one being filled while the other is emptying.

Solids removal is an important step in the treatment process since precipitated metals may under some circumstances re-dissolve if discharged to the aquatic environment.

Settlement effectiveness is affected by factors such as the size and density of particles, and the velocity of flow (in a continuous flow system). The presence of some chemicals may result in poor settlement due to the formation of a colloidal suspension that resists the coagulation into larger particles that fall out readily.

Ferrous and chromium hydroxide readily form colloidal suspensions. Chemicals such as pyrophosphate, carbonates, organic brightening and wetting agents tend to promote such colloid formation. Conversely, ferric chloride and aluminium sulphate may aid settlement and their precipitation as hydroxides neutralises the electrical charge of colloidal particles and provides an opportunity for co-precipitation. Sedimentation may also be assisted by the use of flocculating agents such as long chain polyelectrolytes that entrap small particles and neutralise electrical charges. The use of lime as neutralising agent may also be effective in aiding sedimentation.

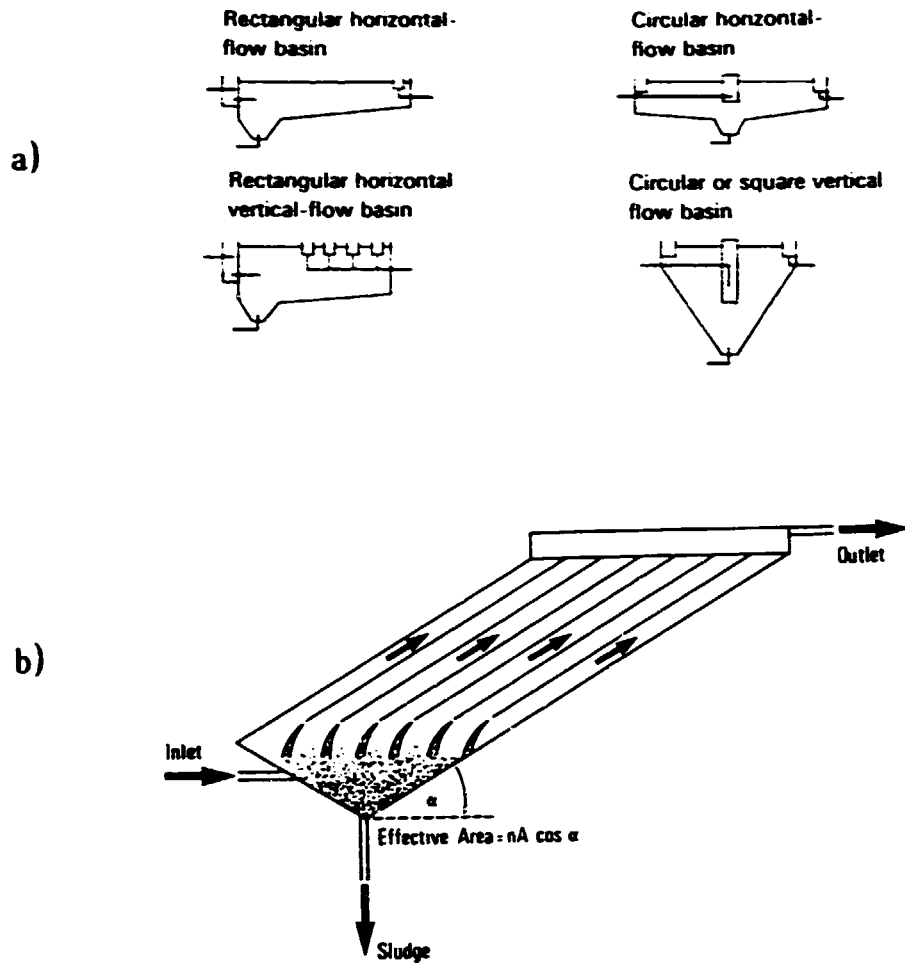


Figure 20 (a) Shapes of some sedimentation basins (From /20/)
 20 (b) Lamellar Flow separator (From W.Regan)

Some common types of sedimentation basins are shown in Fig. 20. The vertical flow basin has the advantage that it can be constructed of steel and mounted above ground, thus taking up a minimum of ground space. The conical bottom allows easy removal of settled solids. Settled solids will usually require further dewatering before disposal. Dewatering may be accomplished by further settlement, drying beds, filter or centrifuge.

The critical design parameter for sedimentation basins is "surface loading", defined as flow rate divided by surface area of the basin (units are metres per hour).

In horizontal flow basins the velocity along the tank may exceed the settlement velocity provided that the tank is long enough. In the case of vertical flow basins however the upflow velocity must be less than the settling velocity, otherwise sedimentation will not occur.

Detention time in basins is normally recommended to be 4 hours or more. If space is a problem a device known as a "lamellar" or "inclined tube" separator may be used. This is illustrated in Fig. 20 (b). The principle of the design is that particles only have a very small distance to settle between a series of parallel plates or tubes. The angle of the plates or tubes allows the accumulated solids to move down the slope to a sludge removal point. Detention time may be reduced to 1 to 2 hours.

Dissolved air flotation is another method of solids removal that may be more effective with solids of low density. Fine air bubbles are introduced to the liquid by various methods, for example, by dissolving air in water under pressure followed by pressure release. Solids are carried to the surface by air bubbles that expand as they rise and are removed by a surface skimming device. Detention time may be of the order of 20 to 30 minutes.

A conical vertical-flow designed basin allows easier collection of sludge than a horizontal-flow basin. Conical or square vertical flow basins are rather easily upset by changes in loading, and in some regions there is increasing use of lamellar flow units. These in turn are relatively sensitive to overloading, so good process control is still required. In all sedimentation basins, it is vital that the inlet and outlet zones be designed to ensure smooth and gentle flow.

Where very high standards of solids removal are required some form of filtration may need to follow sedimentation.

Vacuum or pressure filters can be used, although these are expensive and suitable only for large production plants. More suitable to the small operation is the use of low-cost sand or multi-media filters. The latter are similar in construction to a sand filter, but use media of different sizes and densities such as gravel, silica, or anthracite together in a mixture. As it blocks up, back-washing of the filter is required, with the back-wash water being returned to the sedimentation basin. These filters are used in addition to sedimentation basins: they are not substitutes.

3.2.5 Sludge Dewatering

In order to facilitate the disposal of sedimented material, it is advantageous to dewater the sludge to a more solid form (in many places

the disposal of liquid sludge is now severely restricted). A number of techniques are available for such dewatering.

Prior to dewatering, sludge thickening is becoming an increasingly common step. A typical sludge thickener is a cone-bottomed cylindrical tank in which further compaction of sludge occurs under the influence of gravity, prior to it being withdrawn.

If chemical fixation with cement or silica is carried out to ensure that the sludge remains stable in subsequent landfill, then this is best achieved with thickened sludge.

3.2.5.1 Ambient Air Drying, Natural Evaporation

The simplest, but still a very effective, sludge dewatering method, mentioned already in Section 3.2.4 is the technique used normally by small finishing factories, particularly in warmer countries.

If sufficient ground near the sedimentation pond is available, a suitable drainage basin is constructed and used for drying the sludge by natural evaporation. Construction of the basin must however be controlled by the authorities since the environment can be severely impacted otherwise. Precautions need to be taken against wind or rainfall dispersing the material, and to prevent access by wildlife and unauthorized persons. From time to time the solid earthy-looking sludge has to be transported to a deposition site suitable for industrial wastes. The need for better control over the dewatering process has led most establishments to adopt more mechanized processes.

3.2.5.2 Filterpress, Filterbelts

Filterpressing reduces the volume of the sedimented sludge 15 times or more and yields about 30-35% solids content in the cake. The water pressed out of the filter by hydraulic forces is returned to the sedimentation pond. The filter cake is peeled off the filter material and stored for transportation. Filter presses are relatively inexpensive and simple to operate, and do not require extensive maintenance.

Beltfilters in which the sludge is dewatered by progressively higher pressures on a moving belt are also in common use.

3.2.5.3 Other Dewatering Methods

Several other dewatering techniques are occasionally used. In vacuum filtration a horizontal drum rotates partly submerged in a vat filled with sludge. The surface of the drum is covered by the filter medium connected to a vacuum pump. The dewatered filter cake is lifted from

the drum surface as it rotates. Investment and operating costs are higher than those of filter-presses.

Basket centrifuges are also sometimes used for compressible slurries that settle well. The collected effluent is returned to the sedimentation pond. This technique is not recommended for sludge dewatering in general, because the costs are relatively high.

Following sludge dewatering, some companies practice sludge drying, utilizing various types of equipment. This process further dries sludge filter cake from approximately 35% solids content up to a virtually dry material. The volume reduction to be expected is in order of 4 to 1. Where sludge disposal costs are based on volume, the savings can be substantial.

3.2.6 Treating Oily Waters

Oil and grease are common pollutants in the metal finishing industry. Oil has a high biochemical oxygen demand (BOD) of 1000 to 2000 mg per gram of oil. BOD is a measure of the amount of oxygen consumed while the pollutant is being degraded in the aqueous environment: the higher the BOD, the more polluting is the material.

Wastewater with low quantities of free oil (less than 5 mg/l) is best treated using some form of filtration. Activated carbon, sand or kieselguhr are suitable filter media. Fine coalescer units or combined coalescer/filter units are also on the market. With any of these processes the oil content of the treated water can be lowered to less than 1 mg/l. Thus this method is suitable also for final stages in the treatment of oily waters. Ultrafiltration may also be applicable. For larger concentrations of free oil, gravity separators are used. Water-oil emulsions must be broken before separation by gravity is possible. Oil separators are dimensioned on the basis of surface load and retention time. Compressed air blown into the incoming wastewater line improves the cleaning effect by lifting the oil to the surface in the separation basin. Some designs also work effectively without air, thus reducing considerably the energy consumption of the treatment.

Emulsion-splitting is normally carried out by adding salts (sodium-, calcium-, magnesium-, aluminium- or iron-salts) or acids. After emulsion splitting and sludge separation, the water usually contains between 1 and 50 mg/l of oil depending on the type of emulsion, the chemical additive etc., and should undergo a biological cleaning stage, or be filtered through an absorption agent.

Ultracentrifugation has only recently been introduced for treating oily industrial waste waters. Ultracentrifugation requires a relatively high

level of investment, and skill for operation and maintenance. Final results of about 1 mg/l oil in water can be obtained.

Absorption agents are on the market for treating water containing emulsified oil. They can be directly mixed with the wastewater to convert the oil to an easily removable solid phase. Silicic acid is frequently the active ingredient. Results are comparable to chemical emulsion splitting, however, the treatment time is much shorter: only some 20 minutes. The technique requires little equipment but the price of the material required is relatively high, so that the treatment of large volume of wastewater is not economical. Disposal of the resulting solid needs to be carefully controlled, and should occur only at perhaps after further stabilization and solification of the solid phase.

3.3 CONTROL OF AIR EMISSION

A number of surface treatment operations generate acid mists, particulates and solvent fumes. These pollutants may be toxic to workers, as well as to the surrounding environment.

The control of air emissions can be approached in several different ways:

- substitution of less hazardous materials;
- removal of the pollutants from the collected air stream;
- dispersion of the pollutants to acceptable low concentrations.

Clearly the first alternative is the most preferred. Solvent substitution is a good example of this.

Exhaust hoods and good ventilation can reduce the level of air pollutants in the workplace. Open-tank operation from which mist, spray or volatile gases can escape are particularly in need of such equipment. Every effort should be made to design hoods which enclose as much of the tank surface as possible. This will result in better ventilation using smaller ducts and fans, and lower power consumption.

It is necessary to consider the point at which such vented gases are discharged outside to ensure that no deleterious effects occur there. In many circumstances it will be necessary to treat the off-gases to remove the pollutants prior to discharge.

Particulate pollutants from mechanical surface preparation can be removed by cyclones, or by filters (fabric or bag). Cyclones have low capital and operating costs. Fabric filters are more expensive, but need

to be considered for high efficiency filtration in low volume, low humidity gas streams. Mist eliminators should be fitted over acid cleaning baths and electroplating baths. Fume scrubbers are used on pickling, etching, bright dipping, plating, anodizing and phosphating lines. They are designed to handle high temperature and corrosive gas streams with high efficiency. Both capital and operating costs are relatively high.

4.0 PREVENTIVE MEASURE FOR POLLUTION AVOIDANCE

Previous sections have examined the technical options for reducing environmental impact. Much also depends on the taking of preventive operational and management measures so as to avoid problems in the first instance, and perhaps arrange the situation in the plant so that any necessary corrective action is readily taken.

4.1 OPERATING PRACTICE

Occasional mention has been made above of the need always to operate plant according to the supplier's design specifications. It is true in many instances that current operating practice owes more to history than the original design. This can be particularly true for equipment which is particularly dated, or which has been acquired second-hand rather than new. Concentrations of plating solutions or treatment solutions, plating/treatment time, minimum plating thickness are all areas where best practice may have been overtaken by current practice.

In all events, it is advisable to attempt to determine the operating specifications for which the plant was originally designed. Even for old or second-hand equipment this may be possible, if the original supplier of the equipment can be identified. Alternatively, it may be possible to obtain at least some of the information from alternative sources, such as patent offices in the country of origin. An experienced consultant may also be able to advise on at least some aspects from personal experience.

4.2 GOOD HOUSEKEEPING AND WORK PLACE SAFETY

Untidy and crowded working conditions are a safety hazard to personnel, and can also increase the waste of consumable inputs as well as to a greater number of unplanned discharges to the environment. Good housekeeping is a matter of attitude; essentially the attitude of management, and the degree to which this is transmitted to the shop floor.

Material losses can often be identified by undertaking simple mass balance calculations. Spills can be reduced through careful handling and transfer of materials, and the strategic location of drip and spill trays where these events are most likely to occur. An energy balance calculation can also be used to determine savings that can be made in energy consumptions. Adherence to the suppliers requirements for optimal maintenance cycles can prolong service life and minimise downtime and off specification rejects. Proper receptacles for wastes ensures that contamination of the surroundings of the plant is reduced.

The protection of workers, like the protection of the physical environment, relies largely on appropriate precautionary measures, aided by suitable organisational procedures. Such a combination of measures contributes to reducing exposure to chemical hazards, physical dangers from machinery and handling, and thermal, acoustic and vibrational stress. It should be stressed that the same conditions leading to work place hazards often have an impact on the environment and people surrounding the industry as well.

In Industrie Countries specialist bodies concerned with work place hazard reduction should also pay attention to the external issues so as to support the initiatives of the environmental agencies. In, so called, developing countries it is essential that management familiarises itself with WHO/ILO guidelines on work place safety and ensures that workers are made familiar with these, as well as providing for such equipment and measures as to enable them to be met.

4.3 MANAGMENT OF SPILLS AND LEAKS

In addition to the running rinses that carry many of the pollutants to the effluent stream, large quantities of process effluent are often lost to the environment through accidents and deliberately dumping such material. In some instances, these two sources may account for as much as 80% of the heavy metal load to the environment from a surface treatment plant. The shock effect of introducing high concentrations of pollutants in a short time period may be far more drastic on sewage treatment plants and receiving waters than the same quantity discharged over a long period.

The following possible sources of accidental losses should be the focus of regular inspection, control and prevention measures:

- tanks (for leaks);
- filters and process tanks (for solutions remaining);
- equipment such as filters, pumps, heat exchangers, and their hoses and connections (for leaks);
- overflows (to check for blockage and safe containment);
- valves (for seizure, accidental opening or rupture);
- materials storage and handling (for spillage).

Deliberate, unauthorized release of solutions should never be permitted. Whilst easy to ensure in developed countries, particular effort needs to be paid to this in the, so called, developing countries, where disposal alternatives may be fewer.

4.3.1 Tank Leaks

Unprotected steel tanks should be shielded against stray currents with materials such as PVC. In barrel plating, when the tank is cathodic, insulation should be provided against arcing, which may occur between the anodes and the side of the tank.

In processes where there may be a buildup of chloride that is not itself deleterious to the process, there could nevertheless be accelerated corrosion of an unprotected tank. If improved rinsing does not correct the problem, it will be necessary to line the tank.

4.3.2 Residual Solutions.

These should generally be re-used, or if this is not possible, processed in the effluent treatment plant.

4.3.3 Equipment Leaks.

There is probably more loss of chemicals from equipment leaks than any other. The causes include carelessness, insufficient maintenance, or simple tolerance of a continuing condition. Filter hoses, heat exchanger connections, heating coils, pump hoses and connections are all prone to degenerate and permit leakage. Losses of 2.5 to 5 m³ per day of solution from process tanks through any of these routes may be blamed on evaporation or dragout and go on for long periods.

Filters can be a major source of problems, providing containment around the area of the filter will act as an aid to inspection, allow leakage to be identified, and provide an opportunity for remedying the problem.

Heat exchangers and heating coils deteriorate slowly, developing pin-point breaks or cracks. When steam condenses, a vacuum is created and solution is drawn into the condensate. Since many metal finishers return the condensate to a boiler to save water and energy, there is the likelihood of corrosion damage to the boiler as well as solution loss. In addition, an alarm system can be installed on the boiler condensate return line as an aid to periodic examination.

A similar problem may occur with cooling water, except that it is possible that both overflow of the bath and loss of chemicals to the cooling stream may take place.

4.3.4 Overflows.

Although completely avoidable, almost every shop experiences such events. Overflows usually occur during the "topping up" procedure and are the result of lack of attention.

4.4 REPLACEMENT OF HAZARDOUS CHEMICALS BY LESS TOXIC SUBSTANCES

There are a number of compounds used in surface treatment which are potential dangerous to both the work force and the environment. Opportunities for reducing or replacing process chemicals which have been introduced in developed countries are shown below, accepting that the introduction of some of the substitutions involves the introduction of new, more technologically advanced equipment with all of the associated problems in, so called, developing countries identified above.

4.4.1 Cyanide.

The greatest success so far in the reduction of cyanide in developed Countries has been in zinc plating. Cyanide-free processes for other metals include:

- pyrophosphate copper as a substitute for cyanide copper.

With the cleaners that are now available, there is no need to use cyanide in any cleaning operation. Similarly, there are substitutes for cyanide-containing stripping compounds.

4.4.2 Cadmium.

The high toxicity of cadmium in the work place, and the contribution to its environmental dispersion from plated products, makes cadmium substitution a high priority with many authorities. Some developed countries have banned cadmium from non-essential uses, and discharge limits are often stringent.

The development of highly corrosion-resistant zinc plating has virtually eliminated the necessity to use cadmium except for special applications. For some uses aluminium coatings can also be employed.

4.4.3 Chromium.

As a substitute for hexavalent chromium, the less toxic trivalent chromium should preferably be used in making up baths. Trivalent chromium also rinses more freely and permits simpler waste treatment facilities.

4.5 RECOVERY OF CHEMICALS

Recovery of process solutions provides a simple and economical way of avoiding the discharge of contaminants to the environment. Recovery of process solution has been standard practice for a long time in the metal finishing industry.

To enhance the possibility of recovering the various solutions used in surface treatment, it is advisable to keep the bath solutions as uncontaminated as possible. To this end it is useful either to prevent the baths becoming contaminated with impurities, or to purify the bath solutions more frequently. Regular analysis of the process solution, and making it up regularly is essential.

Profitable recovery of solutions may also be profitable from solutions or solids normally discarded. For example a considerable amount of solution is often left in the treatment tanks used to purify baths and in filters when they are being cleaned. Significant quantities of solution can be lost if these are discarded. In addition, hydroxide sludge containing significant quantities of recoverable metal may still be discarded, even in developed countries. These sludge are potentially saleable for the heavy metal content, particularly if the effluent stream from which they are precipitated is single rather than mixed.

Recovery of chemicals can offer both savings and environmental benefits. Items for treatment should be allowed to drain directly back into the bath. Alternatively, recovery tanks can be used immediately after the process. This procedure is most successful where the contents of the tanks are used to make up for evaporative losses. Some recovery is possible on cold tanks if drag-in can be reduced sufficiently. In extreme cases of drag-out, two recovery tanks may be used, with the first making up the process solution losses and the second making up the first recovery tanks.

Consideration should also be given to mist spraying of parts while they are suspended over the plating bath. This is a very effective way of carrying drag-out directly back to the bath. The quantity of water used in the spray can be controlled to approximate the evaporation rate.

4.6 ENVIRONMENTAL CONTROL TECHNOLOGIES

4.6.1 Waste Water Treatment Technology.

Waste water treatment technologies employed by surface finishers include in-plant water conservation measures to minimise effluent discharges, as well as end-of-pipe treatment. The focus in this section is on the water conservation

aspects, as they are 'good housekeeping' alternatives which are of particular benefit in the developing countries where there is a significant shortage of potable water (see section 3.2).

4.6.1.1 Water Conservation.

Water conservation results in lower water use and less effluent to treat. Savings can be realised in the capital cost of lower capacity treatment equipment, chemical costs, and conserved floor space.

Rinse tanks follow almost all surface finishing operations and are the largest source of waste water (see section 3.1.2). The amount of rinse water used can be reduced by at least 50% by:

- a) counterflow rinsing (at least two stages are required but usually no more than four);
- b) spray rinsing, which consumes less water than the conventional bath;
- c) conductivity meters in rinse tanks so that slightly contaminated water can be re-used to the maximum extent;
- d) flow control valves set at minimum fresh water flow requirement;
- e) delay over plating baths and rinse tanks to reduce dragout to the following tank;
- f) drag-in/drag-out tanks before and after plating tanks.

Unnecessary wastage of process solutions can be prevented by:

- a) the use of holding tanks or dams to retain splashed, spills and leaks;
- b) segregation of acids, alkalis, cyanide and chrome wastes by trenching and piping.

4.6.2 Effluent Treatment.

Effluent treatment options used by surface finishers are summarized below (see sections 3.1.x and 3.2.x).

4.6.2.1 Cyanide Chlorination.

Cyanide-containing effluent from plating, conversion coating and cleaning are oxidized to break down the cyanide to carbon dioxide and nitrogen. The most common treatment method is alkaline chlorination because the operating costs are low, the process can be automated and efficiencies of 99% reduce the cyanide to very low concentrations.

Alternatives to alkaline chlorination have been developed and are commercially available. These include ozonation, ultraviolet radiation, the use of hydrogen peroxide and electrolytic oxidation. However, these methods may be more expensive and require specially trained operators.

4.6.2.2 Electrolytic Destruction of Cyanide

The electrolytic destruction of cyanide is used for heat treatment waste and concentrated cyanide dumps, although it may also be used to treat high-concentration cyanide plating baths.

The use of electrolytic destruction is limited to waste waters with cyanide concentrations over 100 mg/L. Below this level, conductivity is reduced and the reaction normally cannot proceed. Sulphates in the waste inhibit process performance.

4.6.2.3 High-Pressure and High-Temperature Hydrolysis

A hydrolysis process to destroy cyanide in dilute rinse waters and spent plating solutions has been developed recently and may provide surface finishers with an economical alternative to chlorination.

4.6.2.4 Chromium Reduction

Chromium effluent are generated during electroplating, chromate conversion coatings, etching, and any cleaning operation applied to chrome metal. Chromium can be precipitated and removed as a hydroxide after being reduced to its less toxic trivalent form.

Alternatives to reduction of chromium compounds by chemical means are electrochemical chromium reduction, electrochemical chromium regeneration, evaporation and ion exchange.

4.6.2.5 Neutralization and Hydroxide Precipitation

Neutralization is required for the large volume of acidic effluent generated during acid cleaning, acid cleaning rinses and plating rinses. A smaller amount of alkaline effluent results from detergent and alkaline cleaning and is usually combined with the acid stream.

Hydroxide precipitation of metals is the most common treatment process. It has a long history of use, is usually very effective and can be automated.

The use of expensive chemicals and electrical power is avoided. Cyanide and complexed metals must be broken down prior to hydroxide precipitation because they inhibit this process.

4.6.2.6 Sedimentation

After neutralisation and hydroxide precipitation, the suspended solid particles formed can be removed by gravity settling in a sedimentation basin or clarifier. Coagulants or flocculents may be added to shorten the retention time of several hours and increase removal efficiency. Clarifiers are the preferred equipment because they offer a shorter retention time, higher efficiency, and are more compact than sedimentation basins.

Large volumes of metal hydroxide sludge are removed from the effluent but this sludge has no commercially viable recovery potential at present. It may, however, be hazardous and must be disposed of at an accepted landfill site. To reduce transportation and disposal costs the sludge should be dewatered to increase the solids content from about 2% to 40%. Plate and frame filters offer the lowest operating cost but large plants often use vacuum filters for dewatering.

4.6.2.7 Electrodialysis

Electrodialysis is a method separating the ions from solutions by means of an ion-selective membrane under the influence of an electric field, and is a means of recovering and concentrating the metal ions in plating rinse waters for recycle to the plating bath.

Electrodialysis is relatively new and, although there are a wide number of uses for this recovery process, it has not yet gained popularity, perhaps because of its capital cost. It should be considered as one of the technologies whose general application in, so called, developed countries will be limited to particular, large-scale circumstances.

4.6.2.8 Reverse Osmosis

Reverse osmosis is a means of separating solutions by means of a suitable semi-permeable membrane and the application of pressure to the solution. This forces metal ions to permeate through a semipermeable membrane into a dilute solution. Many applications have been found including reclaiming of plating salts.

Other applications (see section 31.4.1) are the recovery of zinc chloride, copper cyanide, zinc cyanide and cadmium cyanide. An important and valuable by-product of reverse osmosis is pure water which can be recycled back to the rinse tanks.

Reverse osmosis has been particularly successful at recovering nickel salts from spent nickel plating and rinse baths. In the context of the commercial environment of developed countries, payback periods of about three years have been realised.

5. UNIDO's Role in Pollution Prevention & Control

The problem of mitigating the rate of environmental degradation in developing countries is receiving increasing attention from the aid agencies, but the programmes in place rarely address the fundamental question of "good housekeeping" in the work place.

UNIDO can support such activities by introducing programmes of training on plant repair and maintenance and quality control and quality control as well as quality assurance of this, but in addition, much more can be achieved by relatively simple and cost effective measures which developed countries governments could instigate themselves (perhaps with a little priming support of UNIDO or some other bilateral or multilateral aid network).

The measures which could be introduced fall without the main remit of the seminar, and are, therefore, not discussed extensively here. Nevertheless, a list is given below of possible measures which could be taken. They are not mutually exclusive, and the benefits would increase more than proportionately if the schemes were to be introduced together rather than serially.

A. Promotion Awareness Campaigns

A government sponsored awareness campaign has the possibility of raising the profile of good housekeeping, and the benefits that it can bring. This would need to be carefully planned, and implemented in such a way that the message was reinforced rather than presented once and then forgotten. It might be that such a campaign could be sponsored by some of the multinationals present in the country, focussing on those with a strong commitment to a corporate environmental policy in their home country.

B. Promotion Good Practice Award

Those companies who can be shown to have a reduced waste, effluent or gaseous emissions could be given an award, which may simply be a question of publicity or could be a combination of this and money (or a government contract).

C. Develop of Economic Incentives

Economic incentives are becoming of increasing importance in some developed countries as a way in which market signals can be adjusted to reflect more accurately the environmental benefits in developing countries is less advanced, but some of those listed below may have applicability in certain developing countries:

× the provision of tax relief on the cost of training the work forces in the quality control and quality assurance of repair and maintenance programmes ("good housekeeping");

× reserving a certain proportion of government contracts for companies with an effective "good housekeeping" programme;

× tax credits for measurable reduction in waste/effluent/gaseous emissions resulting from effective "good housekeeping" programmes.

D. Promotion Education and Continuing Education

The importance of bringing young people fully trained in all aspects of "good housekeeping" into the work force cannot be emphasised. It is for these reason that the technical education facilities in developing countries be encouraged to introduce comprehensive training in this field into the syllabus of technical schools. In addition, provisions for continuing technical education should also incorporate this into the courses they offer.

UNIDO should promote and encourage the implementation of "good housekeeping" projects. A properly implemented good housekeeping programme could provide significant gains in profitability, and that both the environment and profit-related gains could be realised immediately further commends this approach. Good housekeeping programmes, perhaps with some modest pump priming aid from UNIDO or other bilateral and multilateral agencies.

Additionally, UNIDO should instigate demonstration programmes in "good housekeeping" in developing countries to reduce the impact of industry on the environment, either through its own good offices, in association with other divisions of UNIDO, or other elements of the UNITED NATIONS system.

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- 20- The National Swedish Environmental Protection Board 1985, General Advisory 85:1, Committee on the challenges of Modern Society.

APPENDIX 1:
HAZARDOUS WASTES GENERATED BY SURFACE FINISHING

TDGA Code No.	Waste Type No.	Source	Waste Component(s)
Na 9301	1	Solvent degreasing	The following spent halogenated solvents used in degreasing: tetrachlorethylene, trichloroethylene, methylene chloride, 1,1,1-trichlorethane, carbon tetrachloride, and chlorinated fluorocarbons; and sludges from the recovery of these solvents in degreasing operations.
NA 9302	2	solvent degreasing drying painting coating machining miscellaneous	The following spent halogenated solvents: tetrachlorethylene, methylene chloride, trichloroethylene, 1,1,1-trichlorethane, chlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, ortho-dichlorobenzene, and trichlorofluoromethane; and the still bottoms from the recovery of these solvents.
NA 9303	3	solvent degreasing drying painting coating machining miscellaneous	The following spent halogenated solvents: xylene, acetone, ethyl acetate, ethyl benzene, ethyl ether, methyl isobutyl ketone, n-butyl alcohol, cyclohexanone; and methanol; and the still bottoms from the recovery of these solvents.
NA 9304	4	solvent degreasing	The following spent non-halogenated solvents; cresols and cresylic acid, nitrobenzene; still bottoms from the recovery of these solvents.
NA 9305	5	solvent degreasing	The following spent non-halogenated solvents: toluene, methyl ethyl ketone, carbon disulphide, isobutanol, and pyridine; and the still bottoms from the recovery of these solvents.

APPENDIX 1: (Cont'd)
HAZARDOUS WASTES GENERATED BY SURFACE FINISHING

TDGA Code No.	Waste Type No.	Source	Waste Components
NA 9306	6	effluent treatment	Wastewater treatment sludges from electroplating operations except for the following: (1)-sulphuric acid anodizing of aluminium; (2)-tin plating on carbon steel; (3)-zinc plating (segregated basis) on carbon steel; (4)-aluminium or aluminium-zinc plating on carbon steel; (5)-cleaning stripping associated with tin, zinc, and aluminium plating on carbon steel; (6)-chemical etching and milling of aluminium.
NA 9307	7	effluent treatment	Wastewater treatment sludges from the chemical conversion coating of aluminium.
NA 9308	8	electroplating	Spent cyanide plating bath solutions electroplating operations except for precious metals electroplating spent cyanide plating bath solutions.
NA 9309	9	electroplating	Plating bath sludges from the bottom of plating baths from electroplating operations where cyanides are used in the process (except for precious metals electroplating plating bath sludges).
NA 9310	10	cleaning	Spent stripping and cleaning bath solutions from electroplating operations where cyanides are used in the process (except for precious metals electroplating spent stripping and cleaning bath solutions).

APPENDIX 1: (Cont'd)

HAZARDOUS WASTES GENERATED BY SURFACE FINISHING

TDGA Code No.	Waste Type No.	Source	Waste Components
NA 9311	11	quenching	Quenching bath sludge from oil baths from metal heat treating operations where cyanides are used in the process (except for precious metals heat treating quenching bath sludges).
NA 9312	12	salt bath pot cleaning	Spent cyanide solutions from salt bath pot cleaning from metal heat treating operations (except for precious metals heat treating spent cyanide solutions).
NA 9313	13	effluent treatment	Quenching wastewater treatment sludges from metal heat treating operations where cyanides are used in the process (except for precious metals heat and treating quenching wastewater treatment sludges).
NA 9381	81	pickling	Spent pickle liquor from steel finishing operations.
NA 9382	82	effluent treatment	Sludge from lime treatment of spent pickle liquor from steel finishing operations.

**United Nations Environment Programme
Industry and Environment Office
International Cleaner Production Information Clearinghouse
(ICPIC)**

Accessing ICPIC

Equipment: you need

- an IBM (or compatible) PC, an Apple, or a terminal;
- a modem (1200 bauds or 2400 bauds) and appropriate communications software.

Connection: ICPIC is accessible either through public telephone system or any data packet switching network.

Telephone:

- Change your communications parameters*
 - number: 33-1-40588878 ;
 - no parity, 8 data bits, and 1 stop bit;
 - emulated terminal, if necessary, to VT100.
- Save the communications settings.
- Dial ICPIC system.

Packet Switching Network:

- Change your communications parameters*
 - number: local Telenet node** (or local node of your packet switching network);
 - no parity, 8 data bits, and 1 stop bit;
 - emulated terminal, if necessary, to VT100.
- Save the communications settings.
- Dial Telenet (or your packet switching network).
- when connecting to Telenet, enter ICPIC access number 7620 0604 (or 3110 7620 0604 if you are connecting via another packet switching network).

Once connection is established, "Welcome to ICPIC" is displayed on the screen. You are then requested to enter your first name, last name and password in order to log-on.

If your name is not in the list of users, you will be asked if you want to register as a new user. Answer 'Y' and complete the registration procedure in order to add your name to the user list.

ICPIC system is a menu-driven system. Please read carefully the system prompts and answer them correctly. On-line help is available by entering 'H' in response to any prompts.

If you experience any difficulties in using the system, please feel free to contact ICPIC system operator at telephone number 33 (1) 40 58 88 54, or if possible, leave your message to SYSOP before logging-off.

Access to ICPIC is free-of-charge. There is neither registration fee nor monthly charge. Users pay the communication cost directly to local telephone authorities or to the packet switching network which they use to access ICPIC.

For all information related to the system please write to
JNEP - Industry and Environment Office
Tour Mirabeau
39-43, quai André Citroën
75739 Paris Cedex 15
France

Telex: 204 997 F
Telefax: 33 (1) 40 58 88 74

* Refer to your communications software manual for details on how to change these settings.

** ICPIC is actually connected to Telenet (US-Sprint) packet switching network. UNEP can provide you with your local Telenet office address and access number.



IEQ/DIE

INDUSTRY AND ENVIRONMENT OFFICE

Telephone 33 (1) 40 58 38 50
Telex 204 397 F
Cables UNITERRA PARIS
Fax: 33 (1) 40 58 88 74

DEPARTEMENT INDUSTRIE ET ENVIRONNEMENT

Tour Mirabeau
39-43, quai André Côté
75739 PARIS CEDEX 15
France

INTERNATIONAL CLEANER PRODUCTION INFORMATION CLEARING HOUSE CASE-STUDY FORMAT

Guidelines for Case Study Abstractors

- 1.0 **Headline**
A short attention-getting phrase or sentence highlighting the significance of the case study that should include industry or process, waste type, and pollution prevention technique. Describe the problem that was solved.
- 2.0 **SIC or ISIC Code**
Four-digit Standard Industrial Classification code(s) that best describes the industry segment(s) referenced by the case study. Employ the highest level of specificity (i.e. use three- or two-digit SIC codes if information does not allow more detailed identification). Use as many SIC codes as are relevant to the subject study; however, the primary SIC codes should always be the first code listed. Precede all International SIC codes with "I" (e.g. I2261).
- 3.0 **Name & Location of Company**
The name and location of the facility that implemented the case study. Include address if possible (street, city, state, country and telephone number).
- 4.0 **Cleaner Technology Category**
A brief description of the principle(s) behind the pollution prevention technology referenced in the case study, such as:
 - . Periodic assessment
 - . Recycling, reuse and reclamation
 - . Training and supervision
 - . Production planning and sequencing
 - . Process/equipment modification
 - . Material/Product substitution
 - . Housekeeping
 - . Waste segregation and separation
- 5.0 **Case Study Summary**
Summarize information to the level of detail provided in the case study, in the following areas:
 - 5.1 **Process and Waste Information:** A description of the relevant original manufacturing process or area of the plant to which the pollution prevention technique applies, physical state of the target waste streams (solid, liquid, gas, or sludges), changes in the process resulting from the pollution prevention technique, and a description of any positive or negative effects on the wastes, products or production rates after implementing the new technology. Include any changes in:
 - products or production rates resulting from the application
 - new or existing waste stream generation and composition
 - new or existing raw materials and consumption rates
 - energy usage
 - operating procedures

- 5.2 **Scale of Operation:** A description of the size of the process or operation. If possible, include quantitative information on the amount of product being produced or manufactured and the amount of waste being generated.
- 5.3 **Stage of development:** A one-line description of the stage of development the pollution prevention technique was in at the time of the case study (e.g. planning stage, bench test, pilot stage, or fully implemented). Indicate whether quantitative figures are estimated or based on actual production.
- 5.4 **Level of Commercialization:** An indication of whether the technology or process was commercially available at the time of the case study. Indicate whether or not the equipment and/or materials were readily available, or if they were specifically designed for this application.
- 5.5 **Material/Energy Balances and Substitutions:** A tabulation of quantitative changes in material generation and use prior to and resulting from the pollution prevention technique. Include in the following table, information for each waste stream or product, and designate "N/A" when information is not available (provide units of measurement for all numerical data):

Material Category	Qty. Before	Qty. After
Waste Generation:		
Feedstock Use:		
Water Use		
Energy Use:		

- 6.0 **Economics***
A summary of the costs and savings reported in the case study. Include dates and currencies for all economic data reported.
- 6.1 **Investment Costs:** A summary of all capital costs and a detailed description of the purchased items(s) or service. Include specifications (i.e. number, size, capacity, etc.) for each item used.
- 6.2 **Operational & Maintenance Costs:** Changes in operational and maintenance cost (per month or year) and changes in personnel or hours required.
- 6.3 **Payback Time:** The approximate payback period for the particular pollution prevention technology used in the case study (total investment/net savings/year).

* Disclaimer: Economic data will vary due to economic climate, varying governmental regulations and other factors.

7.0 Cleaner Production Benefits

A detailed discussion of the benefits resulting from pollution prevention technique, including but not limited to:

- economic benefits (include source of savings i.e. reduced feedstock)
- improved public relations
- reduced liabilities
- changes in regulatory compliance

Indicate, if possible, what factors were the driving force behind implementing the technique

8.0 A description of the technical constraints that could prevent implementation of the technology (i.e. physical, chemical, or biological limits of a manufacturing or treatment process). Discuss any regulatory barriers in implementing the cleaner technology and indicate what other problems were encountered during implementation of the technology.

9.0 Date Case Study Was Performed

The actual date the pollution prevention measures were initiated.

10.0 Contacts and Citation

10.1 Type of Source Material: The type of source material abstracted:

- book or chapter
- journal or journal article
- organization report
- conference proceedings
- un published material
- other (specify)

10.2 Citation: citation for the document abstracted including: Author(s); title of book, journal article or proceedings; volume; number; and month and year of publication. In addition if the document is available through ISBN, enter the ISBN number.

10.3 Level of Detail of the Source Material: An indication of whether or not additional detail is available in the source document for this case study (applicable only for documents that are publicly available). Indicate what additional information is available (i.e., process, waste, etc.).

10.4 Industry/Program Contact and Address: The name, address and phone number of the person that can be reached for further information concerning the case study.
Authorization must be given by the contact prior including their name in this field.

10.5 Abstractor Name and Address: The name, organization, address and telephone number of the person preparing the case study abstract.

11.0 Keywords

Descriptive keywords selected from the attached ICPIC keyword lists for each of the following categories:

11.1 Waste type: the conventional waste(s) that is/are acted on by the pollution prevention option, not the waste(s) generated after implementing the pollution prevention technique.

11.2 Process type/waste source: The original industrial process(es) or sources of the waste(s) that is/are modified by the pollution prevention technique.

11.3 Waste reduction technique: The techniques that were implemented at the facility and are principally responsible for reducing waste generation.

11.4 Other keywords: Other keyword, as appropriate, that accurately describe the case study and assist users in locating this abstract, including:

- environmental media (air, water, soil)
- product names
- feedstocks
- special incentives
- geographic/institutional keywords (North Carolina, USDA, etc.)

Use as many keywords as are necessary to accurately describe the case study in each category. If ideal keywords are not found on the keyword list, please add new ones to the list

12.0 Assumptions A listing of any assumptions used when abstracting. Reference the sections of the abstract that relied upon the assumption. Any discrepancies encountered in the source document should also be presented.

13.0 Peer Review

An indication of whether or not the source document has gone through a formal peer review process. Indicate: Yes, No or Unknown.

1.0 **Headline: Use of Acid Purification Unit on Concentrated High Temperature Pickling Liquor Reduces Iron Concentration**

2.0 **SIC Code: 2105, Pickling Steel; 2067, Ion Exchange**

3.0 **Name & Location of Company**

Metal Koting
Continuous Colour Coat Ltd.
1430 Martin Grove Road
Rexdale ont. M9W 4Y1
Canada
phone (416 743-7980

4.0 **Clean Technology Category**

Technology Principle: This technology involves the use of an acid purification unit (APU), consisting of filters and an ion exchanger to reduce iron content of the pickle acid.

5.0 **Case Study Summary**

5.1 **Process and Waste Information:** In the original pickling process, no purification of the acidic liquor was undertaken. The liquid was discarded in a continuous "bleeding" process after the "bleed" was neutralized with lime.

The new process involves use of equipment consisting of three basic pieces and one optional piece: an Eco-Tec Acid Purification Unit AP30-24 HT cartridge filter and ion exchanger, a feed pump, an Eco-Tec sand filter and an optional 400 gallon (1100 liter) water supply tank.

The pickle acid is pumped from the reservoir tank through a media filter to remove dirt and oil particles. The acid then passes through a second filter (0.5 μm) to remove very fine particulate and filter media from reaching the resin bed in an ion exchange unit. The following stage contains three steps per cycle: the water displacement stage, the byproduct (iron) removal stage, and the produce (acid) return stage.

The water displacement phase allows the pickle acid into the resin bed, displacing the water from the previous cycle. This water can be reused by sending it to the water supply tank, or sent to drain. This stage lasts approximately one minute.

The byproduct stage allows the pickle acid to continue its flow through the resin bed trapping the sulfate ions and allowing the iron to pass through and sent to drain. This phase also takes about one minute.

The product return phase stops the flow of acid from the reservoir and starts a counterflow of water from a pressurized source (main water line or water supply tank pump). The water picks up the sulfate ions and returns them to the tank of sulfuric acid. This stage takes about two minutes.

This three phase cycle continues automatically until the dirt build-up in the media filter causes the process to automatically shut down. A back flush procedure is necessary to clean the filter before restarting the system again. Backflushing time is approximately one hour.

Using the new process results in the reduction of the iron content of the acid solution from an initial 7.7% to a steady 2-3% during the latter half of the test period. An 89% decrease in use of sulfuric acid and lime also resulted. No new materials are introduced in the process. Since pickling uniformity is a product quality improvement, product quality is at least as good as before using the APU, but this was not quantified.

5.2 Scale of Operation: Information not provided.

5.3 Stage of Development: The installation is fully implemented. Data are derived from the last month of testing.

5.4 Level of Commercialization: The installation is fully commercially available. The vendor seems well equipped and experienced in construction and maintenance of the equipment.

5.5 Material/Energy Balances and Substitutions:

<u>Material Category</u>	<u>Quantity Before</u>	<u>Quantity After</u>
Waste Generation:	N/A	N/A
Feedstock Use:		
Sulfuric acid	629,089	67,558
(lbs/yr)		
Lime (tons/yr)	252	28
(Computed)		
Water Use:	N/A	N/A
Energy Use:	N/A	N/A

6.0 Economics*

6.1 Investment Costs: Investment costs were as follows:

Design and supply of equipment	\$84,000.00
Equipment installation	\$10,000.00
Start-up, supplies, etc.	\$ 2,500.00
	<hr/>
Total	\$94,000.00

These costs do not include the test program nor the management personnel costs for the project.

6.2 Operational & Maintenance Costs: These costs are estimated at \$2500/yr.

6.3 Payback Time: Payback time was calculated as 2.33 years. Annual savings on chemicals were calculated as \$43,937. Not included in the calculations are an estimated \$8,000 saved annually on sludge hauling.

7.0 Cleaner Production Benefits

Annual savings on chemicals were \$25,942 for sulfuric acid and \$17,995 for lime, or a total of \$43,937. An estimated \$8,000 were saved on sludge hauling. The project demonstrated that sulfuric acid used in preparing steel strip for electrogalvanizing could be reclaimed for continuous use.

8.0 Obstacles, Problems and/or Known Constraints

Except for some start-up problems, no other problems seem to have been encountered.

9.0 Date Case Study Was Performed: May 31, 1985 (date of source document)

10.0 Contacts and Citation

10.1 Type of Source Material: Report

10.2 Citation:

Acid Purification Unit for Use on Concentrated High Temperature Pickling Liquor (Sulfuric Acid).

10.3 Level of Detail of the Source Material: More detailed cost information is available in the source document.

10.4 Industry/Program Contact and Address:

Mr. M. Schulz
Head Training Secion
Environment Canada
3439 River Road South
Ottawa, Ontario K1 OH3

Canada
Phone (613)991-1954
Fax (613)991-1635

10.5 Abstractor Name and Address: M. Stein, RIVM, Dept. LAE,
Anthonie van Leeuwenhoeklaan 1, Postbus 1, Bilthoven,
Netherlands. Reformatted: Barbara M. Scharman, SAIC,
8400 Westpark Drive, McLean, VA 22102.

11.0 Keywords

11.1 Waste type: pickle liquor

11.2 Process type/waste source: steel strip

11.3 Waste reduction technique: acid purification, ion
exchange, filtration, iron reduction, acid reclamation

11.4 Other keywords: Canada

12.0 Assumptions

13.0 Peer Review: Unknown

- 1.0 **Headline:** An Experimental Project Using an Electrowinning Cell and Ion Exchange Unit Minimizes Water Usage and Hazardous Waste
- 2.0 **SIC Code:** SIC Code 3471 Electroplating, Plating, Polishing, Anodizing, and Coloring; SIC Code 2067, Ion Exchange

- 3.0 **Name & Location of Company**

Kinetico Engineering Systems, Inc.
Newbury, Ohio

- 4.0 **Clean Technology Category**

Technology Principle: This experimental technology uses an electrowinning cell and ion exchange system to recover copper and reduce water usage.

- 5.0 **Case Study Summary**

- 5.1 **Process and Waste Information:** The line on which the experiment was undertaken is composed of a bath for bright acid copper plating, followed by a "dead" rinse and two rinses in counterflow. Nothing about pretreatment is mentioned in the source document. The dead rinse consists of a tank of 1500 gallons used to replenish the volume lost from the plating bath. The first running rinse, also 1500 gallons, overflowed to the waste treatment facility. The second running of 3000 gallons, was fed with 4 gallons of city water per minute.

In the first stage of the project, an electrowinning system was introduced in a circulating loop with the dead rinse resulting in reduction in the copper content and in drag-out of copper into the running tanks. The electrowinning cell design consisted of a tank using up to 50 square feet of cathode material and 48 square feet of insoluble anode. A 300 Amp, six volt rectifier powered the cell. Current densities could be varied throughout the study. An air sparger was used to agitate the bath liquid, although no heating was used.

After successful reduction of copper in the dead rinse, and thus in the running rinses, an ion exchange unit was installed to remove copper from the drag-out tank. The deionized water was returned to the last rinse bath. The ion exchange system consisted of a pump which supplied four gallons of water per minute to the system. Two ion exchange tanks containing 1.4 cubic feet of a strong acid resin were used. The dual system allowed one tank to be in service while the second tank automatically regenerated or was in standby position.

The technology resulted in reduction of the copper concentration from 15 to 6 g/l in the static rinse tank. In seven months of operation, 360 pounds of salvageable copper have been recovered by the electrowinner. As a consequence, the concentration in the first counterflow rinse dropped from over 200 to below 50 mg/l.

The water coming from the ion exchanger has copper levels well below 0.01 mg/l and is reintroduced into the second counterflow tank. It was necessary to change from city water to softened water at the inlet. Regeneration is necessary every second day and takes about 20 minutes.

The run-off water from the first counterflow rinse contains 6 mg/l of copper. It is transformed into sludge in the waste treatment system.

- 5.2 Scale of Operation: Information not provided.
- 5.3 Stage of Development: Implemented, but tests are continuing.
- 5.4 Level of Commercialization: Information not provided.
- 5.5 Material/Energy Balances and Substitutions:

<u>Material Category</u>	<u>Quantity Before</u>	<u>Quantity After</u>
Waste Generation: Sludge, 60% dry, lbs/day	18.5	2.5
Feedstock Use:	N/A	N/A
Water Use (gpm):	4	2
Energy Use:	N/A	current density 8 ASF, surface area of 20 sq. ft., 6V, 950 W

See "Assumptions" for a discussion of sludge production calculations.

6.0 Economics*

- 6.1 Investment Costs: Information not provided.
- 6.2 Operational & Maintenance Costs: Information not provided.
- 6.3 Payback Time: Information not provided.

7.0 Cleaner Production Benefits

Use of this technology was prompted by tightening control on discharge limits and waste production in the U.S.

Sludge production and water usage are reduced and salvageable copper are recovered.

8.0 Obstacles, Problems and/or Known Constraints

Copper at low concentrations in the electrowinner burned while plating. Lowering current densities also lowers plating to a rate at which the cell cannot keep pace with the drag-out rate. The running rinses had to be fed with demi water.

9.0 Date Case Study Was Performed: November 1990 (date of source document)

10.0 Contacts and Citation

10.1 Type of Source Material: Magazine article

10.2 Citation: Reduce Water Consumption and Hazardous Waste. Jerome Kovach, Kinetico Engineering Systems, Inc., Newbury, Ohio.

10.3 Level of Detail of the Source Material: Additional information is available on the processes in the source document.

10.4 Industry/Program Contact and Address:

Jerome Kovach, Kinetico Engineering Systems, Inc.,
Newbury, Ohio.

10.5 Abstractor Name and Address: M. Stein, RIVM, Dept.
LAE, Anthonie van Leeuwenhoeklaan 1, postbus 1,
Bilthoven Netherlands. Reformatted: Barbara M.
Scharman, SAIC, 8400 Westpark Drive, McLean, VA 22102.

11.0 Keywords

11.1 Waste type: copper plating bath

11.2 Process type/waste source: Electroplating, copper plating

11.3 Waste reduction technique: Electrowinning, ion exchange, drag-out reduction, copper recovery

11.4 Other keywords: wastewater reduction

12.0 Assumptions

No absolute figures on sludge production are given. It is assumed all wastes of the company are sent to the same facility.

As copper concentrations in the runoff water decreased by over 75% (from over 200 to below 50 mg/l) and the runoff was reduced from 4 to 2 gpm, it is assumed that the amount of copper entering the waste treatment facility from the experimental line decreased 87.5%. In the source document, a 75% reduction was claimed. The sludge production decreased by 16 lbs/day. From these figures, the before and after sludge production were computed.

13.0 Peer Review: Unknown

Case Study: Heavy Metal Removal Programme

Programme Applications:

The heavy metal precipitant reacts with soluble metal ions to form insoluble complexes, often in the presence of numerous chelating agents. The insoluble metal complex may appear as colloidal precipitate or as sizeable floc, depending on the particular waste water being treated. Colloidal precipitates require an appropriate coagulant for charge neutralization and, perhaps, a flocculant for adequate floc size formation. The formation of settleable floc is essential to the ultimate removal of the metals, since the presence of precipitate particles in the final effluent can result in unacceptable metals concentration.

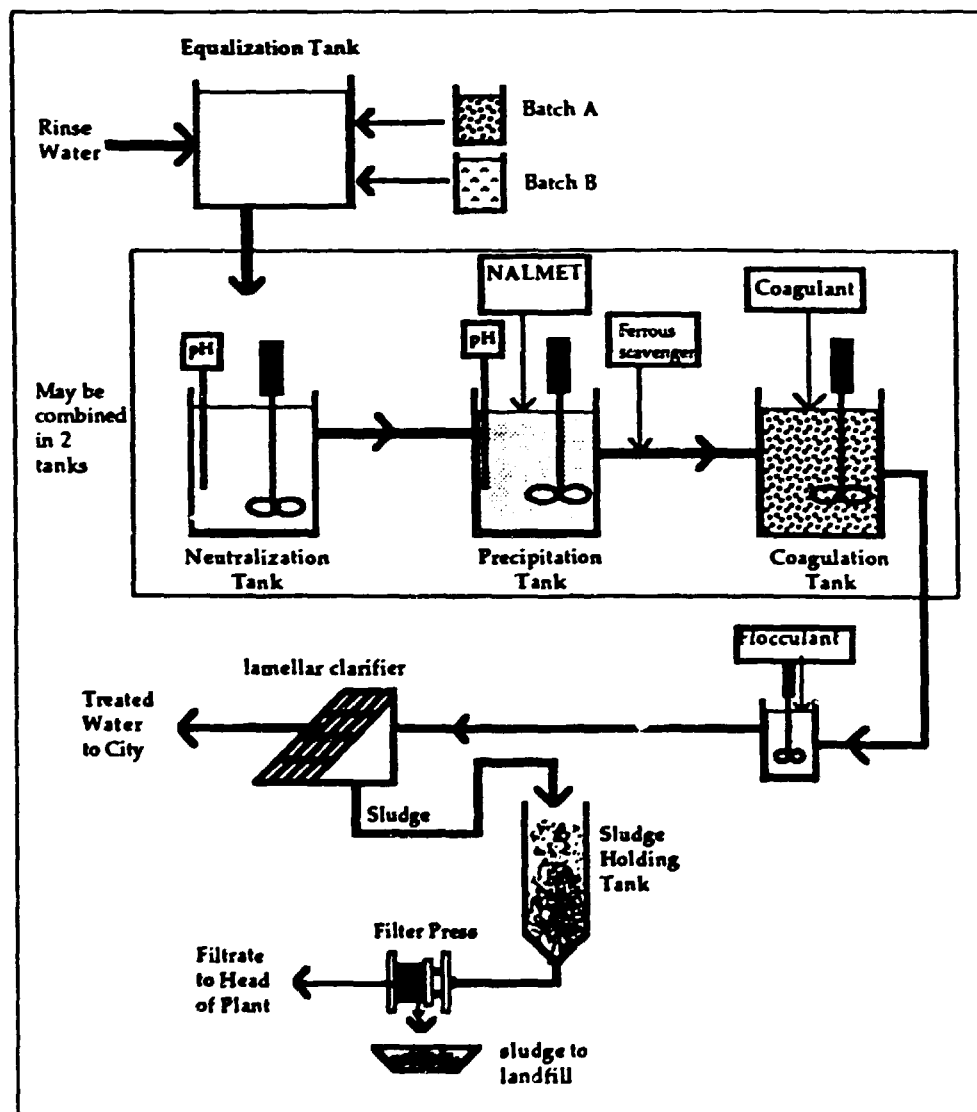


Figure 21: Typical NALMET application treating metal plating waste water (from NALCO Chemical).

Plant Results:

A plating shop recently implemented this programme in their conventional waste water treatment system. Their waste stream contained varying concentration of Copper and nickel with an average of 30 ppm and 10 ppm respectively. Their conventional wastewater treatment system using metal hydroxide precipitation produced copper and nickel levels of 2 ppm and 1.5 ppm, respectively, which did not meet their new discharge requirement of 1 ppm for both metals. This programme, consisting of the heavy metal precipitant, coagulant, and flocculant at a pH of 6.5, reduced their copper and nickel levels to below 1 ppm for both metals.

Case Study D:

- 1.0 **Headline:** Removal of Cations from Chromic Acid and Evaporation Result in Decreased Sludge Production and Energy Consumption
- 2.0 **SIC Code:** 3471, Electroplating; 2067, Ion exchange
- 3.0 **Name & Location of Company**

Koni BV
Langeweg 1
Oud-Beyerland
Netherlands
Phone (01860)12500
H. van Zessen

- 4.0 **Clean Technology Category**

This technique involves use of a cation exchanger for continuous cleaning of drag-out baths and evaporation followed by water reuse.

- 5.0 **Case Study Summary**

5.1 **Process and Waste Information:** The plant operates a three step cascade rinse behind the plating baths and the water is used to replenish the water evaporating from the process baths. This is supplemented with demi water. In the original process, a final rinse with tap water occurred after the cascade.

Because of a build-up of undesired cations such as iron, copper, and nickel in the process baths, drag-out baths are now treated over a cation resin. The water of the final rinse has been substituted with demi water and is also treated over the resin. The process liquor is too aggressive to be treated. By using the waste heat of the cooling system and controlling the process bath temperature, an extra amount of water is evaporated. The resulting wastewater is still treated in a DND installation. Lifetime of the untreated baths was about five years with the original process.

In the original process, the starting power was 10 V and 15,000 Amp. The voltage increased at a rate of 1 V/A. Due to limitations in the transformers, this meant that after about five years the process baths had to be thrown away. In the current situation, the voltage increased two volts in five years of operation, and then remained stable.

Sludge production decreased from 10 tons to 0.4 tons in five years and 60 regenerations of the cation exchanger were performed using 1500 liters of hydrochloric acid. Tap water consumption decreased from 1330 to 15 m³/yr

and demi water consumption went up 1320 m³/yr. Energy consumption decreased from 99 MWH/yr to 59 MWH/yr or more than 40%. The consumption of chromic acid decreased by 2,000 liters/yr and chemicals for the DND installation decreased from 2,000 to 20 liters/yr.

No effects on product quality were reported in the source document although quality should have improved since foreign elements have been removed.

5.2 Scale of Operation: Information not provided.

5.3 Stage of Development: The technology is fully implemented.

5.4 Level of Commercialization: All necessary parts are widely available.

5.5 Material/Energy Balances and Substitutions:

<u>Material Category</u>	<u>Quantity Before</u>	<u>Quantity After</u>
Waste Generation:		
Sludge (tons)	10	0.4
Feedstock Use:		
New chromic acid (tons)	10	N/A
HCl (liters in 5 yrs.)	0	1500
Chemicals for DND (tons)	10	0.1
Water Use:		
Tap water (m ³ /yr)	1330	15
Demi water (m ³ /yr)	N/A	increased by 1320 m ³ /yr
Energy Use:		
(MWH/yr)	99	59

6.0 Economics*

6.1 Investment Costs: Information not provided.

6.2 Operational & Maintenance Costs: Costs for the five year period are as follows:

	<u>Old Process (Dfl)</u>	<u>New Technology (Dfl)</u>
New chromic acid	15,000	--
Waste disposal	3,500	140
Chemicals for DND	40,000	400
Power loss	74,250	44,550
Tap water	8,600	100
Extra demi water	--	33,000
Sewage costs	9,550	100

6.3 Payback Time: Costs over five years have decreased by Dfl 71,710. Since no investment costs were given, a payback period cannot be calculated. However, based on the cost information given and the cost of an ion exchanger, it can be estimated that the payback period would be less than one year.

7.0 Cleaner Production Benefits

The new technology resulted in decreases in power consumption, undesired metals in the deposited layer, sludge production, chromic acid, and chemicals needed for wastewater treatment. The following are savings realized using the new process:

Less chromic acid	3000 Dfl/yr
DND treatment chemicals	8000
Waste disposal	700
Power consumption	5340
Tap water	1900

8.0 Obstacles, Problems and/or Known Constraints

No obstacles or problems were discussed.

9.0 Date Case Study Was Performed: Probably early 1990

10.0 Contacts and Citation

10.1 Type of Source Material: Example report

10.2 Citation

Removal of cations from chromic acid by continuous cleaning of drag-out baths through a cation resin and evaporation before reuse. Jan Ros, RIVM, Dept. LAE, anthonie van Leeuwenhoeklaan 1, Postbus 1, 3720 BA Bilthoven, Netherlands.

10.3 Level of Detail of the Source Material: More detailed information is available on the process.

10.4 Industry/Program Contact and Address

H.W. du Mortier
VOM
Jan van Eycklaan 2
Postbus 120
3720 AC Bilthoven
Netherlands
Phone 030-287111
fax 030-287674

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11.0 Keywords

11.1 Waste type: Plating baths

11.2 Process type/waste source: Electroplating, SIC Code
3471, SIC Code 2067

11.3 Waste reduction technique: Ion exchange, evaporation

11.4 Other keywords: sludge reduction, energy reduction,
Netherlands

12.0 Assumptions

13.0 Peer Review: Unknown

QUESTIONNAIRE

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SURFACE FINISHING INDUSTRY REVIEW

Company Name _____

Do you have any surface finishing operations in your plant such as plating, anodizing, metal heat treating, coating?

_____ YES

_____ NO

SIC Number(s) _____

Address _____

Municipality _____

Province _____

Postal Code _____

Telephone _____

Person Contacted _____

Position _____

Date _____

Interviewer* _____

* Interviewer:

Determine what type of coating operations. Plants with only plastic and/or paint coating operation(s) are not included in the survey.

GENERAL

1. How many years has the business been operating? _____

2. Normal working days per year _____
Normal shifts per day _____

3. Number of employees in finishing operations/shift _____ Total _____

4. Which of the following surface finishing operations are employed?
(check one or more below)

(a) Mechanical deburring, sand blasting _____

(b) Hot dip galvanizing (coating a metallic workpiece with another metal by immersion in a molten bath to provide a protective film) _____

- aluminum _____

- zinc _____

- lead _____

- tin _____

(c) Electroplating (production of a thin surface coating of one metal on another by electro-deposition. Metal ions in either acidic or alkaline or neutral solutions are reduced on cathodic surfaces). _____

Nickel plating bright _____

semi-bright _____

acid _____

black _____

Chromium plating acidic _____

alkaline _____

Chromium plating cyanide _____

pyrophosphate _____

sulphate _____

Zinc plating cyanide _____

chloride _____

sulphate _____

Brass plating _____

tin plating chloride _____

acid _____

alkaline _____

Cadmium plating cyanide _____

acid _____

Gold plating _____

Silver plating _____

Lead plating _____

Iron plating _____

Other (please specify) _____

(d) Electroless plating (chemical reduction process which depends on the catalytic reduction of a metallic ion in an aqueous solution containing a reducing agent and the subsequent deposition of metal without the use of external electrical energy) _____

Copper _____

Nickel _____

Brass _____

Tin chloride _____

alkaline _____

Iron _____

Chromium acid _____

alkaline _____

Cadmium _____

Gold cyanide _____

chloride _____

Silver _____

Other (please specify) _____

(e) Anodizing aluminum or magnesium (electrolytic oxidation process which converts the surface of a metal to an insoluble oxide)

 sulphuric _____

 chromic _____

(f) Solvent cleaning (process of removing oils and grease from surface of workpiece by the use of organic solvents)

vapor - halogenated solvents _____
 • solvent(s) used _____
 • gallons/year (est.) _____

- non-halogenated solvents _____
 • solvent(s) used _____
 • gallons/year (est.) _____

liquid - halogenated solvents _____
 • solvent(s) used _____
 • gallons/year (est.) _____

- non-halogenated solvents _____
 • solvent(s) used _____
 • gallons/year (est.) _____

(g) Alkaline cleaning (removal of oily dirt or solid soils. Detergent nature of cleaning solution provides most of the cleaning action with agitation of work piece secondary)

alkaline solutions used _____
gallons/year (est.) _____

(h) Acid pickling (a solution of an inorganic mineral acid, organic acid or acid salt in combination with a wetting agent or detergent to remove dirt, oil and oxide from metal surfaces)

acidic solutions used _____
gallons/year (est.) _____

(i) Acid bright dipping (a specialized form of etching (k) used to remove oxide and tarnish from ferrous and non-ferrous materials)

acidic solutions used _____
gallons/year (est.) _____

- (j) Stripping Electrodeposits _____
electrolytically _____
immersion only _____
- (k) Etching (production of specific design configurations and tolerances on parts (a metal clad plastic in the case of p.c.b.'s) by controlled dissolution of the metal with chemical reagents of etchants) _____
alkaline _____
acid (type used) _____
- (l) Chemical conversion coating (coating are applied to previously deposited metal or base metal) _____
chromating or passivating
chromic acid _____
other _____
metal colouring
phosphating (immersion in dilute solution of phosphoric acid) _____
- (m) Coating _____
plastic _____
painting _____
electrostatic painting _____
- (n) Electropolishing (process of smoothing or enhancing a metal surface by making it an anode in suitable electrolyte) _____
- (o) Salt bath pot cleaning from metal heat treating operations _____
- (p) Quenching from metal heat treating operations _____
brine solutions _____
water and water-based solutions _____
- (q) Cyaniding from metal heat treating operations _____

(r) Drying operations for electronic components _____

manufacturing

- halogenated solvent _____
- non-halogenated solvent _____

(s) Making, forming and coating operations from electronic components manufacturing _____

- halogenated solvent _____
- non-halogenated solvent _____

(t) Cleaning operations from electronic components manufacturing _____

- cyanides _____
- acid _____
- alkali _____

5. If the information is not considered proprietary, approximately what is your total output of surface finished products per year? (\$/year)

6. What are the major products manufactured at the plant? (printed circuit board, plated screws, hardened metal products, etc.)

7. Are there any water reduction facilities procedures in the plant (for example see below)? Specify.

	_____ YES	_____ NO
- counterflow rinsing		_____
- conductivity meters in rinse tanks		_____
- effluent segregation with trenching and piping		_____
- delay over rinse tanks (manually or by relays)		_____
- spray rinsing		_____
- holding tanks or dams to catch residual spills		_____

- minimization of seepage losses through floors (by timely maintenance, crack repair, etc.) _____
- other (specify) _____

8. Are liquid effluents collected in trenches or drains?

YES NO

Directed to a common collection facility?

YES NO

(Sump or tank) Specify _____

9. Are liquid effluents treated?

YES NO

Method used

- Chemical Treatment _____
 - chlorination _____
 - reduction of chromic acid with sulphur dioxide or meta bisulphite _____
 - neutralization of acid or alkali _____
 - other (specify) _____
- Separation or Destruction _____
 - clarification/gravity settling _____
 - electrolytic destruction _____
 - reverse osmosis _____
 - electrodialysis _____
 - high pressure temperature hydrolysis _____
 - ion exchange _____
 - other (specify) _____
- Evaporation _____
- other (specify) _____

14. For each final effluent stream listed in 13, establish or estimate (in mg/L except for pH). Where other data is available, please specify.

EFFLUENT STREAM	(A)	(B)	(C)
pH	_____	_____	_____
S.S.	_____	_____	_____
chromium	_____	_____	_____
cadmium	_____	_____	_____
copper	_____	_____	_____
nickel	_____	_____	_____
lead	_____	_____	_____
zinc	_____	_____	_____
cyanide	_____	_____	_____

15. How many people are responsible for the operation of efficient treatment equipment and effluent quality control? _____

16. Can you estimate annual cost of compliance with control requirements? Yes _____
No _____

Approximate cost _____
Cost/Volume effluent _____

HAZARDOUS WASTES

17. Are hazardous wastes:

	YES	NO	VOLUME (gal or ft ³)	FREQUENCY of Disposal (d/wk/mo)	METHOD
Segregates?	_____	_____	_____	_____	_____
Treated?	_____	_____	_____	_____	_____
Recovered?	_____	_____	_____	_____	_____
Disposed?	_____	_____	_____	_____	_____
Other (specify)	_____	_____	_____	_____	_____

18. If disposed, what is nature of waste and where is it disposed?

SPENT PROCESS SOLUTIONS (i.e. drainage from process tanks)

19. Where are spent process solutions discharged?

- offsite _____
- sewer _____
- effluent treatment _____
- other (specify) _____

20. If spent process solutions are treated before discharge:

What treatment method(s) is/are used? _____

Materials/solutions recovered? _____

21. State the type(s) and estimate the volume(s) of spent process solutions discharged annually.

Spent Process Solution (Description/Type)	Volume Discharged (gal./yr.)
_____	_____
_____	_____
_____	_____
_____	_____

SOLVENTS & OILY WASTES

22. Are solvent or oily wastes generated from processing?
(degreasing, machining, heat treating, forming, plastic thermo forming)

	YES	NO	VOLUME (gal or ft ³)	FREQUENCY of Disposal (d/wk/mo)	OPERATION(S) GENERATING WASTES
Solvent wastes	_____	_____	_____	_____	_____
Oil wastes	_____	_____	_____	_____	_____

23. Are plant sludges generated?

	YES	NO	VOLUME (gal or ft ³)	FREQUENCY of Disposal (d/wk/mo)	OPERATION(S) GENERATING WASTES
	_____	_____	_____	_____	_____

24. Are sludges generated? (If yes, specify items (1), (2), (3))

	YES	NO	(1) VOLUME (gal or cu ft)	(2) DRY CONTENT BEFORE DISPOSAL (%)	(3) FREQUENCY OF DISPOSAL (daily/weekly/ monthly)
from wastewater treatment processes?	_____	_____	_____	_____	_____
from tank bottoms?	_____	_____	_____	_____	_____
from treatment of spent process solutions? (specify)	_____	_____	_____	_____	_____

25. Are these sludges segregated?

	YES	NO	METHOD
treated? (specify method)	_____	_____	_____
recovered? (specify method)	_____	_____	_____
disposed? (specify method)	_____	_____	_____

26. Are the sludges monitored?

YES _____ NO _____

Who by? _____

If yes, specify content:

chromium	_____	mg/L
cadmium	_____	mg/L
copper	_____	mg/L
nickel	_____	mg/L
lead	_____	mg/L
zinc	_____	mg/L
cyanides	_____	mg/L
solvents	_____	mg/L

If no, would you agree to give us a sample?

YES _____ NO _____

27. Are any materials reclaimed/regenerated or recovered in any way

YES

NO

Specify _____

AIR EMISSION

28. Please identify releases of process emission to the atmosphere surrounding the plant.

29. Composition and quantity of these emissions to atmosphere.

30. Method used to determine information in (29)

emission factors

process material loss estimates

direct measurement

other (specify) _____

31. Are any control devices used to treat process emissions prior to release to atmosphere?

YES

NO

If so, please describe them briefly.

PROPOSAL OUTLINE

A. Development Objective

Reduce the impact on the environment due to the development of the Asia and the Pacific Region's metal finishing industry by means of establishing efficient and integral mechanisms of cooperation among companies and institutions of the region concerning pollution prevention options

B. Immediate Objectives:

1- Establishment of five working-groups in the following areas:

- × Wastewater Methodologies on Environmental Prevention for Metal Production.
- × Methodologies of Training for application of good housekeeping programs
- × Air Pollution control/Prevention
- × Environment Management/Monitoring
- × Legal and Financial Aspects (Incentives) and Regulations

2- Development and Implementation of a Technical Assistance Programm to enhance the capacities of these Companies.

The Objectives of the working-groups could be the following:

- Identify the expertise and resources on environmental aspects available in the Region.
- Identify potential focal points for technology transfer in the Region.
- Prepare comprehensive cooperation programmes (training sessions, seminars, experience exchange, etc.) among the plant members of the work-groups.
- Develop collective research programmes in common problem areas and evaluate their techno-economic characteristics.
- Develop Environment management methodologies i.e. cost-benefit analysis and monitoring.

Activities

- 2.1 Survey of capabilities/capacities of relevant metal finishing plants on the region in cooperation with national Associations.
- 2.2 Selection of the members of the work-groups
- 2.3 Selection of focal points
- 2.4 Design of Technical Assistance Programm to upgrade the focal points
- 2.5 Demonstration programm inviting other industries and governmental and non-governmental representatives.
- 2.6 Design & Implementation of training programmes.