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Technology

*Master thesis*

**Analysis and Assessment  
of Technologies for  
Reduction and Treatment  
of Plating Waste Water in  
Vietnam**

**ENCLOSURE 1**

*Master thesis*

# **Analysis and Assessment of Technologies for Reduction and Treatment of Plating Waste Water in Vietnam**

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# 1 Summary

## 1.1 Procedure

The research covers the collection of information related to the topic from:

Vietnam: Collection of information on current installed process and treatment technologies in plating industry in Vietnam. Assessment of these technologies and outline of optimisation potential.

Switzerland: Collection of data and information from different sources to analyse the current situation of plating technology and waste water treatment in Europe and especially Switzerland.

Based on the collected information, the thesis focuses on the following problems:

- Study on plating, reduction and treatment technology in developed country to gain knowledge and experience of the technical differences and market economy.
- Elaboration of additional preventive measures for plating process in Vietnam considering the methodology of Cleaner Production.
- Study on differences between plating and treatment technologies adopted in developing and industrialized countries especially in Switzerland.
- Identification of the benefits of implementing modern technologies in the plating sector in Vietnam.

## 1.2 Results and findings

The measures are chosen and introduced for changing new plating technology and reduction of wastewater in plating sector in Vietnam now and in the future:

- Changing old rinsing technology (static rinsing) by cascade rinsing in order to reduce the consumption of water that means reduction of wastewater.
- Trivalent chromium replacements for hexavalent chromium plating. This is a modern plating technology. When this measure is implemented, hexavalent chromium will not be in wastewater, so wastewater treatment will become very simple.
- Replacement of hexavalent chrome passivations on galvanized steel. This is also a modern passivation technology. When this measure is implemented, hexavalent chromium will not be in wastewater, so wastewater treatment will become very simple.

The results of appropriate technical solutions are listed in specific guidelines for the project partner (HUT/VNCPC) and Vietnamese companies.

## 2 Introduction

In Vietnam, one of the industrial branches that cause strong pollution in water is plating industry with specific waste water including high concentration of heavy metals.

Metal plating is one of the most effective methods to protect metal from being corroded by influences from the environment. Plated metal has improved properties like high durability, high hardness, better electrical conductivity, more attractive surfaces etc, and therefore a higher value. Metal plating methods have been widely used in many factories for producing e.g. electrical parts, medical implantations as well as components for construction and automotive industry.

In industrialized countries, metal plating industry has developed rapidly and many technical innovations have been introduced. In Vietnam most technologies are old; they have their origin in the 1970s or earlier in the last century. But in recent years, there have been many changes in technology and techniques in plating industry in order to satisfy socio-economic needs in Vietnam. However, the common quality of plated metal is still not high and therefore causes many problems to the end product as well as to the environment. Especially contaminated waste water is a current problem in Vietnam. Vietnamese plating companies may not be able to comply with international regulations and standards when they go competing globally thus hindering their entrance into world market. A substantial change in technology application would sustain many jobs that are not guaranteed at present.

In fact environmental problems especially with waste water still are the local problems of each plating company. There is not any assessment and orientation with long term strategies. This, of course, should be guided by the authorities.

This Master thesis investigates and assesses appropriate technologies to overcome the environmental problems and to reduce the cost of out-spec products respectively. As best available technology in Europe is not transferable to Vietnam in every case, the thesis considers specific Vietnamese factors in order to give an overview of the best applicable technology in plating and plating waste water treatment. This information is compiled in a guideline for Vietnamese industry.



### **3 Status of current studies on plating in Vietnam and goals of this thesis**

#### **3.1 Status of current studies on plating**

Up to now, in Hanoi University of Technology, Vietnam there have been many theses and projects that have studied plating industry. Most of them have been done by graduate students, master students and different departments.

An extract of typical studies are listed in the following:

- Design of waste water treatment systems for plating enterprises with different outputs [5].
- Study to improve the old waste water treatment system in a plating company [7].
- Investigation of plating and environmental problems in Hanoi. Promotion of solutions for those problems [6].
- Build up the model of the environmental management ISO 14001 for plating enterprises [9].
- Cr, Ni treatment in plating waste water. Choosing of the appropriate processes to be applied in a plating company [4].
- Model and optimization of Chromium VI reduction process in industrial plating wastewater treatment [8].

So, there were many projects which have studied different aspects in the field of plating in particular. Through studying those literatures, the projects have always focussed on the specific environmental problems in a concrete plating company. Those solutions were to treat local pollutions in a company. The major reasons for treatment are the pressures of the population living around or pressures of environmental management offices to realize new law, for example: environmental law, tax for wastewater, close or move factory to other place, etc.

Hence, there is no actual project that realize studying and assessment for technologies of reduction and treatment of plating wastewater in Vietnam in general. Therefore this thesis analyses and assesses the realized problems as well as the problems that are still remaining in the measures for reduction and treatment of plating wastewater in order to provide the new approaches for appropriate technologies to reduce and treat plating wastewater.

## 3.2 Goals of this thesis

Because there are many kinds of plating technologies so the limits and scope of this study focuses on the field of Chromium, Nickel and Zinc plating technologies as well as the related environmental problems. Those plating technologies are common in Vietnam. Therefore, the measures for changing the plating technology as well as for reduction of wastewater focus on Chromium, Nickel and Zinc plating technologies.

Contents in this report try to describe very clearly as a referent literature. Hoping that this report will supply more new insights for environmental managers, manufacturers, environmental technological researchers and other people who are interested.

## 4 Situation of plating industry in Vietnam

### 4.1 The role of plated products in Society

We know that the surface of metal dates back to early man using gold decoratively before 4000 BC. Gold and silver plating was well-known by the 13<sup>th</sup> century AD, and tin plating of iron was carried out in Bohemia in 1200 AD. In the mid of 19<sup>th</sup> century, the electro deposition of metals was discovered enabling new possibilities, which are still being extended.

The surface properties of metals are typically changes for: decoration, improved hardness or prevention of corrosion, etc.

The surface treatment of metals does not itself form a distinct vertical industry sector. Surface treatment does not create products. They change only the surface properties of previously formed components of products for subsequent use. The surface treatment of metals is largely a service to many industries, for example: automotive, aerospace, heavy engineering, construction, food and drink containers, domestic, furniture, medical, etc.

Table 1 that is given below shows application of Chromium, Nickel and Zinc plating products

*Table 1. Application of Chromium, Nickel and Zinc plating products [1], [3]*

Treatment type	Substrate	Example workpieces	Achieved effect
(1)	(2)	(3)	(4)
Chromium plating	Steel coil	Food, domestic and commercial products	Corrosion protection Decoration
Hard chromium plating	Steel	Heavy duty engines (marine) Rolling mill bearings (steel and non-ferrous metal). Rollers (in paper mills) Medical equipment	Durability Corrosion protection Decoration
Nickel plating (for subsequent chromium plating)	Steel, aluminium	Bathroom fittings. Furniture fittings. Automotive trim	Corrosion protection Decoration
Nickel plating	Steel	Coins (some kinds of currencies now in Vietnam) Fitting	Corrosion protection Decoration

(1)	(2)	(3)	(4)
Zinc plating and chromium aestivation	Steel	Fastenings (nuts, bolts, screws, nails, specialist design, etc.) for construction, automotive, furniture.  Automobile brake system components, windscreen washer system components.  Chassis and casing for domestic goods (TV, video, washing machine, fridge)	Corrosion protection  Decoration

## 4.2 The size and number of plating enterprises in Vietnam

This part of report gives only information about some typical plating enterprises in Vietnam. Informations include process technology, products, specific environment, realized measures and obstacles during implementation.

According to information from an expert of Vietnam Cleaner Production Centre (VNCPC), up to now there is not any full and exact statistic data about the number of plating enterprises in all Vietnam.

After looking at reference documents, we saw that, the enterprises has been arranged in every cities and provinces in Vietnam, especially in big cities such as Hanoi, Ho Chi Minh city, Hai Phong, Nam Dinh, Dong Nai, etc. The scale of those plating enterprises is mainly small and medium sizes. For example, in Minh Khai Lock Company (Hanoi, Vietnam), the employees are 120 people. The annual production capacity is about 1.500.000 dm<sup>2</sup> plated products, and the turnover is 16 - 17 billion VND per year (approximately US\$ 1.1 million) [5]. Or in Nam Dinh Galvanic Company (Nam Dinh province, Vietnam), there are about 220 employees, including engineers trained in Germany, Russian, Korea, and Vietnam. The annual production capacity is 6000 - 7000 tons of material, and the turnover is 40 - 50 billion VND per year (approximately US\$ 3.5 million) [26]. There are many kinds of goods produced like locks, motor and bicycle accessories, zinc-plated steel wire fencing, etc.

At present, there are three main types of plating companies including State plating companies, Joint-venture plating companies and private plating enterprises.

According to the statistical data of Hanoi Department of Science, Technology and Environment, at present there are about 57 plating plants in Hanoi in which there are 24 private plating enterprises [6]. Those plants were located at every district in Hanoi. The number of those plating plants is shown in Table 2.

*Table 2. Number of plating plants in Hanoi [6]*

No	The name of districts where there are plating plants	Amount of State and Joint-Venture plating plants	Amount of Private plating enterprises	Sub-Total
1	Hoan Kiem	1	1	2
2	Ba Dinh	1	2	3
3	Hai Ba Trung	5	5	10
4	Dong Da	2	11	13
5	Thanh Xuan	5	0	5
6	Tu Liem	1	3	4
7	Dong Anh	6	0	6
8	Thanh Tri	6	0	6
9	Gia Lam	5	2	7
10	Cau Giay	1	0	1
	<b>Total</b>	<b>33</b>	<b>24</b>	<b>57</b>

Some typical State and Joint-Venture plating plants with characteristics of technology and products are shown in Table 3.

**Table 3. Typical State and Joint-Venture plating plants [5], [6]**

No	Name of plating plants	Address	Plating technology	Products	
				Type of products	Quantity of products/year
1	Minh Khai Lock Company	125 Minh Khai street - Hai Ba Trung district	Cr, Ni	quays, locks, hinges	1.500.000 dm <sup>2</sup>
2	Thong Nhat Electromechanics Company	Tuong Mai street, Hai Ba Trung district	Cr, Ni	Electric - fans	3.400.000 dm <sup>2</sup>
3	Instrument Company	Nguyen Trai street, Thanh Xuan district	Cr, Ni	Srews, iron equipment	165 tons
4	Hanoi Motorbike and Car Repairing Company	Thanh Xuan street, Thanh Xuan district	Cr, Ni	Accessories for motobike, car	100 tons
5	Urban Illuminative and equipment Company	Thanh Xuan street, Thanh Xuan district	Cr, Ni	Mechanic equipments	1.200.000 dm <sup>2</sup>
6	Dong Da Motorcycle-bicycle Company	181 Tay Son street, Dong Da district	Cr, Ni	Accessories for motobike, bicycle	2.300.000 dm <sup>2</sup>
7	Export Mechanical Equipment Joint-Stock Company	181 Tay Son street, Dong Da district	Cr, Ni, Zn	Mechanical and medical Equipments, details of motorbike	dm <sup>2</sup>
8	Thong Nhat Motorbike and Bicycle Company	129 Thai Ha street, Dong Da district	Cr, Ni	Rims, frames, and other details of Motorbike and bicycle	100.000 dm <sup>2</sup>
9	Goshi - Thang Long Accessories Company	Sai Dong industrial area, Gia Lam district	Cr, Ni	Accessories for motobike, car	3.000.000 dm <sup>2</sup>
10	Thang Long Metal Company	Sai Dong industrial area, Gia Lam district	Cr, Ni, Zn	Oil stove, cover for street light, traffic lights, marker lamp	2.700.000 dm <sup>2</sup>
11	Thang Long Construction Company	Dong Anh district	Zn	Steel girders	180 tons
12	Viet Tiep Lock Company	Dong Anh district	Cr, Ni	Kind of locks	3.000.000 dm <sup>2</sup>

Note: The plated products were calculated by dm<sup>2</sup> or ton per year.

Some typical private plating enterprises with characteristics of technology and products are shown in Table 4.

*Table 4. Typical Private plating enterprises [6]*

No	Name of plating plants	Address	Plating technology	Products	
				Type of products	Quantity of products/year
1	Trinh Van Dat's plating enterprise	25 Hang Dieu street, Hoan Kiem district	Cr, Ni	Bodywork of motorbike and bike, other bike parts,	120
2	Industrial Mechanical Co-operative 8 March	58 Kim Ma street, Ba Dinh district	Cr	Bike parts, handle-bars	190
3	Toan Thang's plating enterprise	Kim Ma street, Ba Dinh district	Cr, Ni	Bike parts	12
4	Hoa Binh's plating enterprise	29 Vinh Tuy street, Hai Ba Trung district	Cr, Ni	Bike parts	100
5	Quang Tien's plating enterprise	262 Tan Mai street, Hai Ba Trung district	Cr, Ni	Bike parts	50
6	Le Xuan Tien's plating enterprise	62 To Hoang street, Hai Ba Trung district	Ni	Bike parts	50
7	Tuan Tu's plating enterprise	149 Dai La street, Hai Ba Trung district	Zn	Screw nuts, bolts	1
8	Toan Thang's plating enterprise	147 Dai La street, Hai Ba Trung district	Zn	Bike parts	1.2
9	Nguyen Toan Thang's plating enterprise	Nam Dong street, Dong Da district	Cr	Hinges, key positions, door bolts	32
10	Hao Nam's plating enterprise	168 Hao Nam street, Dong Da district	Cr, Ni	Bike parts	5
11	Hai Duc's plating enterprise	140 Van Chuong street, Dong Da district	Cr, Ni	Motorbike's exhaust pipes	80
12	Thang Hai's plating enterprise	62 La Thanh street, Dong Da district	Ni	Bike parts	12
13	Tay Mo plating enterprise	Tay Mo street, Tu Liem district	Ni, Zn	Motorbike and bike parts	30

Note: The plated products were calculated by ton per year. Those private plating enterprises have often small size, the employees are 5 - 20 people, turnover annual about 150 - 180 million VND (Approximately US \$ 10000) [6].

## **4.3 Plating technology in Vietnam**

### **4.3.1 Flow diagram for plating process**

Electroplating processes include the main stages: Cleaning, Pickling, Plating. Rinsing stage is always used after each process. The typical flow diagrams of Cr, Ni and Zn plating are shown in Figure 1 and Figure 2.

#### **4.3.1.1 Cleaning**

Grease on the metal workpieces usually comes from machining, stamping, polishing and preservation stages. Grease of organic nature is removed by saponification with alkali. Petroleum and mineral oil greases cannot be removed by this method and trichloroethylene, benzene, gasoline and carbon tetrachloride are employed. But the most commonly employed method of degreasing is emulsification with alkalis available on the market as metal cleaners. These are usually mixtures of sodium carbonate, caustic soda, trisodium phosphate, sodium silicate, sodium cyanide and borax.

#### **4.3.1.2 Pickling**

Removal of rust and scale from iron articles is usually carried out by pickling with sulphuric acid or hydrochloric acid. Lately, the electrolytic method of stripping has been increasingly used because of its rapid action. In this method, the material to be plated is made the anode. The end-products in both the processes are essentially the same.

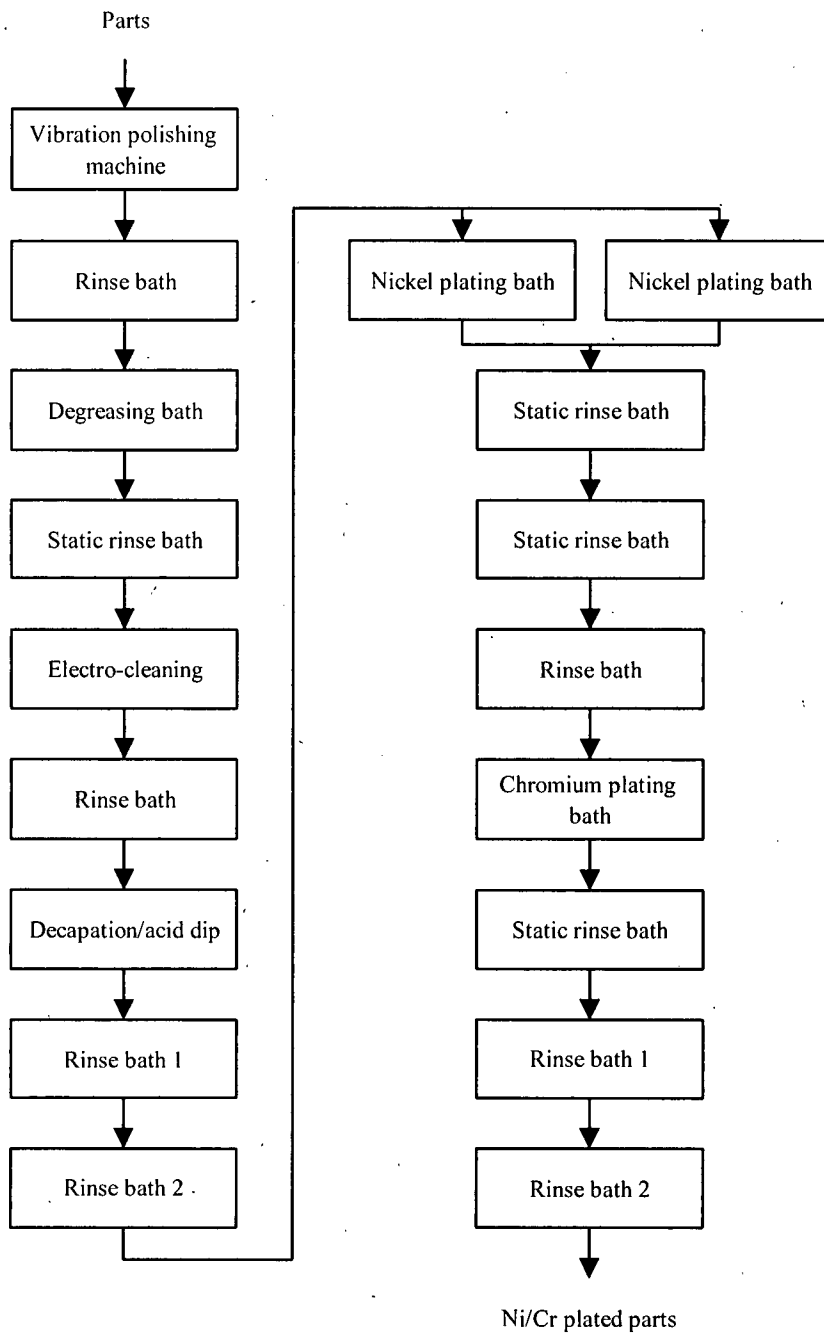
#### **4.3.1.3 Plating**

The pickled workpieces are placed in mild steel vats with special lining wherever necessary or in most cases, tanks made entirely of polymer material. The metal to be plated is made the cathode in an electrolytic cell. Plating baths are acidic in nature and generally contain sulphuric, hydrochloric or nitric acids. Alkaline baths containing sulphide, carbonate, cyanide and hydroxide are also used.

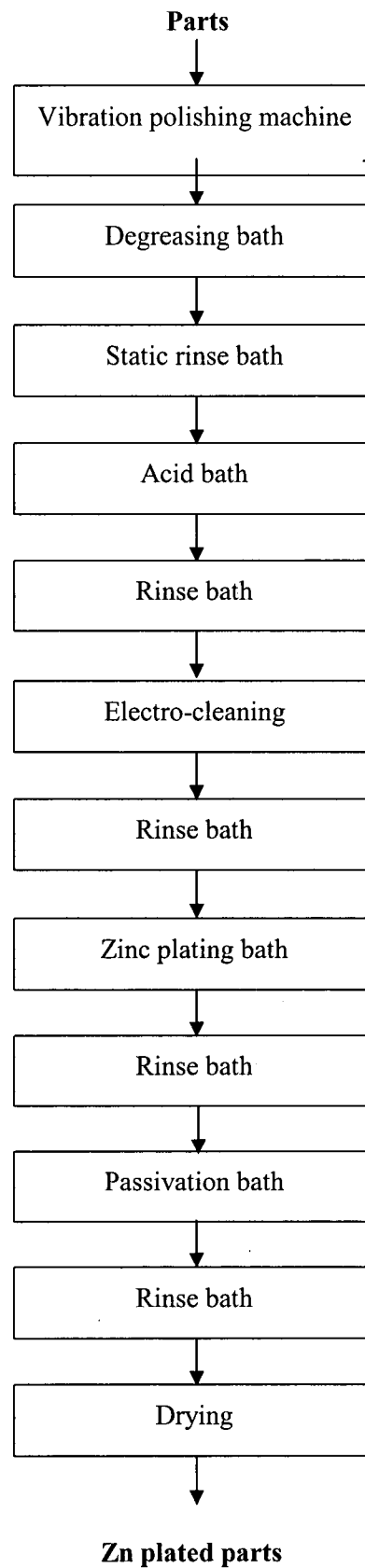
#### **4.3.1.4 Rinsing**

After plating has been done, the plated workpieces are rinsed with water. They are first dipped in stationary water baths, allow draining and then dipped in running water baths to remove the adhering plating solution known as "drag-out". Spray rinsing using nozzles is also used and is well suited for flat work sheets. Stationary baths are re-utilized to prepare solution for the plating operations while the running water baths are discharged into the drains. The quality of drag-out depends upon the nature of the solution, its temperature, shape of the material being plated and the time allowed for draining. Manual plants are known to have higher drag-out losses than automatic ones.





**Figure 1. Flow diagram for a Nickel/Chromium electroplating process**



*Figure 2. Flow diagram for Zinc electroplating process*

## 4.3.2 Technology characteristics of each processes

### 4.3.2.1 Surface preparation processes

The surface must be cleaned of all foreign matter and that it must be chemically prepared for plating. The preparatory steps are dependent on the surface and on the plating bath. Furthermore, there are variations in the preparatory steps that are necessary to accommodate alloys, heat treatments, mechanical stresses in the metal, impurities, and contaminants worked into the surface. As a consequence there are many variations of a plating cycle. The plating cycle can be broadly defined in term of limitations imposed by the basis metal. The preparation of steel, for example, is greatly different than the preparation of aluminium.

### 4.3.2.2 Plating processes

The typical solutions for degreasing, pickling and sulphate zinc plating are shown in Tables 5 to 7.

*Table 5. Typical components of degreasing solution [2]*

Components of degreasing solution, g/l	Solutions			
	1	2	3	4
NaOH	5 - 15	20 - 50	8 - 12	-
Na <sub>3</sub> PO <sub>4</sub> .12H <sub>2</sub> O	15 - 35	5 - 15	20 - 50	15 - 35
Na <sub>2</sub> CO <sub>3</sub>	15 - 35	-	-	15 - 35
Surface active substances	3 - 5	3 - 5	-	3 - 5
Na <sub>2</sub> SiO <sub>3</sub>	-	10 - 30	10 - 30	-
Temperature, °C	60 - 80	50 - 70	40 - 70	60 - 80
Degreasing time, minute	3 - 20	2 - 5	3 - 10	5 - 20

*Table 6. Typical components of pickling solution [2]*

Components of pickling solution, g/l	Solutions		
	1	2	3
H <sub>2</sub> SO <sub>4</sub>	50 - 70	-	-
HCl	-	100 - 150	-
H <sub>3</sub> PO <sub>4</sub>	-	-	120 - 160
Temperature, °C	40 - 60	40 - 60	60 - 70
Pickling time, minute	10 - 20	10 - 15	5 - 10

*Table 7. Solutions for sulphate zinc plating [2]*

g/l	Solutions						
	1	2	3	4	5	6	7
ZnSO <sub>4</sub> .7H <sub>2</sub> O	200 - 300	430 - 500	240 - 360	200 - 220	-	575 - 718	200 - 215
ZnO	-	-	-	-	17.5	-	-
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .18H <sub>2</sub> O	30	30	30	-	-	30	40 - 50
Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O	50 - 100	-	-	70 - 80	-	-	40 - 50
pH	3.5 - 4.5	3.5 - 4.5	4.2	3.5 - 4.5	1.9 - 3.5	3.5 - 4.5	3.0 - 4.4
Tem. °C	25	40	25	25	25	40 - 50	25
Application	Barrel plating	Wire plating	Rack and barrel plating	Barrel plating	Rack and barrel plating	Wire plating	Barrel plating

## 4.4 Specific environmental problems

### 4.4.1 Environmental concern of pre-treatment

Solvents, acids and alkaline solutions used in pre-treatment processes often ends up in the air, in wastewater or as hazardous waste. These chemicals are causing serious environmental impacts when not handled properly.

Wastewater generated from pre-treatment is primarily contaminated wastewater from rinsing baths and process cleanup water. The type of contamination depends on the origin. Most strip baths (pickling) from stripping and cleaning of metals are acidic in nature and consist of solutions of sulphuric, nitric and hydrochloric acid. Alkaline wastewater from alkaline cleaners and rinsing water usually contains soaps, oils and suspended solids. Alkaline cleaners consist of sodium hydroxide, phosphates, silicates, carbonates, some organic emulsifiers and synthetic wetting agents.

The main environmental impacts from pre-treatment processes are listed in Table 8.

**Table 8. Environmental concerns of selected unit operations in pre-treatment**

<b>Selected Processes</b>	<b>Consumption/Waste/Emission</b>	<b>Environmental Concerns</b>
Mechanical treatment	Energy consumption  Particles of heavy metals and dust of blast medium	Resource depletion and air pollution. Especially contribution to the global warming caused by emission of carbon dioxide (CO <sub>2</sub> ).  Poor working environment and noise
Solvent degreasing	Vapours of volatile organic compounds  Hazardous waste	Volatile organic compounds from the solvents are toxic and cause photo-oxidant smog that irritates respiratory passage and causes lung diseases. Some chlorinated solvents are ozone depleting substances and should be phased out according to the Montreal Protocol
Alkaline degreasing	Vapours and wastewater from used alkaline process baths containing oils, metal-ions and chemicals	Risk of toxic impacts on aquatic life if the wastewater is discharged to the environment
Electrolytic degreasing	Aerosols and used process baths containing oils, metal-ions, and chemicals.  Energy consumption	The aerosols may cause a poor working environment. Used process baths may cause toxic impact on aquatic life. Resource depletion, air pollution and contribution to global warming
Pickling	Acid vapours  Used acid process baths containing oils, metal-ions, chemicals	Risk of decomposition of buildings  Risk of toxic impacts on aquatic life if the wastewater is discharged to the environment
Strike	Energy consumption and wastewater containing metal-ions, chemicals	Energy consumption causes depletion of non-renewable resources (e.g. oil), air emission and global warming  Wastewater: as above
Rinsing	Water consumption  Wastewater containing e.g. oils, metal-ions and chemicals from the previous bath	Water consumption may cause depletion of good drinking water in the area  The wastewater is likely to cause toxic impacts on the aquatic environment

#### 4.4.2 Environmental concern of electroplating

Wastes typically generated during electroplating are associated with the metal-bearing solutions. The most commonly electroplated metals and alloys include: brass (copper-zinc), chromium, and zinc.

The character and strength of electroplating wastes vary considerably depending on plating requirements, types of rinsing and the number of pre-treatment operations located in the plant.

Electroplating operations produce air emissions and aerosols. Aerosols arising from electroplating fluids and process gases can be a source of air emissions, which may contain metals or other substances present in the baths. Aerosols and vapours may lead to a bad working environment in the production area.

Wastewater from the electroplating process is primarily rinsing water and the contamination consists of metal ions and in some cases cyanide depending on the composition of the process bath.

Wastewater is normally treated on-site by conventional hydroxide precipitation. Wastewater containing hexavalent chromium must be pre-treated to reduce the hexavalent chromium to its trivalent stage. Wastewater containing cyanide must be oxidized separately. The wastewater treatment results in sludge. The content of heavy metal in the wastewater has thereby been reduced and instead transferred to a concentrated sludge phase of metal hydroxides. The produced sludge phase must be deposited.

Cyanide, mainly in the form of sodium or potassium cyanide, is usually used as a complexing agent for cadmium and precious metals plating and for other solutions as copper and zinc baths. Cyanide salts are desirable since they are good oxide solvents, and in zinc plating they yield a brighter, less porous electroplating.

Cyanide is very toxic to fish and other aquatic life, as well as humans. Even low concentrations in wastes are extremely dangerous and are to be avoided.

Other wastes generated from electroplating include spent solutions which become contaminated during use, and therefore, diminish performance of the processes. Spent solutions may be discharged periodically.

Table 9 shows the environmental concerns from selected process steps in electroplating.

**Table 9. Environmental concerns of selected unit operations in electroplating**

<b>Selected Processes</b>	<b>Consumption/Waste/Emission</b>	<b>Environmental Concerns</b>
Nickel electroplating	Energy consumption	Energy consumption may cause depletion of non-renewable resources (e.g. oil) and air emissions, especially contribution to the global warming caused by emission of carbon dioxide (CO <sub>2</sub> )
	Used process baths containing metal-ions and chemicals	Used process baths causes toxic impact on aquatic life if discharged. There is also a risk of soil pollution
	Minor air emissions and aerosols	The air emissions and aerosols may cause a poor working environment
Acid zinc electroplating	Energy consumption	As above
	Acid vapours	Risk of decomposition of buildings
	Used acid process baths containing metal-ions and chemicals	As above
Rinsing	Water consumption	Water consumption may cause depletion of good drinking water in the area
	Wastewater containing metal-ions and chemicals from the previous bath	The wastewater is likely to cause toxic impacts on the aquatic environment due to its content of heavy metals

#### 4.4.3 Characteristics of waste from some typical plating plants

Some characteristics in air emission from some typical plating plants show in Table 10.

Summary of pollutants and pollution sources in typical electroplating operation shows in Table 11 and 12.

**Table 10. Characteristics in air emission from some typical plating plants [5], [6]**

No	Name of company	Plant inside (mg/m <sup>3</sup> )						Plant outside (mg/m <sup>3</sup> )					
		Dust	NO <sub>x</sub>	SO <sub>2</sub>	CrO <sub>3</sub>	NiO	CO	Dust	NO <sub>x</sub>	SO <sub>2</sub>	CrO <sub>3</sub>	NiO	CO
1	Minh Khai Lock Company	6.1	0.01	0.03	0.00	0.008	0.1	0.57	0.00	0.02	0.003	0.003	12
2	Viet Tiep Lock Company	1.77	-	0.04	0.02	0.017	-	0.52	-	0.020	-	-	-
3	Thang Long Goshi Accessories Company	0.47	0.026	0.02	-	-	3.4	0.26	-	0.009	-	-	1.4
4	Thang Long Metal Company	0.9	0.1	1.36	0.01	-	2.3	0.8	0.02	0.075	-	-	1.55
5	Measuring and Cutting Equipment Company	0.8	-	0.8	-	-	10	0.2	-	0,4	-	-	5
6	Cau Buou Metal Company	0.53	-	0.02	0.00	-	-	0.258	-	0.156	0.000	-	-
7	Thong Nhat Electromechanics Company	0.97	0.5	0.7	0.05	-	0.4	-	0.6	0.004	-	-	-
8	Ha Noi Motor and Car Repair Company	6.8	-	3.5	0.23	0.01	-	0.78	-	4.3	0.032	-	-
9	Dong Da Motorcycle-Bicycle Company	-	-	2.1	0.1	-	0.07	-	0.1	0.4	-	-	4
10	Giai Phong Mechanical Company	0.32	-	0.67	0.2	-	1.45	0.254	0.12	0.016	-	-	1.23
	Standard Vietnam (5937, 5938-1995)	6		2	0.1	0.5		0.2		0.1	0.001	5	5

Notes: Standard Vietnam 5937-1995: Air quality - Ambient air quality standards



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*Standard Vietnam 5938-1995: Air quality - Industrial emission standards - Inorganic substances and dusts*

*Table 11. Characteristics of wastewater of typical State and Joint-Venture plating plants [5], [6]*

No	Name of plating companies	Discharge m <sup>3</sup> /day	pH	Temp. (°C)	Ni (mg/l)	Cr (mg/l)	CN <sup>-</sup> (mg/l)	COD (mg/l)	Zn <sup>2+</sup> (mg/l)	Fe (mg/l)
1	Thang Long Goshi Accessories Company	100	5.0 - 7.5	25 - 26	0.02 - 0.23	100 - 500	< 0.1	320-384	-	-
2	Minh Khai Lock Company	70	6.3 - 7.5	21 - 23	1.2	0.08	-	42	2.5	1.47
3	Viet Tiep Lock Company	70 - 80	4.0	20 - 22	50.2	6.0	0.16	50	-	-
4	Thong Nhat Electromechanics Company	55 - 60	5.8	24	0.62	0.109	-	28.5	-	-
5	Thang Long Metal Company	40	10.8	24	16.00	8.8	0.039	112	-	-
6	Dong Da Motorbike-Bicycle Company	70	8.2	25	1.31	1.4	0.03	4.8	-	-
7	Giai Phong Mechanical Company	50	7.7	24	-	-	-	32.5	-	-
<i>Standard Vietnam 1945 -1995 (Column B)</i>			5.5 - 9.0	40	1	0.1	0.1	100	-	-

*Table 12. Characteristics of wastewater of typical Private plating enterprises [5], [6]*

No	Name of private plating enterprises	Discharge m <sup>3</sup> /day	pH	Temp. (°C)	Ni mg/l	Zn mg/l	Cr mg/l	COD mg/l
1	Trinh Van Dat's plating enterprise	3-5	4-7	21-27	0.01-20.1	14	0.2-5.7	170
2	Industrial Mechanical Co-operative 8 March	4-5	3-11	22-27	0.2-16.7	16	0.02-12.7	154
3	Toan Thang's plating enterprise	1-4	5-12	24-28	-	20.5	-	187
4	Hoa Binh's plating enterprise	2-4	5-10	21-23	5-1706	18.6	-	150
5	Quang Tien's plating enterprise	3-4	6-11	21-23	0.01-12.5	-	0.6-11.2	-
6	Le Xuan Tien's plating enterprise	4-5	2,6-12	23	1-22.3	-	0.43-16.7	300

A summary of the common solid wastes is provided in Table 13.

*Table 13. Summary of solid wastes generated from plating operations*

Solid wastes	Sources
Precipitated metal sludge	Wastewater treatment
Filters and filter sludge	Filtering of cleaning and plating solutions
Oily or greasy rags	Pre-cleaning
Metal polishing residues	Polishing of metal prior to plating
Packaging and general waste	

The largest source of waste from surface treatment plant is solid waste in the form of sludge or filter cake from the effluent treatment plant. For most surface treatment shops the waste is filter cake from a batch pressure filter containing 60-70% water, depending upon the maximum filtration pressure. At this water content, the filter cake has a dry appearance and is easily friable.

The solid waste contains metals in the hydroxide form, together with small quantities of insoluble inorganic salts, organic compounds and general soil. Precious metals are recycled internally.

Filter cake can be dried to a lower content to reduce transport and disposal costs. It does however become dusty at a water content of less than 40%.

Filter cake is of no use to surface treatment shops as recovery technology for the metals is far too expensive and technically challenging for the relatively small quantity involved. Specialist waste handling companies may however be able to recover metals, e.g. nickel, copper, tin or even zinc on an economic basis. Potentially a more significant application may be its use in the building industry as filler for brick making and similar products.

## 4.5 Solution measures

### 4.5.1 Waste water reduction measures

Most plating plants do not care waste reduction by simple methods: avoiding leak, housekeeping, etc. This is problem of awareness.

However, up to now, some plating plants have been interested in and approached on cleaner production step by step in order to reduce wastewater. The obstacles in applying show in Table 14 (see Section 4.6).

#### 4.5.2 Waste water treatment measures

Only a few plants have wastewater treatment. Used method is very simple (Reduce, coagulate, precipitate). Recover of water is not still interested. Most plating plants discharge wastewater to drainage directly.

### 4.6 The difficulties and remaining during implementation of reduction and treatment measures for waste water

Despite the many advantages of Cleaner Production (CP), there is a wide array of barriers preventing or slowing the adoption of CP options. These “roadblocks”, along with measures or that can help overcome them, are presented in the following table:

*Table 14. Barriers to Cleaner Production*

Type of CP barrier	Examples	Enabling Measures
(1)	(2)	(3)
Attitudinal	<ul style="list-style-type: none"> <li>- Lack of management interest and commitment to CP</li> <li>- Ignorance of environmental issues</li> <li>- Resistance to change</li> <li>- Creative blocks</li> <li>- Misunderstanding or distrust</li> </ul>	<ul style="list-style-type: none"> <li>- Increase awareness of CP and environmental issues</li> <li>- Involve employees from start</li> <li>- Begin with “low hanging fruits”</li> <li>- Encourage experimentation</li> <li>- Involve external facilitator</li> </ul>
Organizational	<ul style="list-style-type: none"> <li>- Centralized decision making power</li> <li>- Over-emphasis on production quotas</li> <li>- Ineffective management system</li> <li>- Lack of data</li> <li>- Poor allocation of CP tasks</li> </ul>	<ul style="list-style-type: none"> <li>- Sharing information between managers and operators</li> <li>- Creation of capable CP team</li> <li>- Team ownership of CP options and ideas</li> <li>- Recognition and reward for effort</li> </ul>

(1)	(2)	(3)
Trade	<ul style="list-style-type: none"> <li>- Unreliable supply of materials</li> <li>- Frequent change of products and production</li> </ul>	<ul style="list-style-type: none"> <li>- Establish quality standards for raw materials and suppliers</li> <li>- Optimization of batch size (avoid small production runs)</li> </ul>
Technical	<ul style="list-style-type: none"> <li>- Limited technical access to technical information</li> <li>- Technological limitations of outdated equipment</li> </ul>	<ul style="list-style-type: none"> <li>- Trained staff</li> <li>- In-house technical shops for modifying equipment</li> <li>- Disseminate success stories</li> </ul>
Economic	<ul style="list-style-type: none"> <li>- Low resource pricing and subsidies</li> <li>- Easy availability of raw materials</li> <li>- Limiting economic analysis to direct and short-term financial gains</li> <li>- Ad hoc investment criteria</li> <li>- Inadequate investment planning</li> </ul>	<ul style="list-style-type: none"> <li>- Financial soundness of the company</li> <li>- Prioritization of CP measures</li> <li>- Appropriate cost assignment and investment planning</li> <li>- Financial or fiscal incentives from government or donor agencies</li> </ul>
Governmental	<ul style="list-style-type: none"> <li>- Promotion of end-of-pipe treatment</li> <li>- Immaturity of environmental policy framework</li> </ul>	<ul style="list-style-type: none"> <li>- Financial incentives</li> <li>- Regional volunteer CP groups</li> <li>- Enforcement of environmental legislation</li> </ul>

## 5 Plating technology and related environmental problems in developed countries

### 5.1 Type and size of plating company in Europe

The surface treatment of metals and plastics is carried out in more than 18300 installations in Europe, ranging from small private companies to facilities owned by multinational corporations. The large majority are small or medium enterprises. In Germany the typical number of employees is between 10 to 80. Altogether, the surface of metals and plastics employs about 440000 people in Europe. More than 10000 (55%) are specialist surface treatment installations. The remaining 8300 (45%) [27] are surface treatment shops.

The surface is positioned between initial workpiece or substrate manufacture and final product assembly, completion and packaging. Treatment often has low priority in the production chain, although there are exceptions. This can result in insufficient attention to correct and up to date specifications, insufficient attention given in product design to minimise and reduce consumptions, as well as a lack of investment.

The surface treatment is carried out after the primary metal has been formed into workpieces or shaped substrates, such as nuts, bolts, presses or moduled components, sheets, or coils. They may even be sub - assemblies made of several components, often of different materials. These components and sub-assemblies can be complex shapes which have been pressed, cast and/or machined. In coil processing the substrate used on the largest scale is steel and can vary from wires to steel strip 2008 mm wide.

Process lines are usually modular, and small lines can be easily assembled as a series of tanks. However, large automated lines and the modules in those installations handling steel coil on a large scale. Most installations, particularly the jobbing shops, will operate multiple lines side by side.

As an example of geographic distribution and structure of the industry, in France the industry is widely spread, with concentrations in the south east (21%) and the Paris area (24%). The number of surface treatment installations where the volume of treatment vats exceed  $1.5 \text{ m}^3$  is 2250 (the threshold level for French national legislation), and the number where the volume of treatment vats exceed  $10 \text{ m}^3$  is 1260 [27].

The vats majority of process lines are modular and the actual plant life is difficult to quantify as individual modules are repaired or replaced necessary. Typically, complete production lines are only replaced at long intervals (when maintenance of individual modules is no longer sufficient), or when radically new technology is introduced.

Due to the modular nature of the process lines, some techniques can be installed or changed relatively and cheaply. For instance, some process solutions are changed on a regular basic, others are expensive with a long life and change is an investment decision. Some techniques may require alterations or extensions to production lines. Although the

modular nature facilitates such changes, in many cases other factors will affect the ease of change, such as the limits of transported mechanisms and control systems and the space available in the installation. In house operations tend to be for specific products. Introducing changes for these and for plants handling larger products such as steel coil coating, automotive bodies may be more technically difficult and involve higher capital costs.

The low cost and ease of modular construction of lines is a low barrier to entry. Businesses treating the surfaces of metals using only one or two process lines, often of small vat volumes, are frequently in direct competition for some customers with installations operating large process lines utilising more abatement techniques.

While this industry serves several major manufacturing areas, there is a high concentration of customers in some areas (such as automotive industry) with highly competitive markets, and surface treatment over-capacity. Very few jobbing shops are large enough to serve more than three or four industry types or provide more than three finish options, with most company business strategies focused on specialising in certain finish types. There are some limited opportunities to differentiate the business by providing specialist treatment finished and by specialist quality standards, or for vertical integration such as manufacturing the components to be treated.

The geographic size of the market is often proportional to the degree of specialisation of the treatment. Those treatments that are widely carried out by jobbing shops (such as zinc plating with chromium aestivation) are carried out on a very local basic, with customers usually controlling the price. Other, more specialised, finished where the higher price justifies transport costs maybe carried out on a national scale, or even between neighbouring countries. However, the concentration of surface treatment installations within Europe usually means physically extending markets brings more competitors within range. The extent of the market for the customers' goods is also an important factor. During 2001 and 2002 the volume of business in the light engineering industries fell by 30% across Europe. This was due to the increased exporting of the total manufacture of engineered components and assemblies to Asia.

For continuous electrolytic zinc and zinc nickel coating of steel, since the 1970s, the production of zinc and zinc alloy-coated steel sheet has increased significantly. This has been largely for the automotive industry in response to the demand for anti-corrosion guarantees and longer vehicle lifetimes.

Table 15 shows the various uses for electroplating and the metals employed.

*Table 15. Electroplating applications and principal metals used [30]*

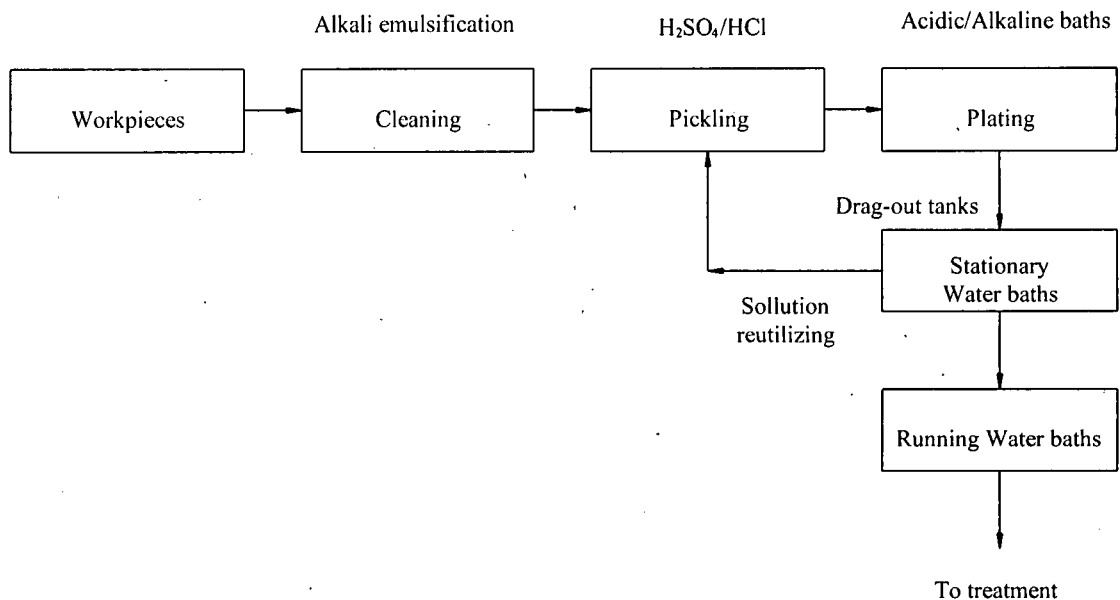
<b>Property/function</b>	<b>Principal plating metals</b>
Decorative	Chromium, copper, nickel, brass, bronze, gold, silver, platinum-group, zinc
Corrosion resistance	Nickel, chromium, electroless nickel, zinc, cadmium, copper and copper alloys
Wear, lubricant, hardness	Chromium, electroless nickel, bronze, nickel, cadmium, metal composites
Bearings	Copper and bronze, silver and silver alloys, lead-tin
Joining, soldering, brazing, electrical contact resistance, conductivity	Nickel, electroless nickel, electroless copper, copper, cadmium, gold, silver, lead-tin, tin, cobalt
Barrier coatings, antidiffusion, heat-treat, stop-off	Nickel, cobalt, iron, copper, bronze, tin-nickel
Electromagnetic shielding	Copper, electroless copper, nickel, or electroless nickel, zinc
Paint/lacquer base, rubber bonding	Zinc, tin, chromium, brass
Manufacturing: electroforming	Copper, nickel
Manufacturing: electronic circuitry	Electroless copper, copper, electroless nickel, nickel
Dimensional build-up, salvage of worn parts	Chromium nickel, electroless nickel, iron

## 5.2 Technology processes

### 5.2.1 Flow process

Electroplating workshops dealt in a rather broad range of end-products as diverse as electronic parts, oil drilling equipment, bicycle parts, typewriters, screws, nuts, locks and other common household appliances. The metals involved in the plating operations include chromium, nickel, zinc, tin, etc. All the plating operations are always wet and the general process sequence by which any metal workpieces must go through are cleaning, pickling, plating and finally followed by rinsing. A flow-chart depicting this sequence is shown in Figure 3. It should be noted here that rinsing is not only encountered as a final stage but, in between processes as wet, as the work-piece are conditioned with intermediate rinses.





*Figure 3 . Schematic flowchart for plating process sequence*

## 5.2.2 Technology characteristics of each processes

### 5.2.2.1 Chromium Electroplating

Chromium plating and anodizing operations include hard chromium electroplating of metals, decorative chromium electroplating of metals, decorative chromium electroplating of plastics, chromic acid anodizing, and trivalent chromium plating. Each of these categories of the chromium electroplating industry is described below.

#### 1. Hard Chromium electroplating of metals.

In hard plating, a relatively thick layer of chromium is deposited directly on the base metal (usually steel) to provide a surface with wear resistance, a low coefficient of friction, hardness, and corrosion resistance, or to build up surfaces that have been eroded by use. Hard plating is used for items such as hydraulic cylinders and rods, industrial rolls, zinc die castings, plastic molds, engine components, and marine hardware.

The process consists of the following steps:

- Pre-treatment (polishing, grinding, degreasing);
- Alkaline cleaning and acid dipping (optional);
- Chromic acid anodic treatment (optional); and
- Chromium electroplating.

The part being plated is rinsed after each step in the process to prevent carry-over of solution that may contaminate the baths used in successive process steps. Either hot or cold water may be used in rinse tanks, but hot water is more efficient than cold water for removing contaminants. Softened, distilled, or deionized water may be required for final rinses.

Pre-treatment steps include polishing, grinding, and/or degreasing the metal part to prepare the surface for plating. Polishing and grinding are performed to smooth the surface of the part. Degreasing is performed either by dipping the part in organic solvents or by vapour degreasing the part using organic solvents. Vapour degreasing is typically used when the surface loading of oil or grease is excessive. The two organic solvents most commonly used in dipping solutions or for vapour degreasing are trichloroethylene and perchloroethylene. In vapour degreasing, the solvent is boiled in a tank and the vapour condenses on the part and removes the oil and grease from its surface. Vapour degreasers must be fitted with a local ventilation system designed to pick up solvent vapours escaping from the tanks without pulling vapour from the machine itself.

Alkaline cleaning is sometimes used to dislodge surface soil and prevent it from settling back onto the metal. These cleaning solutions are typically made of compounds such as sodium carbonate, sodium phosphate, and sodium hydroxide and usually contain a surfactant. Alkaline cleaning techniques include soaking and cathodic and anodic cleaning. In soaking, the metal is placed in an alkaline bath that is agitated mildly. In cathodic cleaning, the metal is placed in an alkaline bath and direct current is applied.

The part acts as the cathode; therefore, when current is applied, hydrogen gas evolves, enhancing the detergent action of the solution. Two disadvantages of cathodic cleaning are that impurities in the cleaning solution may be deposited on the metal and hydrogen may embitter the metal. In anodic cleaning, the part is placed in an alkaline bath and reverse current is applied. The part then acts as the anode so that when the current is applied, oxygen gas is evolved. One disadvantage of anodic cleaning is that oxides may form on the surface of the metal. Also, anodic cleaning is less efficient than cathodic cleaning because oxygen gas is liberated at one-half the rate that hydrogen gas is liberated during cathodic cleaning. During alkaline cleaning, an alkaline mist can be released at a fairly high rate because of the hydrogen and oxygen gases entrapping the solution and releasing it as the bubbles burst at the surface; therefore, adequate ventilation should be provided.

Acid dips may be used to remove any tarnish or oxide films formed in the alkaline cleaning step and to neutralize the alkaline film. Acid dip solutions typically contain from 10 to 30 percent by volume hydrochloric or sulphuric acid in water. Because of the release of hydrogen and oxygen gases, an acid mist is generated from the dip tanks at varying rates and, as with alkaline cleaning, proper ventilation should be provided. A chromic acid anodic treatment step is sometimes included. This treatment cleans the metal surface, with the evolution of oxygen gas scouring the metal. The chromic acid also activates the surface, which enhances the adhesion of chromium in the electroplating step. A typical bath contains chromic acid in a concentration that ranges from 120 to 240 grams per liter (g/l) at temperatures ranging from 49<sup>o</sup> to 66<sup>o</sup>C. Satisfactory cleaning and activation of the surface are usually obtained at 6 volts (V) and a current density ranging from 1550 to 4650 amperes per square meter (A/m<sup>2</sup>) for 1 to 3 minutes. Anodic treatment is typically accomplished by applying reverse current in the hard chromium plating tank.

The anodic treatment also adds a protective oxide layer to the metal so that the chromium can be plated without applying an undercoating of nickel.

The final step of the process is the chromium electroplating operation. Chromium electroplating requires constant control of the plating bath temperature, current density, plating time, and bath composition.

Tanks used for hard chromium electroplating usually are constructed of steel and lined with a polyvinyl chloride sheet or plastisol. The anodes, which are insoluble, are made of a lead alloy that contains either tin or antimony. The substrate is suspended from a plating rack that is connected to the cathode bar of the rectifier. The plating rack may be loaded in the tank manually, by a hoist, or by an automatically controlled hoist system. The plating tanks typically are equipped with some type of heat exchanger. Mechanical agitators or compressed air supplied through pipes on the tank bottom provide uniformity of bath temperature and composition. Hexavalent chromium plating baths are the most widely used baths to deposit chromium on metal. Hexavalent chromium baths are composed of chromic acid, sulphuric acid, and water. The chromic acid is the source of the hexavalent chromium that reacts and deposits on the metal and is emitted to the atmosphere. The sulphuric acid in the bath catalyzes the chromium deposition reactions. Typical operating parameters are given in Table 16.

*Table 16. Typical operating parameters for hard chromium electroplating [30]*

Parameter	Range of values
Plating time, min	20 - 2160
Chromic acid concentration, g/l	225 - 375
Sulphuric acid concentration, g/l	2.25 - 3.75
Temperature of solution, °C	49 - 66
Voltage, volts	Depends on the distance between the anodes and the items being plated.
Current, A	Depends on the amount of surface area plated.
Current density, A/m <sup>2</sup>	1600 - 6500
Cathode efficiency, %	10 - 20

The evolution of hydrogen gas from chemical reactions at the cathode consumes 80 to 90 percent of the power supplied to the plating bath, leaving the remaining 10 to 20 percent for the deposition reaction. When the hydrogen gas evolves, it entrains chromic acid and causes misting at the surface of the plating bath.

## 2. Decorative Chromium electroplating of metals

In decorative plating, the base material (e.g., brass, steel, aluminium, or plastic) generally is plated with layers of copper and nickel followed by a relatively thin layer of chromium to provide a bright surface with wear and tarnish resistance. Decorative plating is used for items such as automotive trim, metal furniture, bicycles, hand tools, and plumbing

fixtures. The purpose of decorative chromium plating is to achieve a combination of the following surface properties:

- Blue-white colour;
- High reflectivity;
- Tarnish resistance;
- Corrosion resistance;
- Wear resistance; and
- Scratch resistance.

The decorative chromium plating process consists of a series of plating operations. The process consists of the following steps:

- Pre-treatment (polishing, grinding, degreasing);
- Alkaline cleaning;
- Acid dipping;
- Strike plating of copper;
- Electroplating of copper;
- Electroplating of nickel; and
- Electroplating of chromium.

As with hard chromium plating, the part being plated is rinsed after each step in the process to prevent carry-over of solution that may contaminate the baths used in successive process steps. Either hot or cold water may be used in the rinse tanks, but hot water is more efficient than cold water for removing contaminants. Softened, distilled, or deionized water may be required for final rinses. Decorative electroplating baths operate on the same principle as that described of the hard chromium plating process: the metal substrate is immersed in a plating solution, and direct current is passed from the anode through the plating solution causing the desired metal (copper, nickel, chromium) to deposit out of the solution onto the metal substrate (cathode).

Pre-treatment steps include polishing, grinding, and/or degreasing the part to prepare for plating. Polishing and grinding are performed to smooth the surface of the part. Alkaline cleaning may be used to dislodge surface soil and prevent it from settling back onto the metal. Acid dipping is sometimes used to remove tarnish or oxide films formed in the alkaline cleaning step. Acid dips are also typically used following strike plating of copper.

The first step following pre-treatment is a copper strike, which consists of applying a thin layer of copper to enhance the conductive properties of the base metal and to protect the part from attack by the acidic copper sulphate baths. The plating bath is typically a copper cyanide solution. The plating time (0.5 to 2.0 minutes [min]) is limited to that necessary for completely covering the entire surface of the part with a thin layer approximately 2.5 micrometers ( $\mu\text{m}$ ) (0.1 mil) thick. Strike plating of copper typically is followed by an acid dip. The part is then usually electroplated with an undercoat of copper to improve the corrosion resistance and to cover scratch marks and other defects.

Copper deposits in the recesses of the part more readily than nickel or chromium, and this enhances the corrosion resistance of the part. The baths used for copper electroplating are either alkaline (cyanides or pyrophosphates) or acid copper solutions. Copper cyanide solution is used most often; however, use of an acid copper bath is growing, due mainly to the low chemical cost and simplified effluent treatment. The acid copper bath requires a copper strike plate for steel substrates before electroplating because the copper cannot be applied directly to steel; however, copper cyanide baths can be directly applied to the steel substrate. Copper cyanide baths are composed of copper cyanide, potassium or sodium cyanide, potassium or sodium hydroxide, potassium or sodium carbonate, and a Rochelle salt. Acid copper baths are usually composed of copper sulphate, sulphuric acid, chloride, and theorem. Another commonly used acid plating formulation contains copper flu borate (instead of copper sulphate) as the active component. Copper may be deposited as a matte finish, or brightening agents may be added to the bath to produce a semibright or bright surface.

When a cyanide bath is used for strike copper plating or copper electroplating, both cyanide and alkaline mist are released from the bath. The potential for release of significant concentrations of these materials into the workroom atmosphere is great enough to warrant the use of local exhaust ventilation. Acid copper plating solutions are capable of releasing the copper salt and sulphuric acid mist into the atmosphere, but because of the generally high electrode efficiencies, acid mist generation is minimal.

However, when high current densities or agitation is used, mist generation can increase and local exhaust ventilation must be provided.

Nickel plating improves the corrosion resistance and strength of the metal substrate and activates the surface of the metal for chromium plating. The nickel is plated on the surface of the part in two layers. The first layer is semibright (sulphur-free) nickel, and the second layer is bright (sulphur-containing) nickel. Pits that form in the outer (bright) layer cannot continue through the inner (semi bright) layer because of the difference in the electromagnetic properties of the two layers. Both the bright and semi bright nickel plating steps uses a Watts plating bath. Nickel plating baths typically operate at 45° to 65°C with current densities ranging from 270 to 1075 A/m<sup>2</sup>.

Generally, gassing from the nickel plating solutions containing sulphate and/or chloride baths is low because the baths are operated at moderate temperatures and low to moderate current densities and have high cathode efficiencies (95 to 98 percent). The need for local exhaust ventilation under such conditions may be minimal.

The final step in the decorative chromium plating process is the plating of chromium itself. Typical operating parameters for this step are presented in Table 17.

*Table 17. Typical operating parameters for decorative chromium plating [30]*

Parameter	Range of values
Plating time, min	0.5 - 5
Chromic acid concentration, g/l	225 - 375
Sulphuric acid concentration, g/l	2.25 - 3.75
Temperature of solution, °C	38 - 46
Voltage, volts	Depends on the distance between the anodes and the items being plated.
Current, A	Depends on the amount of surface area being plated.
Current density, A/m <sup>2</sup>	540 - 2400
Cathode efficiency, %	10 - 20

Decorative chromium plating requires shorter plating times and operates at lower current densities than hard chromium plating to achieve the desired properties of the chromium plate. Some decorative chromium plating operations use fluoride catalysts instead of sulphuric acid because fluoride catalysts, such as fluosilicate or fluoborate, have been found to produce higher bath efficiencies.

#### 5.2.2.2 Nickel electroplating

Nickel plating is used for decorative, engineering, and electroforming purposes. Table 18 summarizes the operating parameters for several types of baths used in both engineering and decorative nickel plating.

*Table 18. Summary of operating parameters for nickel plating baths [30]*

Parameter	Value		
	All chloride	Chloride sulphate	All sulphate
Typical electrolyte compositions, g/l			
Total nickel	75	86.4	70
Nickel chloride	300	158	-
Nickel sulfate	-	188	330
Operation conditions			
Temperature, °C	55	55	55
pH	2.0	3.0	1.5
Current density, A/m <sup>2</sup>	540	540	400
Cathode efficiency, %	93 - 97 %		

Decorative nickel plating differs from other types of nickel plating in that the solutions contains organic agents, such as benzene disulphuric acids, benzene trisulfonic acid, naphthalene trisulfonic acid, benzene sulphonamide, formaldehyde, coumarin, ethylene cyanohydrin, and butynediol.

Nickel plating for engineering applications uses solutions that deposit pure nickel. Table 19 summarizes the operating parameters for nickel electroforming.

*Table 19. Summary of operating parameters for nickel electroplating baths [30]*

Parameter	Value	
Constituents	Watt Nickel	Nickel sulfamate
Typical electrolyte compositions, g/l		
Electrolyte composition, g/l	NiSO <sub>4</sub> .6H <sub>2</sub> O: 225 - 300	Ni(SO <sub>3</sub> ,NH <sub>2</sub> ): 315 - 450
	NiCl <sub>2</sub> .6H <sub>2</sub> O: 37.5 - 52.5	H <sub>2</sub> BO <sub>2</sub> : 30 - 45
	H <sub>3</sub> BO <sub>3</sub> : 30 - 45	NiCl <sub>2</sub> .6H <sub>2</sub> O: 0 - 22.5
Operation conditions		
Temperature, °C	44 - 66	32 - 60
Agitation	Air or mechanical	Air or mechanical
Cathode current density, A/m <sup>2</sup>	270 - 1075	50 - 3225
Anodes	Soluble nickel	Soluble nickel
pH	3.0 - 4.2	3.5 - 4.5

### 5.2.2.3 Zinc electroplating

The most widely used zinc plating solutions are categorized as acid chloride, alkaline noncyanide, and cyanide. Table 20 summarizes the operating parameters for these three types of plating baths.

*Table 20. Summary of operating parameters for zinc plating baths [30]*

Parameter	Value				
	Zinc metal	Sodium	Ammonium	pH	Temperature, °C
	g/l				
Acid chloride zinc					
All ammonium chloride	14.9 - 30		120 - 150	5.0 - 6.0	15.5 - 54
	14.9 - 30		30 - 45	5.0 - 6.0	
Low ammonium potassium chloride	22.5 - 37.5			5.0 - 5.5	
Nonammonium or allpotassium chloride					
Alkaline noncyanide zinc:					
Low chemistry	6 - 9	75 - 105			15.5 - 43
High chemistry	13.6 - 22.5	120 - 150			
Cyanide zinc:					
Low cyanide	7.5 - 11	75 - 90			15.5 - 38
Mid cyanide	13.5 - 19	75 - 90			
High cyanide	26 - 34	75 - 90			

The most widely used zinc alloys for electroplating are zinc-nickel, zinc-cobalt, and zinc-iron. The operating parameters for the baths used in these operations are summarized in Table 21.



*Table 21. Summary of operating parameters for Zinc-Nickel plating baths [30]*

Parameter	Value	
	Rack	Barrel
Acid zinc-nickel bath:		
Zinc chloride, g/l	130	120
Nickel chloride, g/l	130	110
Potassium chloride, g/l	230	--
pH	5.0-6.0	5.0-6.0
Temperature, °C	24-30	35-40
Cathode current density, A/m <sup>2</sup>	10-40	5-30
Anodes	Zinc and nickel separately. In some cases, separate rectifiers and bussing are required.	
Alkaline zinc-nickel bath		
Zinc metal, g/l		8.0
Nickel metal, g/l		1.6
Sodium hydroxide, g/l		130
Ratio zinc/nickel, g/l		5.0
Temperature, °C		23-26
Cathode current density, A/m <sup>2</sup>		20-100
Anode current density, A/m <sup>2</sup>		50-70
Anodes		Pure zinc

### 5.2.3 Material consumption

The highly fragmented nature of the sub-contract sector, the generally small size of most companies (10-20 employees) [28], and the wide range of treatments offered make it difficult to develop quantitative benchmark data. Some indicative data for material and utilities consumptions and emission levels are given below:

#### 5.2.3.1 Input materials

These include process chemicals e.g. inorganic acid, alkalis and salts, proprietary additives e.g. brighteners, anode metals and effluent treatment chemicals. The loss of materials is mainly due to drag-out, but filtration equipment cleaning, leakage and spillage are small but significant contributors. Benchmark material efficiencies for input chemicals for the main plating processes are:

- Zinc plating (all processes) : 70-90%

- Nickel plating (without recycle) : 80-85%
- Nickel plating (with recycle) : 95%
- Chromium plating (without recycle) : 15%
- Chromium plating (with recycle) : 96%

### 5.2.3.2 Utilities

The utilities used in surface treatment are natural gas (or fuel oil), electricity and water.

Electricity is used in the form of direct current for the electrochemical processes. Gas and/or electricity are used for process heating, depending on availability and cost. Electricity is also used for process cooling and fumes extraction. Gas and/or electricity are used for the drying of surface treated work.

Water is used directly for rinsing purposes, or as make-up to recirculation water rinse systems. To a much lesser extent, it is required for making-up evaporation losses from process tanks if the recovery of drag-out is not feasible, and the washing of filtration and heat exchange equipment.

#### 1. Energy

The range of typical energy consumptions for a sub-contract acid zinc plating shop are given below:

- Direct current for pre-treatment and zinc plating : 20-40%
- Process heating for pre-treatment and zinc plating : 20-40%
- Process cooling for zinc plating : 0-17%
- Fume extraction : 5-13%

Drive motors, drying, space heating, and lighting: 13-40%

#### 2. Water

The rinse water usage for a typical automated barrel zinc plating plant is given below:

- Output : 6 barrels/h
- Barrel length : 1200 mm
- Throughput : circa 500 kg/h depending on the components
- Plating electrolyte : acid zinc, 33 g/l zinc
- Plating stages : 5
- Zinc anode usage : 20-25 tonnes/year
- Plating time : 45 min

Even for the same electroplating processes there is a very large variation in the consumption of water. An investigation of 8 Danish electroplating plants in 1991-1992 shows large variations in the water consumption per plated surface area. Water consumption was observed during 1 year and was related to different electroplating processes. One of the conclusions was that it is possible to carry out most electroplating

processes with around 10-20 l water per m<sup>2</sup> surface area by means of cleaner production, management commitment and education of employees.

*Table 22. Collected figures for water consumption per produced surface area*

Type of electroplating	Water consumption, l/m <sup>2</sup>
Barrel-plating, zinc	10 - 210
Vat (still)-plating, zinc	10 - 600
Barrel-plating, nickel	20 - 50
Vat ( still )-plating, nickel	40 - 50
Hard chromium	20
Barrel-plating, tin	50

### 5.3 Specific environmental issues

The main environment issues arising from the surface treatment of metals relate to energy and water consumption, the consumption of raw materials, emissions to surface and groundwater, solid and liquid wastes and the site condition on cessation of activities.

Surface treatment has traditionally been associated with large water usage creating a wet working environment, although many installations have moved away from this way of working. The chemicals used have the potential to cause environmental harm particularly to surface waters, groundwaters and soil. Metals removed from waste water end up in solid wastes and, together with some used process solutions, may need special management for recovery or disposal. The industry can discharge fumes and dust to air, as well as generating noise.

The two major sources of wastewater in the electroplating operations come from batch solutions and rinse water. They are distinctly different in volume and characteristics. Batch solutions from vats are highly concentrated and are discharged intermittently. Rinse waters, made up of preliminary and final rinses, are more diluted but form the bulk of the wastewater of the plating shops. However, the preliminary rinses being more concentrated than the final rinses are often blend together with batch solutions for treatment before discharge to the sewer. The final rinses are treated for reuse in some plating shops.

The volume and characteristics of various wastewater streams vary considerably from one plating plant to another and within the same plant from day to day. Generally, the drains inside the plants are interconnected mainly due to facility layout of the plant and partly to ignorance of the consequences. The ranges of concentration of metals in wastewater are on Table 23.

**Table 23. The ranges of concentration of some typical substances in plating wastewater [12]**

No	Substances	Concentration, mg/l
1	Cyanide	1.0 - 150
2	Chromium (VI)	0.25 - 2600
3	Nickel	0.07 - 125
4	Zinc	0.12 - 140
5	Iron	0.17 - 300

The electroplating wastes may be acidic or alkaline depending on the type of baths used. They may be highly acidic with a pH of 1 or highly alkaline with pH of 12. Total dissolved solids from 131 mg/l to 19500 mg/l and total suspended solids range from 1 mg/l to 3160 mg/l [12].

Due the wide range of process activities, the range of substances used and emitted by the industry is substantial. However, most installations will only use or generate some (and not all) of these substances.

Table 24 Identifies key substances used and the media they may effect when emitted. As most substances are used in aqueous solution, they will be found in process waste water as well as in-plant leakages and spills. Very little is known of the breakdown products in the processes.

**Table 24. Key substances of concern and media potentially affected**

Principal substances of concern	Medium affected			
	Water	Soil	Air	Other issues to be considered
(1)	(2)	(3)	(4)	(5)
<b>Metals</b>				
Chromium	√	√	√	Health issues with aerosols of Cr VI solutions
Nickel	√	√		Health issues in use and products
Zinc	√	√		
<b>Non-metals</b>				
Cyanides	√	√	√	Toxic
Hypochlorite	√		√	Concern for formation of AOX with other substances. Can release chlorine under certain conditions

(1)	(2)	(3)	(4)	(5)
AOX (absorbable organic halogens)	√	√		May be formed in some effluent treatments
Peroxides				Oxidising agent: storage issues.
<b>Surfactants</b>				
Dispersing agents, emulsifiers, detergents, wetting agents	√			NPE is banned. Health and environment issues with PFOS.
<b>Complexing agents</b>				
EDTA	√			
Tartrate, EDDS, NTA,	√			
Sodium dithionite	√			Storage issues
<b>Acids and alkalis</b>				
Hydrochloric, nitric, sulphuric, acetic	√	√	√	Acid fumes, particularly, NO <sub>x</sub>
Sodium and potassium hydroxides, lime	√	√	√	Dusts
<b>Other ions</b>	√	√		Local environmental issues
<b>Solvents</b>				
Trichloroethylene (TRI)	√	√	√	Other legislation applies to air emissions
Tetrachloroethylene (PER)	√	√	√	
Tetrachlorotrifluoroethane (CFC-113)	√	√	√	
Methylene Chloride	√	√	√	
<b>Gases</b>				
Chlorine			√	Used in cyanide treatment
<b>Dusts</b>		√	√	From finishing and polishing
<b>Wastes</b>	√	√	√	

## 5.4 Solution measures

### 5.4.1 Reduction measures

#### 5.4.1.1 Introduction

Spent solvent waste coming from contaminated solvents from parts cleaning operations may be reduced by the following measures:

- Use water-soluble cutting fluids instead of oil-based fluids (this could eliminate the need for solvent cleaning);
- Use aqueous cleaners;
- Use multi-stage counter current cleaning;
- Prevent cross-contamination or drag-in from other processes;
- Prompt removal of sludge from tank; and
- Reduce the number of different solvents used (a single larger waste that is more amenable to recycling).

Solvent loss from air emissions may be reduced by proper operation of equipment as it is designed.

- Use roll-type covers, not hinged covers (up to 50% reduction in emissions);
- Increase freeboard height;
- Install freeboard chillers;
- Use silhouette entry covers;
- Proper equipment layout;
- Avoid rapid insertion and removal of items (less than 11 feet/min.);
- Avoid inserting oversized objects into the tank (cross-sectional area of the item should be less than 50% of tank area to reduce piston effect);
- Allow for proper drainage before removing item; and
- Avoid water contamination of solvent in degreasers.

Techniques to reduce waste rinse water will be discussed in the section on plating. Reduction practices available for minimizing spent plating waste include: use deionized or distilled water for make-up, regenerate plating solution through impurity removal, return spent plating solution to manufacturer, and metal recovery.

Metal recovery techniques include: evaporation, reverse osmosis, ion exchange, electrolysis, and electro dialysis. Many companies have installed such systems to recover metals from waste rinse water and have found that the investment has paid for itself in one to five years. Strategic, in-line placement of metal recovery units, such as ion-exchange columns, can serve to remove metals from spent plating baths and waste rinse

waters. When the ion-exchange resin is regenerated, the metals can be recovered and used to provide plating solutions which can be recycled to the plating baths.

Rinse waters - Conserving water is an effective way to cut operating and capital costs. These methods can be grouped into two major techniques: drag-out reduction and rinse water reduction.

Reducing the drag-out reduces the amount of rinse water needed and the amount of metal in the wastewater. Also, less of the plating solution metals leave the process, which produces savings in raw materials, and treatment and disposal costs. The amount of drag-out depends on the following factors: surface tension and viscosity of the plating solution, shape and surface area of the workpiece and rack, speed of workpiece withdrawal, and drainage time.

Generally, drag-out reduction techniques include:

- Increase solution temperature.
- Use less concentrated plating solution.
- Withdraw workpieces slowly from solution.
- Add wetting agents to plating solution.
- Position workpieces properly on rack.
- Increase drip times (10-30 seconds).
- Use drip boards or pans (direct drips back to origin).
- Install fog nozzles and sprays.

Rinse water reduction involves rinsing off the workpiece in the most efficient manner, using the smallest volume of rinse water. Traditionally, a workpiece would be immersed into a single rinsing bath following a plating bath, and then moved on to the next step in the process. Decreasing water consumption without reducing drag-out will result in a smaller, but more concentrated wastewater.

Several methods exist which use less rinse water than the traditional method, while still adequately rinsing the workpiece. These include:

- Counter-flow multiple tank rinsing.
- Fog nozzles and sprays rinses on simple workpieces, such as sheets.
- Still rinses.
- Flow or conductivity controls.
- Mechanical and air agitation of the rinses.

#### **5.4.1.2 Reduction of rinse water**

The rinsing steps consume up to 90% [12] of the water used by a typical plating workshop. The larger water reduction can be anticipated to come from modification of the rinsing techniques. Cost saving associated with consequent water reduction has resulted in lower cost for rinse water, cost saving on the treatment facilities and reduces chemical costs for wastewater treatment. Rinsing is essentially a dilution step which

reduces the concentration of contaminants on the workpieces. The design of rinsing system for minimum water consumption therefore depends on the maximum level of contamination allowed to remain on the workpiece as well as on the efficiency or effectiveness of each rinsing stage. Some of the practical measures to reduce rinse water consumption are discussed in the following sections.

### **1. Air mixing rinse tank**

Air mixing in the rinse efficiency by providing turbulence between the workpieces rinse water. The air mixing in the rinse tank prevents short-circuiting and allows rinse water to mix completely, resulting in uniform concentration in the tank. The contaminants are removed from the workpiece effectively, thus minimize the rinse water requirement.

### **2. Multiple counter current rinsing**

The basic concept of this operation is to use water from previous rinsing to contact the more contaminated workpieces. Freshwater enters the process at the final rinse stage and then moves counter current towards the work flow to serve as rinse water in the preceding stages. Thus, the concentration of drag-out decreases rapidly from the first to the last tank. The total rinse water flow required to achieve the same degree of cleanliness decreases by about 90% for each additional rinse tank [12] in the counter current sequence as compared to using only one tank.

### **3. Spray rinsing**

Automated control of spray rinsing through nozzle has become popular for application in rinsing operations. It is well suited for flat sheets, particularly for work with holes in it. Spray rinsing is considered the most efficient of the various rinsing techniques. The impact of the spray also provides an effective mechanism for removing drag-out from recesses with a large width to depth ratio. The spray method reduces the water usage by about 30% [12] as compared to other conventional methods.

### **4. Flow control method**

Another form of reducing the water usage in rinsing process is through efficient flow control method. Of the many flow control devices available, the conductivity controller is the most efficient and commonly used by the plating workshops. The device utilizes a conductivity cell to measure the conductance of used rinse water leaving the rinse tank. When the concentration of rinse to a predetermined level in the rinse tank, the conductivity cell operates a solenoid in the effluent line and causes the water supply valve to open and fresh rinse water is added. This system therefore has an advantage over the usual open valve practice which disregards whether the water is needed or not in the electroplating operation. Water usage can be reduced by about 20% [12] when such system is used.

### **5. Reactive rinsing**

Reactive rinsing is a technique to reuse or recycle rinse water. The technique takes the advantage of chemical reactivity of used water. Water consumption will be greatly



reduced by recycling. Rinsing efficiency can be increased by this method, thus improving plating quality. Reactive rinsing is an effective alternative to counter-flow rinsing without the cost of logistical constraints. Reactive rinsing does not require additional rinse tanks or space.

#### **5.4.1.3 Rinse water recycle**

The electroplating workshops require a plentiful supply of water due to thorough rinsing between processing steps. Contaminated rinse water therefore make up the bulk of wastewater. Compared to strong waste from plating bath, rinse water is considerably less contaminated and as such, is eminently suitable for recycle. Also, when valuable metals are involved in plating operations, economic often justified that the waters be treated for recycling with subsequent recovery of valuable materials which would otherwise be discarded.

##### **1. Ion exchange**

Ion exchange is an effective method for recovery of drag-out from rinse waters. Rinse water passed through a series of rinse beds that selectively remove cations and anions. As the rinse water passes through the rinse beds, the rinse exchanges ions with inorganic compounds in the rinse water. Metals are then recovered from the rinse by regenerating the resin with an acid and or alkaline solution. The treated rinse water is of high purity and can be returned to the rinse system.

##### **2. Evaporation**

Evaporation has been successfully used in a number of ways to recover plating bath chemicals. There are basically two types of evaporation systems, atmospheric and vacuum. In the atmospheric evaporator, the rinse water is heated and passes through a packed column in counter current with dry air. In the vacuum evaporator, the rinse water is concentrated by boiling at low pressure. In both systems, the concentrated solution returned to the plating bath. Evaporation technique is a very energy intensive methodology, it is only economically feasible to couple with waste heat recovery system or employed in conjunction with multistage counter current rinse system or other methods that reduce the quality of rinse water required.

A combination of evaporation recovery and counter current rinse system can also be used to accomplish the closed circuit system for the recycling of rinse water. The plating chemicals are concentrated in the evaporator and returned to the plating bath. The water vapour is condensed and returned to the rinse tank. This system provides resources recovery as well as rinse water recycling. The major disadvantage is that the evaporation process consumes large quantity of energy. However, the revenues generated from the resources recovery, rinse capital investment and operation and maintenance costs, but also generate a handsome profit for the plating workshop.

#### **5.4.1.4 Wastewater control technology**

Wastewater is generated in the plating industry as a by-product of:

- Process tank rinses.

- Servicing filters.
- Clean-up of equipment and floor spills.

These sources of wastewater are also the primary targets for source reduction, recovery, recycle and reuse. Most of the emphasis on recovery technology has been on rinse water since it constitutes the majority of the flow leaving an operation and necessitates expensive treatment. Bath dumps are generally of low volume and occur infrequently. Often bath dumps are collected and transported by a waste service provider for final treatment and disposal, but more and more baths are being treated on-site for regeneration and reuse of the bath chemicals. Floor spills include both accidental and intentional waste sources, such as tank overflows, drips from workpieces, leaking tanks or pipes, chemical spills, salt encrustations, washdown water and oil drips-spills from equipment during the operation, transport and handling. Floor spills are managed by the application of good housekeeping, maintenance and operating practices, combined with appropriate operator training. Wastewater treatment following pollution prevention and recovery/recycle/reuse options can be accomplished using one of five general approaches:

- On-site treatment system
- On-site treatment using a mobile treatment system
- Pre-treatment followed by discharge
- Off-site treatment by a centralized waste treatment facility
- Transport of wastewater to an off-site treatment/ disposal facility

Maintaining and operating an on-site treatment facility can be labour intensive and expensive and is usually not a good option for small nickel plating companies. A mobile system can also be expensive for a small plater. Mobile systems are generally used for infrequent site clean-up requirements and are not commonly used by nickel platers. Pre-treatment followed by discharge is a wastewater control option for many platers who are also active in recovery/ recycle programs. Off-site treatment by a centralized waste treatment facility works when several platers are located in the same vicinity, usually in large metropolitan industrial areas. A typical option for most small waste generators is storing the hazardous waste in accordance with requirements until it is economically sound to have the waste transported to an off-site treatment and disposal facility.

#### 5.4.2 Wastewater treatment measures

Plating wastewater contains heavy metals, oil and grease and suspended solids at levels that might be considered hazardous to the environment and could pose risks to public health. Heavy metals, in particular, are of great concern due to their toxicity. Because of the high toxicity and corrosiveness of plating waste streams, plating facilities are required to pretreat wastewater prior to discharge.

The plating process typically involves, alkaline cleaning, acid pickling, plating, and rinsing. Copious amounts of wastewater are generated through these steps, especially during rinsing. Additionally, batch dumping spent acid and cleaning solutions contributes to the complexity of waste treatment.

#### 5.4.2.1 Chemical precipitation

In many cases, metal-bearing wastes contain several constituents at high concentrations. Treatment of spent plating, cleaning, and pickling baths by precipitation often requires special design and operating conditions. More cost-effective treatment may be achieved if wastes are segregated. This is particularly true with wastes that contain cyanide and hexavalent chromium. Segregation of cyanide and hexavalent chromium will allow pretreatment of smaller waste streams requiring smaller tanks and chemical feed equipment, as well as reduced chemical usage for pH adjustment. Jar testing is recommended to compare alternative precipitation processes. Therefore, custom design is the best treatment procedure for the process waste stream.

Either lime, magnesium hydroxide, caustic, or a blend of these alkaline compounds can be used as the source of hydroxide ions for precipitation of metal hydroxides.

Advantages and disadvantages of each of these reagents should be considered in the selection of a system for a particular application. For example, caustic is more expensive than lime, but the cost of chemical feed systems for lime slurry can be substantially more expensive than for caustic. Lime and magnesium hydroxide tend to reduce sludge leach ability and break metal complexes that may be present in the wastewater stream.

Among the more common complexing agents encountered in metal-bearing wastes are ammonia, cyanide, and ethylenediaminetetracetic acid (EDTA). There are a number of treatment procedures for complexed metal-bearing wastes by chemical precipitation and reduction. Most of these complexed wastes contain copper, nickel, zinc, silver, tin and lead. A treatment method that has been investigated and reported to be effective for certain nickel complexes is precipitation at high pH (11.6 to 12.5) utilizing lime. The drastic increase in pH is believed to prompt a shift in the complex dissociation equilibrium to produce uncomplexed metal ions which can then be precipitated.

#### 5.4.2.2 Carbon adsorption

Sometimes it is necessary to pretreat a wastewater stream prior to discharge. Activated carbon adsorption is occasionally used to remove contaminants (usually organic compounds) from such streams. Most carbon adsorption systems use granular activated carbon in flow through column reactors. Since the adsorption process is reversible, it is common to remove the adsorbed contaminants and regenerate the carbon for reuse. It is important to determine if carbon adsorption can produce an effluent of acceptable quality and price for a specific process. For additional assistance for specific waste management applications, consult with an engineering consulting firm, professional trade association, and/or a major activated carbon manufacturer.

#### 5.4.2.3 Alternative treatment

The conventional treatment was replaced by a proprietary treatment agent, based on fast kinetics and synergism. Preliminary jar tests indicated that a dose of 900 ppm of the product was sufficient to bring the concentrations of iron, zinc, chromium, oil and grease and suspended solids below discharge. In light of the quality of treated water, the facility recommended a one-month trial. After evaluating the quality of treated effluent, clarifier

performance, labour requirements and overall treatment cost, the new treatment was adopted.

#### **5.4.2.4 Waste disposal**

Waste produced by the current treatment contains about 50-60% solids and as such has less volume. Conversion to the current treatment was achieved without system reconfiguration or capital expenditure.

The treatment proved very economical and versatile, and the product is easy to work with and safe to handle. The new treatment produces effluents that meet or exceed discharge standards and generates nonhazardous waste. Importantly, the facility has realized a 10% annual cost saving for its wastewater treatment.

## **6 Collection of appropriate reduction and treatment technologies for waste water to apply in plating industry in Vietnam**

### **6.1 Base of collection**

- Methodology of cleaner production: "waste reduction at source"
- Best available technology (BAT)
- Analysis and assessment of plating technology in Vietnam
- The sources of important information about best available technology, measures of reduction and treatment of plating wastewater, collected in Switzerland and other developed countries.

#### **6.1.1 General of principles of cleaner production**

UNEP defines Cleaner Production (CP) as the continuous application of an integrated, preventive environmental strategy applied to processes, products and services in order to increase efficiency and reduce risks to human and the environment. This improved efficiency simultaneously enhances the profitability and competitiveness of a company.

- For production processes, CP includes conserving raw materials and energy, eliminating toxic raw materials, and reducing the quantity and toxicity of all emissions and wastes.
- For products, CP involves the reduction of negative impacts along the life cycle of a product, from raw material extraction to its ultimate disposal.
- For services, CP means incorporating environmental concerns into designing and delivering services.

Cleaner Production avoids or minimizes waste and pollution before it is generated, striving to approach 100% resource efficiency within the barriers of economic feasibility. More than simply a matter of installing new equipment, it involves changing attitudes, applying knowledge, and improving both production processes and the final product.

#### **6.1.2 Best available technology**

BAT means 'the best available technology'. The technology in question should be "Best" at prevention pollution and "Available" in the sense that it is procurable by the industry concerned. Technology itself is taken as the techniques and the use of techniques, including training and maintain etc.

- “Best” must be taken to mean most effective in preventing, minimising or rendering harmless polluting releases. There may be more than one set of techniques that achieve comparable effectiveness - that is, there may be more than one set of “best” techniques.
- “Available” should be taken to mean procurable by the operator of the process in question. It does not imply that the technique has to be in general use, but it does require general accessibility. It includes a technique which has been developed (or proven) at pilot scale, provided this allows its implementation in the relevant industrial context with the necessary business confidence.
- “Techniques” is the term that embraces both the plant in which the process is carried on and how the process is operated. It should be taken to mean the components of which it is made up and manner in which they are connected together to make the whole. It also includes matters such as numbers and qualifications of staff, working methods, training and supervision and also the design, construction, lay-out and maintenance of buildings, and will affect the concept and design of the process.

The objective of the Best Available Technology Guidelines is to provide a list of technologies which will be used for reduction and minimum of waste.

## 6.2 Minimising chemical and waste water

There are numerous reasons why your company will benefit from minimising its chemical and water use:

- Chemical waste levels in the industry are often high. Typically 10 - 20% of the materials from a zinc plating electrode end up as waste. Equivalent figures from a bright nickel electrolyte and from a chromium electrolyte are 25 - 30% and 70% respectively. Such levels of waste mean that you are spending more on chemicals than you should be. You can make substantial savings by reducing your chemical use.
- Waste disposal costs are rising at rates faster than the rate of inflation. Landfill charges for sludge disposal alone are as much as £83/tonne, while current waste disposal policy and pressures on land suggest that charges will rise in the future. You can reduce your waste disposal charges by minimising the quantities of waste produced.
- Water costs are rising faster than the rate of inflation, yet it is relatively easy to save water. You can reduce your water costs by up to 40% by implementing simple, no-cost or low-cost measures. In other words, you can achieve striking results without excessive capital outlay. Even more substantial reductions are possible in the medium and longer term.
- If you fail to implement options for reducing your chemical and water use, you will continue to make less profit than you are capable of making, and could lose your competitive position.
- Companies are required to reduce their environmental impact and comply with increasingly stringent legislative requirements. Taking action now could make compliance easier both now and in the future.

Many plating companies can make substantial cost savings by minimising their consumption of chemicals and water, and improving their end-of-pipe treatment facilities. Chemical and water consumption within the industry varies widely, and there are many instances of waste. Water supply and effluent disposal costs are rising and there is growing pressure on companies to reduce costs and improve both profitability and environmental performance. A waste minimisation programme is a good way of achieving these objectives.

The first step in any waste minimisation programme is to assess what is currently happening on site. The Guide outlines a simple mass balance technique that allows companies to understand the material flows within their processes, determine where wastage is currently taking place, and identify opportunities for waste minimisation.

Drag-out is one of the most significant causes of chemical loss from plating and other treatment baths. Yet these losses can be reduced by up to 40% using simple procedures that involve little or no expenditure. Other techniques for reducing chemical waste include better purchasing and stock control, improved measurement and control of operating conditions, and improvements in the life of process bath chemicals.

Water savings of 15 - 20% [17] can be achieved for zero cost, simply by good housekeeping. Limited investment can increase these savings to 30% [17]. Examples of no-cost and low-cost measures include installing flow controllers and providing better control of hose use. More capital-intensive measures include counter current, spray and fog rinsing.

Where effluent treatment is required, the options range from standard precipitation techniques to more sophisticated approaches such as ion exchange, electrochemical recovery, evaporation, reverse osmosis and ultrafiltration. In many cases, these techniques not only recover chemicals and metals, they also produce clean water for recycling within the process.

The Guide emphasises the need for companies to adopt a systematic approach. In other words, they should consider minimisation throughout the site rather than focusing only on end-of-pipe solutions. Immediate action could be beneficial now and in the longer term.

### 6.3 Determination of the drag-out

The consumption of chemicals in processes of surface treatment is mainly caused by the drag-out of bath solution. Knowing the amount of the drag-out helps to maintain the process stable and is necessary for minimizing waste water and dosage of additives. Mostly, the values of the drag-out only are estimated. Sometimes they are unknown. However, it is very easy to find out how much bath solution is dragged out.

### 6.3.1 General determination of the drag-out

#### 6.3.1.1 Introduction

During the surface treatment with process solutions, a film of the bath solution remains on the parts and on the rack/barrel. The bath solution also remains in cavities and gaps, and is transported into the next baths. Due to this transport, the chemicals of the process get lost. The consumption of additives related to the drag out can be higher than the consumption related to the chemical reaction on the part surface. For instance, the consumption of blue passivation is caused to 90 % [19] by drag-out.

In electroplating processes, especially if high layer thicknesses are deposited, the amount of drag-out is minor to the amount being consumed by electrochemical reaction. Yet, conductivity salts and inert additives are consumed nearly exclusively by drag-out. The amount of drag-out depends on several factors (geometry of the parts and racks, drain times, temperature of the bath solutions, special devices of the plating line) and can differ strongly from one line to another. General values of the drag-out are 20 - 200 ml/m<sup>2</sup> for rack application and 100-400 ml/m<sup>2</sup> for barrel application [19]. But for calculations of the consumption or for instructions of additive dosage these values are indeed too inexact.

#### 6.3.1.2 Practical steps

To measure the amount of drag-out in a processing line, a bath is needed containing ingredients easy to analyse at a high concentration. A hydrochloric pickling or a chromium bath for example is very well suited, since in the following rinse it is easy to analyse the dragged in HCl or chromium. The following steps have to be done:

- Clean the rinsing bath after the chosen active bath, fill it with fresh water and disconnect it from any circuits.
- Determine the exact volume of the rinse by measuring width, length, and level.
- Mix the bath and its rinse well and take a 100 ml sample of each.
- Run 10-50 racks or barrels through the line, using different parts for representative statistics.
- Take samples (100 ml) of the rinse regularly and analyse them.

If the concentration of the chosen active bath (e.g. pickling, chromium bath) is high enough, it can be considered to have a constant concentration for easier calculation.

#### 6.3.1.3 Calculation

Knowing the concentrations of the rinse after different number of racks/barrels, the exact volume of the rinse and the concentrations of rinse and active bath at the beginning, the drag-out can be calculated as follows:

$$V_{d,n} = \frac{C_{r,n} - C_{r,o}}{C_b} \cdot V_r \quad [19]$$



Where:  $V_{d,n}$  = volume, which is dragged out at rack number  $n$

$C_{r,n}$  = concentration of the rinse after  $n$  racks

$C_{r,0}$  = concentration of the rinse at the beginning

$C_b$  = concentration of the bath at the beginning (considered as constant)

$V_r$  = exact volume of the rinse

Dividing the dragged out volume by the number of racks ( $n$ ), which have been run through the line, yields in the average volume being dragged out by each rack. If all analysed concentrations are calculated, the average drag-out of this special line can be found out.

The amount of the drag-out is often unknown or merely estimated. However, sometimes it is responsible for 90 % of the chemical consumption, and it can influence the quality of the plated parts extremely.

To find out the exact drag-out the most important steps are summarised below:

- Choose a bath with components easy to analyse and at high concentration
- Clean the rinse tank directly after the chosen bath and fill up with fresh water.
- Determine the exact volume of the rinse by measuring width, length, and level
- Stop all additions (concentrates and water) to the bath and its rinse, in particular disconnect both from any circuits
- Mix the bath and its rinse well and take a 100 ml sample of each
- Run 10-50 racks or barrels through the line, using different parts for representative statistics
- Take samples of the rinse regularly and analyse them

With the values obtained by this, the dragged out volume can be calculated. This "basic knowledge" of the amount of drag-out in a plating line can help in the following to calculate the consumption of additives, to optimize partly new make-up's, or the dissolution of zinc. Knowing these values will lead to the most wanted result: constant good quality of the plated parts.

### 6.3.2 Drag-out reduction - rack

Prevent drag-out of process solution by a combination of the following techniques:

- Arrange the workpieces to avoid retention of process liquids by jiggling at an angle and jiggling cup shaped components upside down.
- When withdrawing the jigs, allow sufficient draining time
- Automatically or manually inserting a draining pan when draining
- Regularly inspect and maintain jigs so there are no fissures or cracks to retain process solution, and that the jig coatings are hydrophobic (and retaining this property)

- Arrange with customers to manufacture components with minimal spaces to trap process solution or to provide drainage holes.

The reference value for draining time is 20 seconds (withdrawal and drain) as described in Table 25 below:

*Table 25. Withdrawal and dwell times for jig/rack [27]*

Process	Minimum time withdrawal (seconds)	Minimum time dwell (seconds)
Plating	10	10
Cleaning/pickling	8	7
Passivation	10	10
Seals/lacquers	10	5

### 6.3.3 Drag-out reduction - barrel

To prevent drag-out of process solutions by a combination of the following techniques;

#### 6.3.3.1 Ensure the barrels

- Are constructed from a smooth hydrophobic plastic and are inspected regularly for worn areas, damage, recesses or bulges that may retain process solution.
- The bores of holes have sufficient cross-sectional area and thickness of panels thin enough to minimise capillary effects
- Replace holes with mesh plugs
- The proportion of holes in the body is high as possible for drainage while retaining mechanical strength

#### 6.3.3.2 On withdrawing the barrel

- Withdraw slowly to maximise drag-out
- Rotated intermittently
- Have drainage ledges between tanks canted back to the process tank
- Automatically or manually inserting a draining pan
- Incline the barrel where possible

The Reference value for draining time is 24 seconds with 3 rotation periods of 8 seconds on the Table 26 below

*Table 26. Withdrawal and dwell times for barrels [27]*

Process	Minimum time (seconds)		
	Withdrawal	Dwell	Stationary periods (*)
Plating	5	24	3 x 8
Cleaning/pickling	5	24	3 x 8
Passivation	5	16	3 x 8
Seals	5	24	3 x 8
(*) barrel is rotated two or three time through 90 <sup>0</sup> with an 8 seconds dwell period			

## 6.4 Rinse calculations for reduction of waste water

### 6.4.1 Rinsing evaluation

The following steps are recommended as an approach to the rinsing problem:

- Decide on the desired limiting concentration in the rinse
- Measure drag-in by conductivity measurement, and from the drag-in per rack estimate the required flow from the rinse equation
- If the flow is appreciable, estimate the economies of a counter flow rinse
- Install a flow meter so that a definite flow can be maintained
- Calibrate the rinse tank with a conductivity meter so that concentration in the rinse can be measured
- After the flow meter and the rinse tank are calibrated, determine the characteristics of the rinse by measuring the change in concentration with time, under full productions, by means of conductivity measurements.
- After the rinse has been in service for some time, study the plating log to determine of the rinse tank is a source of contamination to the work or to the next tank in line.
- Calculate the savings when operation is kept at equilibrium and estimate the need for continuous control with automatic equipment.

## 6.4.2 Rinsing problems

Close packed parts, as in barrel plating, take some time to rinse. Experiments with barrel rinsing have readily shown what goes on. If a barrel is allowed to rotate in a running rinse while conductivity readings are taken, it will be seen that conductivity will increase for some time. During a typical study this time was two minutes, revealing the time necessary to rinse flow can be halted. This assures proper rinsing in the minimum amount of time. Also, it was found with this approach that rinse flow rates could be increased to shorten the rinsing time.

With automatic control a combined process step is possible that consists of a holding rinse. The controlled rinse will allow water to flow until the equilibrium concentration is established and then shut off the water to maintain this concentration. Following cleaning, some steels can be held in the inactive alkaline rinse to protect the metal until further processing is required.

After pickling, metals may be held in an acid rinse to maintain an active surface and to avoid rusting and so that adherent plating will be attained.

It is believed that troubles can develop from rinse water that is too clean. Rinse waters usually consist of calcium bicarbonate plus contaminants. The calcium bicarbonate can act as a neutraliser both for acids and alkalis and the rinse can become alternately acid and alkaline if it is allowed to run to sufficient dilution. It is possible that metals can lose activity under such conditions or, conversely, that the metals may corrode.

## 6.4.3 Calculation of rinsing criterion and amount of rinsing water

Multiple stage rinsing is particularly suitable to achieve a high rinsing rate with a small amount of rinsing water. The main effect of saving is reached with the transition from the first into the second stage. A smaller rinsing quantity of water can be achieved by selection of the correct rinsing system. The effect of water saving decreases with an increasing number of rinsing stages. However, the volume of water required decreases to the point where direct make up for water losses from process solutions at ambient temperatures can be considered. The achievable recovery rate is, at a given volume of evaporation, directly related to the concentration of process chemicals in the first rinse station.

Rinsing criterion:  $R_i = \frac{c_{i-1}}{c_i}$ , [13]  $c_i$ : concentration in bath  $i$

Rinsing criterion overall:  $R_{overall} = \frac{c_0}{c_n}$ ,  $R_{overall} = R_1 * R_2 * R_3 \dots R_n$  [13]

$c_0$ : concentration in process bath,  $c_i$ : concentration in last bath

Empirically estimated rinsing criterions for different purposes:

- after pre-and after-treatment of surfaces: 500 - 1500
- after deposition of metal (without chromium): 2000 - 5000

- after deposition of chromium: 30000 - 50000

For a one-step rinsing process:  $R_i = \frac{Q_i + V_i}{V_i}$  [13]

$Q_i$ : fresh water volume,  $V_i$ : drag-out volume of process bath

for a rinsing cascade:

$Q = V * (\sqrt[n]{R_{overall}} - 1)$ , [13]

$Q$ : fresh water volume,  $V$ : drag-out volume of process bath

Specific fresh water consumption of rinsing cascades for different rinsing criterion (fresh water demand in l/hour per drag-out of a process bath) shows on the Table 26.

**Table 26. Specific fresh water consumption of rinsing cascades for different rinsing criterion**

Steps	Rinsing criterion, R							
	25000	20000	15000	10000	5000	2000	1000	500
1 step	24999	19999	14999	9999	4999	1999	999	499
2 steps	157	140	122	99	70	44	31	21
3 steps	28	26	24	21	16	12	9.0	6.9
4 steps	12	11	10	9	7.4	5.7	4.6	3.7
5steps	6.6	6.2	5.8	5.3	4.5	3.6	3.0	2.6

#### 6.4.4 Overall achieved environmental benefits for all options described

The zero-discharge (closed-loop or squared) water balance is often seen as the ultimate criterion of the rinsing technology for a surface process low in emissions. This is where the water returned to the process solution from the first rinse station equals the water lost in evaporation and drag-out. Process solutions operated at higher temperatures and with multistage rinsing offer possibilities for this.

By the introduction of multi-stage rinsing systems partly combined with rinsing water recycling system, decreases of wastewater of up to 90% can be obtained.

Generally the installations of multi-stage rinsing techniques is associated with higher space requirement and higher investments (costs for additional tanks, workpiece transport equipment and control). The decrease of water consumption, recovery of process chemicals and the smaller effluent discharge, which requires a smaller wastewater processing facility and less treatment chemicals, reduces the total costs.

## 6.5 Trivalent chromium replacements for hexavalent chromium plating

### 6.5.1 Introduction

Hexavalent chromium has been classified as carcinogenic by inhalation; in addition chromate films do contain hexavalent chromium and may release some of it during the handling and the usage of the finished product. Therefore the labelling of proprietary solutions and/or proprietary solid compounds containing hexavalent chromium do have to show the risk designation, as required for products classified as toxic and carcinogenic. This is the driving force for innovative hexavalent chromium free and other competitive technologies.

### 6.5.2 Hexavalent chromium plating technology

In the traditional chrome plating process, the process steps are generally as follows: activation bath, chromium bath, rinse 1 and rinse 2. The activation bath, if used, is a separate tank of chromic acid. The activation step is typically (depending on the alloy) a reverse current etch to prepare the surface of the parts to accept the plating by removing oxides from the surface of the material.

Sometimes the activation step takes place in the chromium bath itself. The composition of the chromium bath is chromic acid ( $\text{CrO}_3$ ) and sulphate ( $\text{SO}_4^{2-}$ ), with ratios ranging from 75:1 to 250:1 by weight. The bath may be co-catalyzed with fluorides. In chromic acid, the chromium is in the +6 oxidation state, which is reduced to  $\text{Cr}^{+3}$ , then to unstable  $\text{Cr}^{+2}$  and finally to Cr. Some  $\text{Cr}^{+3}$  is necessary in the bath to act as a reducing agent, however, concentrations of  $\text{Cr}^{+3}$  exceeding 2- 3% of the chromic acid content can cause problems. (Many specifications require that this concentration not exceed 1%). The presence of other oxides of metals (e.g., iron, nickel) combined with the  $\text{Cr}^{+3}$  hinders bath performance.

In addition to bath composition, the other important parameters are temperature and current density. Together, these affect brightness and coverage. Current density also affects cathode efficiency. Agitation of the bath is required to equalize the bath temperature. Preheating the parts to be plated, by placing them in the solution with not current applied, may be necessary to obtain a uniform deposit.

The low cathode efficiency of the hexavalent chromium results in the major issue with chromium plating: poor coverage in low current density areas, and excessive build-up in high current density areas (e.g. part edges). The ability of a coating to cover the part uniformly is referred to as "throwing power." In many cases, the part is over-plated, and ground back to final dimensions.

In other cases, auxiliary anodes are used to provide more uniform coating of the part.

### 6.5.3 Trivalent chromium plating technology

In some applications and at certain thicknesses, trivalent chromium plating can replace hexavalent chromium. This is especially true for decorative applications where the trivalent chromium finish closely resembles the hexavalent chromium finish. However, the trivalent chromium process may be more expensive and require more careful control than the hexavalent chromium process.

To more closely resemble the functionality of hard chromium plating, pulse current plating has been used in a trivalent chromium solution. However, they have not quite matched the corrosion resistance of the hexavalent chromium finish.

Trivalent chromium plating has higher cathode efficiency than hexavalent chromium plating which results in less energy use and no misting problem. Furthermore, the reduction step in wastewater treatment is not required (eliminating the use of sodium bisulphate or other reducing agents and additional acid for pH control) and significantly less sludge (by volume) is produced.

Trivalent chromium plating solutions have a lower overall concentration of chromium than hexavalent chromium solutions. Trivalent chromium is also less toxic than hexavalent chromium.

Barrel plating with trivalent chromium solutions is possible, but difficult. Process conditions, part configuration and other variables must be controlled for successful barrel plating.

When trivalent chromium plating was first introduced, customers generally did not accept the different colour tones compared to hexavalent chromium. Additives to the trivalent chromium bath can often adjust the tone to customers' needs.

Trivalent chromium plating can be divided into the following three basic types:

- Single electrolyte bath (chloride- or sulphate-based) using graphite or composite anodes and additives to prevent oxidation of trivalent chromium at the anodes.
- Sulphate-based bath using shielded anodes (lead anodes surrounded by boxes filled with sulphuric acid) which prevent the trivalent chromium from reaching the anodes, thus preventing their oxidation.
- Sulphate-based using insoluble catalytic anode that maintains an electrode potential level that prevents oxidation of the trivalent chromium.

### 6.5.4 Benefits and challenges

While the use of a trivalent chromium process instead of a hexavalent chromium process is more protective of human health and the environment in and of itself, the potential pollution resulting from the trivalent chromium processes can be further reduced by using pollution prevention techniques. For example, static rinse tanks can be used to capture the drag out for return to the plating tank for reuse. In addition, the plating bath can be recycled and recovered for reuse using porous pots, membrane electrolysis, or ion exchange.

The trivalent chromium products share these benefits and challenges for potential users when compared to the hexavalent chromium plating.

#### 6.5.4.1 Benefits

- **Lower Toxicity:** Trivalent chromium is much less toxic than hexavalent chromium, according to EPA.
- **Air Emissions:** The trivalent chromium processes have higher current efficiencies, therefore less chromium mist is emitted into the air requiring treatment.
- **Worker Exposure:** The trivalent processes are inherently less toxic due to the oxidation state of the chromium; therefore they are less toxic to workers. The trivalent processes produce less air emissions and therefore provide less potential for worker exposure.
- **Hazardous Materials Handling:** The lower toxicity of the trivalent chromium chemistries mean less hazardous materials must be handled when compared to the hexavalent chromium processes. In addition, the trivalent chemistries require a lower concentration of chromium in the bath, 5 g/l compared to 130 g/l for the hexavalent chromium bath, so less of a less hazardous material is being handled.
- **Hazardous Waste Generation:** The trivalent chromium processes produce approximately thirty times less sludge (by volume) than the hexavalent chromium baths.
- **Regulatory Compliance:** It is becoming increasingly difficult to comply with air emissions and worker health requirements of hexavalent chromium plating operations. Trivalent chromium is not currently regulated as aggressively due to its lower toxicity.
- **Energy Use:** The trivalent chromium processes require less current density, so less energy is used compared with the hexavalent chromium processes.
- **Quality:** The throwing power is better in the trivalent chromium processes. The trivalent chromium processes can withstand current interruption without sacrificing finish quality, whereas the hexavalent chromium processes cannot.

Advantages and disadvantages of Hexavalent Chromium (Cr VI) plating and trivalent chromium (Cr III) plating show in the appendix 2 to 5.

#### 6.5.4.2 Challenges

- **Chromium:** It is still chromium and may be subject to future increased regulation.
- **Cost:** Trivalent chromium plating may be more costly than hexavalent chromium plating, depending on the properties required and the cost of compliance for the hex chrome system. The actual cost of the trivalent and hexavalent chromium processes are dependant on many factors and are difficult to compare in a general sense. Trivalent chromium plating is slightly more costly than hexavalent chromium plating. However, when the cost of waste disposal and compliance with the restrictions on the use of hexavalent chromium, then the use of trivalent chromium may be a good option for some applications.



## 6.6 Replacement of hexavalent chrome passivations on galvanized steel

### 6.6.1 Introduction

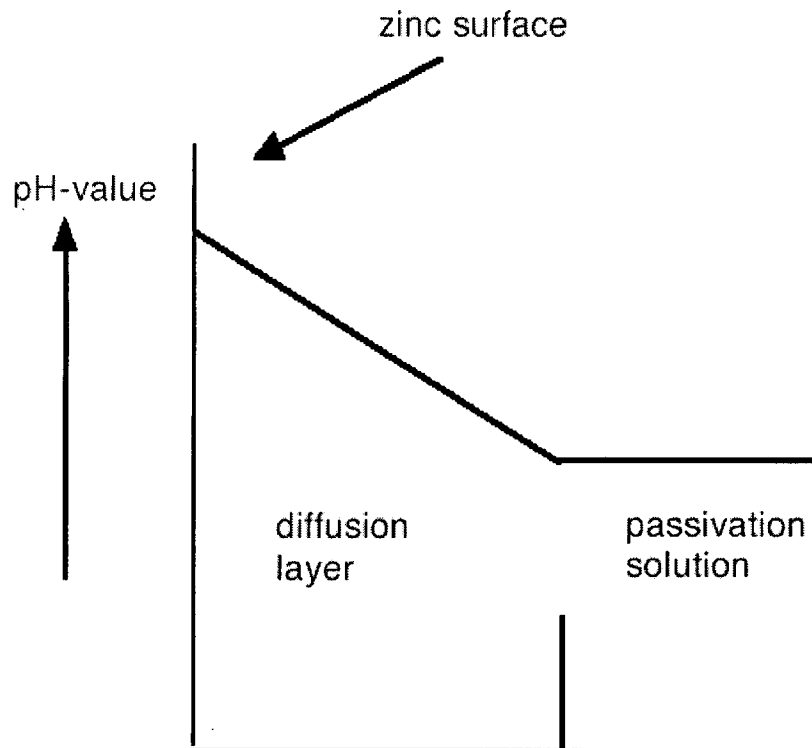
In the year 2000, the EU community released the “End of Life Vehicles Directive” which allows only 2 g hexavalent chrome per vehicle from July, 2003 onwards [20]. Every two years this amount will be compared with the latest technology and possibly adapted. Due to this regulation, car manufacturers in Europe, US and Japan will stop using hexavalent chromates in the year 2002. The electronic industry is planning the same for the year 2006. Hexavalent chrome is known to be carcinogenic, while trivalent chrome and metallic chrome not. The EU-Directive bans the hexavalent chrome but not the trivalent or metallic chrome. The passivation of galvanized steel with hexavalent chrome is used for two reasons; first to achieve a significant increase in corrosion protection, especially for construction and furniture or second as a temporary protection during shipment if the usage of a corrosion protecting oil is not possible. The coating weight of the passivation depends strongly on the application parameter, the thicker, the higher the corrosion protection. In continuous strip plating, the yellow passivations (based on chromic acid) are applied by dip, spray or roll coating (no-rinse coating) with and without further organic topcoats. Alternative systems for replacement must be free of hexavalent chrome or other toxic compounds. The corrosion behavior and the properties as an adhesive layer must be similar or better, but the appearance can be different. Trivalent chrome passivations are known as a non toxic system for many years, however in the past, they could not fulfil the corrosion requirements. Recently developed so called “thick layer passivations” based on trivalent chrome can produce passivation layers with the same or an even better corrosion protection.

### 6.6.2 Layer passivations based on trivalent chrome

Independently whether a hexavalent or trivalent chrome passivation is used, the first reaction is the same:



The acidic passivation solution dissolves the zinc. Due to the consumption of acid in front of the zinc layer, the pH-value increase, see figure 4:



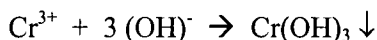
**Figure 4. pH-value increase in front of a zinc layer in a passivation solution**

In case of a hexavalent chrome passivation, the  $\text{Cr}^{6+}$  is reduced to  $\text{Cr}^{3+}$  by zinc and hydrogen:

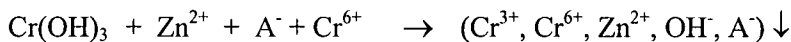


The  $\text{Cr}^{3+}$  intermediate has two reaction paths:

1. Complexing (hex aqua etc.) the trivalent chrome and moving into the electrolyte or,
2. precipitates as chrome hydroxide due to the pH-shift on top of the zinc surface as seen in figure 4:

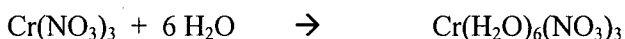


During precipitation of the chrome hydroxide zinc cations and anions as well as hexavalent chrome is incorporated in the layer:

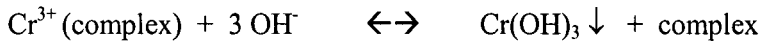


It is interesting to realize that even in a hexavalent chromate the reaction takes place via trivalent chrome and the  $\text{Cr}^{6+}$  are only incorporated during precipitation. The  $\text{Cr}^{6+}/\text{Cr}^{3+}$  ratio in the solution is very important, if the  $\text{Cr}^{3+}$  concentration gets too high a new make up of the passivation is necessary.

In opposite to the hexavalent chrome passivation where a non complexed trivalent intermediate is created the  $\text{Cr}^{3+}$  in a hexavalent free passivation is almost complexed, at least as a hex aqua complex as shown:



The Cr (III)-complex precipitates on the zinc surface because of the pH-shift, to build a passivation layer as described:



For a hexavalent passivation the reaction speed limiting step is the creation of the  $\text{Cr}^{+3}$ -intermediate. For the trivalent chrome passivation it is the reaction of the complex. In contrary to the hexavalent chromating process, the service life of a trivalent chromiting process is only limited by impurities like iron, etc.

### 6.6.3 Comment

The new thick layer trivalent chrome passivation leads to the same or even higher corrosion protection compared to a usual hexavalent chromate with the same short contact time. Depending on the application parameters (contact time, temperature and concentration), the coating weight and therefore the corrosion protection can be adjusted to customer requirements: for example a low coating weight for temporary protection or a high coating weight for a high corrosion protection. In combination with an organic top coat, the original zinc colour is given back, and a further increase of the corrosion protection is observed. An efficient rinsing after passivation is necessary to prevent a dry up of the passivation solution which will reduce the corrosion protection (stack test) or a drag in into an organic top coat which will may lead to coagulation. In opposite to the hexavalent chromate, the rinse water can be recycled into the passivation solution to balance drag-out losses and evaporated water. This will also reduce the consumption of the passivation chemistry. Because the  $\text{Cr}^{+6}/\text{Cr}^{+3}$  ratio is not important for a trivalent chrome passivation solution, its service life for spray or dip application can be longer compared to a hexavalent chromate bath.

## 6.7 Waste water treatment

- Identify, separate and treat flows that are problematic when combined with other flows, such as: Chromates ( $\text{Cr}^{+6}$ ), Cyanide, etc.
- Precipitate anions where required to meet local emission limit values.
- Flocculate the metals and pH adjust according to the composition of the effluent
- Remove solids by precipitation, or filtration
- Monitor and discharge

There is a variety of methods available for the treatment of the electroplating wastes, but two widely used systems employed by the plating workshops are batch and continuous treatment. Batch treatment system is mainly practised in the small electroplating workshops. In the batch treatment system, all wastes are collected in a tank, usually for on shift, and then treated as a single batch. The continuous treatment system, on the other

hand, monitors the volume of incoming wastewater and adjusted the chemicals to the wastewater as it passed through the system.

### 6.7.1 Cyanide treatment

The method commonly used by electroplating workshops for cyanide waste treatment is cyanide destruction by chlorination under alkaline condition, or referred to as alkaline chlorination. Destruction of the cyanide by alkaline chlorination method may be accomplished by direct addition of gases chlorine or chlorine dioxide in the presence of caustic soda, sodium hypochlorite or bleaching powder. When chlorine is added to the wastewater containing free cyanide and sufficient alkali is added to raise the pH to 10 or higher, free cyanide is oxidized to cyanate with cyanogen chloride as an intermediate product. This reaction is normally instantaneous or takes less than 10 minutes. With excess chlorine, cyanate could be further oxidized slowly to carbon dioxide and nitrogen. This second stage of reaction takes 30 minutes to an hour. The overall reaction with excess chlorine in the presence of NaOH for complete conversion of cyanide to carbon dioxide and nitrogen gas is as follows:



Theoretically, 2.75 parts of chlorine and 3.08 parts of alkali (NaOH) are required to oxidize each part of cyanate. Additional 4.09 parts of chlorine and 3.08 parts of alkali for each part of cyanide are required to convert cyanate into carbon dioxide and nitrogen gas. However, chlorine requirement in practice for the complete destruction of cyanide higher than 6.82 parts. Figure 5 shows the schematic flow diagram of cyanide waste treatment in the electroplating workshops:

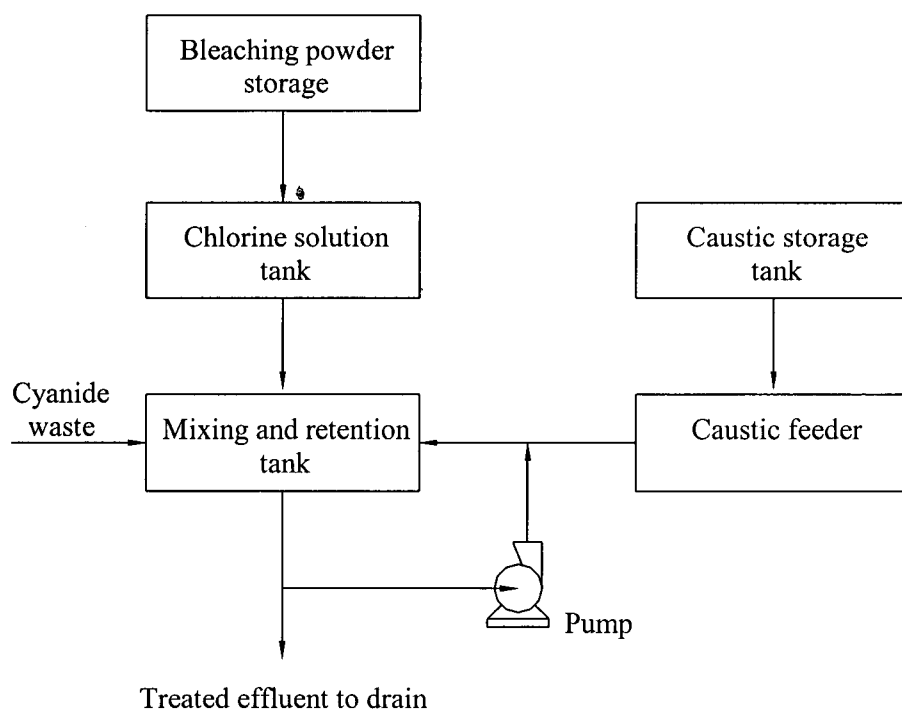
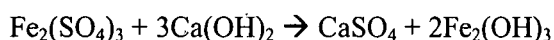
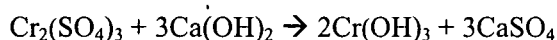
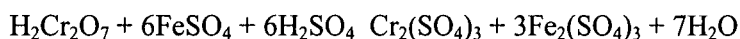


Figure 5. Treatment of cyanide wastes

## 6.7.2 Chromium treatment

The most effective and economical way of chromium treatment is to reduce hexavalent chromium,  $\text{Cr}^{+6}$  to trivalent state,  $\text{Cr}^{+3}$  in an acidic condition, and subsequent precipitation with an alkali. Ferrous sulphate along with sulphuric acid is commonly used for this purpose. Other reducing agents used are sulphur dioxide and sodium bisulphite. Maximum reduction occurs in the pH range of 2.0 to 2.5. The reduction takes about an hour. The reduced trivalent chromium is precipitated by the addition of an alkali, such as lime or caustic soda. Lime is commonly used, since it is cheaper than caustic soda. The step-wise reaction for precipitation by hexavalent chromium with ferrous sulphate and lime are:



Theoretically, 16.03 parts of copperas ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), 6.01 parts of sulphuric acid and 9.48 parts of lime are required for the complete removal of part of chromium. Figure 6 shows the schematic flow diagram of chromium waste treatment:

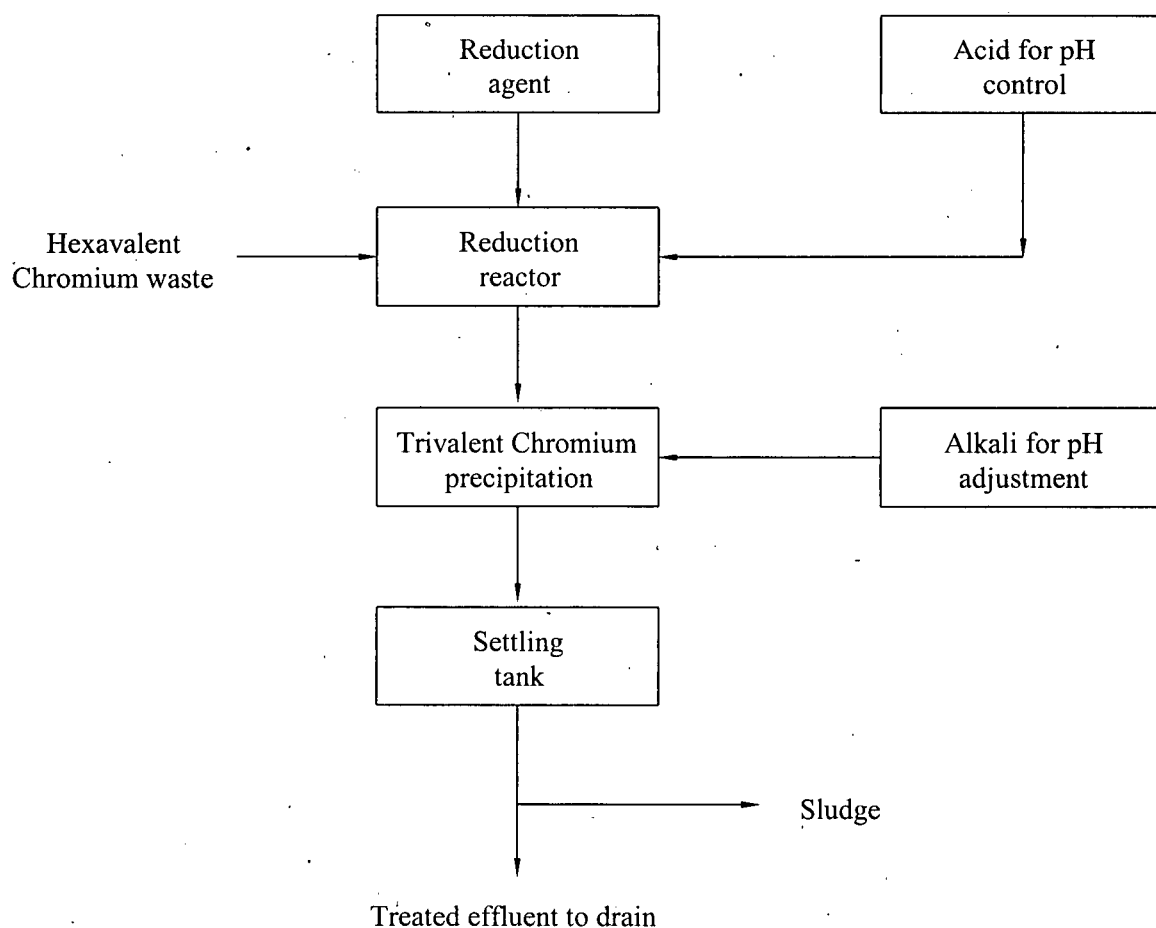


Figure 6. Treatment of hexavalent chromium wastes

### 6.7.3 Treatment of other metal bearing wastes

The most commonly used method of treatment for nickel and zinc wastewater is by chemical precipitation. Almost all the metals precipitate completely in the pH range of 9.5 to 10.5. Lime is commonly used as a coagulant for the removal of the heavy metals. Figure 7 shows the typical treatment processes of electroplating wastewater:

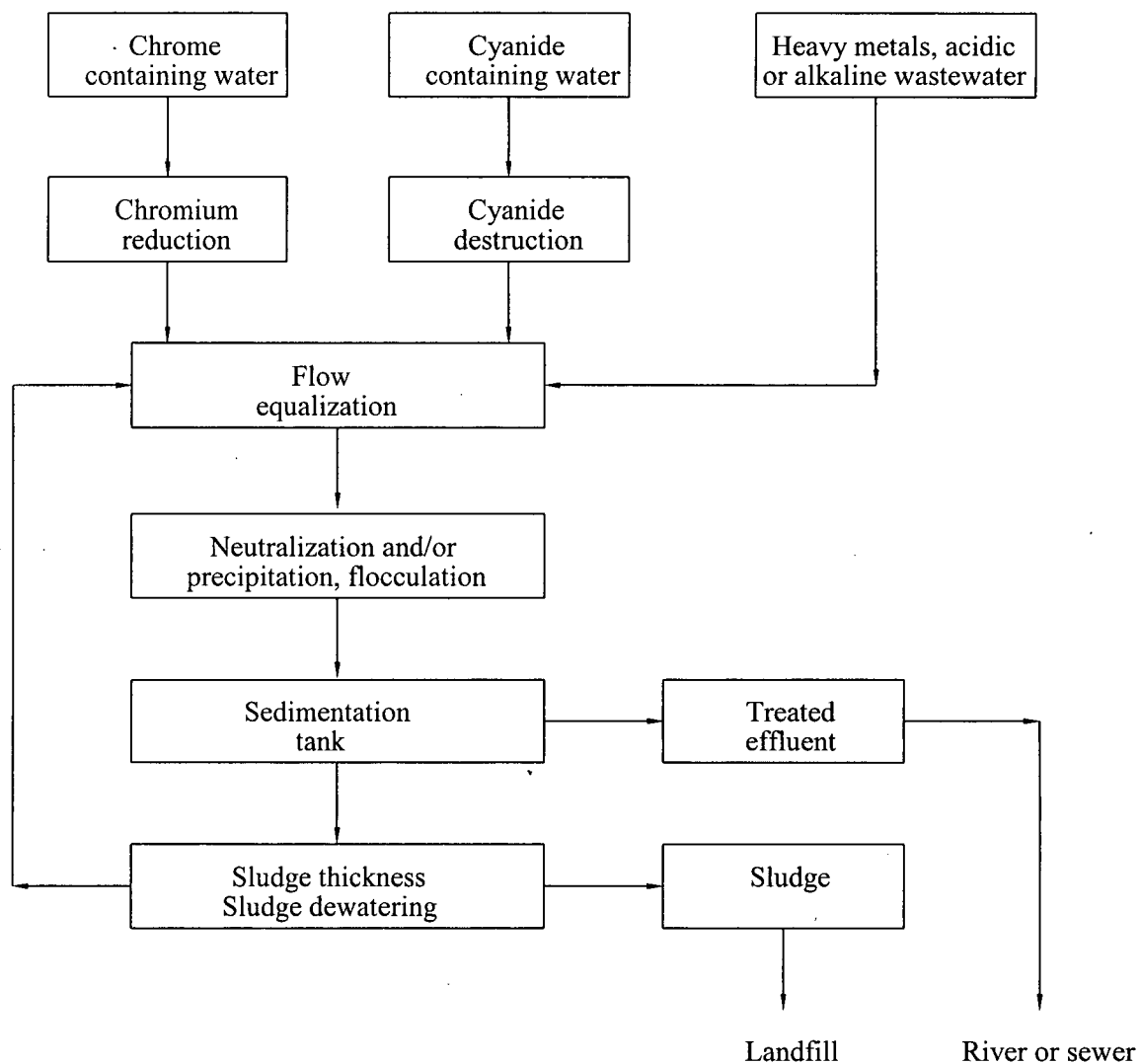


Figure 7. Treatment of electroplating wastewater

### 6.7.4 Sludge disposal

Sludge generated from the treatment processes contains 1% to 3% dry solids. Dewatering of sludge is required to reduce transportation and disposal costs. Centrifugation and vacuum filtration have been used for sludge dewatering. The dry solid concentration by using these two facilities ranges from 15% to 25%. Filter press and belt press are two most effective mechanisms for sludge dewatering. The filter cake produced from these two methods contains 25% to 35% of dry solids. As the dewatered sludge contains high

concentration of heavy metals, the residue may be regarded as hazardous waste. Many countries are now required to use special landfills for disposal of potentially harmful sludge. Secure landfills are sited and designed to preclude the risk that toxic chemicals will leach into surrounding environment and groundwater. The sludge generated from electroplating workshops may have to be stabilized by chemical fixation or cementation to avoid leaching of heavy metals prior to the ultimate disposal in secure landfills.

## 7 Conclusion and recommendation

Based on the results of analysis and assessment of plating technology as well as related environmental problems in Vietnam and in developed countries. Some appropriate solutions are collected in order to reduce and treat plating wastewater in plating industry in Vietnam in the following:

- Minimising chemical and wastewater: show the benefit from minimising the chemical and water use.
- Determination of the drag-out: show the way of calculation for drag-out and reduce the drag-out for rack and barrel plating.
- Reduction of wastewater by applying cascade rinsing
- Reduce hexavalent chromium in wastewater by applying new modern plating technology: Trivalent chromium replacements for hexavalent chromium plating and replacement of hexavalent chrome passivations on galvanized steel. The advantages and disadvantages of these plating technology show in Appendix 1, 2, 3, 4 and 5.
- Collection the appropriate treatment for cyanide, hexavalent chromium and other heavy metals in plating wastewater.

To achieve the goals about reduction and treatment of plating wastewater, some changes can be made:

- Optimize water use with cascade rinsing: Static rinse used in plating companies in Vietnam uses much large amounts of water than cascade rinsing. Drastic reductions in water consumption can be achieved with relatively low-cost measures. In effect, decreased water use corresponds to wastewater with lower volume and higher concentrations of chemicals. Treatment of wastewater would accordingly be more efficient and less costly.
- Changing new plating technology in the future:  $\text{Cr}^{+3}$  plating technology and replacement  $\text{Cr}^{+6}$  by  $\text{Cr}^{+3}$  in passivation are very new technology which Vietnamese plating companies should be interested in for the future. If new technologies are applied, we will not face with  $\text{Cr}^{+6}$  in wastewater and we will reduce hazardous waste from discharge.



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## 9 Appendix

### *Appendix 1. Troubleshooting hexavalent chromium plating*

Problem	Possible Cause	Solution
(1)	(2)	(3)
Milky Deposit	High chromic acid/sulphuric ratio	increase sulphate
	Chloride contamination	remove chloride with silver carbonate
	Iron contamination	dilute bath
	Excess trivalent chromium	clean anodes; reoxidize trivalent chromium
	Poor nickel surface	carbon treat nickel, improve rinsing of nickel, use nickel activator
	High temperature	reduce to normal, check controller
Hazy Deposit	High chromic acid/sulphate ratio	increase sulphate
	High chloride contamination	remove chloride with silver carbonate
	Iron contamination	dilute bath
	Excess trivalent chromium	clean anodes; reoxidize trivalent chromium
	Low temperature	increase to normal
	Current density too high	adjust anode-to-cathode ratio
	Intermittent current flow	check electrical contacts
	Poor nickel surface	improve rinsing and use nickel activator
Gray, Dull but Smooth Deposit	High chromic acid/sulphate ratio	increase sulphate
	Current surge when contact made	reduce current
	High temperature	check temperature controllers
Dull Spots in High-Current Density Areas	High chromic acid/sulphate ratio	increase sulphate
	Passive nickel	improve rinsing; use nickel activator
	Bipolar condition	Use live entry to chromium bath

(1)	(2)	(3)
Blue Deposits	High temperature	reduce temperature to normal
Rough Deposits	Low sulphate	add sulphuric acid
	Low temperature	adjust temperature to normal
	Surface preparation	improve cleaning/rinsing
	Suspended particles in bath	filter bath/eliminate source
Burned Deposits	High chromic acid/sulphate ratio	increase sulphate
	Low chromic acid	add chromium salts
	Excess trivalent chromium	clean anodes/reoxidize trivalent chromium
	Too high current density	reduce current density or increase temperature
	Low temperature	increase temperature/preheat large, cold parts
Brown Spots or Rainbows	Low sulphate or catalyst	increase sulphate concentration/submit samples for analysis
	Inefficient contacts	check racks for build-up on hooks/tip, check for proper contacts on buss bars
Poor Adhesion	Insufficient etch	increase etch time/check etch bath
	Surface contamination	improve rinsing and/or cleaning cycle
	Intermittent contact	clean/check contacts and put work in the chromium bath live
	Poor nickel deposit	check surface prep before nickel plating and nickel bath
Poor Coverage	Low chromic acid content	Add chromium salts
	Low chromic acid/sulphate ratio	precipitate excess sulphate with barium carbonate
	Plating current too low	raise current density
	Oxidized contact	clean contacts
	Scaled anodes	clean anodes
	High temperature	reduce to normal
	Passive nickel	activate nickel surface

(1)	(2)	(3)
Slow Deposition Rates	High chromic acid/sulphate ratio	Add sulphuric acid
	Too low current density	Increase voltage; check part distribution and for current leaks
	Scaled anodes	clean anodes
	Oxidized contacts	clean contacts
	Insufficient power supply	increase rectifier size
	Iron contamination	dilute bath
	Excess trivalent chromium	follow procedure for reoxidation of trivalent chromium
	Too high temperature	reduce to normal
Partial Deposition Rates	Too low current density	increase voltage; clean rack contacts and anodes
	Uneven current density	Improve part arrangement on racks
	Passive nickel	activate cathodically or immerse in 50% hydrochloric acid
	Gas pockets	Suspend parts so gas escapes
No Deposit	Reverse polarity	make proper connections
	Defective contacts	clean contacts
	Excess sulphate	check ratio and correct
	Chloride contamination	remove chloride with silver carbonate
Pitted Deposits	Pitted nickel deposit	filter nickel bath
	Pitting in base metal	Improve preparation
	Solution contamination from magnetic particles on ground surfaces	improves grinding and cleaning procedure
	Gas pitting	reposition work on racks

**Appendix 2. Hexavalent Chromium (Cr VI) plating advantages**

Advantages	Comments
Can build thick layers necessary in hard chrome applications	In some cases there are no alternatives to Cr VI electroplating
High hardness 700 to 1000 HV (harder than from Cr III), corrosion resistant, micro - cracked and retain lubricants, low friction resistant, anti - adhesive, machinable, thermally resistant	Untrue - coatings from Cr III achieve similar hardness values Other attributes from Cr III similar to Cr VI
Widely - used, well - established. Easy applied and low cost	Cr VI Decorative coating: 650 sites in Germany, turnover EUR 2.1 billion/yr CrVI Hard chromium: 285 sites in Germany, turnover EUR 840 million/yr
Glossy coatings are generally deposited from Cr VI solutions	Glossy coatings are also obtained from CrIII solutions
<b>Surface treatment specifications for key applications (e.g. automotive) specify CrVI</b>	

**Appendix 3. Trivalent chromium (CrIII) plating advantages**

Advantages	Comments
(1)	(2)
Lower toxicity	No additional health and safety requirements. Will not trigger Seveso directive limits
Higher cathode efficiency	No hydrogen formed and less spray Energy saving is significant (see case studies) and exceeds increased chemical costs, giving good payback time for change - over and increased profits

(1)	(2)
Better covering and throwing power. Achieves higher racking densities and therefore higher parts throughput per shift	Increased profitability reported in case studies
Lower current density. This requires lighter weight and less expensive jigging.	Increased profitability reported in case studies
Process insensitive to current interruption (hence no whitewashing) and almost impossible to burn. Reject rates down (by 66% reported).	Increased profitability reported in case studies
Widely established in USA, and at least 100 sites. Used by two major cooker manufactures in Europe for 7 years, for parts subject to heat, humidity and cleaning with strong acid or caustic cleaners and abrasive materials.	
Lower chromium content of solutions results in lower viscosity, resulting in lower drag - over, less effluent contamination, and less staining of work	
Less waste produced than CrVI process: up to 80% reported. Also, no dissolution of anodes to lead chromate sludge.	
Overall net profit up due to reduced effluent treatment, reduced waste and waste charges, fewer rejects, reduced air monitoring, increased throughput. Lower insurance premiums are possible for CrIII operators because of lower worker risk.	
Solutions are less concentrated, not oxidising and are cleaner and less corrosive to handle, use and are less corrosive to plant and equipment	
CrIII plating solutions can be regenerated by porous pot or membrane filtration	

**Appendix 4. Hexavalent chromium (CrVI) plating disadvantages**

Disadvantages (1)	Comments (2)	Counter-comments (3)
<p>Very toxic to humans and environment.</p> <p>Current/Proposed classifications</p> <p><math>\text{Na}_2\text{Cr}_2\text{O}_7</math> very toxic</p> <p><math>\text{Na}_2\text{CrO}_4</math> toxic/very toxic</p> <p><math>\text{CrO}_3</math> toxic/very toxic</p> <p>All: very toxic to aquatic organisms</p> <p>Very toxic (human health) triggers Seveso II directive threshold of 5 tones per installation.</p>	<p>Control measures well-understood and can be readily applied: including spray suppression, fume extraction, reduction of Cr VI readily in effluent treatment with flocculation and precipitation. Can be used in closed-loop with counter-current rinsing, evaporation, etc. May be used in specialised, enclosed production lines high volume production of similar-sized components.</p>	<p>Measures for control, such as fume extraction, give rise to other environmental impacts.</p> <p>One key measure involves the use of PFOS in vats to reduce chromium spray formation: PFOS has toxic and bio accumulative effects, and is now under investigation Largest manufacturer ceased production 2002.</p> <p>Insurance premiums for health and safety may be higher as a result of occupational health issues</p>
<p>Low cathode efficiency, poor metal distribution with excessive build up in high current areas and poor coverage in low current areas, lack of coverage around holes, sensitivity to ripples in power supply and 'white washing' (opaque/cloudy finish: a common problem). High reject rates. High energy costs.</p>	<p>Auxiliary anodes can be used to improve throw</p>	
<p>Poor current efficiency due to 85 - 90% electrical power generates hydrogen, causing bubbles which break forming a Cr VI mist.</p>		



(1)	(2)	(3)
<p>Drag-in and etching (sometimes in the chrome vats) in the strong acid electrolyte increase impurities such as Fe, Cu, Ni, and Cr III (this is also generated in the process). These must be removed by chemical precipitation, plating out, ion exchange resin columns, or membrane electrolysis or electro dialysis. Normally ion exchange is on the first static rinse to prevent degradation of the rinse. This is essential.</p>		
<p>High chemical concentration in the vats: typically 180 - 450 g/l.</p>		
<p>High waste production from high solution strengths (where there are discharges from rinsing).</p>		
<p>Typically uses lead anodes, which decompose over time, forming lead chromes (toxic) which slough off the anodes and accumulate in the tank, requiring filtering and removal.</p>		
<p>Cr VI is an strong oxidant and attacks equipment used in its control, such as plastic air dustings etc, causing corrosion in the working atmosphere and deterioration of plant and equipment Dried Cr VI electrolytes have been known to cause fires in plating shops.</p>		
<p>Cr VI plating solutions require specialist regeneration or discarding for recovery of the metal in the waste solution.</p>		

*Appendix 5. Trivalent chromium (Cr III) plating disadvantages*

Disadvantages	Comments	Counter-comments
<p>(1) Solution reactions limit thickness, and hence cannot be built up to the requirement for hard chromium applications</p>	<p>(2) Cr III solutions cannot achieve thick films. A patented process to overcome this is at pre-production trials.</p>	<p>(3)</p>
<p>Corrosion stability, hardness and wear resistance is lower than Cr VI</p>	<p>Reported measured hardness figures are similar from Cr VI solutions. At present, it is not possible to build thick coatings for engineering applications. Corrosion may be due to porosity of the coating or lack of passivation effect. Where high corrosion resistance is not required (e.g. indoor applications) the Cr III coating will outlast the life of the parts. Cr III has been used extensively for about 7 years by major companies making cookers, where parts are subject to heat, humidity, abrasive and strongly acid or alkali cleaning materials, with no reported problems.</p>	
<p>Cr III solution does not passivate in areas where it does not plate. This can lead to corrosion on parts with significant blind areas, such as tubes.</p>	<p>Parts with blind areas should be rinsed rapidly and passivated subsequently with a Cr VI, phosphate or organic passivating solution.</p>	

(1)	(2)	(3)
<p>Dissolution of substrate dissolved from blind areas (Cu, Zn from brass) can give rise to an increase in the contaminants. And other dragged-in contaminants (Ni from previous plating stage) can affect the colour of the plating, causing darkening and decrease in current efficiency.</p>	<p>It is essential to control this by maintenance using ion exchange or precipitating agents followed by filtration. Filtration with activated carbon is essential to remove organic breakdown products.</p>	
<p>Colour is different to Cr VI decorative coatings</p>	<p>Colour is affected by contamination build up. Differences in colour can be matched by the addition of iron (or other additives). The co-deposition with iron and some other irons improve plating properties. If colour match is critical, then parts may have to be produced by the same processes.</p>	
<p>Cr III requires expensive membrane electrodes that are susceptible to damage and poisoning.</p>	<p>Membranes electrodes can be used but are now largely replaced with cheaper and more robust graphite or composite anodes. Organic additives prevent oxidation of Cr III at the anode. Shielded lead anodes and insoluble catalytic anodes maintained at an electrode potential level that prevents oxidation of the Cr III.</p>	
<p>Cr III solutions contain complexing agents that interfere with other waste water treatment</p>	<p>This may be possible hypothetically, but no problems have been observed or reported. In one case study the operator of Cr III with electrolytic recovery of the Cr achieves metals levels low enough to avoid further effluent treatment.</p>	

(1)	(2)	(3)
<p>Cr III solutions contain chloride and release chloride.</p> <p>The oxidation of other materials by chlorine can lead to the production of AOX in effluents</p> <p>The release of chlorine produces lots of small bubbles in the solution and is a source of pitting in the plating.</p>	<p>This problem was resolved 20 years ago by additions which prevent chlorine release. Choice of additives and the usual regular maintenance by activated carbon filtration will prevent release of AOX. No problems have been observed at site visits or reported from case studies or operators.</p> <p>No pitting problems are reported by case studies or site visits, which reports better quality output from Cr III as a key advantage. A large number of hydrogen bubbles are also produced in Cr VI solutions.</p>	
<p>Cr III solutions require more control and costly equipment to maintain solutions</p>	<p>The additional controls are no greater than those required to run the nickel solution that precede the Cr step in decorative plating.</p> <p>The additional equipment (ion exchange, activated carbon filtering) is similar to that required for close-loop Cr VI.</p>	
<p>More complex solution chemistry requires more chemicals.</p> <p>More costly to run</p>	<p>True but case studies report significant overall saving as a key reason for change.</p>	
<p>Cr III cannot be run on a closed loop because it is based on a ligand exchange reaction which cannot be revoked by heating or other processes.</p>		
<p>Make up of Cr III solutions may be more than is normally lost through evaporation and drag-out. Evaporation of the bulk bath is one method of returning to the original volume.</p>		

*Appendix 6. Acid zinc troubleshooting guide*

<b>Problem</b>	<b>Possible Cause</b>	<b>Corrective Action</b>
<b>(1)</b>	<b>(2)</b>	<b>(3)</b>
Black spots on deposit before and/or after chromating. High-current-density areas darker after chromating.	Iron contamination (More than 100 ppm)	Check the bottom of the tank for parts that have fallen off racks or out of barrels.  Treat with hydrogen peroxide. Add 0.25 to 0.5 pint of 30 to 35 pct hydrogen peroxide per 1,000 gal of solution volume. The hydrogen peroxide should be diluted at least 3:1 with water before addition to the tank. The precipitated ferric hydroxide is removed by filtration. If filtering is insufficient, the precipitated iron will again dissolve back into solution and the spots will reappear.
Deposit staining or black after chromating	Copper contamination (5 to 10 ppm) and/or Cadmium contamination (10 to 20 ppm)	Electrolyze solution at two to five and for eight to 12 hr.  Zinc dust treat at one lb per 1,000 gal of solution and filter out zinc particles so as to redissolve the materials back into the bath
White staining	Poor rinsing and/or high brightener	Improve rinsing  Add 0.5 fl/oz of hydrochloric acid to the first rinse after the plating tank Reduce brightener additions
No deposit in low-current-density areas	Chromium contamination (200 ppm)	Add one oz/gal sodium hydrosulphite per 100 gal of solution per 100 ppm of chromium to be removed  Zinc dust treat at one lb per 1,000 gal of solution and filter out zinc particles so as not to redissolve the metals back into the bath Electrolyze solution at two to five and for eight to 12 hr
	High brightener	Reduce brightener additions
Poor adhesion and/or blisters	Chromium contamination (10 to 20 ppm)	add one oz/gal sodium hydrosulphite per 100 gal of solution per 100 ppm of chromium to be removed
	Poor cleaning and/or rinsing	Improve cleaning, pickling and/or rinsing
	Organic contamination	Filter the solution through a carbon filter pack
	Low chloride	Analyze and adjust
	Low temperature	Check and adjust to recommended range
	High brightener	Reduce brightener additions
	Low wetter	Add in 0.5 pct by volume increments until optimum deposit is obtained.

(1)	(2)	(3)
Dull deposit in low-current-density areas	High pH	Check the pH with a calibrated meter (do not rely on pH test strips) and lower with dilute hydrochloric acid.
	Low ammonia and/or chloride	Analyze and adjust to range
	Low brightener	Add in 0.5 pct by volume increments until optimum deposit is obtained.
	High temperature	Lower to recommended range.
	Iron contamination	Treat with hydrogen peroxide. Add 0.25 to 0.5 pint of 30 to 35 pct hydrogen peroxide per 1,000 gal of solution volume. The hydrogen peroxide should be diluted at least 3:1 with water before addition to the tank. The precipitated ferric hydroxide is removed by filtration.
Dark band in medium current density range(20 to 30 asf)	High pH	Check the pH with a calibrated meter (do not rely on pH test strips) and lower with dilute hydrochloric acid.
	Low ammonia and/or chloride	Analyze and adjust to range
Dull or poor coverage medium-current-density to low-current-density areas	Low ammonia and/or chloride	Analyze and adjust to range
	High pH	Check the pH with a calibrated meter (do not rely on pH test strips) and lower with dilute hydrochloric acid.
	Low wetter	Add in wetter 0.5 pct by volume increments until optimum deposit is obtained.
	Low brightener	Add in brightener 0.05 pct by volume increments until optimum deposit is obtained.
Dull deposit across the entire current density range	High temperature	Lower to recommended range
	Low brightener	Add in brightener 0.05 pct by volume increments until optimum deposit is obtained.
	Poor surface preparation	Improve cleaning, pickling and/or rinsing
	Excessive addition of hydrogen peroxide	Leave air agitation on during shutdowns to help dissipate excess peroxide. Add up to 100 ml of brightener per 100 gal of plating solution.
Bright, brittle deposit over 40 asf	High pH	Check the pH with a calibrated meter (do not rely on pH test strips) and lower with dilute hydrochloric acid.
	High brightener	Reduce brightener additions
	Lower wetter	Add in wetter 0.5 pct by volume increments until optimum deposit is obtained.

(1)	(2)	(3)
Pitted deposit in medium-current-density to low-current-density areas	High ammonia and/or	Analyze and adjust to range
	High brightener	Reduce brightener additions
	Low wetter	Add in wetter 0.5 pct by volume increments until optimum deposit is obtained.
	Trivalent chromium (150 - 200 ppm)	Remove with filtration
Streaky deposit	Poor cleaning and/or rinsing	Improve cleaning, pickling and/or rinsing
Soft, spongy or burnt deposit in high-current-density areas	Low zinc	Analyze and adjust to range
	Low ammonia and/or chloride	Analyze and adjust to range
	High pH	Check the pH with a calibrated meter (do not rely on pH test strips) and lower with dilute hydrochloric acid.
	Low wetter	Add in wetter 0.5 pct by volume increments until optimum deposit is achieved.
	Iron contamination	Treat with hydrogen peroxide. Add 0.25 to 0.5 pint of 30 to 35 pct hydrogen peroxide per 1,000 gal of solution volume. The hydrogen peroxide should be diluted at least 3:1 with water before addition to the tank. The precipitated ferric hydroxide is removed by filtration.
Rough deposit	Anode particles in solution	Filter the solution
		Check anode bags for tears and/or holes
	Poor cleaning and/or rinsing	Improve cleaning, pickling, and/or rinsing
	Low wetter	Add in wetter 0.5 pct by volume increments until optimum deposit is achieved.
	Trivalent chromium	Remove with filtration

*Appendix 7. Advantages and disadvantages of typical zinc plating systems*

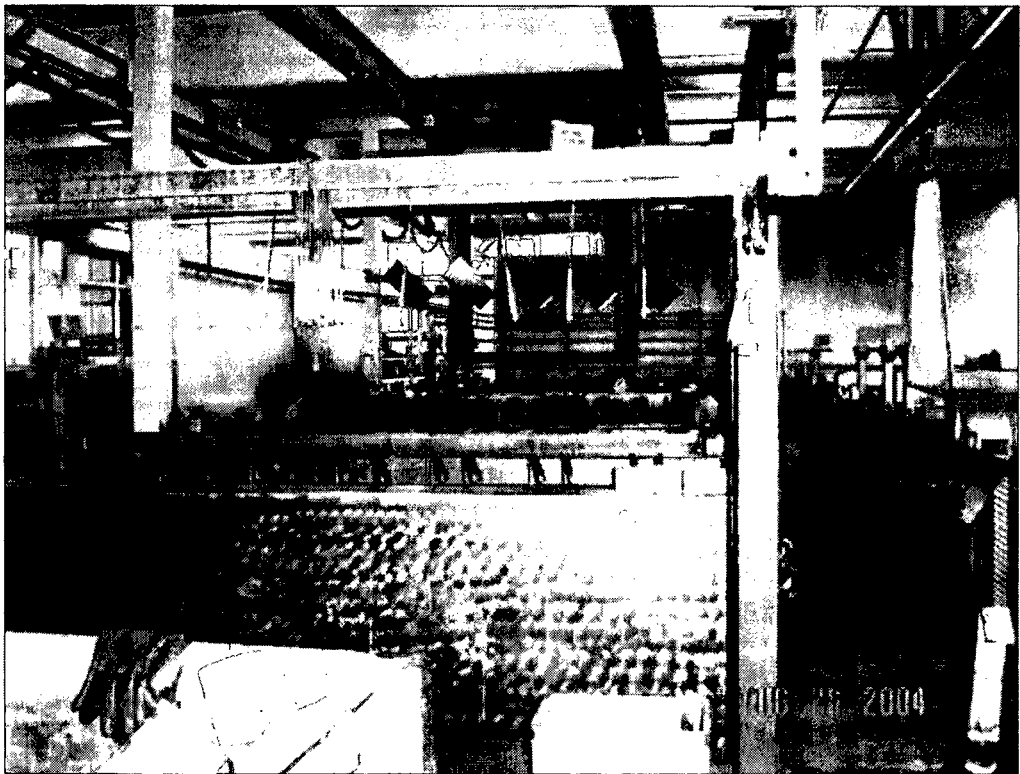
Typical Zinc Plating Systems	Advantages	Disadvantages
Cyanide zinc	Excellent covering power	Toxic materials
	Good throwing power	Safety requirements high
	Easy to control	Expensive waste disposal
	Good corrosion protection	Lower cathode efficiencies at high current densities
	Tolerant to purifiers	Low conductivity of plating solution
	Chromates well	Unable to plate cast iron, some nitrided steels, malleable iron
	Low equipment costs	
Alkaline non-cyanide zinc	Low drag-out	Higher brightener costs than cyanide zinc
	Lowest chemical costs	Blue-bright chromates tend to yellow with age
	Lowest waste treatment costs	Pre-plate cleaning is more critical
	Good coverage	Zinc metal concentrations more critical
	Good plate distribution	Less tolerance to drag-in of complexing agents from cleaners
	Bright deposits	
	Uses same equipment as cyanide zinc	
Acid zinc	Brilliant deposits obtainable	High equipment costs (requires corrosion resistant equipment)
	Good levelling and hiding properties	Requires filtration
	Faster plating rate	Requires bagged anodes
	Ability to plate on cast iron and similar hard-to-plate bases	Requires superior pre-plate cleaning
	Easy to control compared to other non-cyanide zincs	Subject to "bleed-out" problems
	Low waste treatment costs	Blisters or flaking at higher thicknesses
	Requires less voltage	Deposit tends to be brittle
		Poor throwing power



*Appendix 8. Visiting some electroplating companies in Switzerland*



*Metallveredlung Kopp AG*



*Automatic operated plating process, KISTLER ENGINEERING GmbH*



*Cascade rinsing system for rack plating, KISTLER ENGINEERING GmbH*



*A discussion with Swiss experts in the field of plating*