NATSURV 2

# WATER AND WASTE-WATER MANAGEMENT IN THE METAL FINISHING INDUSTRY

Prepared for the

WATER RESEARCH COMMISSION

By

**BINNIE & PARTNERS**

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# FOREWORD

The need for guidelines to reduce water intake and waste-water disposal by industry is of national concern in view of South Africa's water scarcity.

To establish norms for water intake and waste-water disposal, the Water Research Commission (WRC) in collaboration with the Department of Water Affairs (DWA) contracted Binnie and Partners, a firm of consulting engineers, to undertake a National Industrial Water and Waste-water Survey (NATSURV) of all classes of industry. The results obtained in the survey of the metal finishing industry form the basis of this guide on **Water and Waste-water Management in the Metal Finishing Industry.**

It is expected that this guide will be of value to the industry itself and to other interested parties such as municipalities, legislators, researchers and consultants in the water and effluent fields.

# ACKNOWLEDGEMENTS

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| | |
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# SUMMARY

The term "metal finishing" covers a wide range of techniques for the treatment of metallic articles. These techniques give the product a surface which makes it suitable for its intended service conditions as well as providing an attractive appearance.

All field data have been collected from the PWV area where it is estimated that 46% of South Africa's metal finishing operations are located. The electroplating, anodising and phosphating processes have been identified as the most water-intensive of this group; approximately 50 separate factories conducting one or more of these processes have been visited.

Specific Water Intake (SWI) was found to vary from 0,03 to 1,25 $m^3$ per "effective" $m^2$ of surface treated. Many simple yet effective methods are available to reduce water intake, primarily involving minor modifications to the existing plant. Target SWI's should be set at 0,1$m^3/m^2$ "effective" surface for operations treating in excess of 10 000 $m^2$/month; 0,2 $m^3/m^2$ is more realistic for factories treating less than 10 000 $m^2$/month. Results indicate that a uniform target may be set for all three processes.

Specific Pollution Loads (SPL), based on total dissolved solids, were found to vary considerably within each process. Since the bulk of pollution from metal finishing operations derives from dumping of process solutions, it is suggested that initial efforts at curbing pollution be directed at these discharges.

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# GLOSSARY

| | |
|---|---|
| **ANODE** | - The positive electrode of an electrolytic cell, usually composed of the metal to be electro-deposited. |
| **ANODISING** | - A process by which a hard, protective oxide film is formed on aluminium. The aluminium is made the anode in an electrolytic cell usually containing sulphuric acid. |
| **BARREL PLATING** | - A process of electroplating in which the articles to be plated are placed in a rotating container provided with suitable negative contacts. |
| **BONDERISING** | - A proprietary phosphating process for protection against corrosion. |
| **BRIGHTENER** | - An agent added to an electroplating solution to produce bright deposits. |
| **CATHODE** | - The negative electrode of an electrolytic cell which, in electroplating, receives the metallic deposit. |
| **CHELATING AGENT** | - A type of complexing agent (e.g. gluconates or EDTA) which combines with metal ions to form an extremely stable compound from which the metal cannot easily be recovered. |
| **CHROMATING** | - A passivation process, usually used as a pretreatment for paints, by which a protective chromate coating is applied to zinc or cadmium-coated steel. |
| **COMPLEXING AGENT** | - A compound, such as cyanide or an ammonium compound, which combines with metals to form solutions of great stability. See also chelating agent. |
| **DESMUT** | - A nitric acid bath used in the anodising process between the etching and anodising stages to prevent the quick formation of a thin oxide layer on the aluminium being protected. |

| | |
|---|---|
| **DRAG-OUT** | - The water or solution that adheres to work when it is removed from a bath. This liquid is then carried over into the subsequent rinse. |
| **EFFECTIVE SURFACE AREA** | - The area used in this guide to enable fair comparisons to be made between SWI's from different plating shops. The figure is derived by increasing the true surface area by a factor governed by the number of process stages used in the electroplating sequence. It should be noted that historically this term has assumed a totally different meaning in the electroplating industry. |
| **ELECTROLESS PLATING** | - This process employs solutions from which a metal is deposited by chemical reduction instead of electro-deposition. It is also known as autocatalytic plating. |
| **ELECTROLYTE** | - A solution that conducts an electric current by means of ions contained in the solution. |
| **ELECTROPLATING** | - The deposition of a metallic coating onto the cathode in an electrolytic cell. The cell contains an electrolyte composed of a solution of salts of the metal being deposited. |
| **ETCH** | - A caustic bath used in the anodising process to remove the existing oxide layer from work to be anodised. Acidic etching solutions are used in the plating of plastics to provide a keyed surface for subsequent metal deposits. |
| **GALVANISING** | - A process in which a zinc coating is applied to steel to provide protection against corrosion.<br>(a) Electrogalvanising - galvanising by electroplating.<br>(b) Hot-dip galvanising - galvanising by immersion of the base metal in molten zinc. |

| | |
|---|---|
| **JIG** | - An insulated metal rack from which electrical contacts protrude. Work to be electroplated is attached to these points and the whole is immersed in the plating bath, where it forms the cathode. |
| **NITRIDING** | - A process in which a hard surface is provided on special types of steel by heating in gaseous ammonia. Also known as nitrogen case-hardening. |
| **PERPETUAL ETCH** | - An etch solution to which a proprietary agent has been added to prevent aluminium from precipitating out of solution as a sludge at the bottom of the etch bath. |
| **PHOSPHATING** | - A process in which a corrosion-resistant, lubricative surface is applied to steels, often prior to painting. The steel is dipped into a zinc or iron phosphate solution to which phosphoric acid has been added. |
| **PICKLING** | - The removal of oxides or other compounds from a metal surface by means of an acid, usually hydrochloric or sulphuric. |
| **SEALING** | - An operation performed on anodised aluminium by immersion in a tank of hot water (95-100 °C) to close microscopic pores in the surface and prevent staining. De-ionised water is required for optimum results. |
| **SOILS** | - Dust and other dirt deposits which must be removed from work which is to undergo a metal finishing operation. |
| **SPECIFIC WATER INTAKE** | - The volume of water used in a metal finishing process to produce one square metre of finished work. The figure is based on the "effective surface area" of the article being treated and is expressed in $m^3/m^2$. |

**SPECIFIC POLLUTION LOAD** - The quantity of a specified contaminant that is discharged in the final effluent in the processing of one "effective" square metre of work usually expressed in $g/m^2$.

**STRIKE** - A plating solution used to deposit a thin initial film of metal prior to a heavier deposit from a subsequent plating solution. The film itself is also referred to as a strike - e.g. a copper strike from a cyanide solution on a zinc object prior to a heavier deposit from an acid copper bath.

**WETTING AGENT** - An additive which reduces the surface tension of a liquid allowing it to spread more easily over a solid surface.

## ABBREVIATIONS

COD - Chemical oxygen demand

EDTA - Ethylenediamine tetra-acetic acid

RO - Reverse osmosis

SPL - Specific pollution load

SS - Suspended solids

SWI - Specific water intake

TDS - Total dissolved solids

# 1 INTRODUCTION

A reliable estimate of the number of metal finishing installations in the RSA is extremely difficult to establish. The task is made the more difficult as the majority of metal finishing work is performed in-house as an essential part of an overall manufacturing activity. The remainder of the metal finishing work is undertaken on a contract basis by specialist companies, many of whom operate from small, backyard electroplating shops.

The term "metal finishing" incorporates a wide variety of different activities including:-

(a) **Pretreatments**

Chemical surface treatment processes:

degreasing
pickling
phosphating

Mechanical surface treatment processes:

descaling
brushing
scouring
polishing

(b) **Electroplating**

(c) **Post-treatments**

passivation

(d) **Stripping**

chemical
electrolytic

(e) **Anodising**

(f) **Protective coatings**

hot-dip galvanising
powder coating
painting

Of these, only those which were found to use substantial quantities of water or generate substantial quantities of effluent have been studied. Many finishing operations, such as nitriding and powder coating require very little water, as articles are often cleaned prior to treatment using organic solvents. These and other similar processes are not covered in this guide. The electroplating, anodising and chemical surface treatment processes have been found to be the most water-intensive of this group, and this guide deals exclusively with these three processes.

The annual water consumption by the metal finishing industry is in the region of $9 \times 10^6$ $m^3$, accounting for approximately 0,7% of the total water intake of the industrial sector in South Africa.[1] Approximately 80% of this water is discharged as effluent.

The information reported in this guide has been collected from metal finishing operations located within the PWV area, where it is estimated that 46% of the country's metal finishing firms operate.[1] During the preparation of the guide more than 25 separate electroplating shops were visited as well as 15 anodising installations. A number of companies performing some form of chemical surface treatment were also visited.

# 2 PROCESS RESUME

## 2.1 The electroplating industry

### 2.1.1 Process summary

Electroplating is a process whereby a thin coating of metal possessing certain desirable properties is deposited onto a component of a cheaper base metal by means of an electric current. Improvements in corrosion resistance, abrasion resistance and appearance, for example, may be achieved relatively cheaply in this way.

The article to be plated is immersed in a liquid (the electrolyte) and a direct current is passed through the liquid. The articles to be plated form the cathode, whilst the anode is usually composed of the metal to be deposited. The electrolyte is generally an aqueous solution of a salt of the metal being deposited, with various additions to improve conductivity, deposit brightness and surface uniformity.

The most common metals electro-deposited in this way and their major applications are listed below:

cadmium - corrosion resistance;
chromium - decorative appearance, corrosion resistance, wear and temperature resistance;
copper - decorative and many industrial applications;
gold - decorative and industrial;
nickel - in conjunction with chromium for decorative appearance as well as corrosion, wear and heat resistance;
silver - decorative and electrical contacts etc;
tin - food containers and electrical contacts;
zinc - corrosion resistance.

In order that a satisfactory electro-deposit can be applied, the article must first be cleaned from all traces of grease, rust, oxides and other contaminants and the surface activated to ensure maximum deposit adherence. This is accomplished by passing the articles through a series of tanks containing the necessary cleaning and activating solutions. A typical sequence is as follows: hot alkali soak, electrolytic alkali clean, dilute acid dip, electroplate and dry. Each process is followed by one or more running rinse tanks in which traces of electrolyte and other solutions remaining on the article are removed and prevented from entering and contaminating the subsequent process solutions. As indicated earlier, components may receive a series of electro-deposits - such as copper, nickel and a final deposit of chromium.

Articles to be plated may either be mounted on jigs (racks) or else continuously tumbled through the various solutions in perforated barrels. Barrel plating is particularly suitable for small components, where individual attachment to electrical contacts would be very time consuming.

### 2.1.2 Major contaminants and their source

Each process stage within the electroplating sequence is followed by a rinse stage, removing traces of process solution which adhere to the article being plated. These rinse flows obviously contain quantities of the various process solutions which are subsequently carried to drain.

Electrolytic solutions are of two basic types - acidic and alkaline. Acidic electrolytes are primarily used for copper, nickel, chromium and zinc, whilst alkaline cyanide complexes are used for copper, zinc, cadmium, gold and silver. Final choice of which type of solution to use is governed by such factors as base metal, work shape and requirements for deposit uniformity. Hot-soak and electolytic cleaning solutions are generally alkaline whilst the acid-dip solutions are obviously acidic. The rinse flows therefore contain traces of each of these process solutions, in concentrations depending on the rinse flow rates and solution carry-over. The main volume of effluent is provided by the rinse flows. The pollution load, however, is contributed mainly by the dumping of contaminated plating baths as well as the necessary periodic discharge of alkaline cleaners and acid dips.

## 2.2 The anodising industry

### 2.2.1 Process summary[2]

In basic anodising, aluminium components are treated to provide them with a protective oxide layer against atmospheric corrosion. As with electroplating, the surface must first be scrupulously cleaned to remove oil,. grease and soils. After cleaning and etching the article passes through a desmut solution and is then ready for the actual anodising step. Anodised aluminium may be dyed to provide a finish of any desired colour, using special organic dyestuffs. Whether or not a dyed finish is used, the anodised article must be sealed to close the microscopic pores in the surface and prevent any further staining.

As with electroplating, each of these process stages is followed by a rinse stage, ensuring that all traces of electrolyte and process solution are removed prior to immersion in the subsequent stages.

### 2.2.2 Major contaminants and their source

Anodising effluent is of varying pH, but usually has a very high settleable solids content, due to the formation of a milky white precipitate of aluminium hydroxide.

## 2.3 Chemical surface treatment processes

### 2.3.1 Phosphating and chromating[3]

The most common chemical surface treatment process is phosphating. Its major applicaton is to provide improved corrosion resistance under powder coating and paint, for which it also provides a superior bonding surface. In addition, phosphating facilitates subsequent extrusion of wires and tubes as well as providing lubrication for sliding components.

For mass production requirements, conveyor-type spray equipment is generally used; such a line would include spray cleaning, rinsing, phosphating and chromate treatment. For smaller scale production, or where articles are not suitable for spraying, immersion processes similar to those described for electroplating are used.

Chromate treatment of metals prior to painting is also in general use, providing similar benefits to phosphating. On zinc and cadmium coatings, chromate treatment is employed to provide protection against superficial corrosion as well as providing an improved surface for paint adhesion.

### 2.3.2 Electroless plating[3]

Electroless plating may also be considered as a chemical surface treatment. Major applications of this process include plating of nickel onto steel (particularly articles of complex shape) and plating of nickel and copper onto plastics, either for use in printed circuitry or for decorative purposes. Pretreatment of steel is similar to that required for electroplating. Pretreatment of plastics prior to the plating step requires the use of strong etchants, such as chromic acid, as well as various additives used as catalysts and accelerators.

## 2.4 Utilities

Although most of the water usage in the metal finishing industry is used in running rinses, an appreciable quantity is used in utilities. In both electroplating and anodising processes, cleaning solutions are usually maintained at a temperature of around 65°C, whilst some plating solutions, in particular nickel and cyanide copper, are also used at raised temperatures. The sealing operation requires a minimum water temperature of 95°C for satisfactory performance. These temperatures are maintained either by use of electrical immersion heaters or, particularly where larger volumes are involved, by means of steam heated coils. Other plating solutions and refrigeration units controlling the temperature of anodising baths are maintained at their operating temperature by means of open-circuit water-cooling systems.

# 3 SUMMARY OF SURVEY RESULTS

## 3.1 Introduction

Ideally, specific parameters such as SWI and SPL should be calculated on the basis of area of product anodised or plated. Many of the plating shops visited however, were unable to provide this data accurately. In these instances approximate areas have been calculated from quoted deposit thicknesses, assuming small losses of anode onto jigs and in anode bags.

As an example of this calculation, consider a plating shop whose average consumption of nickel anodes is 300 kg/month. The operator quotes a deposit thickness of 7,5 microns. The calculation proceeds as set out below:

Nickel consumed per month = 300 kg
Estimated losses of anode

| | | |
|---|---|---|
| i) | As dust in the anode bags: | 5% |
| ii) | Carried over into the drag-out tank: | 2% |
| iii) | Plated onto poorly protected jigs: | 4% |
| | Total anode losses | 11% |

$$\text{Total anode plated onto work} = \frac{100-11}{100} \times 300 \text{ kg/month}$$

$$= 267 \text{ kg/month}$$

Density of nickel = 8 900 kg/m$^3$

$$\text{Volume occupied by 267 kg nickel} = \frac{267}{8\ 900} \text{ m}^3$$

$$= 0{,}03 \text{ m}^3$$

Approximate surface area plated by 0,03 m$^3$ nickel at 7,5 micron thickness:

$$= \frac{0{,}03 \quad \text{m}^3}{7{,}5 \times 10^{-6} \text{ m}}$$

$$= 400 \text{ m}^2$$

It should also be noted that the "effective" area of an article to be plated may differ from the true physical area of that article. In chrome plating, for instance, it is not unusual to deposit a layer of copper and a layer of nickel prior to the final chrome deposition. (A coating applied in this way is sometimes referred to as a triplex coating). This would give rise to an "effective" area substantially greater than that of the true, physical area, since each deposit has required associated rinses.

The most logical approach to this problem is the use of a multiplying factor by which to increase the surface area in proportion to the number of coatings plated onto the work. The initial cleaning of the object to be plated is only performed once, regardless of the number of subsequent metal layers to be plated onto it. It is therefore not possible to overcome this problem simply by multiplying the physical surface area by the number of metal layers deposited. A simple electroplating sequence requires three preparatory stages and one plating stage; each of these stages is followed by a rinse stage. If it is assumed that each rinse stage is equally efficient, it can be assumed also that they will each use the same volume of water. Therefore each rinse stage contributes 25% to the total water usage. It follows that each additional plating stage requiring an associated rinse stage would increase the effective surface area by 25%.

## 3.2 Water intake

### 3.2.1 The electroplating industry

The SWI obtained from some 22 separate plating shops are listed in Table 1. It should be remembered that where only small quantities of work are being plated, small variations in either work load or water consumption will have an exaggerated effect on the SWI. Attention is also drawn to the fact that some operators have installed additional process stages in an attempt to produce a higher quality product. Each additional process stage will be accompanied by associated rinse tanks and will thus affect the apparent SWI. This is especially true of "in-house" platers who have developed an optimum approach to the plating of a few specific items. The use of an "effective" area plated, as described above, ensures that comparisons remain valid in these instances.

It should not be overlooked that whilst considerable reductions in water usage can often be effected, there is a cut-off point below which product quality becomes unacceptable.

**Table 1** Specific water intake in the electroplating industry

| Factory | Monthly water intake ($m^3$) | Actual surface area plated/month ($m^2$) | "Effective" surface area plated/month ($m^2$) | Apparent SWI ($m^3/m^2$) | "Effective" SWI ($m^3/m^2$) |
|---|---|---|---|---|---|
| A | 350 | 1 250 | 1 250 | 0,28 | 0,28 |
| B | 2 860 | 12 050 | 14 375 | 0,24 | 0,20 |
| C | 420 | 1 500 | 1 500 | 0,28 | 0,28 |
| D | 850 | 3 000 | 4 500 | 0,28 | 0,19 |
| E | 4 875 | 5 200 | 11 700 | 0,94 | 0,42 |
| F | 375 | 200 | 300 | 1,87 | 1,25 |
| G | 500 | 6 000 | 7 500 | 0,08 | 0,07 |
| H | 350 | 900 | 1 125 | 0,39 | 0,31 |
| I | 1 320 | 35 000 | 43 750 | 0,04 | 0,03 |
| J | 800 | 7 500 | 9 375 | 0,11 | 0,08 |
| K | 660 | 3 875 | 3 875 | 0,17 | 0,17 |
| L | 600 | 2 450 | 2 450 | 0,24 | 0,24 |
| M | 650 | 2 000 | 3 000 | 0,33 | 0,22 |
| N | 2 900 | 7 000 | 8 750 | 0,41 | 0,33 |
| O | 350 | 6 750 | 6 750 | 0,05 | 0,05 |
| P | 4 200 | 21 000 | 27 750 | 0,20 | 0,15 |
| Q | 1 430 | 1 000 | 1 500 | 1,43 | 0,95 |
| R | 600 | 750 | 750 | 0,80 | 0,80 |
| S | 750 | 1 600 | 2 800 | 0,47 | 0,27 |
| T | 1 610 | 27 500 | 41 250 | 0,06 | 0,04 |
| U | 1 035 | 15 000 | 15 000 | 0,07 | 0,07 |
| V | 2 000 | 3 000 | 6 000 | 0,66 | 0,33 |
| TOTAL | 28 485 | 164 525 | 215 250 | | |
| Mean | | | | 0,43 | 0,31 |
| Weighted average | | | | 0,17 | 0,13 |

### 3.2.2 The anodising industry

The SWI's obtained from 12 anodising installations covering the full range of existing factory capacities, are presented in Table 2.

**Table 2 Specific water intake in the anodising industry**

| Factory | Monthly water consumption $(m^3)$ | Area anodised per month $(m^2)$ | SWI $(m^3/m^2)$ |
|---|---|---|---|
| A | 10 580 | 105 000 | 0,10 |
| B | 335 | 500 | 0,67 |
| C | 360 | 1 250 | 0,29 |
| D | 800 | 1 500 | 0,53 |
| E | 600 | 8 000 | 0,08 |
| F | 420 | 2 500 | 0,17 |
| G | 260 | 250 | 0,96 |
| H | 155 | 250 | 0,62 |
| I | 5 545 | 47 000 | 0,12 |
| J | 1 150 | 40 000 | 0,03 |
| K | 760 | 2 000 | 0,38 |
| L | 1 600 | 23 500 | 0,07 |
| M | 550 | 800 | 0,68 |
| TOTAL | 23 115 | 232 550 | |
| Mean | | | 0,36 |
| Weighted average | | | 0,10 |

### 3.2.3 Chemical surface treatment processes

The SWI's obtained from several phosphating operations are listed in Table 3.

**Table 3** Specific water intake in the phosphating industry

| Factory | Monthly water intake ($m^3$) | Surface area treated/month ($m^2$) | SWI $m^3/m^2$ |
|---|---|---|---|
| A | 2 335 | 28 500 | 0,08 |
| B | 5 725 | 13 750 | 0,42 |
| C | 2 200 | 29 775 | 0,07 |
| D | 1 635 | 63 800 | 0,03 |
| E | 1 425 | 5 500 | 0,26 |
| F | 585 | 4 515 | 0,13 |
| G | 500 | 12 760 | 0,04 |
| H | 15 900 | 215 000 | 0,07 |
| I | 7 030 | 170 000 | 0,04 |
| TOTAL | 37 335 | 543 600 | |
| Mean | | | 0,13 |
| Weighted average | | | 0,07 |

## 3.3 Effluent

### 3.3.1 Introduction

The calculation of SPL's presents several additional problems to those associated with the calculation of SWI's. The samples taken during this survey were either instantaneous grab samples or, in the case of larger concerns, composite samples collected over a period of 24 h. Neither sampling technique is able to take into account the periodic dumping of pretreatment and process solutions. Dumping of cleaning solutions and acids occurs approximately once every six weeks and provides the bulk of the salt load leaving a plating shop. An additional problem is the collection of samples from those establishments where both electroplating and anodising are conducted simultaneously. Effluent stream segregation is often not practised and some operators cascade rinse flows between the two processes, further exacerbating the problem of obtaining a truly representative sample.

Definite trends can nevertheless be identified from the results which are tabulated below.

### 3.3.2 The electroplating industry

Pollutants from the electroplating industry are predominantly dissolved metal salts. Particular attention is usually drawn to the cyanide content and heavy metal content of these effluents. As was explained in 2.1.2, cyanide-based plating solutions are only used for the deposition of certain metals. Most of the plating shops visited ran several plating lines, only some of which used cyanide-based solutions so that although total cyanide loads being discharged from the premises could be calculated relatively easily, it was rarely possible to compute a specific cyanide load. Table 4 indicates the full range of concentrations of various parameters encountered in the survey.

Specific parameters have been calculated as explained earlier, and the COD, TDS and total heavy metal content were selected for purposes of comparison. The specific pollution loads for several plating shops appear in Table 5.

**Table 4 Effluent analyses in the electroplating industry**

| Factory | pH | COD (mg/l) | TDS (mg/l) | Total heavy* metals (mg/l) | CN⁻ (mg/l) |
|---|---|---|---|---|---|
| A | 7,0 | 150 | 2 525 | 40 | 15 |
| B | 8,6 | 30 | 645 | ND | ND |
| C | 8,5 | 110 | 390 | 10 | 10 |
| D | 9,5 | 355 | 595 | 5 | 10 |
| E | 6,4 | 1 280 | 1 470 | 70 | 40 |
| F | 2,8 | 145 | 710 | 100 | ND |
| G | 9,4 | 675 | 3 365 | 140 | ND |
| H | 2,9 | 35 | 570 | 80 | ND |
| I | 3,5 | 110 | 900 | 145 | 55 |
| J | 7,8 | 60 | 265 | 5 | ND |
| K | 8,3 | 460 | 2 475 | 30 | 30 |
| L | 7,5 | 50 | 435 | 80 | 5 |
| M | 9,8 | 555 | 475 | 40 | 20 |
| N | 8,7 | 425 | 1 235 | 15 | 10 |
| O | 7,8 | 300 | 355 | 25 | 5 |
| P | 8,5 | 195 | 910 | 40 | ND |
| Q | 7,4 | 10 | 260 | 10 | ND |
| R | 10,4 | 3 760 | 24 500 | 760 | 1 580 |

ND - not determined

* Total heavy metals could include Cr, Ni, Cu, Zn, Cd, Sn, Ag and Au.

Note: Average monthly effluent discharges for factories A to R are listed in Table 5.

The values recorded at factory R indicate the influence that the discharge of process tank contents has on effluent quality. The generally higher than expected COD values are attributable to various organic additives in the cleaning and plating solutions.

**Table 5** Specific pollution loads in the electroplating industry

| Factory | Monthly effluent discharge ($m^3$) | "Effective" plated area per month ($m^2$) | COD ($g/m^2$) plated | TDS ($g/m^2$) plated | Total heavy* metals ($g/m^2$) plated |
|---|---|---|---|---|---|
| A | 4 000 | 27 750 | 22 | 365 | 6 |
| B | 2 700 | 14 375 | 6 | 120 | ND |
| C | 1 250 | 43 750 | 3 | 10 | 1 |
| D | 335 | 6 750 | 18 | 30 | 1 |
| E | 1 550 | 38 625 | 51 | 60 | 3 |
| F | 570 | 750 | 110 | 540 | 76 |
| G | 400 | 1 500 | 179 | 900 | 37 |
| H | 620 | 3 000 | 7 | 120 | 16 |
| I | 1 900 | 6 000 | 34 | 280 | 46 |
| J | 715 | 2 800 | 16 | 70 | 1 |
| K | 760 | 9 375 | 37 | 200 | 2 |
| L | 1 360 | 1 500 | 47 | 390 | 71 |
| M | 980 | 15 000 | 35 | 30 | 3 |
| N | 2 750 | 8 750 | 133 | 390 | 5 |
| O | 630 | 3 875 | 48 | 60 | 4 |
| P | 4 630 | 11 700 | 77 | 360 | 15 |
| Q | 475 | 7 500 | 1 | 15 | 1 |
| R | 570 | 2 450 | 875 | 5 700 | 175 |

ND - not determined

* Total heavy metals could include Cr, Ni, Cu, Zn, Cd, Sn, Ag and Au.

### 3.3.3 The anodising industry

The pH of effluent from the anodising operation was found to range between 2,2 and 12, both ends of the scale being well represented. The low pH effluents usually emanated from small establishments or else from those incorporating a brightening step, used to provide the finished article with a very high decorative sheen. This step is often accomplished by the use of a phosphoric acid dip tank prior to the anodising step. This additional stage can reduce pH drastically from the usual value of 10 to 12 found for large installations to a value nearer 3 as a result of the scrubbing of extracted acid fumes with insufficient quantities of alkaline rinse flows. Phosphate values from such an installation rose to as high as 800 mg/l. The parameters selected for comparative purposes were COD, TDS and SS. Table 6 indicates the effluent qualities encountered during the survey; Table 7 shows the SPL's calculated from these analyses.

Factory C uses a chemical brightening step employing phosphoric acid and this accounts for the low pH and very high phosphate level. High sulphate concentrations indicate excessive carry-over of sulphuric acid from the anodising tanks.

**Table 6 Effluent analyses in the anodising industry**

| Factory | pH | COD (mg/l) | SS (mg/l) | TDS (mg/l) | $Al^{3+}$ (mg/l) | $Na^+$ (mg/l) | $SO_4^{2-}$ (mg/l) | $PO_4^{2-}$ (mg/l) |
|---|---|---|---|---|---|---|---|---|
| A | 11,5 | 185 | 1 375 | 6 915 | 1 440 | 1 200 | 825 | 1 |
| B | 10,9 | 240 | 3 370 | 3 595 | 40 | 1 500 | 480 | 3 |
| C | 3,1 | 735 | 22 270 | 10 040 | 160 | 2 000 | 1 210 | 760 |
| D | 10,2 | 0 | 850 | 950 | 50 | 350 | 300 | 0 |
| E | 8,8 | 20 | 115 | 870 | 5 | 3 335 | 325 | 2 |
| F | 8,9 | 70 | 480 | 800 | 5 | 205 | 90 | 1 |
| G | 7,7 | 130 | 1 945 | 3 820 | 1 | 800 | 5 040 | 1 |
| H | 2,2 | 595 | 80 | 655 | ND | ND | 270 | 1 |
| I | 3,3 | 10 | 45 | 455 | 15 | 20 | 180 | 1 |

ND - not determined

Note: Average monthly effluent discharges for factories A to I are listed in Table 7

### 3.3.4 Chemical surface treatment processes

These effluents contain traces of the various salts used in the pretreatment and treatment stages. Since these vary considerably, SPL's have been calculated from the total quantity of dissolved salts found in the final effluent streams. Tables 8 and 9 list respectively the actual analyses and the SPL for the phosphating operations surveyed.

Proprietary formulations are reused in the phosphating industry and these contain widely varying compounds. Nonetheless TDS values for factories A and F indicate excessive carry-over of process solution to drain.

**Table 7** **Specific pollution loads in the anodising industry**

| Factory | Monthly effluent discharge ($m^3$) | Area anodised per month ($m^2$) | COD ($g/m^2$) anodised | TDS ($g/m^2$) anodised | SS ($g/m^2$) anodised |
|---|---|---|---|---|---|
| A | 5 100 | 47 000 | 20 | 750 | 150 |
| B | 9 735 | 105 000 | 22 | 330 | 310 |
| C | 1 100 | 40 000 | 20 | 275 | 610 |
| D | 150 | 250 | 0 | 570 | 510 |
| E | 760 | 1 500 | 10 | 440 | 60 |
| F | 570 | 8 000 | 5 | 60 | 30 |
| G | 1 450 | 23 500 | 8 | 235 | 120 |
| H | 725 | 2 000 | 215 | 240 | 30 |
| I | 525 | 800 | 6 | 300 | 30 |

**Table 8** **Effluent analyses in the phosphating process**

| Factory | pH | COD (mg/l) | TDS (mg/l) | $Na^+$ (mg/l) | $PO_4^{2-}$ (mg/l) |
|---|---|---|---|---|---|
| A | 5,8 | 605 | 2 210 | 550 | 805 |
| B | 9,1 | 135 | 150 | 100 | 25 |
| C | 8,5 | 140 | 405 | 100 | 5 |
| D | 3,9 | 75 | 425 | 35 | 5 |
| E | 7,8 | 15 | 260 | 35 | 0 |
| F | 7,3 | 3 240 | 3 970 | ND | 305 |
| G | 7,1 | 1 080 | 620 | ND | 130 |
| H | 7,1 | 530 | 515 | ND | 5 |

ND - not determined

Note: Average monthly effluent discharges for factories A to H are as listed in Table 9.

**Table 9** Specific pollution loads in the phosphating process

| Factory | Monthly effluent discharge ($m^3$) | Area treated/ month ($m^2$) | COD ($g/m^2$) | TDS ($g/m^2$) |
|---|---|---|---|---|
| A | 2 220 | 28 500 | 50 | 170 |
| B | 5 350 | 13 750 | 50 | 60 |
| C | 1 620 | 29 775 | 10 | 30 |
| D | 1 450 | 63 800 | 5 | 10 |
| E | 1 360 | 5 500 | 5 | 60 |
| F | 555 | 4 515 | 400 | 490 |
| G | 6 850 | 170 000 | 45 | 25 |
| H | 10 600 | 215 000 | 25 | 25 |

# 4 CONCLUSIONS: WATER INTAKE

## 4.1 The electroplating industry

Electroplating shops in the PWV area operate on an SWI ranging from 0,03 to 1,25 $m^3/m^2$ "effective" area plated. The mean SWI obtained from the plating shops was 0,31 $m^3/m^2$; the weighted average SWI, based on the total water intake of the shops visited and the total "effective" surface area treated by those shops was 0,13 $m^3/m^2$ (see Table 1). This indicates that the larger plating shops operate more efficiently, in terms of water use, than do the many smaller plating shops.

## 4.2 The anodising industry

SWI's for the anodising industry were found to range between 0,03 and 0,96 $m^3/m^2$. The difference between the mean SWI and the weighted average again indicates the greater water efficiency of the larger installations. The mean SWI and the weighted average SWI were 0,36 and 0,10 $m^3/m^2$ respectively (see Table 2).

## 4.3 Chemical surface treatment processes

The range of SWI's found in the various phosphating operations was 0,03 to 0,42 $m^3/m^2$. The mean SWI was 0,13 $m^3/m^2$, whereas the weighted average was 0,07 $m^3/m^2$, indicating a similar, though less pronounced trend of the larger premises being more water efficient than the smaller (see Table 3).

## 4.4 Target specific water intakes

Comparison of the three sets of SWI figures obtained for the electroplating, anodising and phosphating operations suggests an achievable norm for the three industries. The figures indicate, however, that target SWI's should be governed by the factory throughput. Such targets could be set at 0,1 $m^3/m^2$ for operations treating more than 10 000 $m^2$ "effective" area per month, and 0,2 $m^3/m^2$ for those treating less than 10 000 $m^2$/month (see Figure 1). Various water saving measures that may be employed to achieve these targets are set out overpage.

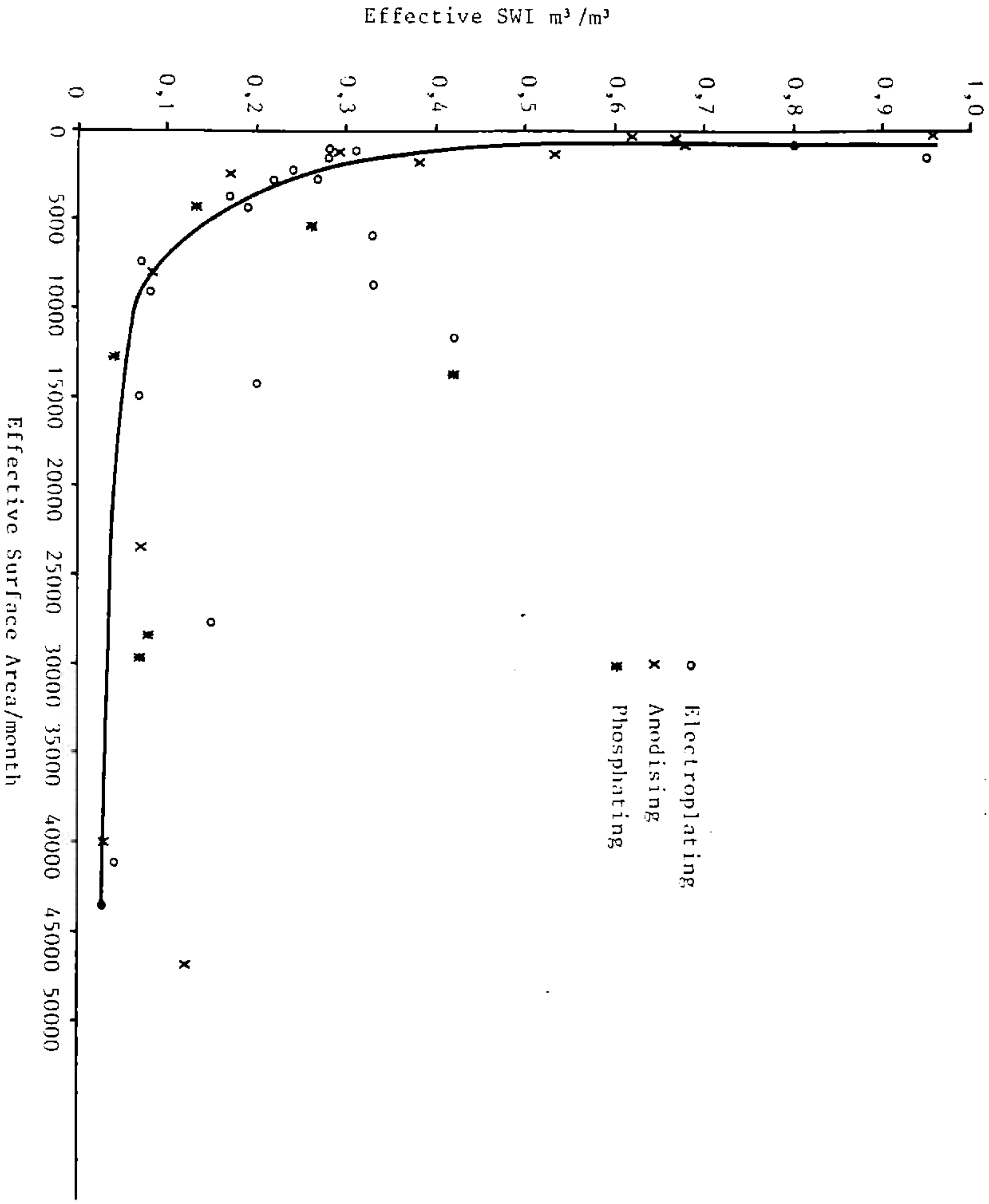


Figure 1 Variation of SWI with monthly throughput

## 5 RECOMMENDATIONS: WATER INTAKE

### 5.1 Rinse tanks

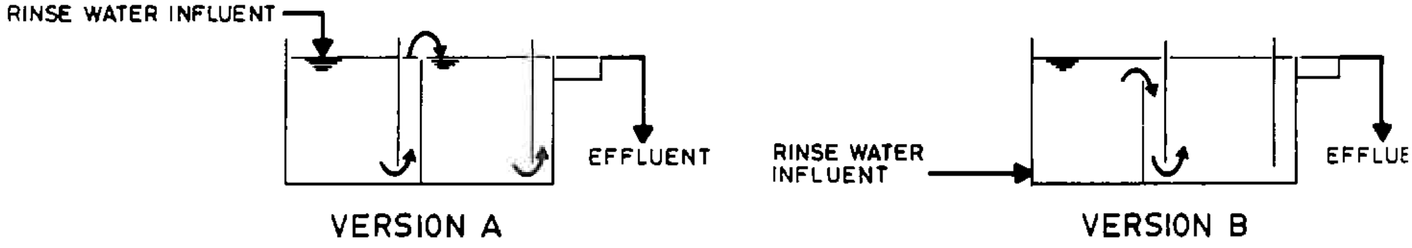
Rinse tanks achieve maximum efficiency when optimum mass transfer patterns are set up. These can be achieved by ensuring that water inlets to rinse tanks are placed at the bottom of the tanks, at the point furthest away from the outlet weir. The use of distributor type outlets - a series of small holes along the final horizontal section of the inlet pipe - will further augment these beneficial mixing patterns. The use of two tanks at each rinse stage increases the rinse efficiency. These tanks should be arranged so that water is introduced into the second rinse tank and flows counter-current to the work before leaving over a weir in the first rinse tank. By ensuring that the weir in this first tank is lower than the weir in the second (inlet) tank, this type of counter-current cascade can be implemented without the use of pumps. The flow rate required for this type of counterflow rinse system has been shown by various authors to be approximately[4]:

$$Q_n = D \left( \frac{C\ in}{C\ out} \right)^{1/n}$$

Where: $Q_n$ = volumetric rate of rinsing for each tank
n = number of rinse tanks in series
D = volumetric rate of drag-out
C in = concentration of constituents in the plating bath
C out = concentration of constituents in the final rinse tank

Close attention should be given to the design of such systems to ensure that short circuiting between influent and effluent rinse water does not occur. Failure to consider this aspect could result in inadequate mixing and non-uniform concentrations in the tank. Figure 2 shows two versions of rinse tank design, with version A being a more efficient design than version B.

**Figure 2 Rinse tank design**



Rinsing efficiency can be increased further by placing static (i.e. non-flowing) rinse tanks, known as drag-out tanks, immediately after each plating solution. A drag-out tank installed in this way not only reduces carry-over to subsequent running rinse tanks but also effects savings in electrolyte, particularly attractive in the case of expensive nickel salts.

Theoretical calculations demonstrate that the use of more than two cascading rinse tanks after a drag-out tank does not provide a worthwhile increase in rinse efficiency.[4;5;6] Where existing plant conditions make it impossible to add extra rinse tanks into a process line, consideration should be given to cascading flows between rinse tanks positioned at different stages in the line. The final rinse used prior to drying could for instance, be returned as the rinse water following an acid dip. This approach is frequently used in the anodising industry but few examples have been encountered in the electroplating industry.

## 5.2 Regulation of rinse flows

Water flows to rinse tanks should be regulated. Several methods are in use:

(a) The use of conductivity or pH meters to activate valves only when these parameters reach levels unacceptable for adequate rinse performance. Several systems are available on the market for this purpose.

(b) The use of time regulatory valves. These can be set to deliver water for a prescribed period, shut off for a period and then reopened. This provides a simple and effective means for water conservation.

(c) The use of in-line meters. Two basic types are available:

  (i) In-line meters permitting visual inspection of instantaneous flow rate. Operators can adjust valves until a predetermined optimum flow rate is achieved and fluctuations from this optimum can be quickly spotted and remedied.

  (ii) In-line volumetric meters. These meters indicate the volume of water that has passed through the pipe: regular reading of these meters will quickly bring to attention any irregularities in water usage around the plant.

(d) The use of ring mains. Wherever possible rinse water should be extracted from ring main systems. This ensures that water pressure at each outlet is maintained, thus obviating the need to have valves wide open to provide sufficient water pressure at the end of supply pipes.

## 5.3 Adequate drainage

Carry-over of process solutions to rinse tanks should be kept to a minimum. This can be achieved in a number of ways:

(a) Inclined drain boards should be provided between each tank, ensuring that drips from overhead work return to their source and not the subsequent tanks.

(b) Draining time above each process tank should be sufficient to ensure excess solution returns to the source tank.

(c) Jigs should be well maintained to ensure that the coatings are not cracked and no metal build-up occurs which can provide additional crevices in which liquid can collect.

(d) Article orientation on jigs should be carefully considered to ensure that minimum liquid carry-over can be expected.

(e) Jigs should be allowed to drain inclined at an angle to the horizontal, particularly where tubular or lengthy sections are being treated, as frequently occurs in anodising, to allow any trapped solution to drain.

(f) Where possible barrels should be left rotating above each process stage to ensure better drainage.

(g) Wetting agents should be used where possible to reduce surface tension and improve drainage.

(h) A low-flow cold rinse after the electrocleaning stage may be returned to the hot cleaning solution to make up for evaporation losses. This not only recovers cleaning material but also reduces the discharge of strong alkalis.

## 5.4 Use of cooling water circuits

Where water is required for cooling purposes, open-circuit evaporative cooling should be employed. Where the heat load does not justify the use of such plant, once-through cooling water should subsequently be used as rinse water.

## 6 CONCLUSIONS: EFFLUENT

Specific pollution loads, calculated from the analysis of rinse water flows, can provide valuable information on the performance of metal finishing installations. Tables 5, 7 and 9 indicate however, that the setting of target SPL's for parameters such as total heavy metals and total dissolved solids would be very difficult. It can be concluded therefore, that initial efforts at reducing pollution loads from these industries should be directed at controlling wilful dumping of cleaning and process solutions.

These provide the major source of pollution from the metal finishing industry and are particularly harmful to local sewage treatment works where such toxic slugs can bring normal sewage purification to a standstill.[4]

Good water management as outlined earlier will greatly reduce effluent generation from the regular rinse flows. Nonetheless, certain additional measures should be adopted to further reduce pollution loads received by sewage treatment works. Some of these are outlined in the following section.

# 7 RECOMMENDATIONS: EFFLUENT

## 7.1 The electroplating industry

### 7.1.1 Prevention of bath contamination

The life of cleaning and process solutions may be prolonged by ensuring that adequate rinsing is provided between each treatment bath. The life of plating solutions in particular may be prolonged by preventing contaminants from entering the plating baths.[4] Contamination may be prevented by:

(a) Using only anodes and chemicals of highest purity.

(b) Providing sufficient anode area to prevent exhaustion of the plating solution.

(c) Providing sufficient rinsing at the operation ahead to avoid the drag-in of incompatible constituents.

(d) Using only coated racks in good order to prevent carry-over of solution in cavities and crevices.

(e) Providing a sufficient thickness of protective layer to guard against corrosion - e.g. of the copper cyanide strike on a zinc object prior to acid copper or nickel plating.

(f) Frequent analytical control of bath solution.

Although these measures will not eliminate the need for periodic dumping of various tanks, they will at least reduce the frequency with which such dumpings have to be made.

### 7.1.2 Prevention of shock loads

However well process solutions are preserved, it is necessary to replace these solutions when they become exhausted. Alkaline cleaners require replacement every 6 to 8 weeks, whilst other solutions such as the acid dips also require occasional replacement. Plating solutions, if maintained as indicated in 7.1.1 above are only infrequently discarded as suitable purification and filtration systems are now available. If discharged directly to drain these solutions form severe shock loads to subsequent sewage treatment works, and this should be avoided.

The provisions of one or more holding tanks into which discarded solutions may be pumped provides an elegant solution to this problem, as well as offering several other benefits. These benefits are listed below:

(a) Discharge of the solution to drain may be controlled and shock loads avoided.

(b) Off-spec solutions may be treated and brought back up to working quality without requiring a loss in production time, since fresh solution may be used while off-spec solution is being restored.

(c) An opportunity is provided for limited batch treatment prior to discharge, e.g. neutralisation, oxidation or precipitation.

(d) Tank repairs and/or cleaning can be performed without wasting tank contents.

(e) Discarded solutions may be removed by waste contractors, either for controlled discharge elsewhere or for treatment at a centralised plant set up to handle such toxic effluents.

### 7.1.3 Effluent treatment

Discharges from the electroplating industry usually contain cyanide complexes and hexavalent chromium as well as salts of several heavy metals, such as copper, zinc and nickel. The toxic nature of these compounds can cause severe problems to biological sewage treatment works and for this reason most receiving authorities stipulate maximum concentrations which should not be exceeded. In order to comply with these limits some form of treatment is often necessary. Such treatment can be performed either batchwise or using continuous flow through plant. Unless very large volumes of effluent require treatment - in excess of say 250 $m^3/d$ - batch treatment is usually the more attractive option.[4] The requirement of sophisticated control systems and continual maintenance for the continuous type plants usually outweighs advantages of space saving and constant effluent quality.

Before the usual methods employed for heavy metal removal can be applied successfully the cyanide and hexavalent chromium content of the effluent must first be treated.

#### 7.1.3.1 Oxidation of cyanides

Where cyanide-based solutions are in use, the cyanide content should be oxidised to less toxic cyanate. Metals complexed with cyanides are not easily removed, so that cyanides must first be destroyed before subsequent treatment. The most common method is alkaline chlorination, usually effected by the addition of sodium hypochlorite.[4;6;7] This can be done most easily in static tanks placed after drag-out tanks, or, where this is impractical, in a collection sump prior to final discharge. It is important that solutions containing nickel salts be kept away from cyanide solutions until after the cyanide has been treated, since nickel-cyanide complexes are extremely stable and highly resistant to oxidation. Since the rate of destruction of the cyanide complex is pH-dependent,[8] careful pH control (at about pH 12) must be exercised and mixing will need promotion by means of a small impeller. The use of ozone as an oxidation agent for cyanides is growing in popularity, since strict pH control is unnecessary. This involves on-site ozone generation, which, however, is relatively expensive.[1;5] Where cyanide is present in high concentrations - above 1 000 mg/l - electrolytic oxidation becomes the most suitable form of treatment, effecting 40-60% savings over chlorination. Once the cyanide concentration has been reduced by anodic oxidation, conventional chlorination oxidation should be used for complete destruction.[4;9]

### 7.1.3.2 **Chromium reduction**

Chromate bearing waste must first undergo reduction from the hexavalent to the trivalent state to facilitate subsequent precipitation and removal. The simplest way of achieving this is by placing a tank filled with sodium metabisulphite (at a pH of 2,5-3)[8], immediately after the chrome drag-out tank. Sodium sulphite, sodium bisulphite and ferrous sulphate may also be used for the chemical reduction. The tank will require periodic dumping and recharging. If necessary the trivalent chromium can be precipitated from solution as chromium hydroxide by pH correction.[8] Other methods available for the treatment of hexavalent chromate bearing streams include cementation and ion exchange. In the process of cementation, scrap metal (such as iron, zinc or aluminium) is used to electrochemically reduce the hexavalent chromium.[1;5;8] Anion exchange resins enable the recovery of concentrated regenerated solutions of up to 6% chromium acid, suitable for recycle.[8;10]

### 7.1.3.3 **Removal of heavy metals by precipitation**

Local authorities in the RSA impose limits on the concentration of heavy metals allowed in final effluent streams. In most cases at least two limits are set: one for the concentration of individual metals and a separate limit for the total of all heavy metals present. Of the many methods available for the removal of heavy metals, precipitation is the most common. As indicated above, precipitation will only be an effective treatment if the cyanide and hexavalent chromium streams have first been treated separately. After treatment the separate waste streams are combined and let into a tank where the heavy metal content may be precipitated out.

Metals precipitate at various pH values depending on such factors as the metal itself, the insoluble metal salt that has been formed (hydroxide or sulphide), and the presence of complexing agents (e.g. EDTA, ammonia, gluconates, acetic acid). Furthermore the presence of two or more heavy metal ions mixed in the same stream will alter the precipitation characteristics from those found when only one metal is present. As a general rule however, minimum solubility of the hydroxides of the metal salts most commonly found in electroplating effluent occurs at pH 8,0-8,5.[1] In order to determine the optimum pH for precipitation, a laboratory scale testing programme should be conducted. The use of a polymer to improve settling of the resultant floc should also be investigated at this stage. As indicated earlier, metals may be precipitated as either the hydroxide or the sulphide.

(a) **Hydroxide precipitation**

Heavy metal precipitation is usually brought about by the addition of caustic soda or lime, with the use of lime becoming more widespread as concern over sodium levels discharged to sewer grows. Lime has a low solubility and therefore requires a more complicated dosing system than caustic soda. Lime also produces a greater volume of sludge than caustic soda. Caustic soda addition however, forms a very light and gelatinous metal hydroxide sludge that settles poorly and is difficult to dewater. Although lime produces more sludge and is more difficult to handle, its superior dewatering characteristics often outweigh these disadvantages.[4;6;7]

Neither lime nor caustic soda addition is able to precipitate heavy metals satisfactorily from the various metal complexes often present in electroplating effluents.[1;7;10]

(b) **Sulphide precipitation**

Sulphide precipitation has several attractive features compared with hydroxide precipitation and has been demonstrated to be an effective alternative. Sulphides have a high reactivity with heavy metal ions and form highly insoluble precipitates over a wide range of pH. Sulphide precipitation can also achieve low metal solubilities in the presence of certain complexing and chelating agents.[1;5;10]

Sulphide precipitation is accomplished with either the "soluble" or "slightly soluble" process. In the soluble process, sulphide is added in the form of a water soluble sulphide, such as sodium sulphide or sodium hydrogen sulphide. Excessive sulphide addition - and the resultant odour of hydrogen sulphide gas - is prevented by use of a sulphide ion-selective electrode controlling the supply of sulphide. The slightly soluble process uses a freshly prepared solution of ferrous sulphide as the source of sulphide ions. As sulphide ions are consumed, the iron sulphide dissociates into ferrous ions and sulphide ions so as to maintain the equilibrium concentration. In alkaline solutions, the excess ferrous ions are precipitated as ferrous hydroxide, whilst the heavy metals precipitate out as sulphides. Thus, since chemical equilibria control the concentration of sulphide ions in solution, sophisticated control loops are not required.

The absence of any detectable hydrogen sulphide odour and the simultaneous reduction of $Cr^{6+}$ to $Cr^{3+}$ are attractive features of the slightly soluble process, but these advantages over the soluble system must be set against the higher reagent consumption and the greater sludge volume produced.

(c) **Sludge handling**[7]

Once precipitation has taken place the floc is usually settled out in a clarifier which often incorporates inclined plates for improved efficiency. The resultant sludge is removed at 1-2% solids and either pumped to drying beds or forced through a filter press. Filter cake from a filter press typically contains up to 40% solids by weight.

### 7.1.3.4 Integrated waste-water treatment

In general it becomes progressively more expensive to remove contaminants from solution as the concentration of that contaminant decreases, since treatment plant has to be designed to handle progressively larger hydraulic loads. For this reason it is usually advantageous to remove such contaminants as close to their point source as possible. In the case of heavy metals this is most easily done using a "drag-out" tank - a static rinse tank placed immediately after a plating tank that retains the plating solution adhering to the work. As noted above, this enables considerable savings in metal salts necessary for replenishing plating baths. Subsequent rinse flows will remove final traces of electrolyte from the work. The metal ions in these rinse waters may be removed in several ways allowing the reuse of the water and also recovery of the metal. Two such techniques are ion exchange and reverse osmosis.

(a) **Ion exchange**[9;11;12]

Ion exchange equipment basically comprises one or two cation columns containing an exchange resin which absorbs the heavy metal and replaces it with hydrogen or sodium ions. Several configurations are possible, the final choice depending on several factors including the type of metal being recovered and the concentration at which it is required. The exchanged metal ion can be stripped from the resin in the form of the sulphate, using sulphuric acid, and the recovered sulphate may be returned to the plating tank. This system has the advantage of recovering the metal free from complexing brighteners often added to plating solutions as well as providing pure water suitable for reuse. The major disadvantage of the system is that the exchange resin requires regular regeneration with acid to remove the collected metal ions from the saturated or exhausted resin.

(b) **Reverse osmosis[1;5]**

Reverse osmosis can also be used to concentrate the electrolyte in rinse flows. Osmosis is the transport of water from a less concentrated solution through a semipermeable membrane to a more concentrated solution. When pressure greater than the osmotic pressure is applied to the more concentrated solution, the flow through the membrane is reversed providing a permeate of purified desalted water and a reject stream of enriched solute. In this way salts can be concentrated up to 20 times. The final concentration is limited in practice by the osmotic pressure of the solution, so that for the salt stream to be recycled, RO has to be used in conjunction with evaporation. The natural evaporation from hot baths (e.g. Watts nickel) is sufficient and supplementary evaporation is not required. Alternatively, the reject stream could be neutralised and the metal content precipitated out as the hydroxide.

The major difficulty with RO is the problem of maintaining membrane performance. The pH must be kept within prescribed limits to ensure reasonable life and additional steps are necessary to prevent the accumulation of biomatter from fouling the membranes. Fines must also be prevented from entering the system as these will tend to blind the membranes: cartridge type filters will usually be required for this service.

### 7.1.3.5 Specialised treatments[1;5;7;13;14;15]

Treatment of effluent discharged from the electoplating industry has been the subject of much research work over recent years. While it is outside the scope of this guide to describe the results from this research, some of the processes that have been successfully applied to effluent treatment on an industrial scale:

(a) sodium borohydride (total effluent treatment);
(b) insoluble starch xanthate (total effluent treatment);
(c) sacrificial iron anodes ($Cr^{6+}$ to $Cr^{3+}$ reduction);
(d) ultra and microfiltration (fine particle removal);
(e) evaporation (concentration and reuse of plating chemicals);
(f) electrodialysis (concentration and reuse of plating chemicals);
(g) electrolytic cell processes (destruction of concentrated cyanide, recovery of elemental metal).

## 7.2 The anodising industry

In the anodising process the contents of the sealing tank are dumped regularly. These tanks usually contain only small quantities of contaminants and so present no pollution problem. The etch solution requires dumping occasionally when excess quantities of sludge accumulate in the bottom. This problem, however, can be overcome by adding proprietary additives to keep the aluminium sludge in solution. This is known as a perpetual etch.

The major contaminant in the effluent from anodising is the aluminium hydroxide precipitate formed when the aluminium dissolved at the etching and anodising stages comes out of solution upon neutralisation. This sludge is difficult to dewater but a flocculant may be used to improve settling characteristics. Inclined plate settling tanks have been found to give satisfactory results and the use of several holding tanks in which to store the removed sludge prior to collection by waste disposal companies enables more complete settling to take place.

## 7.3 Chemical surface treatment processes

Rinse waters from chemical surface treatment processes usually only require pH correction. This can be effected by the addition of caustic soda to bring the pH up to an acceptable value. Neutralisation with caustic soda however, increases the sodium content of the final effluent and various municipalities are now insisting that lime be used instead. Lime addition also has the advantage of precipitating dissolved phosphates from the final effluent as calcium hydroxyapatite.[16] The flocculated mass can then either be removed by sedimentation or by means of a filter, typically of plate and frame construction.

## 8

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