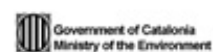


MEDITERRANEAN

Alternatives for preventing
pollution in the
Surface treatment industry

CLEANER

Regional Activity Centre for Cleaner Production (RAC/CP)
Mediterranean Action Plan



Note: This publication may be reproduced in whole or in part and in any form of educational and non-profit purposes without special permission from the Regional Activity Centre for Cleaner Production (RAC/CP), provided acknowledgement of the source is made. RAC/CP would appreciate receiving a copy of any publication that uses this material as a source.

No use of this publication may be made for resale or for any other commercial purposes whatsoever without prior permission in writing from RAC/CP.

If you consider that this study could be improved or there if you find any lack of accuracy, we would appreciate if you could notify it to us.

Study finished on November 1999

Published on May 2000

Updated on March 2002

For additional copies or information, please contact:

Regional Activity Centre for Cleaner Production (RAC/CP)

C/ París, 184 – 3ª planta

08036 Barcelona (Spain)

Ph. +34 93 415 11 12 - Fax. +34 93 237 02 86 - e-mail: cleanpro@cema-sa.org

Web site: www.cema-sa.org

TABLE OF CONTENTS

1. INTRODUCTION	5
2. DESCRIPTION OF SURFACE TREATMENT PROCESSES	7
2.1 SURFACE PREPARATION BATHS	7
2.1.1 Mechanical pre-treatment	7
2.1.2 Mechanical abrasion	8
2.1.3 Chemical degreasing	8
2.1.4 Ultrasonic degreasing	9
2.1.5 Electrolytic degreasing	9
2.1.6 Acid activated / pickling	9
2.2 THE MAIN ELECTROPLATING PROCESSES	10
2.2.1 Electrolytic zinc plating and passivation	11
2.2.2 Sublayers and finishes	13
2.2.3 Surface conversion processes	18
2.2.4 Electropolishing	21
2.3 RINSING	23
2.3.1. Costs deriving from the excessive use of water	23
2.3.2. Relationship between the quality of rinsing and the amount of water necessary	24
2.3.3 Single rinsing	26
2.3.4. Rinsing in stages	27
2.3.5. Sealed recovery rinsing	29
2.4 WATER TREATMENT	30
2.4.1 Treatment prior to the process	30
2.4.2. Treatment following the process: physico-chemical treatment	31
2.5 WASTE FLOWS	34
2.5.1 Introduction	34
2.5.2 Waste flow generation	34
2.5.3 Summary of the waste flows generated	37
3. POLLUTION PREVENTION ALTERNATIVES	46
3.1 POLLUTION REDUCTION AT SOURCE	47
3.1.1 Raw material and process material replacement	47
3.1.2 Good housekeeping practices	54
3.1.2.1 Lengthening bath life	54
3.1.2.2 Drag-out reduction	55
3.1.2.3 Rinsing and washing improvements	62
3.1.2.4 Application of good housekeeping practices	72
3.2 RECYCLING AT SOURCE	81
3.2.1. Recovery of raw materials	81
3.2.1.1. Degreasing	81
3.2.1.2. Pickling	83
3.2.1.3. Products involved	85
3.2.2 Reuse of water	86
3.2.2.1 Skip technique	86
3.2.2.2. Recycling by ion exchange	86
3.2.2.3 Recycling by inverse osmosis	88
3.2.3 Drag-out recovery	89
3.2.3.1. Electrolysis	89
3.2.3.2. Electrodialysis	90
3.2.3.3. Electro-electrodialysis	91
3.2.3.4. Inverse osmosis	91

3.2.3.5. Ultra-filtration.....	92
3.2.3.6. Evaporation.....	93
3.2.3.7. Ion exchange.....	94
3.2.3.8. Other measures.....	95
4. ALTERNATIVE TREATMENTS.....	97
4.1. THE BREAKDOWN OF METAL COMPLEXES.....	97
4.2. CYANIDE OXIDATION.....	98
4.3. HEXAVALENT CHROMIUM REDUCTION.....	99
4.4. COAGULATION.....	99
5. OTHER ASPECTS TO BE CONSIDERED	102
5.1. PRODUCT STORAGE LOCATIONS.....	102
5.2. MANAGEMENT OF THE STORAGE LOCATION.....	102
5.3. RETAINER TRAYS	102
5.4. WATER FEED.....	103
5.5. PROTECTION OF PIPES.....	103
5.6. DESIGN OF THE PROCESSING LINES	103
5.7. EFFLUENT TRANSMISSION	104
5.8. EFFLUENT COLLECTION	104
5.9. THE WORK ENVIRONMENT.....	105
5.10 PROCESS AUTOMATION AND PROGRAMMING	105
6. ANALYSIS OF THE TECHNICAL AND ECONOMIC VIABILITY OF SOME OF THE ALTERNATIVES	106
7. CONCLUSIONS	132
8. SOME REAL EXAMPLES FOR THE PROPOSED ALTERNATIVES.....	134
9. REFERENCES.....	135
10. ENTITIES AND INDIVIDUALS THAT HAVE COLLABORATED IN THE PREPARATION OF THIS REPORT.....	136
11. USEFUL WEBSITES RELATED WITH THE PROJECT.....	137
12. PHOTOGRAPHIES ON MINIMISATION ALTERNATIVES	138

1. INTRODUCTION

The Regional Activity Centre for Cleaner Production (RAC/CP) of the Mediterranean Action Plan has carried out the **Study on the Alternatives for Pollution Prevention in the Surface Treatment Sector**, with the aim of presenting those pollution prevention options that can be implemented by the Mediterranean companies of this sector.

The surface treatment industry is made up of mainly small and medium-sized companies that specialise in modifying the basic structure of a surface - metal or otherwise - to give it certain conditions of resistance to external agents, a decorative finish, etc. Companies are fundamentally workshops with middle to low level of technical development on average. Another characteristic of the industry is the use of a wide variety of chemical compounds, many of which can be highly toxic and pollutant.

Rationalisation of consumption and in-house improvements focused on pollution prevention and eco-efficiency give economical and social advantages to the companies that implement them, as they reduce the impacts on the environment. Waste flows generated are also reduced, water and raw materials are saved and the public image of the company is improved. All these advantages provide an added value to the company and improve its competitive capacity.

The study is divided into 5 chapters and a final chapter of conclusions and recommendations. The first chapter¹ describes the main processes of the sector: the pre-treatment baths, the most important metal plating processes, and the rinses, key step of the process, in order to find the main alternatives to reduce the volume of the effluents generated. A section is also included that describes the waste flows generated during the different steps in the electroplating process.

The second chapter describes those pollution prevention alternatives focused on waste reduction at source: change of materials and the application of environmentally sound processing procedures, and recycling at source: recovery of raw materials, the reuse of water and recovery of drag-outs.

The third chapter describes the classical wastewater treatment and some alternatives to the same.

The fourth chapter describes, by use of examples, a series of recommendations that aim to reduce the risk of pollution, either in the workplace or in the environment.

¹ The first chapter corresponds to chapter 2 of this study and so on.

Finally, the fifth chapter uses examples to show those aspects to be taken into account when making a technical and economical feasibility analysis of the alternatives detected, in order to implement them in the company.

In addition, a final section is included showing some real-life examples of companies that have implemented pollution prevention alternatives, related to practical cases of Med Clean published by the CAR/PL.

This study is mainly addressed to experts and industrialists of the surface treatment sector with the aim of presenting them pollution prevention opportunities, to reduce unnecessary costs and non-efficient practices that are really applicable to the sector according to the present situation of each company.

2. DESCRIPTION OF SURFACE TREATMENT PROCESSES

2.1 Surface preparation baths

All electroplating processes involved in the surface finishing of a part require a preliminary preparation of the surface to eliminate all traces of grease and oxides that may be on it. These traces in general come as one with the part and are produced when it is mechanically formed.

Parts can also be mechanically polished to improve their surface and also eliminate any trace of grease.

Parts can be prepared in many different ways, according to the base material and the nature of the remains that are to be eliminated. The most frequent ones in the industry are:

- mechanical pre-treatment
- mechanical pickling
- chemical degreasing
- ultrasonic degreasing
- electrolytic degreasing
- acid activated / pickling

2.1.1 Mechanical pre-treatment

Pre-treatment is where parts are prepared for subsequent electroplating processing and is usually classified into two groups, either preliminary or end pre-treatment.

Preliminary pre-treatment is where dirt and residual elements, such as polish, dust, grease, drops of oil, rust marks, etc. are mechanically removed from the surface of a part. It is normally done prior to the production process although it can form part of the actual process itself.

End pre-treatment mechanically removes just the large traces of oil or grease remaining and prepares the part for the electroplating process itself.

It is good practice in any pre-treatment cycle where parts that are being treated have traces of either oil or rust to mechanically remove these pollutants before introducing them directly in the processing line, for this will facilitate the more uniform removal of oil and oxides afterwards.

2.1.2 Mechanical abrasion

This consists of projecting an aggressive solid state material (silica sand, slag, steel powder, etc.) at high speed with compressed air onto the surface in question. This system removes the layers of impurities that have adhered to the surface that is to be treated. The aggressive material used depends on different factors such as how the part responds, the possibilities of recovery, the desired finish and the base material of the part.

2.1.3 Chemical degreasing

Here, the surface is treated by being immersed in a chemical solution containing solvents or detergents or by electrolysis for a pre-established period of time.

Degreasing using solvents is done either with vapour or as a cold process. Grease, paint and varnish can be removed in this way.

Chlorate solvents are normally used in the vapour deposition phase, and are evaporated in the bath to produce solvent vapours.

The following solvents are the ones that are most frequently used in this process at present:

- trichloro-ethanol, trichloro-ethylene and ethyl perchloride,
- methyl chloride,
- trichloro-fluorethanol,
- chloroform, as bases.

The same compounds are used in cold solvent degreasing but they are applied by immersion.

In **chemical degreasing using detergents** (commercial ones), all types of grease are removed due to the presence of surface-active elements that reduce the surface tension of the bath and that are added to an alkaline solution.

The following formulation is typical for the alkaline medium used for degreasing parts:

- caustic soda40 g/l
- sodium carbonate.....25 g/l
- trisodium phosphate 12·H₂O.....10 g/l
- sodium metasilicate 5·H₂O.....10 g/l
- humectants..... 2-5 g/l

The optimum working conditions in this medium are:

- pH.....12-14
- temperature.....60-90°C

The medium is also normally agitated mechanically in some way to help the mechanical cleaning effect. This can be done, for example, by using air.

2.1.4 Ultrasonic degreasing

This system consists of a chemical medium, as in the previous example, to which an ultrasonic generator is added, which creates an impact effect on the surface of the part and helps the mechanical cleaning process.

2.1.5 Electrolytic degreasing

One of the most frequently used systems is electrolytic degreasing which consists of using an alkaline solution in which the parts act as cathodes. Saponifiable grease is attacked and is saponified by the action of the alkaline solution. The hydrogen that originates from the electrolysis of the cathode loosens any grease from the part. The metal oxides also fall off due to them being reduced by the hydrogen.

The basic formulation for the medium is as follows:

- caustic soda..... 50-60 g/l
- trisodium phosphate 12·H₂O..... 10-20 g/l
- sodium gluconate..... 10-30 g/l

The most frequent working conditions with this are:

- pH..... 12-14
- temperature..... 80 °C
- current density..... 5-10 Amp/dm²

2.1.6 Acid activated / pickling

This operation eliminates especially the metal oxides on the surface being plated.

Either hot or cold acid baths are used according to the type of oxide to be eliminated.

The main compounds are:

- chlorhydric acid
- sulphuric acid
- inhibitor agents

A mixture of both acids together is used, although some special metal activators use ammonia bifluoride ($F_2H_2NH_4$) as an activation substance.

After the pickling, the surface contains chemical products that are generated by the action of the acids on the oxides. Neutralising and subsequent rinsing with running water remove these products.

2.2 The main electroplating processes

After a surface that is to be plated has been completely cleaned of any type of grease or metal oxide, it is put through an electrodeposition process with a material that gives it corrosion-inhibiting and the desired decorative properties.

Different techniques and materials are used, according to the material being plated and the final characteristics that are required of the plating. Below is a description of the main treatment processes that are carried out.

In the case of electrolytic plating, the plating mechanism consists of cleaning the surface with one of the aforementioned processes and then submerging it in a suitable electrolyte containing the metal ions, with the part itself acting as the cathode in the electrolytic tank. Pure bars of the metal being deposited act as the anode and maintain a constant concentration of the metal ions in the electrolyte.

The thickness of the plating is regulated by varying the intensity of the current and the time that the process lasts. Various different humectants, lustering and complexing agents, etc. that have different functions, also form part of the bath.

The main industrial processes in the surface finish industrial sector are described below.

2.2.1 Electrolytic zinc plating and passivation

This is one of the most widespread processes in the surface treatment industry and is possibly becoming one of the most widely used plating methods for protecting iron, given its corrosion-inhibiting and decorative characteristics.

There are three basic ways of electrolytically plating zinc at the present time:

- acid zinc
- alkaline zinc
- cyanide zinc

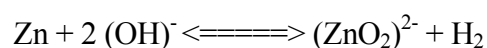
The **acid zinc** process is not a very extensively used technique nowadays. The metal is chemically active and is attacked by the diluted acids, although this occurs slowly when the acid is concentrated. In some cases, this is difficult when controlling the parameters of the processing bath. The acid solution is mainly formed of zinc chloride or sulphate, sodium or potassium chloride, boric acid, as the main elements. The acid formulations are:

- zinc chloride.....62-85 g/l
- potassium chloride.....186-255 g/l
- boric acid.....30-38 g/l
- humectants.....60-90 g/l
- lustering agents.....0.5-1 g/l

The working conditions for this formulation are:

- Temperature..... 21-35 °C
- Current density..... 1- 4 Amp/dm²
- Voltage..... 1-18 V
- pH..... 4.8-5.4

More use is made of the **alkaline zinc solution**. Here, zinc reacts with the alkalis to give soluble zinc platings, according to the following reaction where hydrogen is also given off:



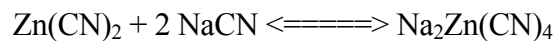
In this case, the most widely used basic formulation is as follows:

- zinc oxide..... 9.5 g/l
- sodium hydroxide..... 90-120 g/l
- lustering agents..... 10-50 ml/l

The working conditions in this case are:

- Temperature..... 20-30 °C
- Cathode current density..... 2- 4 Amp/dm²
- Voltage.....2-15 V

The last type of zinc plating, which is used more frequently than either acid or alkaline zinc plating, is the alkaline form of **cyanide zinc plating**, which is based on the following reaction:



The basic formulations fundamentally depend on the concentration of sodium cyanide, which varies as follows:

Type of bath	High conc.	Mid. conc.	Low conc.
Zinc cyanide	60	30	10
Sodium cyanide	42	20	7.5
Caustic soda	80	75	65
Sodium polysulphide	2	2	-
Lustering agents	1-3	1-4	1-5

Table 1

values in g/l

The most usual working conditions are the following:

- Temperature..... 20-30 °C
- Cathode current density..... 2- 6 Amp/dm²
- Voltage..... 2-15 V

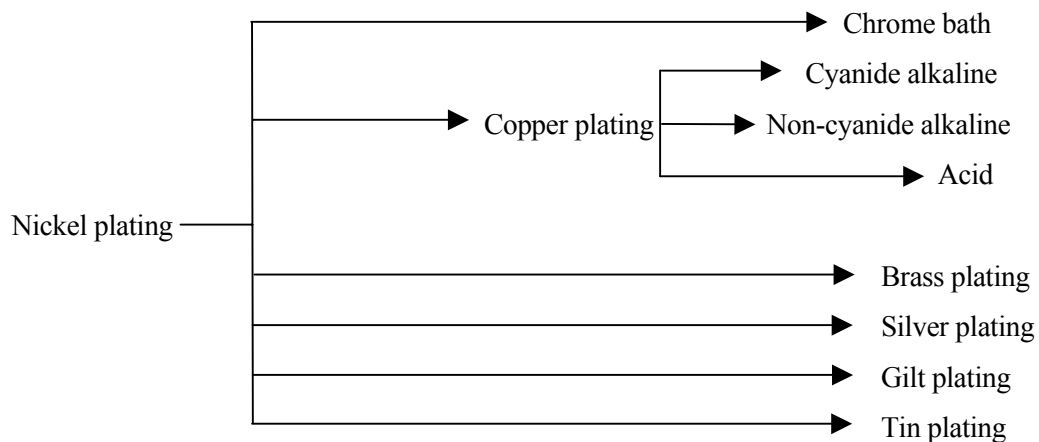
Once the parts have gone through the zinc plating process to increase their resistance to corrosion, they are put through a **chromic** or **chromatising passivation process**. There are four types of passivation:

- blue passivation (low resistance to corrosion)
- green passivation (high resistance to corrosion)
- yellow passivation (similar resistance to corrosion as the previous one)
- black passivation (average resistance)

Up to here, hexavalent chromium is still used in the formulations for passivation.

2.2.2 Sublayers and finishes

The surface treatment section produces a great many anticorrosive and decorative finishes. In many cases, before the final finish, we will find a sub coating of nickel, which enhances corrosion resistance and favours the subsequent electroplating of the final metal finish. The following diagram summarises the main coating and finishing baths.



As a result, it can be seen that electrolytic nickel plating is used in a wide number of cases as a base for being plated with other metals, such as:

- chromium
- gold
- silver
- brass, amongst others.

This is called a general type of process.

The **nickel plating** process normally uses one of the following as a sublayer for treatment:

- iron
- aluminium and aluminium alloys
- brass
- copper
- zinc and zinc alloys

In certain cases, parts are finished with a chemical plating of nickel with special characteristics (hardness, lubrication, etc.).

Good adherence and very clean parts are very important in the treatment because the reactions that take place in the chemical nickel plating process are catalytic ones (i.e. they are started by the material itself that is being plated).

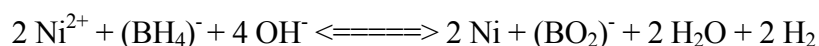
The basic formulation used is:

- nickel sulphate 7·H₂O.....250-350 g/l
- nickel chloride 6·H₂O.....60-90 g/l
- boric acid.....30-60 g/l
- lustering agents.....20-30 g/l
- humectants.....2-5 g/l

The required working conditions with these raw materials are as follows:

- temperature..... 50-65 °C
- current density..... 1-10 Amp/dm²
- pH..... 4 - 5
- voltage..... 1-16 V

The general reaction that takes place with nickel deposition is as follows:



As has already been pointed out, electrolytic nickel plating is used in many cases as a base that helps the deposition of another metal (mainly chromium).

The most extensively used raw materials in the **chromium baths** studied are as follows:

- chromium trioxide.....150-400 g/l
- sulphuric acid..... 2.5-4 g/l
- catalysts..... 0.5-1 g/l

The working conditions that are used are:

- temperature..... 40-50 °C
- current density.....5-55 Amp/dm²
- insoluble anodes.....93 % Pb, 7 % Sn

The **copper plating** bath is also quite extensively used in the industry. The formulation for the bath varies and can be classified according to:

- alkaline cyanide copper
- alkaline copper without cyanide
- acid copper with sulphuric acid
- acid copper with boric acid

The composition for the alkaline cyanide copper is:

- Copper cyanide..... 22.5 g/l
- Sodium cyanide..... 34.0 g/l
- Sodium carbonate..... 15.0 g/l
- Sodium hydroxide..... pH control

The working conditions are as follows:

- temperature.....32-43 °C
- current density.....10-15 Amp/dm²
- pH..... 12-12.6
- anodes..... copper and steel

It is used for fine thicknesses on all types of base metal and acts as a base layer for new layers of other types of copperplating. It is very extensively used for this reason. There is also a high concentration version that has as much as 120 g/l of copper cyanide and 135 g/l of sodium cyanide.

The alkaline copper bath without cyanide has the following composition:

- pyrophosphate copper..... 345.0 g/l
- potassium hydroxide.....18.0 g/l
- ammonium (29%).....1 ml/l

The working conditions for the plating process are:

- temperature.....43-60 °C
- pH.....8.2-9.2
- current density.....1-7.5 Amp/dm²
- anodes.....copper

This is a substratum for nickel bright and chromium plating processes. It can be applied to any metal with a layer of copper. It is also used in printed circuit boards.

In the case of acid copper with sulphuric acid, the composition of the bath is made up of:

- Copper sulphate.....195-248 g/l
- Sulphuric acid.....30-75 g/l

The working conditions are:

- temperature.....21-49 °C
- current density..... 2-10 Amp/dm²
- anodes.....copper

This is a bath that can be applied to any ferrous metal with a prior copper base; it can also be used as a treatment under nickel-chromium plating processes to give more resistance against corrosion. It is used a lot in the manufacturing of printed circuit boards for it gives very fine layers of plating, although thick coats are also possible.

In the case of the acid copper bath with boric acid, the composition is as follows:

- copper fluoborate..... 225.0 g/l
- fluoboric acid..... pH control

Working conditions:

- pH.....0.8-1.7
- temperature.....27-77 °C
- current density.....7.5-12.5 Amp/dm²
- anodes.....copper

This is a process that can provide any thickness to parts of any kind of base metal having a copper base. It is also used in the manufacture of printed circuit boards.

Another type of plating that uses nickel as a base is **brass plating**. Here, the most commonly used formulation is as follows:

- copper cyanide60-75 g/l
- zinc cyanide8-30 g/l
- sodium cyanide.....130 -150 g/l
- caustic soda.....3 - 4 g/l
- ammonia.....1 - 5 g/l
- lustering agents.....1-10 g/l

In this process, the working conditions are:

- temperature.....40-60 °C
- pH..... 9.5-11.5
- current density.....0.5-2 Amp/dm²
- Cu-Zn anodes.....80% Cu, 20% Zn

Another plating process that requires prior treatment with nickel is **silver plating**. The formulation in this process is:

- silver cyanide..... 30-40 g/l
- potassium cyanide.....160-200 g/l
- lustering agents.....0.1-10 g/l

The working conditions are as follows:

- temperature..... 22-30 °C
- current density.....0.5-2 Amp/dm²
- anodes..... silver (99.99 %)

One final process that is very common and that also requires a preliminary layer of nickel is **gold plating**. In this case, the formulation used is as follows:

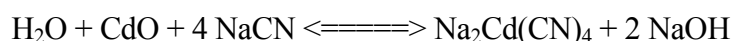
- double gold and potassium cyanide.....0.5-2 g/l
- disodium phosphate.....10-20 g/l
- lustering agents.....1-5 g/l

The working conditions most used are as follows:

- temperature..... 50-70 °C
- pH.....11-12
- current density.....0.2-0.6 Amp/dm²
- anodes.....platinised titanium (inert)

Although it is not as common as the previous ones, mention should be made of the **electrolytic cadmium plating process**, where cyanides (mainly sodium cyanide) and cadmium oxide are involved.

The reaction that takes place is the following:



The excess free cyanide in the solution helps stabilise the cadmium complex that is formed.

Within these types of general treatment, reference should also be made to the **electroplated tin** plating process which involves sodium stannate, sodium acetate, caustic soda, sodium perborate and water. The working temperature is 70°C. The process takes place basically because the sodium perborate oxidises the stannate ion into stannic.

2.2.3 Surface conversion processes

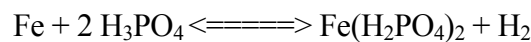
In this group of plating processes, a chemical reaction takes place with the base metal.

There are two important industrial processes:

- **phosphating and blueing**, in the case of iron and steel.
- **anodising of aluminium** and its alloys.

Phosphating consists of the formation of layers of phosphate on the surface of the metal that is being treated. The process protects against corrosion, as well as making treated metals easier to work with mechanically.

The phosphating process is achieved by introducing the part to be plated in a diluted solution of phosphoric acid, which reacts with the iron and proceeds according to the reaction:



Blueing basically consists of the oxidation of the surface by controlling the process in such a way that the hard ferric oxide that is formed protects the iron.

This oxidation can be achieved in different ways:

- electrolytically (anodic oxidation), in a solution of water with hyposulphite.
- chemically (alkaline oxidation), by using sodium hydroxide and sodium or potassium nitrate.
- chemically (salt bath), in a bath with a mixture of sodium and potassium nitrate, with added manganese dioxide.

There is also the **aluminium anodising** process. The anodic oxidation of aluminium can be considered a passivated process that is accelerated by a continuous current. What actually happens is that it is oxidised by electrolysis with the part being treated being the anode. This is a very important application that serves, in the majority of cases, to protect parts made of aluminium for use in the construction industry.

The mechanism that takes place is the following: when the electric current passes through the electrolyte, where the aluminium parts to be oxidised act as an anode, a layer of aluminium oxide (alumina) is formed that slowly grows until it reaches a thickness of around 25-60 microns.

During this process of oxidation, the oxygen that forms at the anode oxidises the aluminium. Given the excessive heat that is given off during oxidation, it dehydrates and forms aluminium oxide (a layer of alumina).

Unlike the other processes, the aluminium here is treated in the following way:

- | | |
|-------------------------------|-----------------------------|
| 1. chemical degreasing | 7. sulphuric acid anodising |
| 2. rinsing | 8. rinsing |
| 3. aluminium burnish (alkali) | 9. colouring |
| 4. rinsing | 10. rinsing |
| 5. nitric acid pickling | 11. sealing with hot water |
| 6. rinsing | |

The most frequently used formulation for chemical degreasing is as follows:

- sodium carbonate.....40 g/l
- sodium metasilicate.....20 g/l
- sodium gluconate..... 10 g/l
- Disodium phosphate..... 20 g/l
- humectants.....1-5 g/l

For the aluminium burnish process, the basic formulation is:

- caustic soda.....50-60 g/l
- sodium gluconate.....20-30 g/l
- humectants.....1-5 g/l

For the pickling process with nitric acid, the formulation is:

- nitric acid.....500 ml
- water.....500 ml

The process is worked at room temperature.

As far as the anodising process itself is concerned, different types of electrolyte are used in anodic oxidation, the most important being sulphuric acid at 20% weight.

The working conditions are:

- temperature.....21-23 °C
- anodic current density.....0.5-1.5 Amp/dm²

The sulphuric acid attacks and partially dissolves the surface during the anodic treatment of the aluminium so when the concentration of aluminium in the medium reaches a specific value, the electrolyte needs to be diluted.

In some cases, the aluminium has to be coloured by the use of appropriate organic or inorganic dyes. The concentration of the dye varies according to each case.

The working conditions also depend on each specific dye, together with the degree of absorption intensity required.

Lastly, distilled water at 98 °C is used in the sealing process to hydrate the layer of alumina.

The following description of the electropolishing process ends this study of the electroplating processes.

2.2.4 Electropolishing

Electropolishing consists preferably of dissolving a very small amount of the part to achieve a stainless steel mirror sheen.

The part acts as an anode in a bath containing hot concentrated acids.

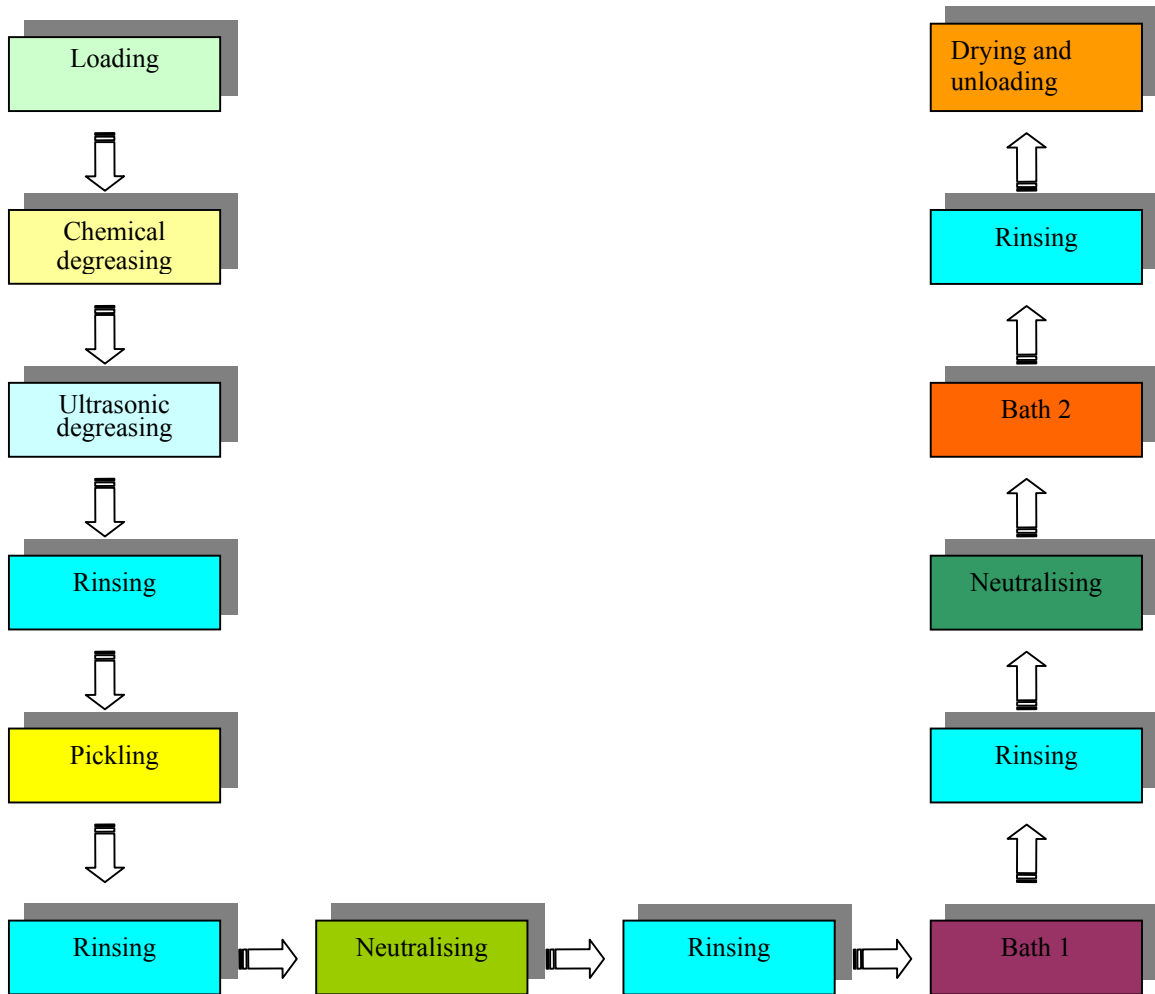
In this case, the composition of the electrolyte is as follows:

- phosphoric acid.....90 % (weight)
- sulphuric acid.....10 % (weight)
- glycerine.....1 % (weight)

The working conditions are as follows:

- temperature.....80-90 °C
- time.....2-3 minutes
- anodic current density.....10-50 Amp/dm²

Having described the main processes that make up an electroplating line process, the following table shows the sequence for a theoretical processing line:



 Path followed by the parts

2.3 Rinsing

Rinsing operations are fundamental in electroplating processes. The volume of water necessary for rinsing the treated surfaces correctly is a parameter that is normally determined by the size of both the management and follow-up treatment systems.

The volume depends on many factors and can be much greater than the necessary minimum, according to how the electroplating plant has been designed. This, unfortunately, is very often the case.

It is thus essential that the selected rinsing system provide the necessary quality of rinsing with a minimum amount of water consumption, which will moreover also result in the reduction in the volume of wastewater.

One of the factors that has the greatest influence in the rinsing volumes is drag-out. This, on the other hand, is conditioned by the shape and surface roughness of the parts, the viscosity of the process solution, etc.

2.3.1. Costs deriving from the excessive use of water

Producers in some Mediterranean countries have to take into account that there are other costs that must be added to the cost of water, according to the requirements for bringing the disposal of waste water into line with prevailing regulations. The most important of these costs are as follows:

1. Taxation (levies and taxes). Moreover, many of these are progressive, i.e. the more water used, the higher the tax.
2. Distribution costs inside the workshop.
3. The cost of maintaining the supply facilities.
4. Energy for the pumps and suppressors for conveying or agitating the water.
5. Investment in conditioning treatment processes according to the characteristics of the water (desalinisation, delimers, etc.).
6. Investment in the collection of polluted effluents.
7. The maintenance costs of efflux installations.
8. Investment in decontamination treatments (physico-chemical purification).
9. Operating costs of decontamination (personnel, energy, reagents, replacements, sludge management, etc.).

Reductions in the consumption of water lead to reductions in all or part of these different costs to the company.

Experience shows that rationalising the handling of water and, by extension, of materials in the electroplating workshop leads simultaneously to improvements in the production cycles by limiting idle time, reducing the deterioration of the working environment and disinclination on the part of the workers, and by consequently improving product quality and the productivity of the company as a whole.

The following goals in relation to the use of water by the industry can be established:

1. In some countries in the Mediterranean Basin, a maximum water consumption of around 8 l/m² is considered acceptable for each rinsing position depending on the surface being treated.
2. Optimum reductions in the use of water with the same dilution ratio, or improvements in the quality of rinsing without increasing the water consumption.

2.3.2. Relationship between the quality of rinsing and the amount of water necessary

When a worker in an electroplating workshop removes a part from a tank in the processing line, both the part and its support carry part of the aqueous solution where they were submerged, for they are moist and covered with a fine liquid film when removed from the tank. This volume of liquid is known as **drag-out** and corresponds to a volume (q), which is usually in litres per hour (l/h). Part of the liquid thus gets transferred from one tank to another and "contaminates" it.

Parts and their support mechanism need to be rinsed to avoid cross-contamination between processing tanks. This is where another fundamental concept in the industry comes to the forefront and one that is frequently forgotten about or unknown by manufacturers i.e. the **dilution ratio** (Dr). This concept measures the quality of the rinse in question, and by definition has to be established in each particular case.

With the following parameters:

Co = initial concentration of the bath

Cr = mean concentration of the bath and rinsing water

q = drag-out (l/h)

Q = volume of rinsing water (l/h)

Dr = dilution ratio (rinsing quality)

The relationships that exist between them are:

$$\mathbf{Dr = Co / Cr = Q / q}$$

In this way, once the quality of rinse (Dr) in question has been established together with the drag-out (q) derived from it, the manufacturer can determine the volume of rinsing water necessary for each rinsing position².

The basic issue is that drag-out has to be eliminated in rinsing water to prevent the concentration of rinsing salts. So, if *q* is the volume of drag-out and *Q* is the rinsing volume:

- **q Co** is the quantity of products that enter the rinse and
- **Q Cr** is the quantity removed for rinsing.

So this gives:

$$\mathbf{q Co = Q Cr}$$

That is to say:

$$\mathbf{Q = q Co / Cr = q Dr}$$

$$\mathbf{Q (rinsing volume) = q (drag-out produced) Dr (dilution ratio or quality of rinsing)}$$

The result of all of this is that *increasing the rinsing volume is not the only means that is available for improving the quality of rinsing*. High-level quality rinsing (high Dr) can be achieved by:

- Reducing the drag-out volume (q);
- Reducing the rinsing volume by modifying the rinse structure.

² For determining the maximum permitted concentration of water in the cleaning tank, it is possible to take the concentration of some element that endangers the cleaning quality. For example, for a final clean, it would be sufficient to determine the Cl⁻ concentration, or a characteristic preparation bath product (Ni, Zn, CN⁻, etc.) can be taken as a reference.

Details of some standard examples of rinsing quality (Dr) taken from the bibliography are given in the following table:

Type of process	Dr = Co/Cr
Preparation (degreasing, pickling)	500-5000
Multilayer finishes (Cu, Ni, Cr, etc.) and most deposition baths	5000-10000
Hexavalent chromium passivation	1000-2000
Iron phosphatisation, aluminium anodising	2000-5000
Critical final rinsing	> 10000

Table 2

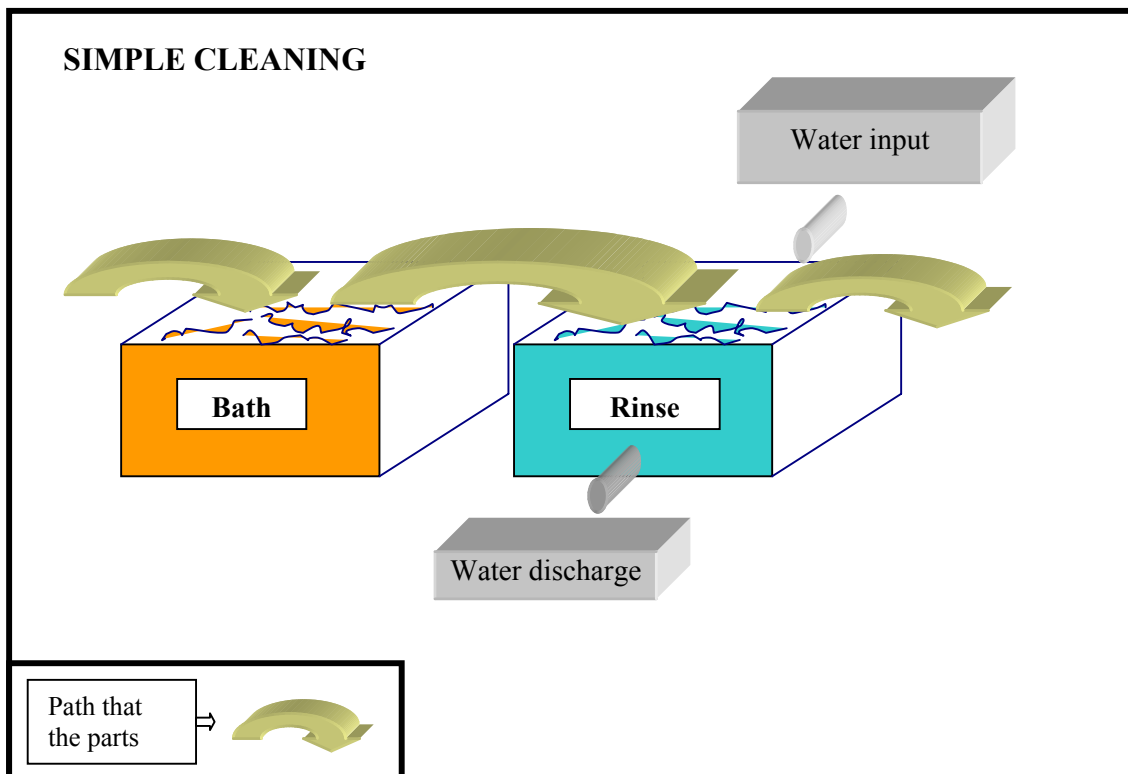
The structures and systems used in the industry are as follows:

2.3.3 Single rinsing

This is the most extensive system used in the majority of the companies in the electroplating industry.

Here there is just one rinsing tank with running water after the treatment bath.

A large volume of water is usually necessary to guarantee suitable dilution.



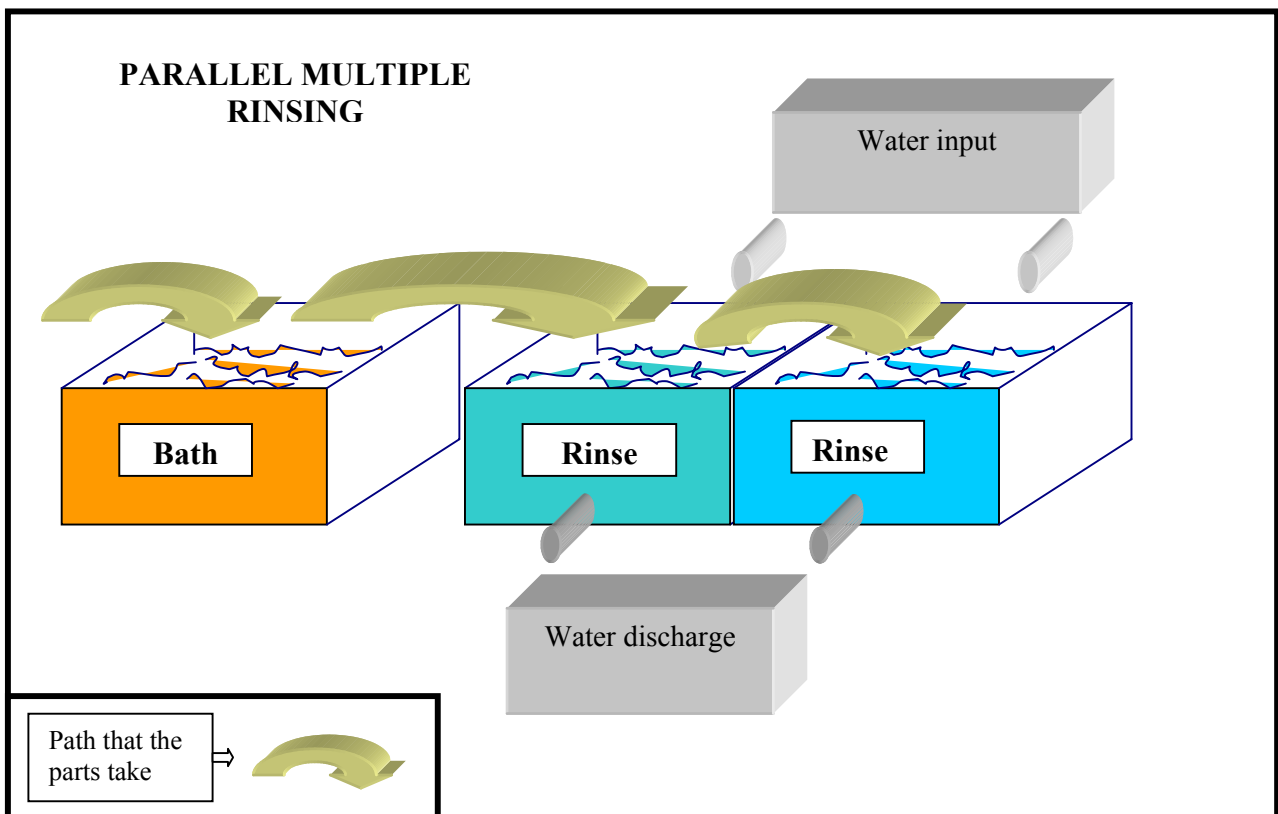
2.3.4. Rinsing in stages.

This is also called multiple rinsing and usually involves a two-fold rinsing process (with two vats).

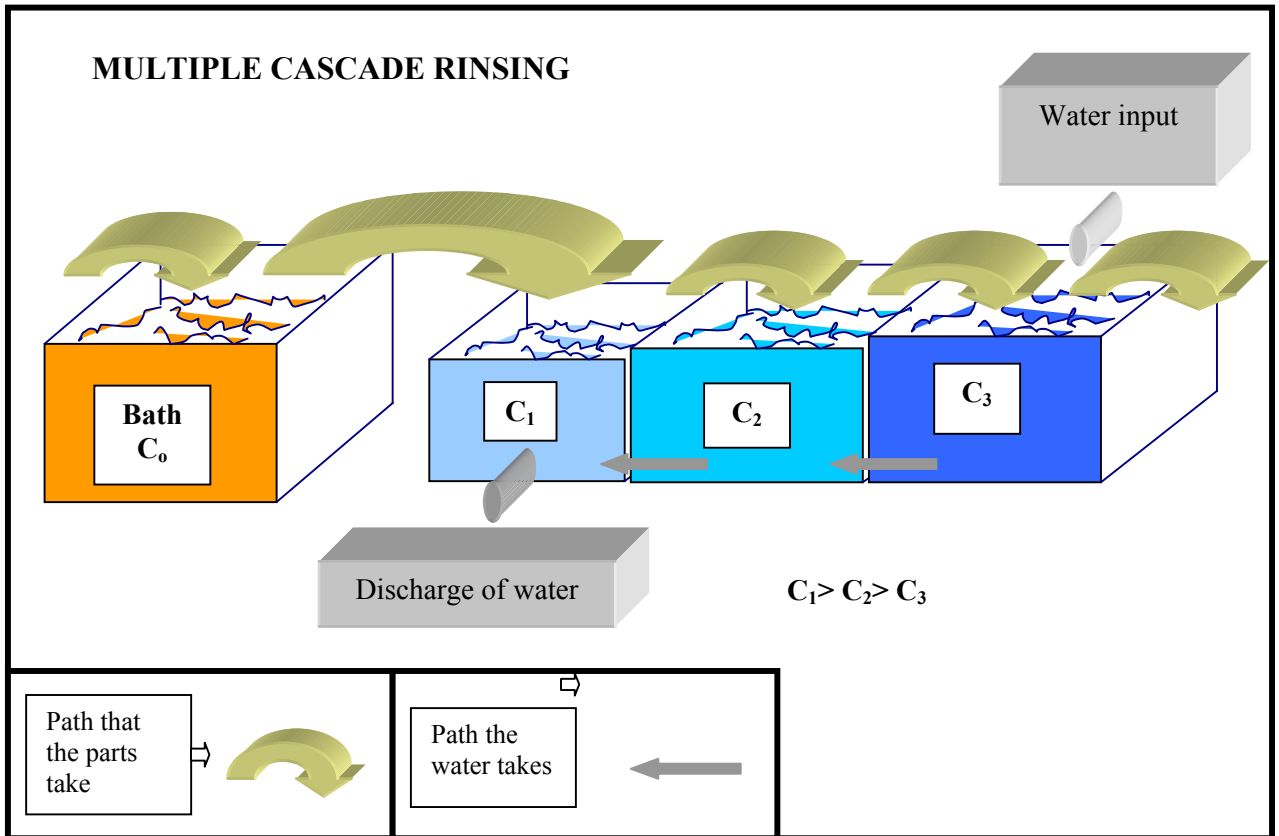
This system of rinsing can be one of two types:

- **Parallel multiple rinsing.** This is a good alternative for making considerably large reductions in water consumption.

This is for where there are various rinsing tanks, each one being fed separately (in parallel) with water.



- **Multiple cascade rinsing (mass).** This is generally the most recommended system (provided that the company has enough space).



A simple economic analysis reveals the unquestionable fact that the investment necessary to install this system is minimal compared to the saving of water that is achieved.

Fresh water is supplied to the rinse tank farthest from the process tank and overflows to the preceding tank (in cascade form) until it reaches the tank immediately following the process tank. The system thus works via a counter-current flow (the circulation of water goes in the opposite direction to that of the part being worked). The parts thus come into contact with water that is cleaner and cleaner.

It can be demonstrated, as is shown very clearly in section 3.1.2 of this research study, that the volume of water necessary for a multiple rinse system is much less than that which is needed in a simple system.

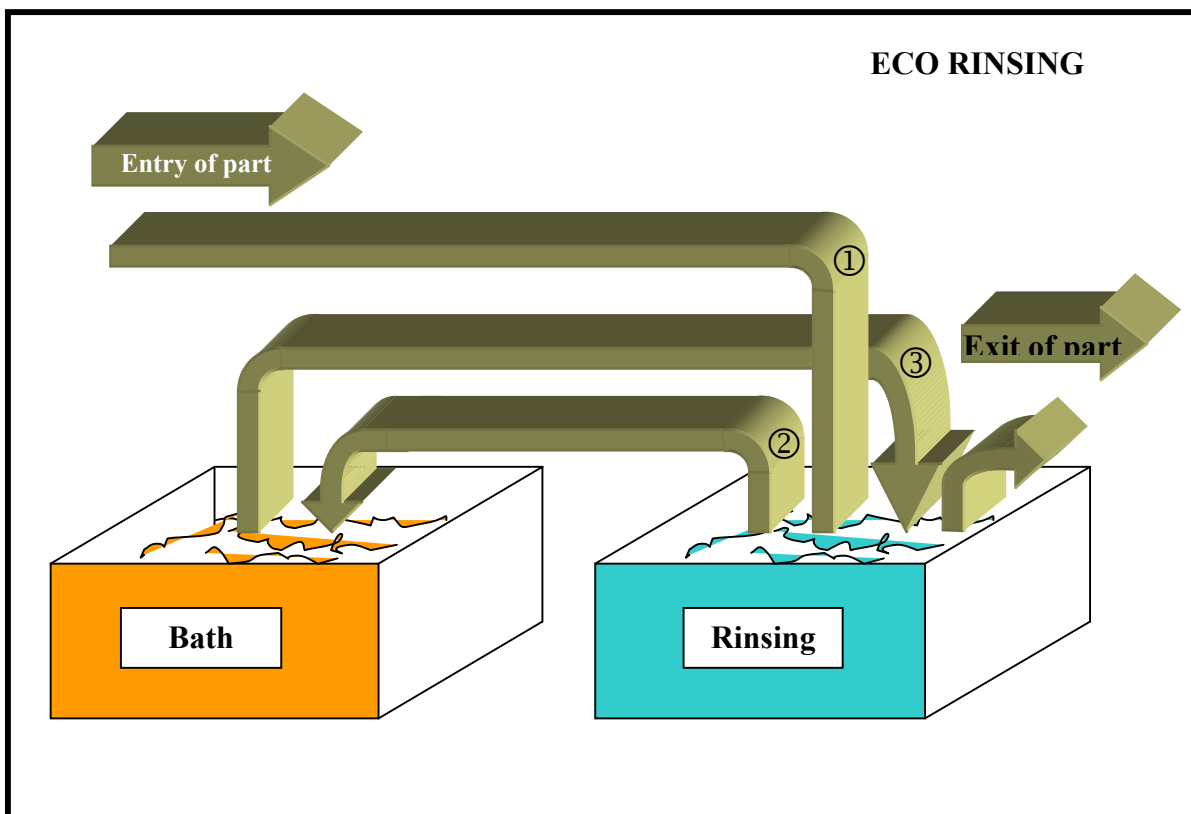
2.3.5. Sealed recovery rinsing

This is a pre-rinse process that retains part of the drag-out from the treatment bath and thus helps to economise the use of raw materials.

As its name indicates, the water is totally renewed periodically instead of being fed continuously. Apart from this function, the use of sealed recovery rinsing helps to reduce the contamination of the liquid by "drag-in" from the parts and thus reduces the water requirements in later rinsing processes.

This type of recovery rinse can be located after a hot process solution. In such cases, it can be used to replace the losses undergone in the previous bath due to evaporation.

For some baths that are worked at room temperature, one rinse can be carried out before and another afterwards in the recovery tank itself so that the drag-out entering the process bath comes from the recovery system itself. The result is partial recovery on a process where there is no evaporation. This type of rinse is named ECO.



2.4 Water treatment

2.4.1 Treatment prior to the process

With surface plating, the level of manufacturing quality depends on the quality of the input water. The input water is often not suitable for direct use in the processing baths and it can even contain so many impurities that this causes problems in the rinsing stages, especially final rinsing processes, and rapidly saturates the recovery equipment with the element/s in question.

As a general rule, an initial chemical analysis needs to be carried out to determine the presence of iron, calcium, magnesium, manganese, chlorides, etc. for these can cause problems in the electrodepositing process. Seasonal variations in the quality of the water should also be taken into consideration (for example, there is an increase in the saline concentration in many places during the summer). Even so, it is difficult to set optimum values because the quality of the water is a function of the particular conditions of use. In any case, water with a TH³ of 15-20 °F and a TAC⁴ of 10-15 °F is considered as being acceptable for preparing most process baths and rinses.

The use of input water that is polluted obviously shortens the operating life of the baths, it affects their efficiency, it makes the recovery of wash water more difficult, it causes the breaking of parts and contributes to the pollutant load that needs purifying.

As far as the chemical quality of the input water is concerned, electroplating processes should take the following general recommendations into account:

- Alkaline baths and washes: in general, soft water is best for avoiding depositions and stains.
- Hot baths: the most highly recommended is demineralised (or decarbonated) water to avoid the mineralisation of the bath due to the progressive concentration of salts.
- Final rinses: the quality of these rinses needs to be strictly controlled to avoid the formation of stains (presence of salts) and the subsequent corrosion of the finished surface (presence of chlorides).

The most important elements used to modify the input water are the following:

- delimers
- ionic exchange demineralisers
- reverse osmosis.

³ The hydrotimetric title is the total unstable Ca and Mg (bicarbonates) and stable (carbonates, chlorides, sulphates, etc.) salts.

⁴ The complete alkalimetric title is the concentration of Ca and Mg bound to the bicarbonates.

2.4.2. Treatment following the process: physico-chemical treatment

As a general recommendation, producers should take the following aspects into account before deciding on one treatment system or another:

1. Carry out an exhaustive study of all of the wastewater generated at the different points in the electroplating line process.
2. Adopt all measures for making reductions at source that are appropriate for the problems at hand, including modifications to equipment, processes and current practices.
3. Analyse and ultimately implement the means aimed at recovering waste flows.
4. Lastly, choose the most appropriate treatment systems in terms of a satisfactory level of decontamination by minimising the quantity and toxicity of waste generated in the treatment process.

As has already been mentioned, conventional processes for treating waste water in the surface finishing industry require the elimination of metal through the forming and precipitation of relatively insoluble metal hydroxides. The only chemical requirements for this process are that the metals be free of effluent and the pH high enough to ensure optimum precipitation with hydroxides.

The requirement that the metals be free of effluent is very difficult with water full of cyanide, EDTA, NTA, lustering agents, humectants, etc., especially when complexing compounds are added to certain process baths to regulate the amount of free metal in ionic form in the electrolyte. A very typical example is the case of copper cyanide baths. Experience shows that most wastewater treatment plants do not take these precepts into account.

It is advisable for waste water generated in surface treatment workshops to be collected in different waste flows (according to its chemical characteristics) and treated separately, and in the same way follow the same criterion for the discharge of depleted concentrates that are produced from time to time. This is already done in some Mediterranean countries.

It is preferable for treatment plants to be located below the outlet pipes so that effluents are fed by a gravity flow system into the processing reactors where they are treated. Once the chemical aggressiveness has been removed, they are pumped to a destination point.

Treatment is carried out by way of a chemical process and the quantity determination by automatic control. This is the most common method, although this does not permit any kind of recovery of valuable materials that are lost.

To be able to totally understand how a treatment plant works, the different mechanisms involved in the chemical reactions that take place in the treatment operations need to be explained.

All types of treatment can be grouped into operations either of destruction, transformation or separation of the components in waste water.

The most important effluents produced by the surface finish industry are inorganic, such as heavy metals or anions such as cyanides and chromium. In many cases, oil and grease are present and sometimes need to be separated. Bacteriological contamination, on the other hand, is not a problem in this industrial sector and is not considered here.

** Cyanide treatment*

Cyanide is a very common component in the waste flows produced by the surface treatment industries because, as has already been seen, many types of metal electrodeposition bath have a high potassium or sodium cyanide content. It is also found in the water from iron and steel tempering installations where diluted or highly concentrated cyanide salts are used. The concentrations of free cyanide to be found in these effluents range from 20 to 100 mg/l and in some cases even more.

A distinction must be made between the simple cyanides, such as sodium or potassium, and the complex, heavy metal cyanides, such as copper, nickel, zinc and others. Residual effluents from electroplating processes contain both types of cyanide and must be treated. The toxicity of both types is different and depends on the specific kind of chemical is present.

The usual process consists of the oxidation of the cyanide ion using an oxidising agent. The most common is sodium hypochlorite, although chlorine gas is also used.

The simple cyanides are easily oxidised with these oxidising agents. The reactivity of the metal complexes varies, on the other hand, according to the metal content. Zinc and cadmium complexes oxidise fairly rapidly. On the other hand, silver and nickel complexes oxidise very slowly. The copper complex comes between the two. The reaction time thus depends on the metals that are present in the effluent. If this is not taken into consideration, there is the risk of the reaction being incomplete. Likewise, if the reaction conditions are not totally adequate, insoluble metal cyanides can be produced. These can get decanted and thus escape treatment.

Nickel cyanide complexes take between 10 and 20 hours to be destroyed, which is an extremely long reaction time (and impossible to achieve in practice). As this kind of cyanide only forms when water

containing cyanide mixes together with nickel-containing water, it is extremely important to keep these two types of effluent separate.

Cyanide is destroyed by oxidation, and gets transformed into cyanate (CNO⁻). Cyanates oxidise into carbon dioxide and nitrogen in the presence of an excess amount of an oxidiser. Cyanate is not normally considered to be excessively toxic, for its toxicity level is around a thousand times lower than that of the cyanide ion. Cyanate can hydrolyse in an acid medium to form ammonium and carbonate. As ammonium is more toxic than the cyanate itself, this must be avoided.

If hypochlorite is used for oxidation, ensure that the conditions are appropriate (pH, excess of reagents, etc.) to prevent cyanogen chloride from being given off, which is a volatile gas that is just as toxic as hydrocyanic acid.

The treatment of complex heavy metal cyanides occurs at variable rates and also in various stages. In the case of complex copper and potassium cyanide (K₃Cu(CN)₄), for example, three cyanide groups are destroyed relatively quickly whereas the fourth is very resistant. The iron complex cyanides hardly get attacked by the hypochlorite so some other process must be used, such as precipitation through the addition of an iron salt (II) in the form of Prussian blue (hexacyanoferrate (III) of iron (II)). The toxicity of these hexacyanoferrate complexes is low, for example, with 200 mg/l of complex corresponding to 0.1 mg/l of cyanide.

** Chromic acid treatment*

Chromic acid is one of the most toxic and dangerous compounds in waste water. In addition, its relative cost is high compared to other products used in electroplating and special interest is thus taken in its recovery.

The treatment process that is most used at present consists of using an acid medium to reduce hexavalent chromium to trivalent chromium, which can be precipitated in the form of a hydroxide during the neutralising stage.

In theory, 156 kg of sodium bisulphite and 74 kg of sulphuric acid are necessary to reduce one kilo of chromic acid. In real life situations, however, the use of reagents is much higher and can reach up to 300 % of the theoretical amount.

The precipitation of trivalent chromium is normally carried out after all of the waste waters with the heavy metal content have been collected together. An alkali, such as caustic soda or limewater is then added and the metal hydroxides are precipitated. Chromium hydroxide precipitation is done with a pH

between 7.8 and 8.5. With pH levels that are higher, there is the danger of resolution due to the formation of chromites whenever neutralising is done with caustic soda. This risk is considerably reduced when neutralising is done with limewater.

** Precipitation and separation of metal hydroxides*

The separation of toxic metals in solution by precipitation in the form of hydroxides is a widely developed purification technique. This process takes place simultaneously with the neutralising of the effluent, for the margin of values admitted for the discharge pH is suitable for ensuring the precipitation of most common metals.

The formulation of this stage of the treatment requires a prior in-depth analysis that considers concepts such as the solubility of the metal according to the reagent, the pH, the temperature, the use of coagulating and flocculent agents, the precipitation of chelates, the alkali used for precipitation, etc.

2.5 Waste flows

2.5.1 Introduction

Waste flows in the plating baths sector result basically from raw material loss during process activities. Part of this material loss is deliberate, as in the case, for example, of the emptying of a degreasing bath that is no longer effective due to oil pollution; replacement with a new bath gives rise to a waste solution that creates a waste flow. Involuntarily loss of material also occurs, however, as in the case of loss from drag-out (the fine liquid film that covers parts when removed from a process bath). The need here to rinse the parts in order to clean off the drag-out generates a waste flow that is polluted by a material that is being lost at the same time.

The most important waste flows in the sector are described below.

2.5.2 Waste flow generation

Generically speaking, the waste flows resulting from the wide variety of activities connected with electroplating processes are as follows:

a) Storage of raw materials:

- Waste generated by spoilt materials in storage,
- Loss of chemical products during handling and decanting operations by runoff, leakage of products due to drum breakage and tap losses,
- Loss of product that clings to the walls of containers and drums in container-emptying operations,

- Empty containers and drums with remains of product.

b) Process operations:

- Particulates and dust originating from mechanical pre-treatment operations,
- The emission of solvents in degreasing operations,
- Degreasing baths that are dirty with oil, grease, polish, etc.,
- Pickling baths polluted with the base metal of the parts being processed,
- Used baths that are inactive but still contain products for coating, bisulphite, anodisers, phosphatisation, chroming, etc.,
- Waste water polluted with liquid drag-out as parts are removed from the different process baths,
- Diffuse emissions from baths that work at a certain temperature ($>50^{\circ}\text{C}$),
- Flue gas emissions from the heating of baths and the drying of parts,
- Liquid from baths dripping onto the ground between process tanks and when crossing over an aisle in manual installations.

c) Auxiliary activities:

- Dirty absorbent material and sludge from bath maintenance,
- Concentrated solutions from the regeneration of ion exchange resin and inverse osmosis equipment,
- Concentrated solutions and dirty material from the rinsing of baths,
- Concentrated solutions from the release of emissions into the atmosphere,
- Sludge containing metal hydroxide from effluent treatment,
- Concentrated solutions from rack demetalising,
- Sludge, etc., from the cleaning of piping, pumps, etc.,
- Filter material for treating water, depleted or dirty, resins, filters, etc.

A classification of all of these waste flows according to the generally accepted pollution vectors is given below:

Waste water

- Regeneration eluates from resins and osmosis
- Diluted effluents from the rinsing of parts
- Depleted and polluted concentrated bath solutions
- Polluted solutions from fume treatment equipment.

Industrial waste

- Depleted surface preparation baths: degreasing and pickling.

- Polluted and depleted process baths: anodising, neutralisation with bisulphite, chromium baths polluted with heavy metals and trivalent chromium.
- Demetalising solutions.
- Solutions and treatment filters from emissions into the atmosphere.
- Empty drums and containers.
- Sludge from effluent treatment.
- Different types of filter and absorbent material: filters, active carbon, absorbents, dirty rags, etc.
- Material used in waste water treatment: depleted ion exchange resins, inverse osmosis filters, etc.

Emissions into the atmosphere

- Emissions of dust and particulates from mechanical pre-treatment operations (shot peening, polishing, etc.).
- Diffuse emissions from the baths (pre-treatment and process), consisting basically of water vapour from solutions that work at a certain temperature (>50°C).
- Emissions of volatile organic compounds from baths for pre-treating parts.
- Vapour containing chromic acid from chroming processes.
- Pollutant gases from combustion boilers used to heat baths or to dry parts.

The following table shows the relative importance of the three vectors analysed in terms of environmental problems, and consequently the efforts that need to be made by the manufacturer:

Waste flows	Relative importance (%)
Industrial waste water	50
Industrial waste	40
Emissions into the atmosphere	10

Table 3: Source: Author

2.5.3 Summary of the waste flows generated

DESCRIPTION OF THE WASTE FLOW	ORIGIN	DESCRIPTION
VECTOR: Water		
Diluted effluents	Rinsing of parts	Liquids and treatment and metal coating baths (electroplating, anodising, phosphatisation, pickling)
Concentrated process solutions (when treated by the same company)	Depleted and polluted process baths	Liquids and treatment and metal coating baths (electroplating, anodising, phosphatisation, pickling)
Regeneration eluates	Concentrated solutions from the regeneration of ion exchange and inverse osmosis resins	Regeneration eluates from ion exchange resins
Concentrated solutions from emissions into the atmosphere	Polluted water from gas and vapour treatment systems	Chromium non-cyanide coating liquids and baths Non-chromium non-cyanide coating liquids and baths
VECTOR: Waste		
Dirty halogenated solvents	Halogenated solvents (trichloroethylene, perchloroethylene, etc.) dirty with oil, grease, etc.	Solvents, dirty mixtures containing solvents and halogenated organic liquids
Concentrated pre-treatment solutions (when managed externally)	Preparation baths (alkaline degreasing and acid pickling) that are depleted and polluted with oil and metals	Non-chromium non-cyanide coating liquids and baths Acid pickling solutions, passivation agents, non-chromic acid degreasers Alkaline pickling solutions, passivation agents, degreasers. Other pickling solutions, passivation agents, degreasers.
Concentrated process solutions	Depleted and polluted plating baths (anodising, phosphatation, chroming, bisulphite, etc.).	Chromium non-cyanide coating liquids and baths Non-chromium non-cyanide coating liquids and baths Acid pickling solutions, passivation agents
Alkaline solutions with surfactants	Alkaline solutions with dirty surfactants containing grease, oil, etc. (chemical degreasing)	Alkaline pickling solutions, passivation agents, degreasers
Concentrated solutions in installation maintenance	Solutions used for rack demetalising	Chromium non-cyanide coating liquids and baths Non-chromium non-cyanide coating liquids and baths Other pickling solutions, passivation agents, degreasers
Absorbent material used in treating emissions into the atmosphere	VOC filtering material Material for filtering emissions with heavy metals into the atmosphere	Absorbents, filter materials, cleaning rags and protective clothing polluted with heavy metals
Empty drums and containers	Plastic drums and metal containers that have contained materials	Plastic containers and packaging Metal containers and packaging
Sludge from waste water treatment	Sludge from the physico-chemical treatment of waste water	Effluent treatment sludge (pre-treatment, and treatment plants)
Effluent treatment sludge	From sedimentation, settlement, filtration, pressing.	Effluent treatment sludge (generated in the treatment of waste water)

DESCRIPTION OF THE WASTE FLOW	ORIGIN	DESCRIPTION
		produced before any subsequent chemical treatment and appropriately separated and treated)
Filter material used in water treatment	Active carbon and depleted ion exchange resins	Ion exchange resins Active carbon
Filter material and different types of absorbent	Material for bath filtering and maintenance: filters, rags, etc.	Inorganic residues that contain metals not specified previously Adsorbents, filtering materials, cleaning rags and protective clothing polluted with heavy metals
Particulates from mechanical pre-treatments. Sand	Shot peening, mechanical polishing, etc.	Shot, filings, scrap and metal particulates.
VECTOR: Emissions into the atmosphere		
Process water vapour	Vapour from tanks that work at a certain temperature (>45-50°C)	
Vapour containing chromic acid	Vapour that contains drops of chromic acid from chroming	
Polluting gases from sources of combustion	Combustion gases from the heating of baths and the drying of parts.	

Table 4

Details are given below of the various waste flows described and for the different production processes.

Mechanical pre-treatment

Shot peening, mechanical polishing and other similar operations basically lead to the emission into the atmosphere of dust and metal particulates that are almost always collected by filtering systems, and produce industrial waste. Furthermore, once the abrasive material that is used becomes depleted through friction with the metal parts, it turns into another form of industrial waste that must be managed.

Part degreasing

The waste flow that is generated depends on the type of degreasing used. The two main types of degreasing either use a halogenated solvent (TRI, PER, etc.) or an aqueous degreasing alkali.

In the case of the use of halogenated solvents, these become polluted with oil, grease, polish, etc. that are on the parts prior to the electroplating process. Unless they are recovered by distillation, these dirty solvents turn into a highly polluting form of waste that is produced fairly regularly. Moreover, the use of these solvents also generates emissions into the atmosphere of volatile organic compounds (VOCs).

As for aqueous degreasing alkalis, the most usual pollutant compounds besides oil and grease are sodium salts (hydroxide, carbonate, phosphate and metasilicate), and surfactants and organic complexing agents (EDTA, NTA, etc.). Sodium cyanide used to be added to baths in the past – examples thereof can still be found – to reinforce the degreasing effect; although this has practically died out today as a result of technological improvements in bath formulations. This type of waste is created more regularly than halogenated solvents although, on the other hand, the process of managing this is much more economical and it can be treated by the company itself in a treatment plant (installations permitting). In the case of hot baths, there is also a diffuse emission of water vapour. Different types of system are available for quantifying this diffuse loss of water through evaporation; in the case at hand, the following table is provided for calculating the values for evaporation per square metre of tank and per hour according to the temperature and density of the working solution. An extrapolation can be made for data that do not coincide.

Solution density	Example of solution	Temperature (°C)	Evaporation value (l.m ² /h)
1	Water	50	1
		70	9
		90	23
1.2	Nickel bath	50	0.8
		70	7
		90	20
1.4	Hard chromium bath	50	0
		70	2
		90	5

Table 5

These values for evaporation must be increased by 50% if there is a gas exhaust or air-stirred solution system.

Pickling

Most types of pickling involve a dilution (more or less concentrated, although the most frequent is 30%) of acid in water. Hydrochloric and sulphuric acids are the most important ones, and nitric, phosphoric and hydrofluoric acids are of secondary importance.

As the base metal is attacked in the pickling process, batch waste is generated when part of the metal is dissolved by the acid, which in turn gets contaminated and loses its pickling function. At this point, a type of waste is generated that, due to its characteristics, can be treated in a physico-chemical treatment plant by the company itself. Generation of this type is more sporadic than with aqueous degreasing alkalis.

Plating processes

The pollutants generated depend on the type of process, composition, concentration, etc. Basically, pollutants in the plating process can be classified as follows:

- Diffuse emissions of steam into the atmosphere and chromium particulates in the chromium baths in the case of solutions that work over 50°C,
- Flue gas emissions from boilers used to heat process baths and/or to dry parts,
- Acid baths: nickel plating, acid zinc, acid copper, tin plating, anodising of aluminium, ferrous phosphatation, and white passivation, amongst others;

- Alkaline baths: non-cyanide alkaline zinc, non-cyanide alkaline copper, and blueing are the main ones;
- Alkali cyanide baths: zinc coating by cyanide, copper cyanide, gold plating, silver plating, etc.;
- Chromic acid baths: chromic and yellow passivation are the most extensively used.

The presence of heavy metals depends on the composition of the bath (Ni, Cu, Zn, Fe, Al, Sn, Au, Ag, etc.), and the anions that accompany this in the form of salt (Cl⁻, SO₄²⁻, PO₄³⁻, CO₃²⁻; OH⁻, etc.). In the case of cyanide baths, in addition to the corresponding metal and different kinds of salt, there is also the CN form - in its different expressions of dynamic equilibrium. Cr⁶⁺ is found in most chromium baths.

This chemical classification of the waste flows generated in the electroplating process has its physical equivalent, which consists of the following types of waste flow:

- Diluted
- Concentrated

Diluted flows refer basically to rinsing water between treatment processes whereas concentrated flows refer to the bath itself or a concentrated sealed rinse that has to be renewed.

Diluted waste flows are usually generated continuously throughout coating activities as the parts are rinsed between the different process baths whereas concentrated flows are batch produced at the end of the useful life of the bath or when the maximum accepted concentration of a sealed rinse is reached.

Storage of raw materials

As described above, a large part of the waste flows generated in this area of the company occur in storage conditions and/or inadequate operational conditions; i.e. inappropriate environmental practices in most cases. These include poor management of stocks in storage, defective storage systems and/or decanting of materials, personnel in charge of the storage location with low levels of training and that are poorly informed, etc. This results in products that have expired, accidental runoff that is not properly cleared up, losses during decanting, empty containers that are not drained correctly with remains of the product inside, etc. All of this comprises a waste flow that needs to be managed appropriately.

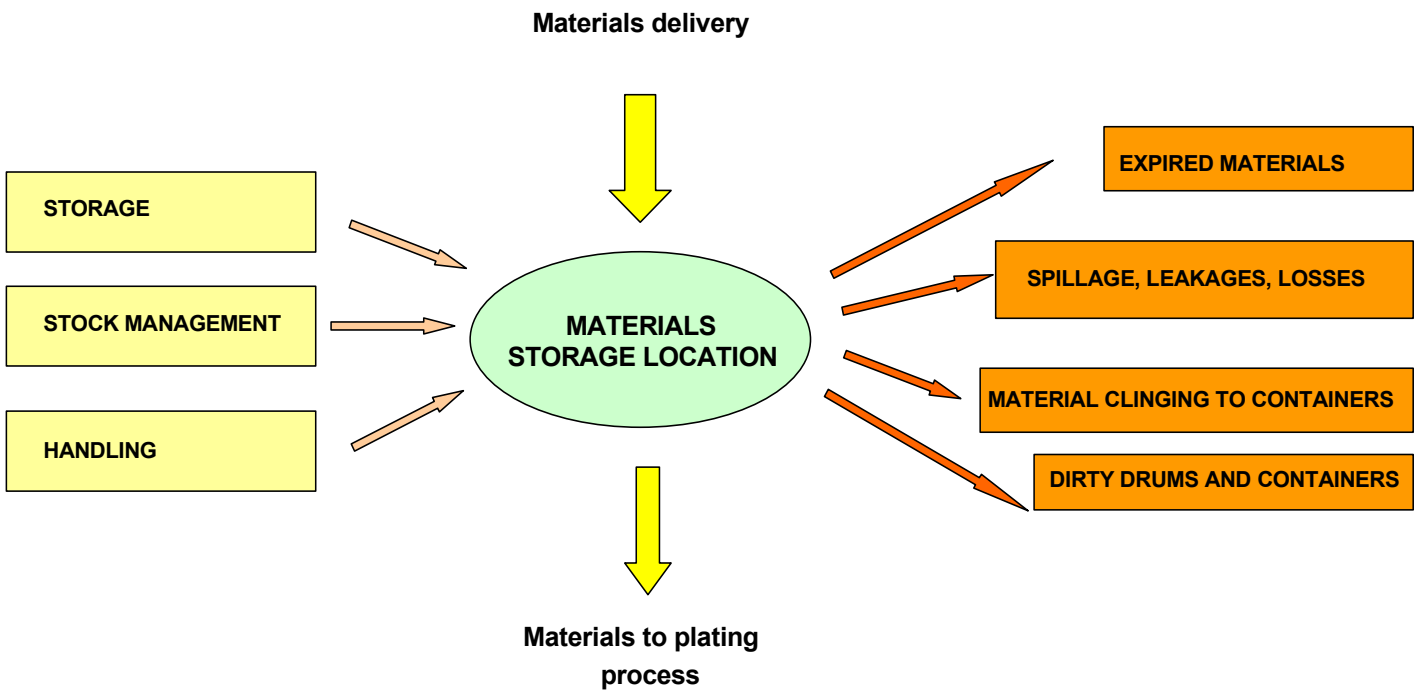
Auxiliary activities

In terms of waste flow generation, the most important auxiliary operations are as follows:

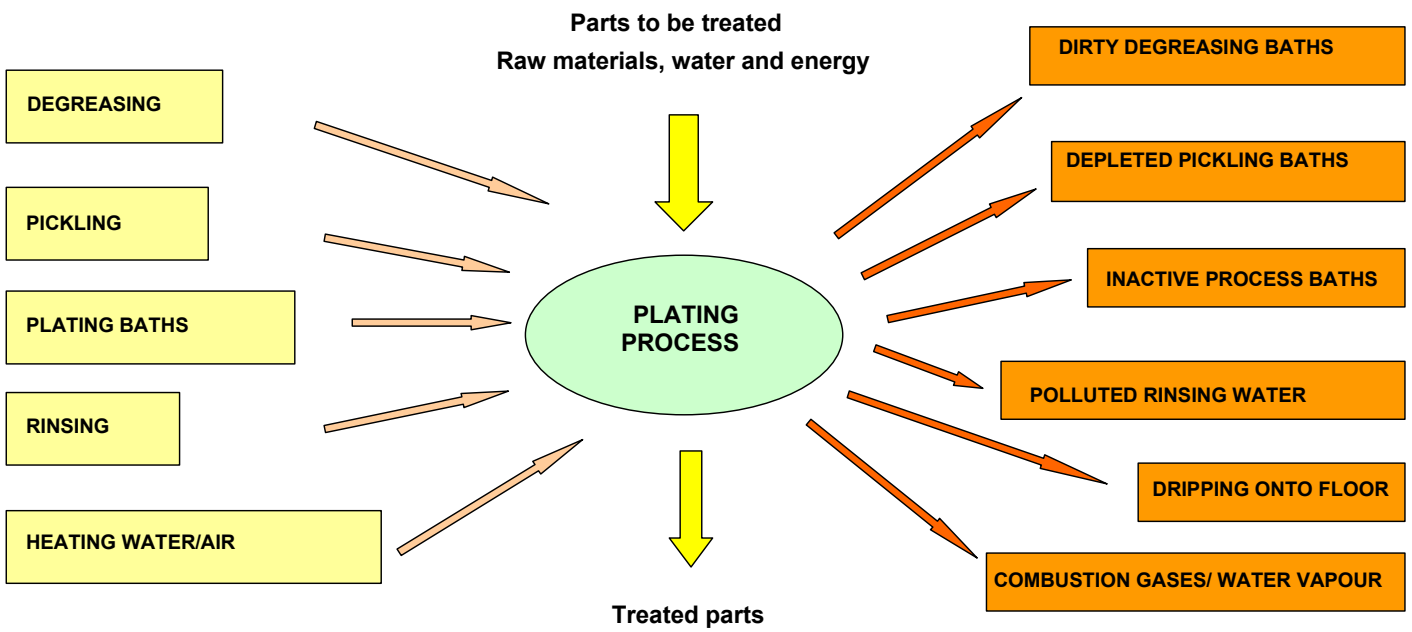
- Waste water treatment: this gives rise to a quantity of sludge in the form of metal hydroxides that, depending on each case, can be very significant (the case of aluminium anodising, for example). In the treatment process as such, the company usually manages most of the waste flows (in liquid form) generated in the plating process, which means diluted rinse water and concentrated solutions or baths that are depleted. Depending on the type of baths used by the company, cyanide and chromium hydroxide may also be present.
- Bath cleaning and maintenance operations: a dirty filtering material, together with the filtered material itself in the form of sludge, sediment or a polluted adsorbent material, are produced here.
- Rack demetalising: this is a highly polluting operation because only solutions containing complexing agents, cyanide or acids that are difficult to treat afterwards (as in the case, for example, of nitric acid) are used; the situation here is complicated because there are high concentrations of metal that have to be removed from the rack.
- Resins from ion exchange and inverse osmosis, etc are another material from waste water treatment equipment that very occasionally produce solid waste that needs to be treated (depleted resins, polluted active carbon, filtering materials such as membranes, etc.).

A series of diagrams are given below with a summary of the information given in this chapter.

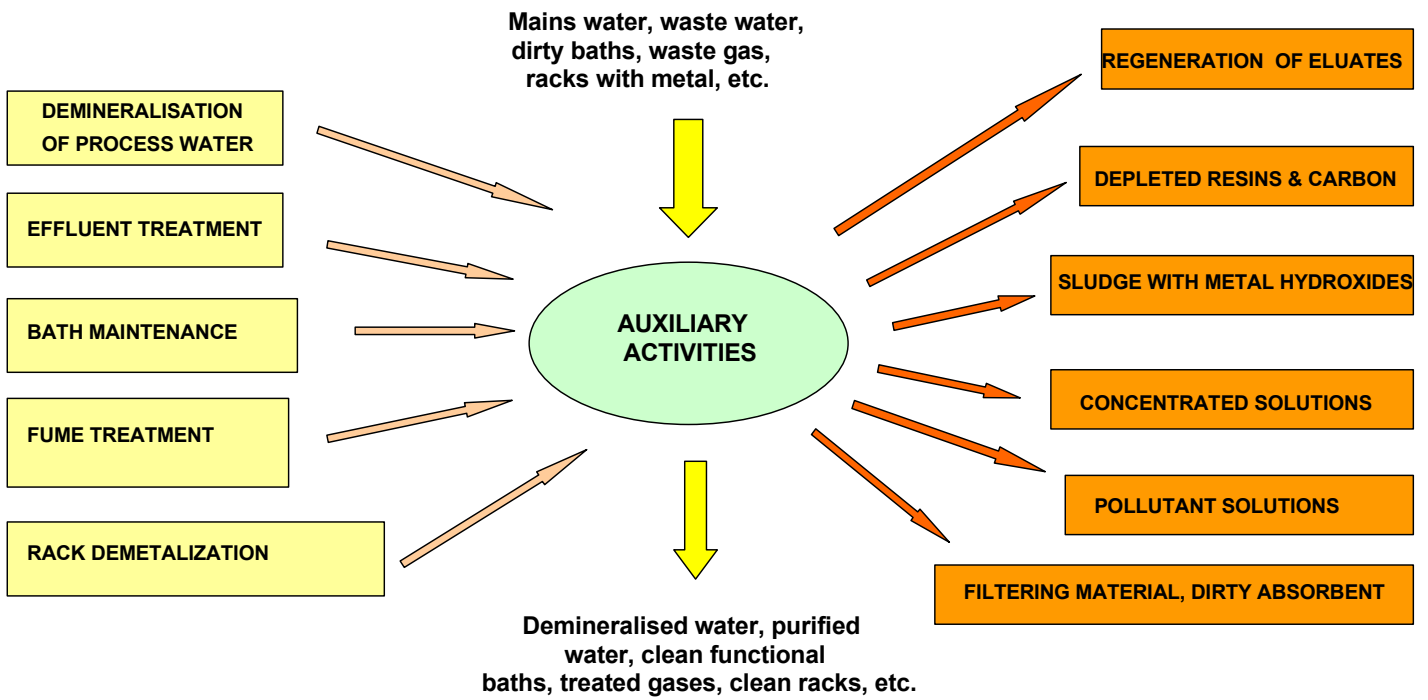
FLOW DIAGRAM. MATERIALS STORAGE LOCATION



FLOW DIAGRAM. ELECTROPLATING PROCESS



FLOW DIAGRAM. AUXILIARY ACTIVITIES



3. POLLUTION PREVENTION ALTERNATIVES

The *prevention at source* of pollution implies above all, avoiding it being generated. Apart from the environmental improvements achieved, the implementation of a pollution prevention policy decreases the cost of environmental management, allows the design of waste flow treatment installations with appropriate dimensions, improves the corporate image, and contributes to an optimal level of protection for people and the environment.

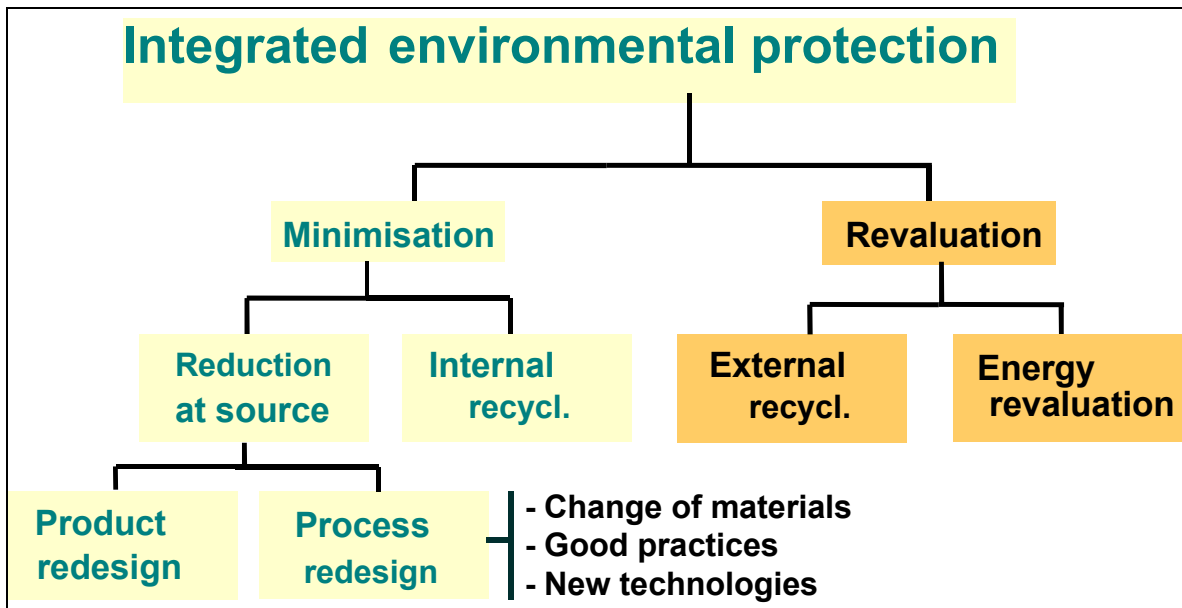
The *minimisation* of waste, wastewater and emissions polluting the atmosphere is a concept that is equivalent to pollution prevention at source and can be defined as the combination of reduction and recycling at source.

The *reduction at source* consists in avoiding or in decreasing the waste flows (or their damaging effect on the environment), before they are generated, by means of modifications in the production process, of the application of good environmental practices, of the change in materials and/or product or using technologies that are more environmentally respectful.

As the second option, once the applicable types of reduction at source have been considered, , we find the *recycling at source*, in other words the reusing of the waste flow that will inevitably have been produced, in the same process, or within the same company that generated it.

An appropriate environmental policy will only take into consideration the procedures at the end of the line and/or in the management of the waste flow, once the company's viable minimisation options have been analysed and/or applied.

The following diagram summarises the concept of minimisation or prevention at source:



Study and knowledge of the electroplating sector bring to light a series of factors that cause the companies concerned to operate badly and with a poor environmental management.

The main objective of this third section is to give a series of alternatives to current practices. These alternatives are geared to a reduction in the production of waste flow and towards efficient management of the waste that is inexorably produced. The object of our study in the following sections is drag-out reduction, replacement of raw materials with others that pollute less, reuse of water, its treatment and good housekeeping practices by operators.

3.1 Pollution reduction at source

3.1.1 Raw material and process material replacement

Raw material replacement is one of the alternatives used in order to reduce the generation of waste flow. In many cases highly-pollutant raw materials are being used in preparation processes for parts or in processing baths. Nevertheless, there are alternatives to these materials, already giving good results based on chemical products that do not attack the environment in the way traditional products have done up to now and that, at the same time, carry out the same function or provide the same results as these. We shall examine the alternative available for each bath.

- Degreasing

The use of different chlorate solvents such as trichloroethane, trichloroethylene, perchloroethylene, etc., is tending to progressively disappear due to the impact that these compounds have on people's health and on the environment.

This has caused the appearance of different alternative products from some companies dedicated to the supply of raw materials.

It is true that, in some cases, the substitute for the chlorate solvent improves on its action since it is more effective in the job of degreasing.

Of all alternative products it is necessary to highlight in the first place **p-cime-based mixtures** since they are perfectly effective degreasing products and at the same time are made up of totally biodegradable surfactant products. These are monocyclic hydrocarbons (1,8 (9) P-Menthadie) with characteristics that make them suitable for numerous applications: aroma and perfume production, composition of solvents and detergents, substitutes for chlorofluorocarbons in some cases. They also substitute 1,1,1 trichloroethane, trichloroethylene, perchloroethylene degreasing detergents for steels and general metals, etc. Their main characteristics are, among others, that they are non-toxic and totally biodegradable and do not alter the ozone layer nor harm the atmosphere. The disadvantages are that they are applied wet, which could prevent their use in some of the later applications; their high cost is also a hindrance.

The difficulty involved with this substitute is that automatic sprinkling equipment is required for product distribution and for the movement of the parts to be degreased so as to enhance the mechanical effect of degreasing.

Recently, using **hydrofluoroethers** (HFEs) with good degreasing qualities can become an option. Furthermore, the product emerges dry. The main characteristics of these products are low toxicity, thermal and chemical stability, low viscosity and surface tension. They are excellent moisteners, penetrate well and have a low water solubility. They are not inflammable and are without burning point. The product, like chlorate solvents, may be acquired along with distillation equipment which allows for the recovery of the greater part of the waste liquid that is generated. The cost of these products is currently rather high in comparison with halogenated solvents. Although the initial investment may be high, their pay-offs make them an economically viable option.

As regards the other large group of degreasing agents, **chemical and electrolytic agents**, it is necessary to highlight the limitation in the use of those containing high levels of phosphates, as well as derivatives of EDTA in order to avoid the formation of soluble complexes between these compounds and metals. The problem lies in the need to free the metal, by its later precipitation, from the complex formed. To achieve this freeing, conditions must arise in which the purifying process is non-viable since, among other conditions, lengthy treatment time is necessary and thus a more than considerable increase in the cost of waste water purification. As a technically viable alternative, we propose the use of **sodium gluconate**, a totally biodegradable compound, compound that makes up a more complex type of lower-strength metallic compound, with which the subsequent precipitation of the metallic compound is not as difficult.

- Pickling

As regards **pickling** it can be said that the normal trend is to use hydrochloric acid. This increases the attack speed on the metal when the concentration of dissolved iron increases. This makes it difficult to control this attack speed. The most common alternative is the **replacement of this acid with sulphuric acid** that enables metal attack to be controlled through monitoring the temperature of the bath.

- Electrolytic Nickel Plating

There does not exist, for the moment, any alternative to the process of electrolytic nickel plating. The only measures that can be introduced are derived from rationalisation of rinsing after the process and from its recovery in the work solution.

- Chromium plating process

As an alternative solution with respect to the existing bibliography **the use of trivalent chromium instead of hexavalent** is being considered since the former is considerably less toxic than the latter.

The problem caused by the use of a trivalent form, instead of a hexavalent one, is that certain dark deposits appear on the surface of the part after the bath, and the required quality of the product is not achieved.

Other options, to be used when it is not possible to substitute the trivalent chrome, could be:

- the use of evaporation techniques that allow for the recovery of more water from the recovery rinses, and therefore return a greater amount of product. Increasing the consecutive number of

recovery rinses, achieves the avoidance or the reduction to the minimum of the wastewaters containing chrome.

- the use of ion-exchange resins, with the subsequent recovery of the runoff in the form of concentrated chromic acid.

- Copper plating bath:

Of all existing possibilities among copper plating baths, the most extensively used, because of its features, continues to be the alkali cyanide bath. It is, however, possible to **replace the cyanide bath with a non-cyanide (alkaline or acid) option in specific circumstances**. Nevertheless, tests for each case should be analysed and tests should be done to see whether the quality of the part is appropriate.

- Brass plating baths

Currently, **there is no viable alternative to the use of cyanide compounds** that make up brass plating baths.

Thus, it will be necessary to apply minimisation measures such as the reduction in the concentration of cyanide compounds in the bath, the incorporation of recovery rinses and consistent correction measures in cyanide oxidation and metal precipitation.

- Silver plating baths

In this case **the same problem is found as in the case of brass plating baths** with cyanide oxidation and subsequent silver precipitation and recovery being the only alternative.

- Gold plating baths

Since it is a high cost metal it can be said that **currently all used solutions are already recovered** and they are involved in the production process whether it be by precipitation or by means of ionic exchange resins.

In this way, gold cyanide and potassium (AuKCN_2) whether it be in an acid or alkali medium dissociates in order to leave a deposit of gold whilst the small quantity of free cyanide resulting from the process automatically oxidises at the anode of the electrolytic bath thus minimising pollution from such a toxic compound.

To obtain the precipitation of the remaining gold from the rinsing baths, separating it from the rest of the cyanide molecule, zinc dust, aluminium or sodium dithionate are generally used. These break the gold cyanide molecule and make the gold precipitate. The little cyanide that remains free may oxidise later without difficulty.

- Zinc coating process

As we have seen earlier, zinc is deposited in three ways:

- by acid,
- by alkaline cyanide,
- by alkaline without cyanide.

Evidently, the three processes involve the formation of different compounds depending on the way used. Thus, it is interesting to promote those processes that, on one hand produce fewer compounds and fewer toxins and, on the other, have good subsequent treatment.

Following these criteria, the current state of the art is in favour of replacing the cyanide processes with **acid or alkaline processes without cyanides** (due to the toxicity of cyanide and its complexes). In this way, these alternatives, which are technologically very effective, have already been on the market for several years.

The two other technically viable alternatives to be considered are therefore those of **non-cyanide acid and alkali zinc coating**. Below is a description of their possibilities with regard to pollution prevention at source.

In the **acid zinc coating process**, the main pollutants produced are chlorides, boric acid and ammonia.

Of these, ammonia is a compound that can be eliminated in the formulation of this process: This is done by **replacing ammonium chloride with potassium chloride** by which process pollution can be substantially reduced.

As regards substituting the acid zinc coating process for another alternative, this is not possible today. Furthermore, a cathode yield of nearly 100% converts it into an essential process in treating tempered steel and synthesised material, since these materials are very difficult to treat with processes with a low

cathode yield because of the high production of hydrogen that is deposited on the material thus making the deposit of zinc impossible.

The other process, that of **non-cyanide alkali zinc coating**, has meant a great technological breakthrough. Thanks to its formulation based on zinc oxide and sodium hydroxide, it can be used alternatively in many industries while decreasing considerably the degree of pollution (compared with cyanide).

Furthermore, later treatment of waste waters is a lot simpler and faster than with the use of cyanide since it can be purified by a simple adjustment of the pH to 9.2-9.5, by using dilute sulphuric acid or calcium hydroxide.

- Zinc passivation

The currently used method for zinc passivation involves some of these acid compounds: chromic, hydrochloric, sulphuric, nitric, acetic, phosphoric, and formic. These compounds produce different chrome finishes on the surface of zinc.

Most passivation processes use chromium VI as a basic component.

These solutions should be changed frequently and, as well as the afore-mentioned pollutants, the following are also noteworthy: Zn, Fe and Cr III, that come from the attack on the zinc-coated parts and the oxide-reduction reaction CrVI to CrIII.

Once again we find ourselves with an especially pollutant element as is Cr VI. Unfortunately, despite the efforts being made to replace it, there is no element that can effectively do so, from the point of view of the attractive appearance of the product and not to the properties that it confers to the surface.⁵

⁵ It should be stated that a few years ago some European countries began to **use Cr III** as an alternative, above all for the products where the aesthetic quality is not excessively important.

Furthermore, the future limitation of the use of Cr VI in passivation coating in the European automobile sector will favour research into alternatives among which the use of Cr III will be dominant.

- Aluminium anodic oxidation

With regard to this process, we will distinguish the two stages that make it up: surface preparation and true anodising.

Among the main pollutants found are alkalis, phosphates, surfactants, aluminium, oils and greases.

In the degreasing and burnishing process of aluminium, a large amount of the described pollutants are produced since it is currently difficult to propose a less pollutant alternative process. A possible alternative could be to recycle the degreasing baths, after having treated them with equipment for separating and concentrating oils.

During anodising part of the aluminium is dissolved in the processing bath. There comes a point when its concentration is so high that it decreases bath yield considerably and as a result this must be diluted and concentrated again with fresh sulphuric acid. This causes two types of main pollutants: sulphuric acid and aluminium sulphate.

The only totally tried and tested technique to be applied today is the **use of ion exchange resins or ion delay** that allows for the separation of the aluminium from the sulphuric acid that may return to the work tank.

- Electropolishing

Stainless steel electropolishing processes are based on the use of concentrated mineral acids. Currently there do not exist alternative processes that pollute less. Likewise, neither the compound-type or volume-type waste flows generated represent a difficult problem to solve.

Measures to be proposed are based on an improvement of purifying systems by neutralising the effluents generated with calcium hydroxide. This treatment will allow for the reduction in both heavy metal pollution (iron, chrome, nickel, etc.) and the presence of undesired anions (sulphates and phosphates).

- Cadmium plating

In many countries the cadmium plating process has been replacement for health reasons since its carcinogenic effects have been demonstrated. The alternatives have been the use of tin and silver

plating that provide the necessary conductivity and ability to solder. Zinc alloy baths are also being used to achieve an anticorrosive effect.

Other alternatives from outside the electroplating bath sector are thermal treatments or even vacuum sputtering that require, however, special facilities.

3.1.2 Good housekeeping practices

3.1.2.1 Lengthening bath life

The industrial surface treatment sector should reflect upon the processing baths that it has and, in accordance with the technical evolution of manufacturers, decide whether or not those being used are the most suitable for their needs. To be considered in this analysis are:

- gamma technology (succession of operations to be carried out),
- the type of bath to be used.

Once the bath type has been decided, taking into account the environmental problems that this may imply, the following key aspects in bath management have to be considered:

- Choose the lowest possible salt concentrations, compatible with the intended objectives as regards finishes.
- Product salt adjustments have to be made with objective criteria according to the electrical consumption of the process (the more amps, the greater the salt consumption) and according to periodic bath concentration analysis. Of the analyses to be carried out, the following are fundamental:
 - free cyanides, carbonates;
 - total and free acidity;
 - total and free alkalinity;
 - pH, chlorides, etc.;
 - specific metals: Ni, Cu, Cr⁶⁺...
- A special control form is recommended for each bath where the following information is stated:
 - bath constituent formula;
 - analysis results;

- adjustments made;
 - bath maintenance operations.
- As regards bath maintenance, the following can be noted as generic:
- filtration on active carbon
 - oxidation with hydrogen peroxide
 - precipitation of impurities and subsequent filtration
 - regular elimination of parts and tools that fall into the processing bath
 - elimination of impurities on inert cathodes (stainless steel for example), especially for undesirable metals that pollute the bath.
 - withdrawal of the anodes when the bath is not in use
- Section 3.2.1. of this report details how to lengthen the life of the two processing baths that should be emptied more frequently and made up again: degreasing and pickling.

3.1.2.2 Drag-out reduction

Drag-out is the amount of liquid that is extracted involuntarily from a bath with the performance of part extraction between two stages of any electroplating process. It is normally measured in litres per hour (l/h) although it can also be measured in accordance with production (l/dm², for example).

This is the most significant source of raw material loss from the processing baths and of rinsing water pollution⁶. It can be stated that the volume of sludge generated is directly proportional to the level of rinsing water contamination, which is the drag-out level that takes place.

Despite the afore-mentioned, it must be stated that drag-out does not only have negative implications for the company (rinsing water consumption, loss of raw materials and generation of pollutants); it also has a beneficial aspect: drag-out, as well as carrying away raw materials from the bath also takes out its possible pollutants causing a diluting effect. In fact, a typical case is the presence of impurities on the anodes that end up in the bath, polluting it. Drag-out allows the concentration of these impurities to be maintained at a level that does not affect the life and performance of the bath.

Having arrived at this point, it is essential to go back and relate the concept of drag-out with the “need to rinse” or the “rinse ratio” or “rinsing criteria”, understanding as such the *number of times that the liquid dragged out with the parts must be diluted in the rinsing process so that the final*

quality of the process is not affected. This concept gives us a quantitative measure of the rinsing process efficiency. This parameter is inversely related to the concept of drag-out, according to the formula:

$$C_0 / C_r = Q / q$$

Where:

C₀ = initial bath concentration

C_r = average rinsing water bath concentration

q = drag-out (l/h)

Q = rinsing water volume (l/h)

Taking into account the above formula, it is easy to determine how drag-out may be estimated. The industry may determine it empirically by applying the following formula derived from the previous one:

$$q = C_r / C_0 \cdot I / t$$

Where in this case:

C₀ and **C_r** are the same factors as in the previous case

I: Volume of rinsing tank

t: time in hours

Thus, the industry should carry out analyses to determine some type of chemical that may be used in the latter formula and in this way be able to determine the drag-out levels caused by the company activity.

From all this, one can deduce that these two ideas that we have dealt with up to now, drag-out and rinsing criteria, are of key importance and are unfortunately unknown or not specified by the vast majority of companies in the sector. Since the drag-out caused by the operation process is not known and neither is the necessary rinsing quality specified, we find ourselves with rinsing volumes that are far higher than necessary (with all that implies, as previously stated) or, in a few cases, insufficient rinsing volumes and consequent pollution between baths and a defective final finish to parts.

⁶ Drag-out is, in fact, considered to be the cause of the greater part of waste generation because of the necessary water treatment.

The importance of establishing *rinsing criteria* or *dilution ratio (Dr)* is therefore clear in order to offer the sector real minimisation alternatives.

Average standard drag-out values are:

- rack: 150 ml/m² processing
- drum: 1-3 l/drum

Knowledge of the conditional factors that contribute to drag-out is of key importance if it is to be reduced. The main factors are the following:

1. size and shape of the parts
2. viscosity and chemical concentration of the bath
3. bath surface tension
4. bath temperature and,
5. work method

With all these factors, we can establish that drag-out is directly proportional to the surface area of the part, viscosity, concentration and bath surface tension and inversely proportional to temperature and bath density.

Once factors favouring drag-out are determined, it is easier to deal with the fundamental idea of *drag-out minimisation*.

There are different techniques to reduce it significantly and efficiently. Some of these systems do not represent any additional cost to the company since they only involve working in different conditions; the investment required is usually small anyway and otherwise they reduce drag-out considerably⁷. In certain cases, other factors may make it difficult to introduce the measure; factors that condition the process and lack of space for example.

We have tried to make the alternatives we have proposed below as exhaustive as possible and they are explained in some detail in order to establish their importance clearly; they are ordered by the level of investment required beginning with the lowest amount.

⁷ And thus great reductions in the company's costs.

- Keep the bath at the lowest possible concentration to reduce its viscosity.

In general, the bath supplier recommends concentrations higher than those really necessary in order to ensure the quality of the finished product and obtain maximum yield.

It is very important for the company to establish empirically the minimum possible work concentration for its baths, based on, for example, a reduction by means of the addition of a more diluted bath until it is detected that this no longer operates suitably. At this point, the company may identify the processing bath's optimum concentration that gives suitable quality in the finished product.

- Work at the maximum possible bath temperature, also producing a decrease in its viscosity and aiding liquid drainage. This measure also increases the bath's evaporation range that allows for the introduction of sealed recovery rinses that contribute especially to drag-out reduction as we will see later on.

However, it is necessary to make sure that the wetting liquid that emerges with the part is not allowed to dry on its surface and form deposits that affect the quality of the process.

- Addition of wetting agents, in order to reduce the surface tension of the bath. This measure may reduce drag-out by up to 50%.

There are industrialists, however, that prefer not to use these products because they form a scum on the bath and dirty the part when it is taken out. In this case, it is necessary to indicate that their use must be evaluated according to the bath's own characteristics and the desired finish.

- Incorporation of blowing systems, acting on the bath and easing the drainage of liquid trapped by the parts.

- Introduction of vibration systems, also with the rack on the bath giving rise to greater liquid drainage.

- Use of spray rinsing systems, on the processing bath itself and especially suitable for those systems working with heat. It is necessary to add the mechanical effect of the spray to the effect of rinsing with water.

Moreover, on carrying out the first rinse over the bath we return most of the liquid dragged-out by the part, (up to 50%). The only conditioning factor presented by the system, as has been stated, is that the bath operates at a certain temperature (>40°C) and so the evaporation that takes place can be compensated by sprinkler rinsing of the bath itself.

- Incorporation of joint-covers between the bath tank and that of the subsequent rinse. If this element is suitably angled with the bath all the dripping from the parts and between tanks that takes place can be returned by this.

- Introduction of liquid suction systems in the drums: this is the application of a small negative pressure on the drum to recover the liquid contained in it.

This measure, not very widespread, allows a reduction of about 30% of loss through drag-out.

- Choice of racks: in some cases the racks may represent a surface area greater than that of the parts being treated. It is therefore necessary to carry out a detailed study of the shape and structure of these racks so as to obtain the greatest possible surface area.

Plasticised racks have a hydrophobic surface anyway and so drag-out much less solution than metallic racks.

- Sealed recovery rinses: these are very likely one of the most efficient methods of reducing drag-out into rinsing waters, at the same time enabling raw materials to be recovered in the original bath.

Furthermore, they indirectly allow for the reduction in water renewal flow for the subsequent rinse: if a sealed rinse has a bath concentration of 20%, the subsequent bath flow can be divided by 5. The method consists in placing one or more sealed water tanks between the processing bath and subsequent rinses.

Water from this rinse should preferably be distilled, since water from the mains that contains salts could end up polluting the bath.

Since it is a sealed rinse, another interesting recommendation that is often lacking in companies, is to agitate the rinse by air - or mechanically - so as to increase its efficiency.

The rinse gets concentrated with salts from the processing bath and, at a certain concentration, at 20% of the bath's on average, part of this liquid is withdrawn and it is introduced again in the

processing bath from which the salts came. This volume is determined by the range of evaporation from the bath. In this way, just as with the spray, the bath must operate at a certain temperature, in this case also higher than 40°C so that the system may be applied.

Some companies impede the use of sealed recovery baths for fear of polluting the bath⁸. In some specific processing baths it also may occur that some of the components are destabilised when they are in diluted form, changing the chemical composition of the initial bath; this is the case of chemical nickel and copper baths. The sealed rinse may also be polluted because an operator has rinsed parts from another processing bath in it accidentally (cross-bath pollution). In this case, if there is a risk of pollution from impurities or metals, there is a chance to “purify” the sealed rinse before returning it to the bath by using, for example, ion exchange resins.

In spite of everything, the system is so important that once a specific case has been studied, it should be introduced whenever possible.

A very interesting variant on the system, with clear drag-out reduction repercussions, is the chance of combining 2 or even 3 “cascade” sealed rinses; i.e. connected with each other. This arrangement is converted into a system of rinse flow cascades that has a sufficiently small volume to be directly and continuously recycled and taken to the processing bath. The system allows for maximum raw material recovery and thus a reduction in drag-out. If a sealed bath can achieve a drag-out reduction of 70%, 2 consecutive recoveries may reach up to a 90% reduction in drag-out loss.

- ECO Rinse: this, like the previous case, is a sealed rinse in which the parts are submerged before and after the treatment bath. Unlike the recovery rinse that slowly empties to compensate for the loss by evaporation from the bath, in the ECO rinse this never empties. Its concentration stabilises 50% of the bath. Drag-out concentration is thus half of that at the beginning.

It is used in baths working at low temperatures (<40°C). It is not recommended for surface preparation baths (degreasing and pickling) or finishes (passivation) since contact between the part and a relatively concentrated solution (even though it is only 50%) may cause reactions harmful to the quality of the following treatment.

In this case it is estimated that the drag-out reduction is lower than the recovery rinse and is between 30 to 50%. In spite of this, the ECO rinse has the same environmental advantages as the sealed recovery rinse.

⁸ Before it was mentioned that drag-out has a positive factor in that it dilutes the possible pollution of the bath caused by external agents (impurities from the anodes, metal emission from the surface of the parts being treated, etc.).

Finally, it should be stated that in both the cases of the recovery rinse and the ECO rinse it is necessary to respect the principles of good rinsing:

1. Relatively turbulent movement between part and water.
2. Adequate contact time between part and water.
3. Presence of enough water during contact time.

- Position of parts on the rack: they should be placed in such a way as to ease emptying when coming out of the bath and not allowing zones where liquid is trapped to form. Thus it is necessary to state that parts should preferably be placed flat since the thickness of the liquid film that is dragged-out on extracting the parts will be reduced.

Whenever possible, placing one part on another should be avoided so as to stop the drainage of an upper part falling on a lower one. In this respect, the design of the chosen rack for the work in question is very important.

It is also important for the operator to lean the rack appropriately on extraction from the bath in order to aid emptying.

The design of the drum is also fundamental in easing drainage of the liquid dragged out from the bath: with the largest possible holes that do not reach the edges in the case of solid angle drums (since liquid would be trapped in the drum ribs).

- Velocity of extraction of parts from the bath, that must be slow: the faster the part is taken out, the thicker the film of wetting liquid.

Plant supervisors should train and supervise operators in this.

- Drainage time: this should be the maximum possible whilst preventing the liquid from drying on the surface of the parts or the possibility of “passivation” on the surface.

To ease this task, rack-hanging bars are useful (very practical especially when there is considerable weight to be supported) in the case of manual processing lines.

It has been proved that drainage time does not present these problems in pre-treatment baths (degreasing and pickling); in these cases the operator can operate the rack again once this has released all drag-out.

For drums, as well as drainage time it is also important to make them turn 90°, and to maintain them well so as to prevent orifice closure. The racks must also be kept in good condition because if they are not, liquid may remain inside cracks and holes.

Average standard drainage time values are:

- for racks: 10 sec.
- for drums: 20 sec.

To end a section that is so important in the possibilities of preventing pollution generated in surface treatment at source it can be concluded that:

1. Drag-out is the main source of waste flow generation in the electroplating bath sector, involving a loss of raw materials and water at the same time. It should thus be the object of detailed analysis by each specific company and the main focus upon which the company should base its efforts to reduce the waste flow generated.
2. The majority of companies do not know the average drag-out they are producing as well as the necessary rinsing criteria for their specific case.
3. The majority of companies do not know the factors that contribute to drag-out minimisation either and so take no action in this respect.
4. There are a good number of alternatives and options to minimise drag-out, the majority of which do not involve any investment cost for the company or it is low enough for the pay-back period to be very short, considering the great reduction in the cost of purchasing raw materials, water consumption and waste management.

3.1.2.3 Rinsing and washing improvements

With all the ideas described in section 2.3. corresponding to rinse systems we are able to analyse different methods to reduce water consumption in the electroplating plant.

The industrialist must therefore be able to define the optimum structure for his rinses taking the main selection parameters into account.

The means within the reach of the electroplating industry to reduce water consumption are the following:

- Rinse rationalisation: choice of rinse system.

a) Simple rinse.

This is one of the worst rinse systems that the company can have although it is almost the most widespread in the sector

It consists, as we have seen, of having a single rinse tank of running water after the bath treatment. In this case the volume of rinsing water for specific dilution ratio (Dr) is:

$$Q = q Dr$$

It can be generally stated that the flow (Q) of rinse necessary to ensure a satisfactory dilution ratio is very high compared to other possibilities.

b) Double (and multiple) parallel rinse.

We find it in the situation in which each rinse tank after the bath (2 or more) is fed separately (in parallel). In this case, the mathematical expression that determines rinse flow is given by the following:

$$Q = Q_1 + Q_2 + \dots + Q_n = n q \sqrt[n]{Dr}$$

where n = number of rinse tanks.

It is not a widely used system since, for the same number of rinse tanks, with the following system a much greater rinse water flow reduction is obtained for the same dilution ratio.

c) Double (and multiple) series rinse (cascade).

This is one of the best available rinse systems. The system consists in introducing clean running water in the last position of the rinse system. It passes by a cascade to the first tank. Parts to be rinsed move in the opposite direction, i.e. against the current. Unlike the previous case there is only feeding with clean water (to the last tank).

In this case, the necessary water volume is given by:

$$Q = q \sqrt[n]{Dr}$$

in which n also corresponds to the number of rinse tanks that make up the system.

In this case, the saving obtained in water consumption as a result of the increase in the number of tanks (n) is important. Given in the following table is a specific example of water consumption with regard to the number of tanks in a cascade. The considerable reduction in flow as the number of rinses increases can be appreciated:

Rinse system	Rinse flow Q (l/h)
Simple rinse	10,000
Double cascade rinse	220
Triple cascade rinse	65

Table 6

Supposing:

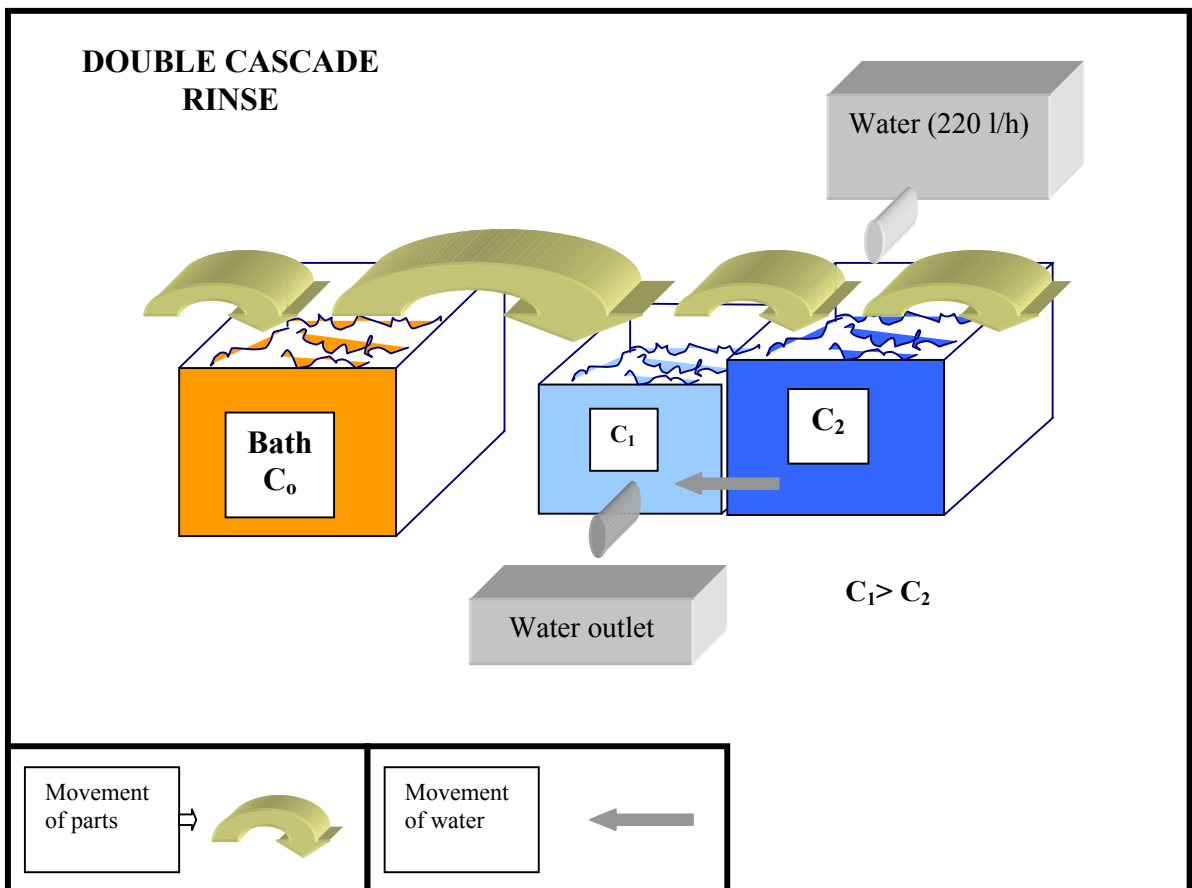
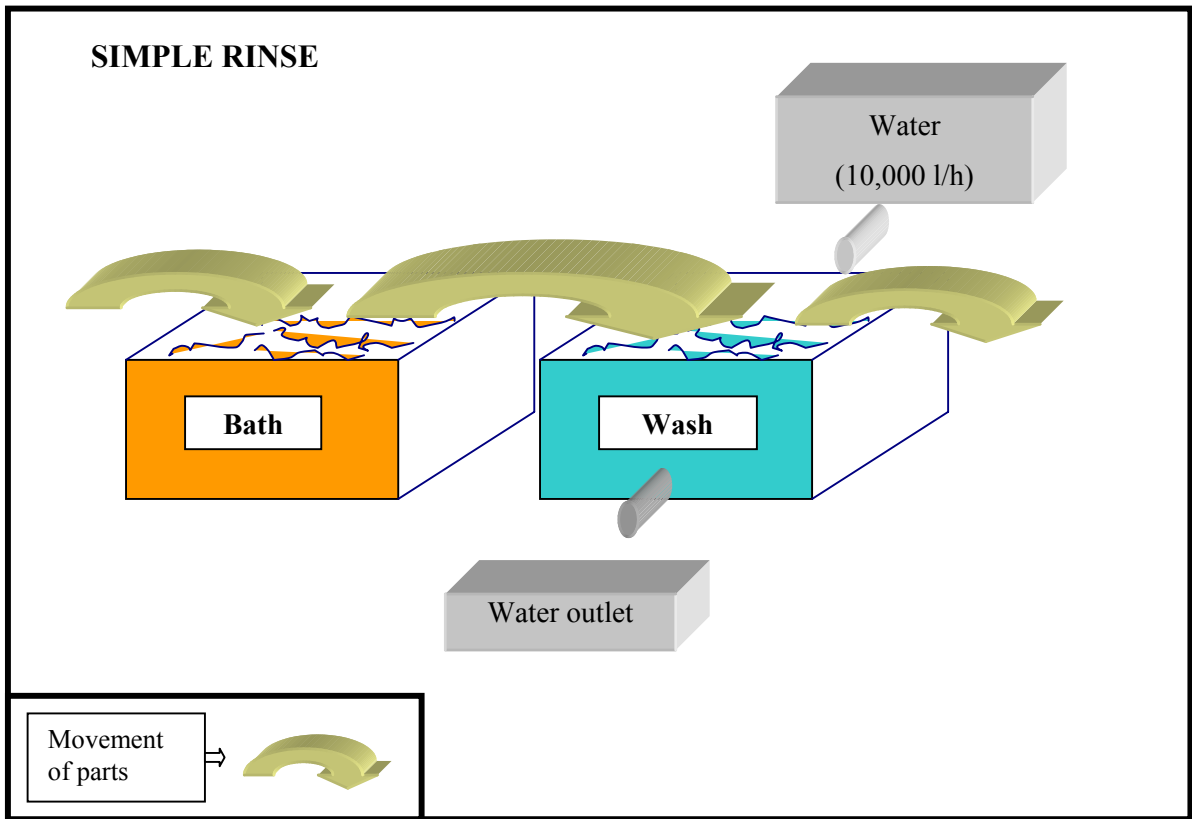
$$\text{Drag-out (q)} = 5 \text{ l/h}$$

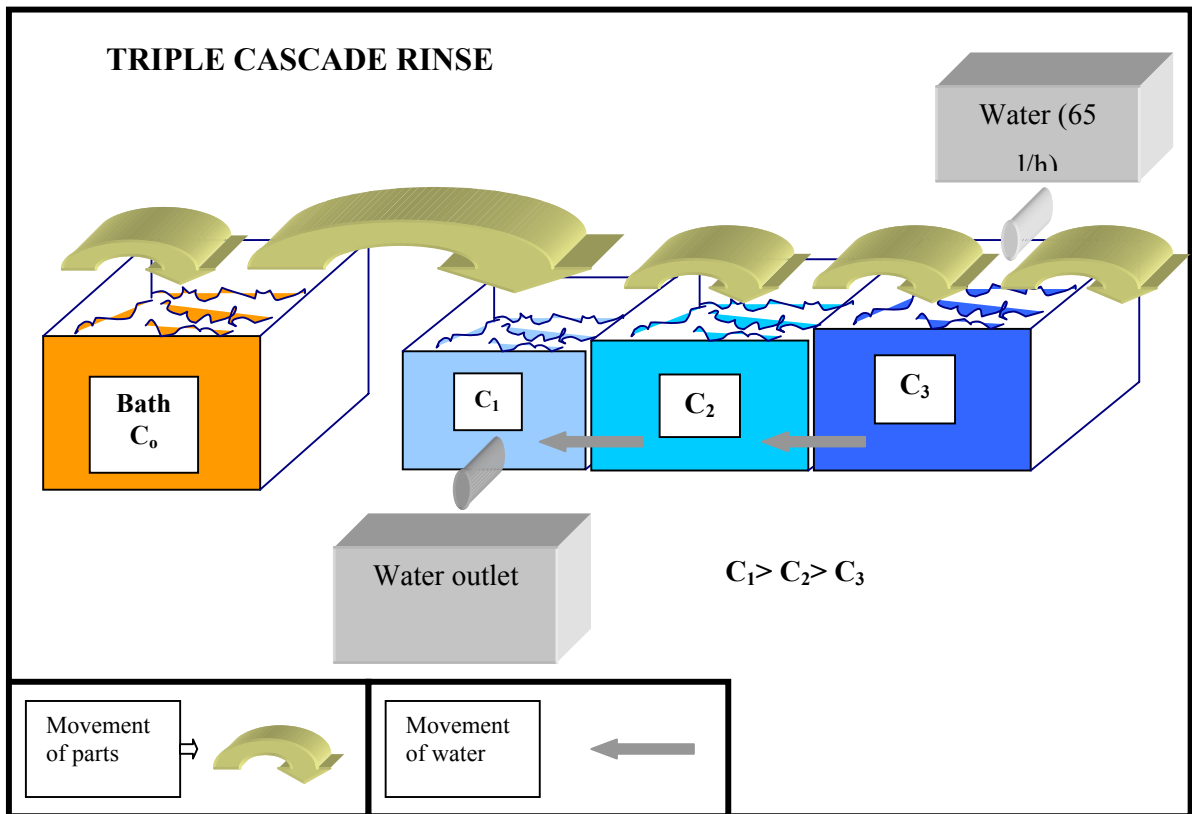
$$\text{Dilution ratio (Dr)} = 2000$$

This example demonstrates the importance of rinse rationalisation allowing for:

1. the consumption of less water for the same dilution ratio,
2. the consequent reduction in the costs of water consumption and purification,
3. an increase in rinse quality without having to increase water consumption.

Therefore, the graphic form would be the following:





d) Sealed rinse.

This is a non-renewal rinse that enables much of the drag-out from the processing bath to be retained. Thus, as well as reducing the subsequent rinse needs – and water consumption – it makes the recovery of bath salts possible.

Although it is sealed, in order to prevent progressive salt concentration from the processing bath, it has to be renewed periodically. If the preceding bath is hot – more than 50°C – this renewal will reintroduce the loss of water through evaporation and of water and salts through drag-out.

Sealed rinse concentration values of between 10-20% of the bath are perfectly acceptable for this double function.

A very effective system is to maintain 2 or more sealed rinses connected by cascade, redirecting recovered liquid back to the bath from which it came. In this way, maximum product can be recovered simply. In this case, it must be ensured that the volume of water entry at the last tank position is the same as the volume of evaporation from the processing bath.

There will be greater product recovery the higher the evaporation from the bath and the more sealed rinses there are connected in cascade.

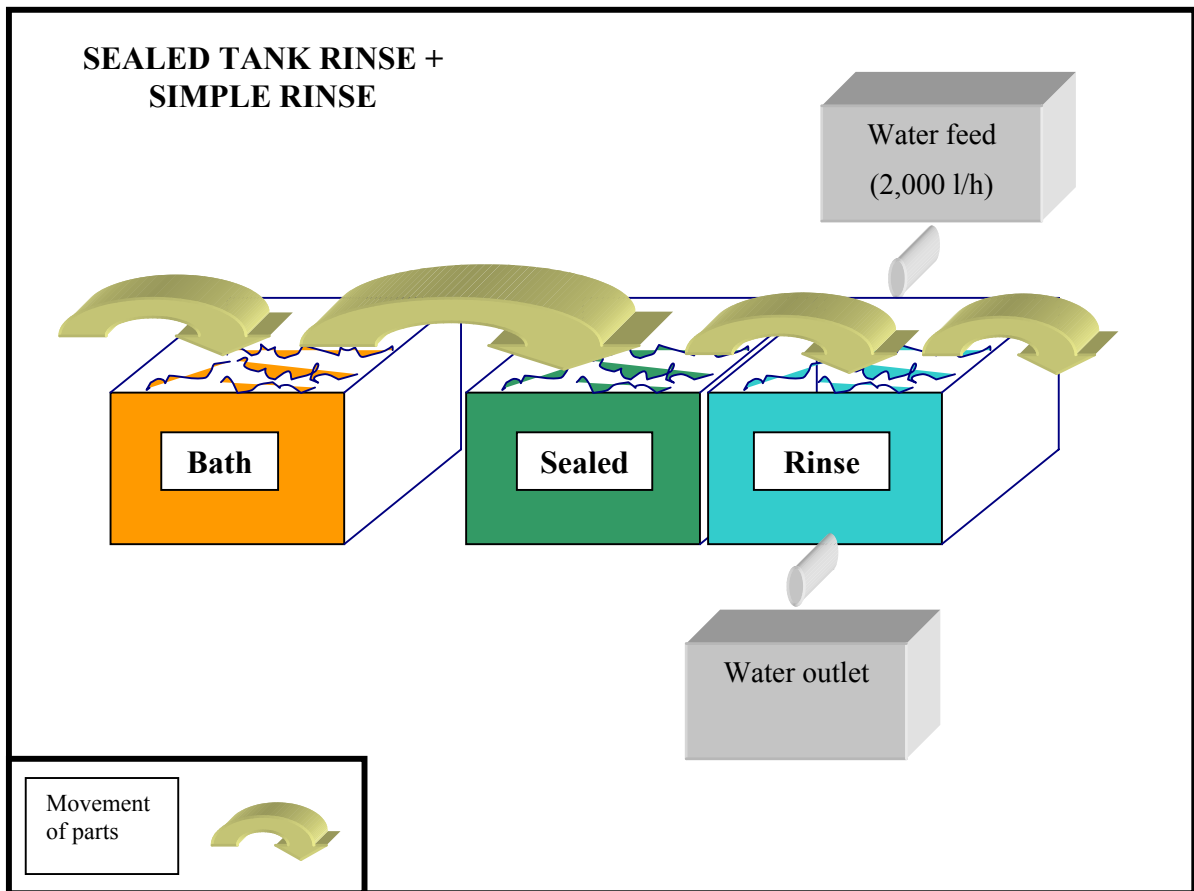
The following table gives a comparative example with this special case:

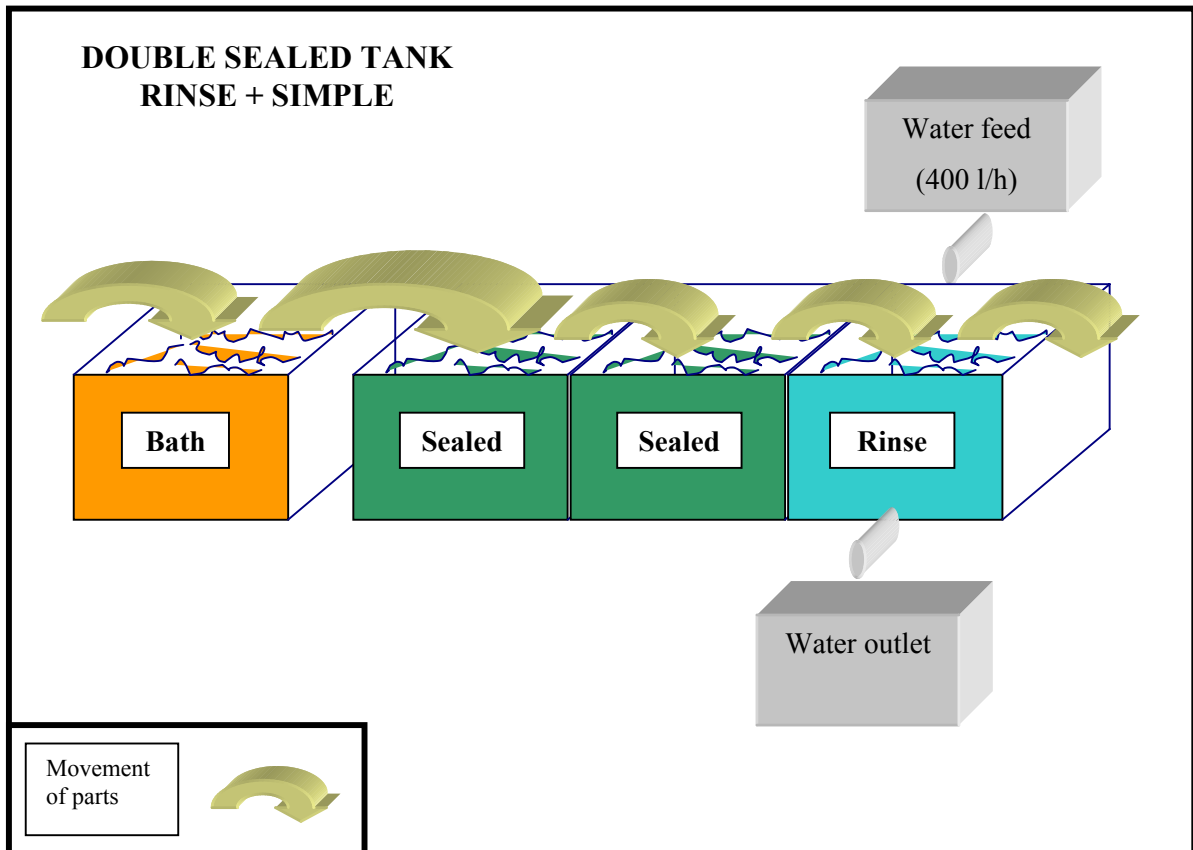
Rinse system	Rinse volume Q (l/h)
Simple rinse	10,000
Sealed rinse + simple rinse	2,000
Double sealed rinse + simple	400

Table 7

Supposing:

drag-out (q) = 10 l/h
 dilution ratio (Dr) = 1000





e) ECO Wash.

The ECO rinse is also a sealed rinse in which the parts are submerged before and after the treatment bath. It is never, not even partially, emptied and its concentration is established at half that of the processing bath. Thus, half the initial drag-out concentration is achieved. This neither implies a tank volume variation since it is normally applied cold or not very hot baths - 40°C-.

In spite of these advantages, its application in preparation baths (degreasing and pickling) or final baths (passivation) is not recommended, or in chemical processing baths (chemical copper or nickel) because, as the concentration of this rinse is half that of the bath, reactions with the surface of the part may occur which could harm subsequent treatment.

ECO rinses allow for:

- recovery of raw materials ,
- limitation of drag-out –in theory between 30 and 50%–
- thus, a reduction in subsequent rinse water consumption.

f) Rinse by sprinkling.

This consists in projecting a fine mist of water directly onto the parts that come out of the processing bath either directly over the bath, – if working at heat -, over an empty tank or even over the subsequent rinse.

The system has the following advantages:

1. Reduction in rinse water consumption. A sprinkler rinse is like a cascade rinse.
2. Improvement in rinse quality as a result of the hydro-mechanical effect of the water drops when they fall against the surface of the part to be rinsed.
3. Chance to recover salts in the case of baths at temperature by performing a first rinse over the processing tank

Sprinkler cleaning, as we see, has important advantages as regards efficiency and water economy.

Nevertheless, sprinkler rinsing presents some problems to be taken into account:

- Complicated installation and considerable maintenance.
- Need for quality water.
- Danger of aerosol formation that could affect work safety.

To conclude this point, the parameters that the electroplating industry must consider at the same time as defining its rinse system are listed:

- Desired rinse quality for each position: determination of dilution ratio (Dr);
- water availability and inlet volumes (Q);
- bath concentrations and their composition;
- estimated drag-out volume (q);
- capacity to redirect drag-out to baths;
- available workshop space;
- plant operating conditioning factors;
- compliance with dumping limits.

- Other methods to reduce water consumption.

a) Reduction of excessive consumption.

On certain occasions it is observed that many electroplating workshops have an extraordinarily high water consumption that cannot be justified with the optimum rinse needs. Among the main reasons for this excessive consumption the following can be stated:

- unnecessary water feed in rinse positions, without production, for example;
- rinse excessive in certain positions above the dilution ratio;
- excessive rinsing of tanks, cans, facilities and floors, etc.;
- diverse losses: badly turned off taps, leaks, etc.;

The scale of this consumption may be, in some cases, up to 40-50% of total company water consumption.

As minimisation alternatives, the following can be applied:

- fitting electro-valves that shut off water supply if there is no processing, either by water conductivity or by temporisers;
- clean facilities and equipment with pressurised means, reuse of second-rinse water for first rinses, etc.;
- correct facility maintenance, control and supervision, training of personnel, etc.

b) Improvement in rinse quality.

Once the rinse structure has been chosen, rinse quality can still be significantly improved. For example:

- by reducing drag-out volume and concentration;
- by heating certain rinses;
- by introducing rinse agitation systems;
- by using very high quality water for critical rinses and some final rinses.

In fact, at the same time as improving rinse efficiency, three strategies that can be used should be taken into account:

- Controlling contact time between part and rinse system. It is easy to demonstrate that this time is normally lower than is really necessary.
- Bringing about a slight turbulence (through agitation) in the rinse water to produce a more efficient rinse.
- Achieving sufficient water volume during the time of contact between part and rinse system.

The combination of these three strategies increases rinse operation efficiency considerably and contributes to a decrease in the necessary water quantity.

c) Reuse of certain waters.

Another possibility, seldom used in industry, is reusing the waters from certain rinses, for another rinse position, compatible with the first one, for example. It is possible to reduce water consumption at the two rinse positions by half with this simple measure. It is necessary, however, to ensure compatibility between baths.

The following are given as examples:

- a second rinse after degreasing can be reused for a rinse after acid or alkali pickling or vice versa;
- a rinse after activation (passivation or neutralisation) can be used as a rinse after pre-treatment;
- a rinse after zinc chromic passivation can be reused for a rinse after chromium plating (except in the final rinse);
- if the waste water purification process is correct, purified water can often be reused for different pre-treatment rinses (its conductivity must be watched however to avoid excess salt concentration). This water may also be reused for connected activities: washing floors and facilities, etc.;
- reuse of bath cooling water for rinses.

As a general precaution, it is important to state that before taking a decision to reuse certain water types it is necessary to examine the conditioning factors that determine their use.

3.1.2.4 Application of good housekeeping practices

Some good housekeeping practice recommendations have already been mentioned when the improvements to reduce water consumption or minimise drag-out were being suggested. The recommendations described here are more generic and affect other company activities. Good housekeeping practices are of an integral type, since they act upon different waste flows at the same time.

In general, they are measures without any economic cost (at least direct), or they involve a small cost and have a very favourable repercussion on the reduction of raw materials consumption and waste flow generation and they greatly improve overall control and management greatly in certain areas of the company.

Measures of good housekeeping practices in the company are defined and organised according to their field of application into:

- Material and waste storage

Deficient waste storage is a potential source of waste production such as the generation of products past their best-before date and a high risk of material spillage, etc. and at the same time constitutes a danger and risk to the workers themselves.

All the processes developed by the company include the storage of raw materials, products, by-products and waste and their transfer from one area of the factory to another. Correct storage therefore presents very great minimisation possibilities.

The following are recommended among the main generic proposals:

- Carry out a regulatory control of the state of dirtiness (grease, dust, etc.) of the parts received to be treated by electrolysis so as to ensure that they arrive in as clean a state as possible.
- Have separate and suitable storage areas for raw materials, products, by-products and waste. These areas should be protected from the elements – light, rain, heat, etc. – to avoid deterioration in the packaging or in the material itself and there should be a waterproof concrete floor and a waste water collection system separate from the general system. The area in question should be suitably sign-posted and lit.
- Maintain the established order in the warehouse and the distance between materials in order to provide for their accessibility and inspection. It is also necessary to maintain distances between incompatible chemical products. The different containers should be organised according to hazardousness and frequency of use, easing their loading and unloading. All materials should be

suitably labelled with descriptions of their characteristics and special handling regulations. It is also of interest to store the containers according to the packager or manufacturer's instructions.

- When materials are stored, liquids should always be stored under solids and the recipients should be kept well closed.
- Clean surfaces just before their collection for electrolysis in order to prevent them getting dirty while they are stored.
- Establish a stock management system according to the FIFO system (*"first-in-first-out"*), that guarantees that the materials that have been in the warehouse for longest are the first to leave.
- Use recipients with dimensions suitable for their intended purpose and for the product's characteristics, aiming for bulk purchase except in products with a short shelf life or those which are not consumed in large quantities. All in all, this will reduce the number of containers and thus the material lost by sticking to the walls of the recipient. Likewise, reusable containers are preferable, such as polyethylene that can be used again and are also easier to transport and clean. Recipients, however, should be emptied completely to reduce the quantity of necessary cleaning agents.
- In the special case of waste, a specific and differentiated area should be provided and adapted for its storage, as has been stated earlier, with a sufficient number of containers to allow for their correct segregation into liquids and solids and dangerous or inert materials. Separation should be carried out according to their composition. Finally, the different types of waste that can be valued should be separated (scrap iron, plastic, cardboard, paper, etc.) to allow for its external management and reduce its volume.

- Inventory control

A fundamental consequence of inventory control is that the company does not have more materials, products and by-products in the plant than are strictly justifiable. Besides the space that it occupies and the building involved, a lack of inventory control may cause the generation of waste that comes from raw materials and unnecessary, out-of-date and badly-made products. This implies double the cost for the company.

As good housekeeping practices, we suggest the following:

- Define the frequency of and responsibility for the inventories.
- Avoid excess purchases that may become out of date and cause waste.
- Standardise, as far as possible, purchased materials, using the minimum possible number of compounds for the same purpose. This means a reduction in purchasing cost and maintenance, simplifying inventory control, improving monitoring and use of materials and may allow for a reduction in the quantity and variety of waste to be managed.

- Label and register all products received, indicating the name of the product, the date of entry in the warehouse and the expiry date (if it is appropriate). Check, at the same time, that the material comes suitably labelled.
- Buy the amount of material strictly necessary for each specific production stage so that no material is left over.
- Control all materials on reception, verifying that they fulfil manufacturer's specifications. Return those materials that do not.
- Follow supplier and manufacturer specifications on the use, handling, storage and treatment of the materials received.
- With regard to materials consumption, as has already been mentioned, undertake a FIFO management system, carrying out a rotation of containers that are located at the back of the shelves and bringing them forward when new material arrives. In any case, give written instructions and train the operators to use first the products that expire first.
- Reduce the quantity of partially full containers by promoting the use of excess material from previous operations. In this respect, it is very important to suit the size of the container to the amount necessary for each occasion, as it has also been stated previously.

- Material handling

During handling, transport and decanting operations etc. both materials and waste must comply with a series of measures to avoid spillage, leakage, pollution of materials, etc. that bring with them losses and generate waste flows. For example, waste pollution as a result of incorrect handling or segregation may generate a higher volume of waste, reduce the chances of it being valued or define its classification as special.

Amongst other things, the following can be recommended as good housekeeping practices:

- Loading and unloading areas must be well lit, sign-posted, clean and free of obstacles especially in transit ways.
- Establish special written procedures for loading, unloading and decanting operations paying special attention to physical loading and unloading: handling of pallets, barrels, lifting trucks, transpallets, pumps, etc. Checking and inspecting equipment to be used –pumps, filters, joints, valves – is highly recommended before beginning any decanting operation, especially when dealing with liquid products (for degreasing baths for example).
- It is also necessary to prepare written procedures for maintenance and periodic review of the facilities used in the loading, unloading and decanting of products: connections, joints, valve closures, hoses, pumps, etc.

- Arrange deposits and recipients in such a way as to prevent their breakage, making the detection of cracks or corrosion easier. Metal drums, for example, must be separated from the ground by pallets to avoid corrosion caused by ground humidity.
- Use recipients following the manufacturer's instructions and only for their intended purposes, ensuring that all these receive a control and maintenance programme and are in good condition.
- Reserve impermeable and clean areas of containment around the tanks or storage areas that include elements – tanks and baths – to collect possible spillage material. In these areas respect should be shown to the separation of materials according to their chemical nature and potential hazardousness and contact avoided with the facility's general water collection network should be avoided.
- Ensure that the correct liquid is being decanted into the container for which it is necessary to observe labelling regulations that make it possible to know the content of stored barrels at any time, as mentioned previously.
- Have systems that give, at any time, the volume of liquid in the deposits that the company has, preventing excess filling of deposits or containers and always checking the level in the container to which the liquid is being decanted before the beginning of the operation so that this is not insufficient.
- In decanting areas, provide systems that allow the operators to let the elements used drain for long enough, especially in areas for the decanting of liquids. It is necessary for this drainage to be carried out in a container that enables the product to be recovered.
- Proceed with special care in liquid decanting operations and avoid possible splashing and spillage by using equipment in the correct way (pump, funnel, etc.).
- Avoid unnecessary movement of materials by using a precise plan and transporting the right quantity to the right place.
- Quick access to absorbent materials suitable for the products that are normally handled so as to act in case of leaks. These should, therefore, be available near the handling areas and should be easily accessible to the people responsible for the operations.

- Plant operations

Indicated below is advice to be followed during the electroplating bath process and all other related activities with the aim of preventing the pollution generation. Some of these recommendations have been made previously:

- Use of potentially less polluting baths, provided that it is technically possible. Beginning with preparation baths and ending with processing baths, it is a good idea to consider whether the composition or concentration of each bath can be modified so as to reduce the generation of waste flows and to produce parts with quality at least as good as the bath that has been substituted.

- Cleaning parts just before they are electroplated so as to prevent them from getting dirty during periods of storage.
- Optimise the cleaning of parts to reduce the generation of waste and emissions. By using the exact amount of cleaning product and lengthening the life of the preparation baths as much as possible.
- Use of cleaning products that pollute less. Hence, the order of choosing a cleaning product is: air, water, abrasive medium, aqueous detergent solution, alkaline solutions, acids and finally solvents.
- Agitating the baths in order to increase cleaning operation efficiency whether it be by mechanical or ultrasonic methods.
- Slow extraction of parts from preparation and processing thus giving time for excess liquid to drain into the tank.
- Correct placing of parts on racks to minimise raw material drag-out.
- Maximise drainage time of parts as much as possible. This important point is often forgotten. A minimum drainage time of 10 minutes is recommended for racks.
- Ensure the emptying of parts during drainage. If it is convenient, different vibrating movements should be performed by the racks that are recently taken out of the baths to ensure that the liquid that may have been retained on the parts is emptied.
- Installation of joint-covers to collect liquid that drips from the parts on taking them out of the corresponding tanks.
- When recovering defective parts, mechanical cleaning systems should be used before using liquid systems.
- Carry out a regulatory control on the condition of parts after the cleaning and preparation process in order to reduce the number of defective parts that are electroplated.
- Workers should be informed about the importance of reducing environmental pollution and the need to use ideal personal protection systems: use of masks, helmets, earplugs goggles and gloves, etc.
- Suitable professional training for operators responsible for production lines so that work can be performed with professional know-how.
- Let product pots and barrels drain well.
- Know the composition of the products used by the company and possible toxic components. It is thus very important to request and update product safety sheets.
- Calculate the necessary amount of raw material for each task, attempting to programme changes in order to reduce cleaning and material residues to a minimum.
- Study the facility's tube, pump and deposit connection design so that the part to be drained and cleaned is minimal.
- Do not mix non-corresponding products.
- Avoid spillage and splashing.
- Periodically check that taps and connections do not drip.

- Understand how the machinery and equipment to be used works properly. The better it is understood, the higher the yield that will be obtained and there is less chance of pollution happening.
- Check that the surfaces to be treated by electrolysis are in perfect condition and show no irregularities that may affect the final quality.

- Facility equipment maintenance and conservation

Normal machine and equipment operation causes them to wear out and affects their yield, bringing with it the generation of products not included in specifications, leaks and spillage, etc. All in all, they can generate waste flows that cannot be ignored.

Preventative maintenance consists in the periodic inspection and cleaning of the equipment and facilities and includes the lubrication, the checking and replacement of parts in bad condition constituting good housekeeping practices to prevent the production of pollution. Generally, the quantity of waste and emissions caused by leaks and non-standard products can be reduced, the working life of equipment can be increased and the productivity of the company improved.

Among the main good housekeeping practices that contribute to the correct conservation of facilities and minimisation of waste are:

- Preparation of sheets or maintenance procedure for all equipment and machinery with instructions for use. It is important that these be found near the equipment and detail its characteristics, optimum performance and correct maintenance. Each sheet should, furthermore, include the frequency and method of cleaning of the equipment, the performance of small adjustments, the checking of the equipment and the replacement of small parts. It is also advisable to keep a written register of breakdowns experienced, changes of parts, adjustments performed, servicing and repair data, etc. It should also be indicated where used parts are put and possible waste generated –oils, metal parts, dirty cloths, etc.- These sheets may be in the form of data cards or on a computer.
- The preparation, also, of incident sheets for each line or area of production where the personnel write down breakdowns, valve or joint dripping, equipment stoppages, etc. that may affect manufacture or cause the generation of unnecessary waste flow.
- The teaching and training of personnel responsible for maintenance is fundamental so that they get used to the written procedures and respect the periods established for services. This aspect is especially important with regard to the management of waste that is generated as a result of maintenance operations (dirty cleaning liquids, dirty sawdust, dirty cloths, etc.). It is important, in this case, not to mix them and to store them in a place especially for this purpose.

- For certain elements and equipment (combustion apparatus, fork-lift trucks, for example), it is preferable to subcontract external preventative maintenance from a specialised company.

- Equipment and facility cleaning

As it has been mentioned previously, there are various means of avoiding accidental spillage and leaks by handling products correctly and by using suitable elements for decanting, etc. However, despite all the afore-mentioned prevention measures, there is always an undesirable part of the materials that dirties the equipment and company facilities.

Should it be necessary to clean up, the recommendable sequence of action is: isolate the spilt product, in order to stop it covering more space, collect it in such a way that it may be reused, or reduce its volume and finally clean the floor or whatever it has dirtied. This sequence will enable cleaning detergents and water to be saved, reduces the pollutant quantity in the waste water poured away and, should it not be possible to use the product again, will enable it to be segregated and managed as waste.

The following are recommended to the company as general rules for the cleaning of equipment and facilities:

1. Inform, train, raise awareness and supervise personnel responsible for cleaning.
2. Substitute manual systems for more efficient automatic systems.
3. Establish written cleaning procedure.

Specifically, some recommendable good housekeeping practices in this section are those described below:

- Establish and make known written procedures that describe, according to the spilt product, the action to be carried out, the order in which it must be done and the materials to be used. Maximum cleaning efficiency with the minimum resources is the aim, as well as reducing the number of cleaning operations to a minimum and avoiding any unnecessary cleaning.
- The first objective, as has been stated, is, whenever possible, the isolation of the focus as a first step and then the collection of the spilt material in a way that allows for its reuse. With liquids it is important to build retention cups in the decanting and storage areas that should not be connected to the drains or the internal drainage network. It is sufficient, with solids, to avoid contact of the solid with water or other products that will cause them to spread out.

- Have suitable material available to isolate the different types of products that are normally handled in the company and that may be accidentally spilled. These include trays or containers to put under the barrel and that act as retention cups to collect the liquid that may fall.
- Have suitable material available to clean the floor or site affected by a leak or spillage once the focus has been isolated and the spilt product collected. This material should be easily accessible by personnel and therefore it must be located near the points where it may be most necessary. Mechanical cleaning should be used instead of chemical whenever possible.
- Cleaning processing equipment (filters, tanks, pumps, etc.) periodically to maintain them in the correct condition and at the same time make cleaning them easier.
- In cleaning equipment, attempt to use the cascade rinsing system or, against the current for the first rinse, the liquid coming from other rinses, followed by another which is half dirty and finish the operation with the least possible quantity of clean cleaning liquid.
- Should chemical cleaning methods be necessary (such as the cleaning of the floor with water and a degreasing solution) the control parameters to be considered are time, temperature, concentration and the turbulence necessary for efficient operation. To reduce the quantity of cleaning solution the following order should be followed:
 - clean mechanically and not chemically at the suitable moment and place such as scrapers, brushes, vacuum cleaners, etc.
 - use hoses or pressurised aerosols to save water and/or products (water, steam),
 - make use of water with surfactants or other products, (such as suspension agents and emulsifiers),
 - reuse water with detergents from a previous clean for a first rinse in order to achieve pollutant concentration and a lower volume of dirty cleaning water.

- Operation procedure development and fulfilment

The existence of written documents or operation procedures that gather all the data, operations and instructions performed in the different processes carried out assure that each task is well-defined and, as well as improving production efficiency, may reduce the generation of waste flow. If is not so, by squandering raw materials and inefficient processes, etc., it may be found that as a whole these contribute to a greater generation of waste and an increase in the risk of accident.

The involvement at all operational levels of everyone in their area of responsibility in the preparation and implementation of these operation procedures is especially relevant to this section.

As special recommendations the following can be noted:

- First, the choice of normal operating procedures carried out most frequently in the factory. Those operations that may have environmental repercussions, should be detailed more such as:
 - manufacturing processes,
 - maintenance operations,
 - equipment and facility cleaning,
 - material storage and decanting,
 - action in response to leaks and spillage.

It is important that each procedure incorporate an overall description of the processes and define each one of the individual jobs, indicating the tasks to be carried out by each operator or person in charge, the operation method and the intended means, etc.

- Create respect for the content of the procedures prepared by avoiding improvisation and omissions for the established instructions.
- With leaks or spillage it is necessary to have, as previously mentioned, a generic procedure where the first action to be carried out is described, indicating the people responsible who should be informed.
- Keep a data register on the generation of waste flow for every process line or area of the company as well as associated costs. The object of this is first to identify the areas that are in most need of improvement and subsequently to be used to evaluate the results of the improved practices.

- Waste segregation

The correct segregation of the different types of waste flows generated by the company allows for minimisation, facilitating a more suitable management of each type of waste by increasing recycling and recovery potential with the consequent economic saving associated with treatment. If this is not done, the mixture of different types of waste causes the squandering of raw materials by reducing the chance of reusing them, the pollution between wastes, a larger volume and finally, an increase in the costs of their management.

It is therefore necessary for the company to separate the waste that is produced according to its characteristics. This is certainly recommendable:

- Have the written means and instructions so that the waste generated can be separated in accordance with the following:
 - separate the waste according to its physico-chemical characteristics: isolate liquid from solid waste, separate special from non-special and inert waste, as well as segregating

toxic waste according to its main component types. With inert waste or ordinary refuse it is of interest to segregate it by types so that it may also be externally valued (wood, paper, cardboard, scrap iron according to its composition, plastic, etc.).

- This segregation presupposes having specific containers that should be sited near each work area either in the factory or the offices, warehouses or the company's outside premises.
- As mentioned in the chapter referring to the company's warehouse, it is necessary to provide for, adapt (lay asphalt, cover, etc.) and sign-post the area where the different containers are stored until they are withdrawn by an authorised manager. It is also necessary to label each container suitably with an indication of the waste, code, storage conditions and handling, manager's name and telephone number, etc. as has been mentioned previously.
- Assign people to make sure of the correct use of each container and storage area and who should inform the managers of each type of waste to be emptied or of replacement of the container when it is full.
- Promote the reuse of packaging material whether it be from the company itself or by means of its return to the supplier.
- Teach, train and give incentives to company personnel about the need to segregate waste.

3.2 Recycling at source

As we have seen throughout this study, the electroplating industry consumes a lot of raw materials and, furthermore, deals with potential pollutants. There are different techniques to reduce loss, by reducing and/or valuing these materials, to avoid their transformation into waste.

Below, is a series of simple methods for product use and of other more elaborate methods that involve rather costly investment.

3.2.1. Recovery of raw materials

3.2.1.1. Degreasing

As oil and grease is removed from the parts, the degreasing mechanism becomes charged with oils, greases and impurities from the parts.

It is generally observed that these preparation baths are removed when they have lost their degreasing power as a result of these impurities.

As a technical (economically viable) alternative to this way of operating, the introduction of separating equipment that separate impurities from the degreasing solution is recommended. This equipment allows for product recovery and grease and oil elimination.

Within this alternative there are different systems to implement in companies:

* When degreasing forms an *emulsion*:

- **Ultra-filtration**: This separates the oils and recycles active and solvent products from degreasing processes. In this process, the different components should have a molecular weight lower than the cut limit value of the membrane under consideration.

* For *non-emulsion* oils:

- **Superficial floating and decanting sweeping system** and *“oil skimmer”*: consists in installing a pump in the degreasing bath that blows air onto its surface and displaces the oils and greases on the surface towards a concentration department. This system is only useful in the case of non-emulsion oils in degreasing. It is generally a method with mediocre efficiency even though implementation cost is relatively low. Oils can also be removed by using mechanical drag-out equipment.
- **Centrifuging equipment**: brings about the separation of the two phases since oil and grease weight is higher than that of the degreasing product. Efficiency is quite good although investment and operation costs are considerable.
- As well as these possibilities there is another method of extending the useful life of degreasing by means of the **introduction of pre-degreasing**. When the pre-degreasing tank has to be emptied, it is filled once again with the contents of the degreasing bath. This is made up again. In this way the life of the bath is increased by 20-30%.
- Finally, another simple alternative to recover product, in the case of degreasing that works at a certain temperature (>40°C), is the **introduction of a sealed recovery rinse** allowing evaporation loss to be recovered. For example, an aqueous degreasing alkali that works at around 70°C, has an evaporation loss of between 6.5 and 31.1 l/h/m².

3.2.1.2. Pickling

One of the main problems of the chemical pickling process is the acid attack on the base metal surface itself. This has two effects:

- premature ageing of the pickling bath due to metal pollution;
- and as a consequence of this more frequent emptying of the bath with the consequent increase in the consumption of raw materials and the generation of waste flows.

Thus it is necessary to be able to influence base metal acid attack speed to control the process.

As regards iron, the operation parameters in a sulphuric and hydrochloric sulphuric acid medium are:

- the concentration of acid;
 - bath temperature⁹;
 - dissolved iron concentration¹⁰.
- A system to reduce the attack on the oxidised zones of the base metal consists in introducing into the bath some type of **attack inhibitor**. Given the great variety of attack inhibitors available on the market, (organic amines, etc.), it is recommended that it should be chosen taking into account its compatibility with the following treatment operations.
- It is also possible to purify the pickling baths either by charging or continuous. In the case of sulphuric acid iron pickling, the system called **electro-electrodialysis** can be used. The method consists in concentrating the sulphuric acid by ion migration across a membrane subject to a magnetic field and the elimination of iron by deposition on the cathode. For more information, see point 3.2.3.3. Electro-electrodialysis, later in this study.
- In the case of the hydrochloric acid pickling bath, anionic-type **ion exchange resin** equipment can be used to fix the iron chloride formed in the bath. Subsequently, the

⁹ Sulphuric acid pickling speed increases notably with temperature.

¹⁰ In hydrochloric acid pickling, pickling speed increases slightly with the presence of dissolved Fe²⁺.

resin is regenerated with water, obtaining pure hydrochloric acid. See also section 3.2.3.7. Ion exchange in this study.

- For sulphuric acid copper pickling baths **continuous electrolysis** can be used on the bath which enables metallic copper to be obtained directly at the cathode.

Other more simple systems to consider are:

- **Introduction of pre-pickling** before pickling (as in the degreasing), that is fed by emptying the pickling bath.
- Also in the case of hot pickling (of iron and copper with sulphuric acid for example), the **introduction of a sealed recovery rinse is of interest** to allow for the recovery of bath evaporation losses whilst recovering the acid. Furthermore, this recovery rinse may act to **reformulate new pickling** once that has been changed. Very often, however, it is necessary to proceed with continuous purification of the bath since base metal becomes more concentrated.
- To end this section, the introduction of a **mechanical pre-pickling** is recommended providing that the part allows it and that it reduces - or sometimes disperses with – the use of chemical agents.

In large pickling quantities to be regenerated, three technically-viable alternatives are noted. However, investment is costly:

- Installation of an **iron sulphate crystalliser**: the mechanism consists in allowing the pickling agent within the crystalliser to cool to a temperature at which the precipitation of iron in heptahydrate sulphate form occurs. This is a variant of the system that heats it in order to obtain the monohydrate form of iron sulphate. Between 40 and 70% iron sulphate elimination is achieved by this method, with a 30-50% reduction in the consumption of new acid. The product obtained may be valued as a coagulant in physico-chemistry wastewater purification processes. The cost of investment is very high and it is only recommended for large recovery volumes (500 l/h or more).
- **Oxidation incineration** system, consists in converting the pickling agent into powder form in a kiln at high temperature by which HCl is recovered in gaseous form as well as Fe₂O₃. The system allows for the recovery of a concentrated acid that has less than

10 g Fe /l. It is also a highly expensive system, only worthwhile for large pickling facilities (more than 1 m³/h).

- **Liquid-liquid exchange**, consists in the extraction of heavy metals in pickling baths (Fe, Ni, Cr, etc.) by the addition of tributylphosphate in kerosene. The system allows for nitric acid recovery and up to 70% of hydrofluoric acid. Like the other three systems, the investment can be very high and only justifiable for large pickling plants.
- **Ion delay**. Consists in separating the dissolved metal in the acid and allows for the recovery of the acid to a degree of purity sufficient to be reused in the process.

3.2.1.3. Products involved

In this section, all those products that make up the different processing baths are considered (degreasing agents, pickling agents, additives, metal salts, etc.).

It is necessary to begin with the idea that a large part of product loss can be avoided, essentially in two ways:

- prevention of losses, preventing them from occurring or reducing them:
 - choice of bath (nature, composition, concentration, etc.)
 - correct management of bath (respecting optimum work conditions, choice of minimum concentrations, bath maintenance, etc.).
- recovery and valuation of losses through the introduction of equipment:
 - systems allowing for the recovery of all bath salts:
 - reverse osmosis: nickel baths
 - electro-dialysis: nickel, copper and silver baths
 - electro-electro-dialysis: tin and chrome baths, certain pickling purification (of sulphuric acid, for example)
 - evaporation: chrome, cadmium, zinc and silver
 - ultra-filtration: degreasing purification
 - ionic delay: recovery of acids from pickling or anodising
 - systems that allow for the recovery of metals without the other constituents:
 - electrolysis: all metals
 - specific ion exchange resins: silver, gold, copper, boron, etc.

3.2.2 Reuse of water

3.2.2.1 Skip technique

One of the systems that can be used to reduce water consumption is the skip technique. This technique consists in using the same rinse in different stages that are chemically compatible, like, for example, using the rinse after a pickling stage, as a rinse prior to an acid bath or using the water from a pickling rinse (slightly acid) as degreasing rinse water. With this the number of rinse tanks and water consumption is reduced.

In order to apply this technique coherently, it is necessary to consider the fact that stages sharing rinsing must be as close as possible and located in such a way that drag-out can also be minimised; otherwise the intended effect of the technique is devalued by drag-out increase.

3.2.2.2. Recycling by ion exchange

Ion exchange recycling systems are gaining popularity especially in industries that decide to install effluent treatment plants.

The system is very useful as it achieves some very important objectives:

- reduce water consumption from the mains by a high percentage;
- clean parts with a large volume of water that is also a closed circuit and is not lost;
- clean parts with very high quality water (This equipment eliminates practically all ions in the water, transforming it in demineralisation);
- avoid as far as possible pollution of the baths due to drag-out;
- purify a much smaller and more concentrated volume of effluents increasing purifying treatment efficiency and reducing its operation cost;
- reduce the investment cost in effluent treatment facilities.

The use of water recycling systems using ion exchange resins should be studied very carefully, with regard to the types of chemicals present in effluents and their degree of concentration.

The presence of certain substances may affect recycling systems since they may block the active resin groups and thus render the equipment useless. It is also very common for incompatible toxic substances to be retained and concentrated at the same time. This could be the case for water with the presence of chromates and also cyanides. As both substances are anionic, they are retained by the same anionic resin in a way that, on regeneration of the resins, both pollutants are present together.

If that happens, purification of the pollutants cannot be carried out by usual methods and it is greatly complicated. Therefore, **waters that contain chromate and cyanides should never be mixed.**

Another typical difficulty may be the mixing of effluents with the presence of nickel as a cation with free cyanide ions. In these conditions, compounds may be formed with nickel tetracyanide which is very difficult to destroy using traditional methods and, as a result, they escape from the purifying systems that are dealing with them. It is therefore necessary to foresee this situation in order to avoid the formation of the mentioned complex.

The second great problem associated with water recycling using ion exchange resins is related to the maximum concentration of pollutants present in the water to be recirculated.

Industrial recycling equipment has a defined fixed maximum capacity. If the salt concentration in recycled water is high, this capacity is exhausted in very short time intervals, forcing the equipment to regenerate often. This effect is related both to the cost of exploiting the recycling system and to the generation of effluents with high salinity.

The maximum salt concentration in recycled water is a very important parameter to be considered in achieving a good recycling operation.

In most cases, this forces working lines to be remodelled so that a minimum of two consecutive rinses always intervene after each treatment process. The first works at high volume recirculating within the recycling equipment.

The final problem with the recycling systems, even though they are well designed, is the increase in salinity (or conductivity) of the effluents removed. This problem is difficult to solve since first, water consumption is reduced and thus the concentration of its pollutants is increased making purification necessary, which becomes more effective, and is translated into an increase in salinity. The recycling equipment, furthermore, is regenerated through acid (often hydrochloric) and an alkali (often soda), in variable quantities but that, on average, are 100g of hydrochloric acid at 100% per litre of cationic resin and 80g of sodium hydroxide at 100% per litre of anionic resin.

In practice, this involves very high conductivity in regeneration effluents due to the presence of sodium and chlorides, with both substances being very difficult to eliminate. This increase in water salinity may cause big changes in the ecosystem in certain areas.

3.2.2.3 Recycling by inverse osmosis

This recycling system is an alternative to ion exchange using rinse water recycling. Its level of use is currently low even though it is technically viable.

Inverse osmosis is based on separation of dissolved salts from the solvent, which in this case is water, by means of external pressure that makes the solvent pass through an osmotic membrane and does not allow the passage of saline ions.

In this way, from a volume with a determined salt concentration, two different solutions are obtained. One has the majority presence of the solvent, known as the permeate, the volume of which is high and the saline concentration low, and the other, known as the concentrate, has a low volume and a high salt concentration. In this way, it is possible to recycle the permeate for rinsing operations.

The separation is produced by mechanical effect by applying pressure and so there is no addition of chemical products to separate the pollutants (unlike ion exchange). The saline content of the polluted effluents therefore does not increase, controlling the effect of the high conductivity.

Another advantage of inverse osmosis is its capacity to work on more concentrated effluents than ion exchange, in such a way that it is not necessary to carry out dilution before rinsing with recycled water. On the other hand, the quality of the recirculated water does not reach the quality of purity of the resin systems and so in some cases these would still be needed.

However, this type of equipment presents some practical operating problems that make its use on an industrial level difficult. The performance of the membranes used up to now has improved a lot but they still show problems of chemical resistance with aggressive agents such as hexavalent chrome, chlorine, persulphate, etc. especially above certain concentrations.

These membranes, moreover, present important saturation problems that must be provided for using combinations of sand filters beforehand and finalising filters of a pore size of 5 micros. This filtration is also necessary to eliminate organic materials that could damage the membranes. It would even be recommendable, in some cases, to install active carbon filter beds.

Another associated problem is the presence of cations in the water that produce incrustations such as calcium and manganese. It is thus indispensable for all the water that penetrates the system to be softened by a decalcifying agent.

As can be observed, the final system is very complex composed to the benefits that it provides which implies an installation cost that is somewhat higher than ion exchange resin recycling systems. However, the operating cost is somewhat lower since it does not require a high level of chemical product consumption.

3.2.3 Drag-out recovery

In spite of all the measures taken to reduce drag-out (see section 3.1.2.2. Reduction in drag-out), an inevitable waste drag-out persists that, in the worst cases, ends up on the floor of the shop or in the rinse tanks with water. As has already been seen, this drag-out can be recovered partly by improvement in rinse structure (see also 3.1.2.3. Improvements in rinses and washes.).

There are, however, other more sophisticated systems that also allow for the recovery of a good part of the drag-out produced. Let's see what they are:

3.2.3.1. Electrolysis.

This system enables a metal in solution to be recovered. The separation is carried out within an electrolytic cell with the deposition of the metal in question on its cathode. In section 3.2.1.2. Recovery of raw materials: pickling, some examples of recovery have already been noted.

System operation is identical to any other electrolytic cell and so it is necessary to:

- control bath concentration,
- periodically control the electrical equipment
- replace the cathodes.

Besides the recovered metal, the rest of the bath's salts and compounds are not recoverable. The recovery of the metal deposited on the cathodes requires their destruction, normally by incineration, and so a recuperation service is necessary, normally external, the cost of which must be added to the total recovery cost.

It is also necessary to mention that the electricity consumption is high in relation to the quantities recovered and it is therefore used to recover precious metals, the value of which compensates for the costs of recovery.

3.2.3.2. Electrodialysis

This also consists in an electrochemical system that allows for the extraction of the ions contained in a solution by migration across selective membranes subject to the influence of a magnetic field. Normally an electrodialysis cell is formed by a cationic membrane that demarcates two compartments between two anionic membranes. One of the compartments contains the solution to be diluted (rinse) and the other, the solution to be enriched (bath). The anionic membranes only let the anions and the cationics, the cations, pass. Both of them are impermeable to liquids. The cations migrate in the direction of the electric current from the anode towards the cathode, crossing the cationic membrane and are retained by the anionic.

This enables the dissolved electrolytes to be concentrated on one side and not the other and therefore allows:

- separation of certain ions in a solution
- concentration of a solution that can be returned towards the processing bath.

It is therefore a system for the recovery of salts in hot baths where natural evaporation takes place. It is thus placed between the processing bath and the sealed recovery rinse, concentrating the drag-out salts towards this rinse and returning them to the bath.. In this way, two objectives are achieved:

- returning part of the salts lost by drag-out to the bath,
- maintaining low concentration in the sealed recovery rinse so that the following rinse water is polluted less. The water flow can thus be reduced.

This type of facility is useful for sealed rinses of copper, nickel and silver.

Disadvantages of the system are:

- controls and daily equipment maintenance: control of work pressure, checking of filters and electrodes;
- carbonate removal from membranes: quarterly.

Given that its yield of between 95-97% is very high and operating costs and maintenance are not very high, the average investment pay-back period is estimated at less than one year.

3.2.3.3. Electro-electrodialysis

This system combines the effects of electrolysis with those of electrodialysis, interposing an electrodialytical membrane (anodic and cathodic) between two electrodes. Two compartments, one anodic and the other cathodic, are in this way separated from each other. The anodic compartment is limited by an anode and a membrane while the cathodic compartment is limited by the same membrane and a cathode. The choice of membrane type depends on the elements to be passed from one compartment to another. This means selective anion and cation filtration is obtained.

The other phenomenon that takes place is electrolytic: oxidation at the anode and its reduction of the element at the cathode.

As a technically viable application, we find the regeneration of chromic acid and sulphuric acid in a sealed rinse tank. Chromic acid is recovered in the anodic compartment of the apparatus and can be reintroduced whether it be to the processing bath itself or to the rinse prior to the bath to introduce it slowly with the drag-out.

As a limiting factor to the system, we can state that the work concentration of chromic acid is 300 g/l.

Other disadvantages in the system are in the maintenance and control methods that are very similar to those of electrodialysis. Furthermore, as the equipment produces solutions that are directly useable, cases may arise of pollution of the solution because of the impurities that there are and that are also reduced on the cathode.

The main operating cost is energy since there is consumption of between 25 and 30 kWh per kg of recovered chromic acid. With the high initial investment cost, operating costs and chromic acid market price, the data indicates that the system is only of interest to facilities that have to recover large quantities of chromic acid.

3.2.3.4. Inverse osmosis

The system has already largely been described in section 3.2.2.3. on inverse osmosis recycling as well as its main use as a water recovery element. In this section, we shall only add its possible use to recover materials from drag-out that exists between tanks.

In the case of salt recovery, metal ions are well-retained by osmosis membranes with efficiency percentages of up to 90% in many cases.

One system that is used is the recovery of nickel salts, contained in a sealed recovery rinse. On the other hand, recovery of polishes from the bath is less than recovery of nickel, reaching values of only 60%. Because of this, an analysis and reconstitution of the bath is necessary to achieve optimum work parameters.

Another disadvantage presented by the facility is that, unlike other selective separation systems, the impurities received by the bath also concentrate, in this case meaning there is a high risk of its contamination as all salts are concentrated.

It is high-cost equipment that needs installation annexes to work well, with periodic maintenance such as cleaning of the membranes with a solution of citric or acetic acid to eliminate possible calcium or carbonate deposits. All in all, along with the low price of the salts that can be recovered, it means that pay-back periods are normally very high.

3.2.3.5. Ultra-filtration

This idea has already been dealt with in section 3.2.1.1. Recovery of raw materials: degreasing. Here, it can be added that, as in the case of osmosis, the system works by separating the solution by means of membranes as a result of external pressure applied to the system. The important difference is that in this case selective membranes are used according to what is being filtered. It is therefore necessary to determine – habitually and empirically – the membrane type and the desired pore size.

Currently, there are two types of membranes available:

- organic membranes: cellulose acetate, polyamide, etc.
- mineral membranes: the main one being zirconium oxide.

While the first are less costly, they have more limited applications; minerals can be used on liquids at high temperatures (between 50 and 120°C) and with the presence of aromatic solvents or chlorates, factors which organic membranes cannot tolerate.

The following are possible applications within the surface treatment sector:

- separation and concentration of electrophoresis effluents in the tempering of metals;

- salt recovery in degreasing baths by means of the separation of oils.

However, among the disadvantages of the system is the need to clean the ultra-filtration module using a lactic acid or butyl-butane with successive subsequent rinses with distilled water.

Furthermore, it is expensive equipment that offers no economic justification for degreasing recovery. In certain cases, however, (with parts heavily charged with oil that cause real problems when purifying exhausted degreasing baths) their installation may be of interest.

The advantage of this technique is that it gives a constant degreasing quality, suitable for processes requiring high-quality degreasing.

3.2.3.6. Evaporation

This is a system of material concentration that uses energy in the form of heat to evaporate the liquid part, concentrating the salts that are dissolved in it.

Given this salt concentration factor, it can be used to reintroduce them into the processing bath. It is an especially suitable system for baths working at low temperatures ($< 40^{\circ}\text{C}$), in which natural evaporation loss is not significant enough to introduce sealed recovery rinses.

Furthermore, evaporated water when condensed may be used to feed the rinse system of the processing line.

The evaporation system may be introduced in the line at different levels:

- in a multiple cascade rinse system against the current
- on a sealed rinse level subsequent to the processing bath
- even on the processing bath itself, concentrating it

Evidently, only in the first two levels can we achieve drag-out recovery.

In order to avoid both a high-energy cost in heating the solution up to boiling point and also avoid the degradation of certain organic constituents present in the electroplating baths, the most recommendable evaporation system is that of vacuum. With this system an evaporation process of an aqueous solution can be achieved at only $30\text{-}40^{\circ}\text{C}$.

The following examples are practical applications of the system:

- evaporation of soluble oils
- zinc recovery (in this case, given that the zinc bath is quite hot, on bringing about solution vacuum, it is possible to make it boil without the need for extra heat)
- concentration of a chromate bath to allow for the introduction of sealed baths after the bath.
- recently, the implementation of this equipment has been observed to reach “*zero material*” in waste water, combined with water recycling equipment using ion exchange.

Furthermore, the only disadvantage of the system is the high investment cost in the apparatus. Since it is quite robust, equipment maintenance is low. The only critical element that needs to be controlled is the vacuum pump that requires thorough attention given its high cost. As regards equipment use, it is important to control pressures, work temperatures, evaporated liquid levels and condensation and distillation volumes. To obtain maximum benefit from this technique an analysis should be made, where necessary, of the electroplating line to include multiple rinses; combining this technology with ion exchange equipment is recommendable.

3.2.3.7. Ion exchange

This system has largely been dealt with in section 3.2.2.2. Ion exchange recycling with reference to the process water generated.

Here, the different possibilities for the recovery of certain ions lost with drag-out will be added.

In addition to the afore-mentioned continuous recovery applications of rinse water, resin equipment can be used for the following:

- To purify recovery from chromic acid baths or chromic passivations using resin retention of undesired cations: Cr^{3+} , Zn^{2+} , Cd^{2+} , Fe^{3+} , Cu^{2+} , etc. During their decontamination, they can be reintroduced in the bath, enabling the drag-out produced to be recovered.
- Recovery of metals present in rinse water using anionic resin types (Ag^+ , chromic acid, etc.).
- Regeneration by hydrochloric acid pickling, through the elimination of Fe^{3+} ions. The hydrochloride can be recovered (it is only necessary to adjust its concentration) and the iron chloride obtained can be valued if it is concentrated beforehand.

As regards problems and disadvantages of the facility, refer again to section 3.2.2.2. Ion exchange recycling in this study.

This section can be concluded by stating that ion exchangers allow for the concentration and extraction of pollutants (specific ions). In spite of everything, the concentration level reached does not allow for the direct reintroduction of the recovered salts, which would require a higher concentration. This means that they are not often used for this purpose. They are especially suitable, as has already been seen, for very dilute solutions such as rinses that must recirculate to the rinse line.

Finally, to end this section on drag-out recovery, some of those simpler systems will be detailed, many of which, as mentioned in previous sections, can be combined with all the other recovery systems seen so far.

3.2.3.8. Other measures

- Rack support bars

This system is used in manual-type installations in which operators have to handle heavy racks that make drainage operations difficult.

The operation is certainly simple but unfortunately it is not very widespread.

Actually, it only requires a few more operations than the hanging of the racks. Thus, while a draining hook moves on to the next process, a second will be in the draining position and this continues successively.

This system is used a lot over work baths at room temperature and recovery rinses but not much on hot processing baths since the solution may end up drying on the parts and creating problems with the finished product. In these cases its use is limited to recovery rinses.

- Joint-covers between the different work baths

This consists in putting an inclined surface between two consecutive tanks in the production process.

In practice, these types of apparatus are hardly ever used, even in automated facilities even though their use is unquestionable.

In manual processing plants, the use of joint-covers and a suitable process apparatus will provide for the recovery of much of the drag-out at the same time as avoiding its dripping onto the floor to generate another problem that is difficult to solve.

- Drainage tanks

When the production type is such that there is prolonged drainage such as, for example, in drum production, it is advisable to consider the use of a drainage tank.

This consists in an empty tank over which the transporter can be suspended for a time while the parts are drained. For drums, this may rotate while it is in this position to ensure maximum drainage. When a certain quantity of solution accumulates at the bottom of this tank, it can be returned by pumping to the treatment tank.

- Sprinkler drainage tanks

A variation on drainage tanks is sprinkler drainage tanks. Parts are wet in these by a small quantity of water in the form of finely sprayed drops that form a mist that condenses on the surface of the parts. This drains to the bottom of the tank. This system cannot be considered as a rinse because of the small quantity that is used.

As a result of the vaporous nature of this mist, it reaches the most inaccessible areas of the parts. The solution that accumulates at the bottom of the tank is quite concentrated and so it can be reused in the treatment tank itself.

This system is of little use for concave parts where drag-out solution may be retained.

- Sealed recovery rinses

As we have previously seen, this system is ideal for the recovery of raw material constituents of the processing baths especially if they are operating hot.

In some special cases of baths that operate at room temperature ECO recovery systems can be implemented.

4. ALTERNATIVE TREATMENTS

Various alternatives to this treatment are given below. They are orientated towards reducing waste that is generated in the process, basically in the form of sludge containing metal hydroxides, and minimising the amount of substances that are present in the purified water.

A good alternative to the treatment unfailingly involves the **correct segregation of these effluents** from the rest. This is the only way to get all of the metals to precipitate correctly.

4.1. The breakdown of metal complexes

Once the effluent that is to be treated has been segregated, alternatives to the conventional process that separate the metal from the complex and cause it to be precipitated include, amongst others:

1. Treatment with **calcium chloride, hydrogen peroxide and sulphuric acid**. As well as breaking down the complex, the system reduces the copper to the cupreous form that precipitates very well in an alkaline medium.
2. Another variation on the previous one, which is more effective and has been introduced more recently, is the addition of ferrous sulphate prior to the conventional treatment. **Ferrous sulphate and hydrogen peroxide at pH 9** also reduce the copper to the cupreous state, at the same time that it forms part of the complex due to the presence of ferrous or ferric ions. The main drawback of the method is the high consumption of ferrous sulphate and the large quantities of sludge that are generated.
3. There are also alternatives in similar applications that involve the use of **sodium polysulphide** and **sodium hydrosulphide**. The advantage over the previous ones is that it generates much less residual sludge but offsetting this is the risk of gaseous hydrogen sulphide being produced, which is highly toxic. Strict control of the pH must thus be ensured, together with good ventilation in the premises where the compounds are applied.
4. A very recent alternative to these treatments, which is completely developed, consists of the use of an **insoluble starch xanthate (ISX)**. One possible use of this organic molecule is the regeneration of cationic ion exchange resins, for it releases magnesium ions that take the place of the absorbed metals. Purification treatments that combine this compound with other sulphurous ones can notably reduce the presence of heavy metals in waste water. As a rule, the sulphurous compounds are much more insoluble than formats with hydroxides.
5. Lastly, to eliminate complex metals and other components that are difficult to eliminate with physico-chemical means, mention is made of the possibility of using **specific ionic exchange resins**. Chelating resins are available on the market for Cu, B, NO₃⁻, amongst

others. To avoid problems with the regeneration eluate, the best advice is to centrally regenerate the resin in waste treatment plants.

4.2. Cyanide oxidation

With respect to cyanide oxidation, the alternatives to hypochlorite in an alkaline medium involve the following:

1. Alternative cyanide oxidation with **chlorine gas**. This possibility is especially adequate in the case of large water purification plants given the lower operating costs and the smaller quantity of sludge that the system generates.
2. Oxidation with **hydrogen peroxide**, that converts it into cyanate and without the formation of any intermediary compound. As has already been mentioned, this compound facilitates the breakdown of metal compounds, enabling them to be precipitated afterwards.
3. Destruction of cyanide by using a **monoperoxide sulphuric acid**, which acts as a triple acid salt. The process that takes place is complex; comment is just made here of the fact that the method notably increases the speed of reaction with the cyanide by achieving optimum levels of purification of the compound.
4. Cyanide oxidation using **oxygen or air, with the presence of active carbon**. Just as with the second case, the cyanide oxidises due to the presence of oxygen. In order to facilitate the contact between the liquid and the oxygen (or air), it is passed by a counter-current flow through a column full of active carbon. Here, the catalytic oxidation of the cyanide takes place on the surface of the carbon. It is also possible to aerate the cyanide-containing water in a tank with active carbon particles in suspension. The final result in both cases is the formation of a cyanate, with the advantage that less residual sludge is produced at the end of the treatment than in the conventional case with sodium hypochlorite.
5. Destruction of cyanide by way of a **process of anodic oxidation**. The reaction mechanism that takes place is extremely complex due to the large number of reactions that take place. The system consists of oxidising the cyanide in an electrolytic cell under different working conditions. The cyanide oxidises in the anode. This is a slow method and is only useful for small, concentrated quantities of solution (for example, the purification of baths containing precious metals). Interesting aspects of the method are that the reaction is totally irreversible, and the formation of cyanide by the reduction of the cyanate in the cathode is impossible. An ideal case is where the metal dissolved in the solution is reduced along with the oxidation of the cyanide in the anode of the electrolytic cell.
6. Destruction of the cyanide by **precipitation with Fe (II) salts**. The ferrous ions form an extraordinarily stable complex with the cyanides that can be precipitated out (the so-called

hexacyanoferrates or ferrocyanides). This is a good system for eliminating cyanide in concentrated solutions and gives an easily filtered precipitate. A serious drawback is that the cyanide is not oxidised in the sludge formed, which makes the sediment toxic.

7. There is another alternative, although it is just mentioned briefly for it is expensive and requires extensive controls. This is the **thermal destruction of cyanide** through the use of sources of combustion. Cyanide can be hydrolysed and subsequently burnt at high temperatures (between 140 and 220 °C).

4.3. Hexavalent chromium reduction

Alternatives to the conventional treatment are as follows:

1. Reduction with **sulphur dioxide** gases. The system consists of mixing the residual liquid with the gas in a reaction tank. The reaction is very fast and good levels of reduction are achieved. As it is a gas, the main advantage is that it does not generate so much sludge as in the case of sodium bisulphite. Moreover, with the gas being acidic, hardly any additional acid consumption is necessary to reduce the pH in the process.
2. Chromium reduction through the use of **Fe (II) compounds**. The main advantage of the method is that the process is practically independent of the pH, within certain limits. This means that the pH does not need to be reduced to values of 2 - 2.5 u.pH, as is the case with sodium bisulphite. This is particularly interesting for reducing acid consumption, as well as alkali consumption that is used to increase the pH to the precipitation values for metals. The presence of ferric ions in the system acts as a flocculating agent by helping the elutriation of metal hydroxides that are formed afterwards.
3. **Cathodic reduction** of hexavalent chromium. Chromates, just like cyanide, can be reduced in the cathode of an electrolytic cell. The process is only effective, however, at low chromate concentrations (<0.5 mg/l). In any case, the method is not adopted in practice because of the various technical difficulties that are involved (an electrochemically complex process, high electricity consumption, inverse reactions with the new formation of the compound, etc.).

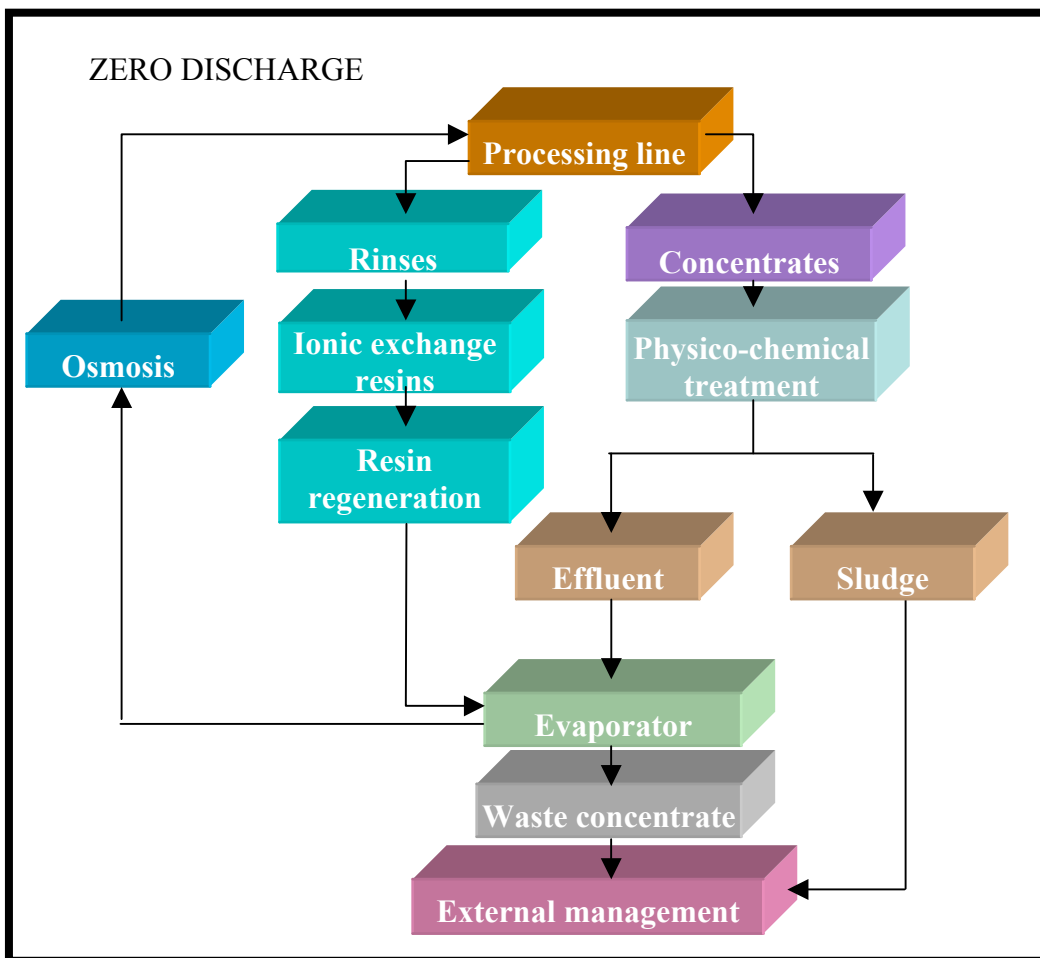
4.4. Coagulation

With reference to the usual process of coagulation with ferric chloride, brief mention is made of the **electrocoagulation** plant technology used by companies in the sector. The system consists basically of the *in-situ* production of ferrous or ferric ions that are indispensable for the good formation of coagulants, prior to the stage of neutralising and metal precipitation.

The method itself uses an electrolytic cell through which an electrical current is passed to produce the formation of ferric ions from an anode made of an iron plate. The producer in fact thus manufactures his own coagulant.

The main advantage is the reduction of the conductivity of the water. In the traditional case, a ferric chloride solution is used for the ferric ions, and the chlorides of this then remain in soluble form in the purified water. There is also less need for an alkaline solution to raise the solution pH and there is therefore a slight reduction in the volume of residual sludge generated. The main drawback is the high cost of the electrocoagulation unit. This technique is applicable in cases where there is very little variability in the characteristics of the water and even then it is advisable to have homogenisation tanks available to achieve uniformity. According to the kind of water being homogenised, an agitation system to avoid precipitation will need to be installed.

As a way of finishing this section, mention is made of the different uses of the prevalent equipment used for recovering and recycling water in the industry during recent years with the purpose of achieving "*zero discharge*" rates. As all of them have been dealt with in previous sections, reference is only made here to the type of installation that is gaining ground in the field. This involves the combination of rinse water recycling systems through the use of ionic exchange resins, which are sometimes combined with reverse osmosis equipment, combined with vacuum evaporators to concentrate the eluates originating from the regeneration of resins and the depleted pre-treatment baths. The final result is a residual concentrate that has to be managed as special waste.



5. OTHER ASPECTS TO BE CONSIDERED

A series of recommendations are considered in this section that aim to reduce the risk of pollution, either in the workplace or in the environment. Many of these proposals have already been made in previous sections, especially in reference to good housekeeping practices.

5.1. Product storage locations

As a general rule, storage locations must be situated as close as possible to where products are consumed, although the best recommendation is to have just one storage location.

It obviously needs to be situated to give easy access to transportation vehicles.

5.2. Management of the storage location

Only a certain number of people who have enough information and basic training concerning the characteristics and hazards of the stored products should have access to the storage location.

As has been mentioned in previous sections, products must be distributed in such a way as to avoid them being mixed together, via visible labelling visible, separator retainer trays need to be installed (base acids and especially cyanide), etc.

It is also advisable to make out stock-check forms to control the movement of items in and out of the storage location and reduce the risk of ending up without an adequate supply of products.

5.3. Retainer trays

These should enable any possible overflows to be adequately collected and guarantee a high degree of imperviousness.

It is advantageous when the tray can collect both vertical and horizontal spills from leakages in high tanks.

As has already been mentioned on various occasions, the trays should act as separators to avoid the mixing of acid and cyanide or other mixtures which, because of their nature, make the reuse of spilt products difficult or impossible.

5.4. Water feed

Ideally, there should be just one water-feed input in the electroplating workshop with a meter and an electrically operated valve connected to a volume measurement system. If consumption shoots up in a sustained way, an electrically operated valve is activated and the feed system is closed.

A recommendable system is the installation of a sufficiently large water storage tank that can operate for several hours, so that poor quality purified water can be stored. Direct external dumping is thus avoided in the case that incorrect purification or accidents occur.

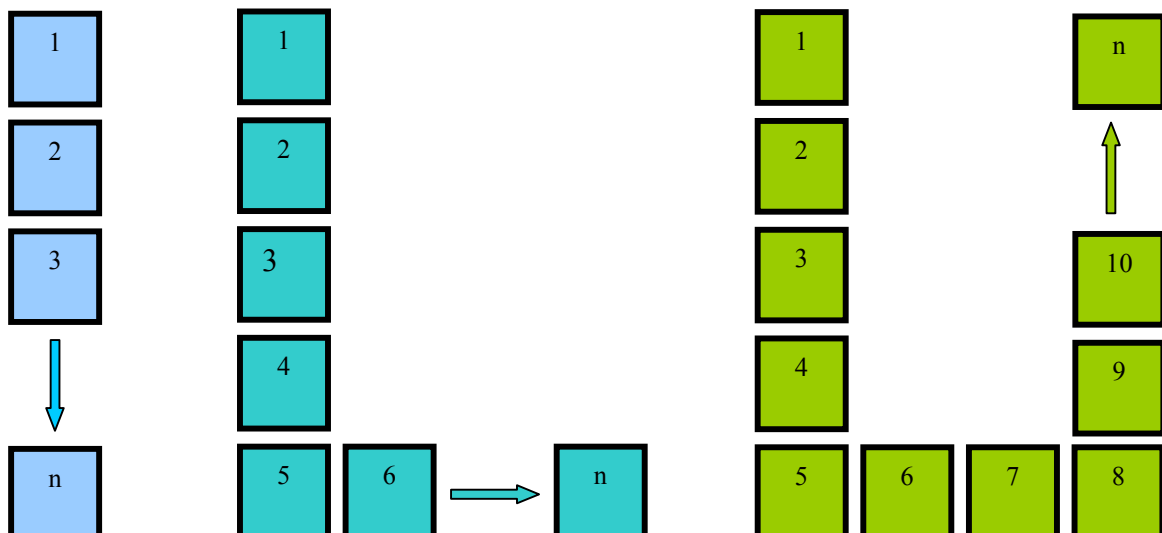
5.5. Protection of pipes

Effluent and reagent pipes that have been poorly installed or that are insufficiently protected can turn into sources of waste flow generation as the result of breakage or cracks.

They thus need to be adequately supported and protected with resistant elements to avoid this occurring.

5.6. Design of the processing lines

Given that the main environmental problems of the industry are caused by drag-out, provision needs to be made for the minimum number of passageway intersections in the layout of the electroplating plant in order to specifically avoid part of the drag-out produced in the movement between tanks from ending up on the factory floor.



As this is not always feasible, especially in plants using manual operations for different final finishes, trays need to be positioned under the aisles to collect any drips and above all prevent them from ending up on the ground. These trays need to be connected to the corresponding tank, preferably to concentrates, for the subsequent purification of the effluent.

5.7. Effluent transmission

Pumping equipment for effluents and other liquids also have to comply with a series of requirements:

- The quality of the pumps needs to be adequate for the type of liquid being pumped. Care has to be taken, for example, of the interior of pumps used for pumping effluents or chromium liquids due to the iron and even stainless steel being attacked;
- Take the precaution to double the number of pumps that send diluted effluent to the water treatment plant, for these are the ones that contribute the most volume to the plant;
- In specific cases, it can be useful to set up meters that show the number of hours that the pumps have been in operation.

5.8. Effluent collection

Effluent collection should be done by way of closed feed lines, one for each type of effluent and resistant material. As a precautionary measure, take account of the customary periodic emptying of the degreasing baths which can reach temperatures of around 65-70°C; PVC pipe, for example, will not resist being heated to this temperature and will warp. The same pipe made of iron, which will resist temperature changes very well, will not stand up to attack by caustic soda, for example, and will be perforated over time. A good material for this effluent is stainless steel.

As to the segregation of effluents, at the very minimum piping is necessary for:

1. Acid and chromium concentrates
2. Alkaline concentrates
3. Cyanide concentrates (do not mix with the previous ones for the risk of forming complexes between the metals from the cyanate baths and the chelating agents present in the degreasing processes).
4. Diluted non-cyanide acids and alkalis.

5. Diluted chromium
6. Diluted cyanide

The system used for the collection of effluents must take any future modifications in the processing plant into account. The ideal system consists of an accessible passageway where piping is fixed securely.

5.9. The work environment

A workshop with water everywhere, a slippery floor and a damp, corrosive atmosphere all enhance the possibility of accidents and illnesses occurring at work. Work must be carried out in adequate conditions in terms of cleanness and orderliness, with the suitable equipment, etc. necessary for each job that is done.

If this is not the case, general untidiness is being encouraged, the repercussions of which are the poor quality of production, a deterioration of the work environment and, more than likely, an increase in the generation of waste flows.

Experience shows that a dirty, polluted workshop is generally less competitive in terms of productivity.

5.10 Process automation and programming

One way to optimise production activities and to minimise waste flow generation is by establishing the process control parameters and automating them. Moreover, it allows all parts to be processed in the same way in accordance with the quality standards defined by the company.

The viability of the application of this alternative is highly dependent on the specific characteristics of the company (size, space, etc.).

6. ANALYSIS OF THE TECHNICAL AND ECONOMIC VIABILITY OF SOME OF THE ALTERNATIVES

Two models of real companies that carry out surface treatment processes (company A and company B) have been used as the basis for this chapter, and an evaluation has been made of the different costs and savings that are involved when implementing certain alternatives. The objective of this chapter is to obtain a fairly reliable estimate of the period of return on investment (PRI) suggested for some of the identified alternatives for minimisation.

Company A:

A small, family-type concern, with five workers and manual rack lines for nickel and chromium finishing.

Company B:

A medium-sized company with forty workers and automatic lines and that specialises in the anodising of hard aluminium.

A study is made below of the technical feasibility and economic viability of most of the minimisation alternatives covered up until now.

COMPANY A:

Type: very small family-type concern specialising in nickel and chromium finishing using manual rack lines.

General description:

Number of workers: 5 *Job time hours day:* 8 *Working shifts:* 1

Activity: electrolytic coatings of decorative nickel and chromium on parts made of iron and brass.

Type of installation: small manual installation, with aisles between the tanks.

Production: around 2.3 million dm²/year for illumination and lighting.

Turnover: 19,833.99 €/year.

Main pollutants produced:

Waste water:

- Characterisation: continuous diluted and concentrated batch effluents with:
 - Very alkaline or acid pH, according to the concentrate;
 - Presence of heavy metals, such as iron, nickel, copper and zinc;
 - Presence of hexavalent chromium;
 - Other compounds present, such as soluble salts (chlorides, sulphates and boron).
- Discharge rate: the company continuously disposes of 1.4 m³/h throughout the 8 job working hours of the day.

Industrial waste:

- Characterisation:
 - Hazardous:
 - ⇒ Waste water and depleted concentrated bath solutions;
 - ⇒ Effluent treatment sludge;
 - ⇒ Empty, dirty raw materials containers.
 - Non-hazardous:
 - ⇒ General waste (non-selectively collected)

Current management of the pollutants produced:

Waste water: physico-chemical treatment consisting of the reduction of hexavalent chromium to trivalent chromium using sodium bisulphite, coagulation with iron chloride, neutralisation with sodium hydroxide, flocculation with an anionic polyelectrolyte, sludge sedimentation, concentration and press filter drying.

Industrial waste: apart from waste water and depleted concentrated bath solutions that are treated in the company itself, the remaining waste generated by the company is managed externally through authorised companies.

Current cost of waste management:

Through losses of raw materials and water: 9,616.19 €/year.

Waste water: 23,439.47 €/year.

Industrial waste: 2,704.55 €/year.

DESCRIPTION OF MINIMISATION ALTERNATIVES

Waste flow analysed: pollution of rinsing water.

Minimisation alternative: reduce drag-out.

Minimisation options: attachment of joint covers between the bath tanks and subsequent rinsing.

Other flows affected: none.

Raw materials affected: all of those that comprise the different process baths.

Processes or products affected: the entire electroplating plant.

Possible economic saving in the use of raw materials and auxiliary materials: 30% of drag-out.

Process bath or component	Loss due to drag-out	Economic saving through reduction of loss (30%)	Total economic saving (€/year)
Ultrasonic degreasing	88.70 kg	26.61 kg	14.38
Electrolytic degreasing	68.90 kg	20.67 kg	31.31
Pickling	24.64 kg	7.39 kg	14.44
Nickel chloride	78.85 kg	23.65 kg	50.47
Nickel sulphate	266.10 kg	79.83 kg	199.11
Boric acid	49.28 kg	14.78 kg	11.11
Polishes	24.64 kg	7.39 kg	49.54
Additives	3.94 kg	1.18 kg	3.43
Chromium oxide	147.84 kg	44.35 kg	217.25
Chromium trioxide	177.40 kg	53.22 kg	391.19
TOTAL	930.29 kg	279.07 kg	1,009.41

Table 8

In terms of water from the mains network, if a reduction of 30% can be made in the pollutant load in the rinsing water, then volume renewal can also be reduced by the same proportion; that is to say, 2,443.7m³/year could be reduced by 733.1m³. This would mean an economic saving of 1,005.02 €/year.

The same line of reasoning can be applied to distilled water, so out of 9.9m³/year, the company could make an economic saving of 2.97. This gives an economic saving of 62.48 €/year.

Possible pollution reduction: the same reduction of 30%, needs to be applied here, as all raw materials lost due to drag-out turn into waste water.

Technical justification for each option:

Comparison of technology: Attaching joint covers does not imply any substantial change in the production process used by the company; only part of the dripping that is lost through drag-out returns to the bath.

Effect on process or product quality: none.

Space requirements: practically none; the intention is precisely to occupy an empty space in order to avoid the dripping onto the ground of product salts from the process baths.

Implementation time: very little; attaching joint covers is done directly on the tanks involved.

Requirements for use: it is important to angle the joint covers suitably so that the liquid can be returned to the process bath..

Economic justification for each option (in €):

Expenditure:

- *Equipment:* 3.01€ each. x 6 process tanks = 18.03€.
- *Installation:* 2 h x 15.03 €/h = 30.05€.
- *Engineering*
- *Servicing*
- *Set-up*
- *Value of equipment at end of useful life*
- *Training*
- *Raw materials*
- *Waste management*
- *Operation*
- *Maintenance*
- *Others*
- **TOTAL: 48.08€.**

Income:

- *Sale of existing equipment*
- *Increase in selling price of the product*
- *Increase in production*
- *Sale and/or revaluation of by-products*
- *Saving of raw materials and auxiliary materials:* 2,076.91 €/year (see adjacent table).
- *Economic saving as result of waste management:* (733.1m³ of mains water + 2,97 m³ of distilled water that would no longer need treating) x 0.9 €/m³ waste water treatment and transportation and management of treatment sludge = 663.58

€/year.

TOTAL: 2,740.48 €/year.

Period of return on investment: approx. 6.4 days.

DESCRIPTION OF MINIMISATION ALTERNATIVES

Waste flow analysed: pollution of rinsing water.

Minimisation alternative: reducing drag-out.

Minimisation options: the use of sealed recovery rinses after certain process baths.

Other flows affected: sludge generation.

Raw materials affected: all those comprised in the different process baths involved.

Processes or products affected: the entire electroplating plant.

Possible saving in the use of raw materials and auxiliary materials

Process bath or component	Number of sealed recovery rinses	Economic saving through reduction of loss	Total economic saving (€/year)
Ultrasonic degreasing	1	62.09 kg (70%)	97.02
Electrolytic degreasing	1	48.23 kg (70%)	73.05
Nickel plating	2	380.51 kg (90%)	940.95
Nickel chloride		70.96 kg (90%)	151.40
Nickel sulphate		239.49 kg (90%)	597.33
Boric acid		44.35 kg (90%)	33.32
Polishes		22.17 kg (90%)	148.62
Additives		3.54 kg (90%)	10.28
Chromium plating		3	318.73 kg (98%)
Chromium oxide	144.88 kg (98%)		709.66
Chromium trioxide	173.85 kg (98%)		1,277.66
TOTALS	7	809.56 kg	3,098.54

Table 9

As for rinsing water, the volume of water in subsequent rinsing per sealed recovery rinse could be reduced to 1/5. This would give:

Prior process bath	Water volume renewal (l/h)		Reduction in rinsing volume (l/h)	Economic saving (€/year)
	Current	With recovery		
Ultrasonic degreasing	560	112	448	1,080.93
Electrolytic degreasing	280	56	224	540.47
Nickel plating	2,800	112	2,688	6,485.47
Chromium plating	4,480	36	4,444	10,722.48
TOTALS	8,120	316	7,804	18,829.48

Table 10

Possible pollution reduction: the same reduction of 1/5 of the necessary volume per sealed recovery rinse that gets converted into waste water to be treated needs to be applied here as well; there would thus be a reduction of 13,735 m³/ year of waste water.

Technical justification for each option:

Comparison of technology: As can be seen from this report, sealed recovery rinses are especially recommendable for process baths that operate at temperatures higher than 40°C, as they enable water and salt losses due to evaporation to return to the bath.

Effect on process or product quality: The introduction of sealed recovery rinses, as has been mentioned, can lead to the reintroduction into the bath of certain pollutants generated by impurities in the anodes, the surface of the metal being attacked, etc. Analytical control criteria need to be applied systematically in order to avoid the bath being contaminated.

Space requirements: A tank needs to be added to the current process line for every sealed recovery rinse. One thus needs the necessary space in order to be able to extend the lines.

Implementation time: Relatively little; the necessary modifications to the process lines can be carried out in 3 to 4 days.

Requirements for use: As this involves an additional rinse, no special measure is required in process. It is important, however, to remember that the company will need to return losses due to evaporation back into the bath every day. This is done by adding the last recovery losses to the previous ones, and so on successively back to the initial losses, which are then all returned to the bath.

Economic justification for each option (in €):

Expenditure:

- *Equipment:* 721.21€ each x 7 rinsing tanks = 5048.5 €.
- *Installation:* 2 x (32 h x 15.03 €/h) = 961.62 €.
- *Engineering*
- *Service:* modifications to the rinsing water piping: 1,502.53 € .
- *Set-up*
- *Value of equipment at end of useful life*
- *Training*
- *Raw materials*
- *Waste management*
- *Operation:* ½ h daily to return losses due to evaporation x 220 days/year x 15.03 €/h = 1,652.78 €/year.
- *Maintenance*
- *Others*

- **TOTAL INVESTMENT: 7,512.65€**
- **TOTAL OPERATING COSTS: 1,652.78 €/year**

Income:

- *Sale of existing equipment*
- *Increase in selling price of the product*
- *Increase in production*
- *Sale and/or revaluation of by-products*
- *Saving of raw materials and auxiliary materials: 21,928.02 €/year (see adjacent tables).*
- *Economic saving as result of waste management: 13,735 m³/year of mains water that would no longer need treatment) x 0.9 €/m³ of waste water treatment, and transportation and management of waste water sludge = 12,382.35 €/year.*
- **TOTAL: 34,310.37 €/year.**

Period of return on investment: approx. 2.8 months.

DESCRIPTION OF MINIMISATION ALTERNATIVES

Waste flow analysed: contamination of rinsing water.

Minimisation alternative: reduction in the consumption of rinsing water.

Minimisation options: incorporation of a reverse current multiple cascade rinse system.

Other flows affected: generation waste water sludge.

Raw materials affected: none.

Processes or products affected: rinsing structure in the plating plant.

Possible economic saving in the use of raw materials and auxiliary materials: saving in the consumption of rinsing water:

Process bath or component	Current single rinse with volume (l/h)	Double cascade rinse (l/h)	Reduction in water consumption (l/h)	Total economic saving (€/year)
Ultrasonic degreasing	560	18.0	542.0	1,307.74
Electrolytic degreasing	280	12.5	267.5	645.42
Pickling	400	15.0	385.0	928.92
Nickel plating	2,800	39.6	2,760.4	6,660.28
Chromium plating	4,480	50.0	4,430.0	10,688.70
TOTAL	8,520	135.1	8,384.9	20,231.07

Table 11

Possible pollution reduction: The same reduction needs to be applied for each rinsing position, given that all rinsing water ends up as waste.

Technical justification for each option:

Comparison of technology: reverse current multiple cascade rinse systems are used by many companies in the sector and they offer all of the aforementioned advantages in terms of the important reduction in rinse water volume for the same quality rinse.

Effect on process or product quality: no negative effect, and if anything, an improvement on current rinsing methods.

Space requirements: The use of these double rinses makes the process line longer and tanks need to be installed between the existing ones.

Implementation time: merely a short period of time is necessary to move the tanks in order to make space for the double rinses and install new water pipes.

Requirements for use: none in particular; the only requirement is to respect the direction of the parts through the two connected tanks, entering by way of the dirtier water and coming out from the cleaner water.

Economic justification for each option (in €):

Expenditure:

- *Equipment: 1,502.3€ each x 5 process tanks = 7,512.65€.*
- *Installation: 20 h x 15.03 €/h = 30.05€.*
- *Engineering*
- *Service*
- *Set-up*
- *Value of equipment at end of useful life*
- *Training*
- *Raw materials*
- *Waste management*
- *Operation*
- *Maintenance*
- *Others*
- ***TOTAL: 7,813.16€.***

Income:

- *Sale of existing equipment*
- *Increase in selling price of the product*
- *Increase in production*
- *Sale and/or revaluation of by-products*

- *Saving of raw materials and auxiliary materials:* 20,231.07 €/year (see adjacent table).
- *Economic saving as result of waste management:* $14,757\text{m}^3 \times 0.9 \text{ €/m}^3$ waste water treatment, transportation and management of sludge = 13,303.70 €/year.
- **TOTAL: 33.534,77 €/year.**

Period of return on investment: approx. 2.8 months.

DESCRIPTION OF MINIMISATION ALTERNATIVES

Waste flow analysed: contamination of rinsing water.

Minimisation alternative: reduction in the consumption of rinsing water.

Minimisation options: fitting of flow meters at each rinsing position.

Other flows affected: generation of waste water sludge.

Raw materials affected: none.

Processes or products affected: none.

Possible economic saving in the use of raw materials and auxiliary materials: saving in the consumption of rinsing water:

Process bath or component	Single rinse usual volume (l/h)	Single rinse volume (l/h) with flow meters	Reduction in water consumption (l/h)	Total economic saving (€/year)
Ultrasonic degreasing	1,000	560	440	1,061.63
Electrolytic degreasing	500	280	220	530.81
Pickling	700	400	300	723.83
Nickel plating	5,000	2,800	2,200	5,308.16
Chromium plating	8,000	4,480	3,520	8,493.05
TOTAL	15,200	8,520	6,680	16,117.49

Table 12

Possible pollution reduction: The same reduction needs to be applied here for each rinsing position, given that all rinsing water ends up as waste.

Technical justification for each option:

Comparison of technology: The installing of flow meters makes it possible to establish and regulate the real needs for rinse water volume, and does not involve any technical difficulty in the process; on the other hand, it offers all types of advantage concerning the control and regulation of rinsing water volume.

Effect on process or product quality: No negative effect provided that the dilution ratio at each rinse position is respected.

Space requirements: No space requirements are required concerning the installation of flow

meters with regard to the plating line.

Implementation time: Around five hours for all of the tanks.

Requirements for use: None in particular; only the rinse volume needs to be regulated by way of a valve on the device itself.

Economic justification for each option (in €):

Expenditure:

- *Equipment:* 270.46€ each x 5 rinsing tanks = 1,352.28€.
- *Installation:* 5 h x15.03 €/h =75.13€.
- *Engineering*
- *Service*
- *Set-up*
- *Value of equipment at end of useful life*
- *Training*
- *Raw materials*
- *Waste management*
- *Operation*
- *Maintenance*
- *Others*
- ***TOTAL: 1,427.40€.***

Income:

- *Sale of existing equipment*
- *Increase in selling price of the product*
- *Increase in production*
- *Sale and/or revaluation of by-products*
- *Saving of raw materials and auxiliary materials:* 16,117.49 €/year (see adjacent table).
- *Economic saving as result of waste management:* 11,757m³ x 0.9 €/m³ waste.
- *water treatment, transportation and management of sludge = 10,599.15 €/year.*
- ***TOTAL: 2,676.15 €/year.***

Period of return on investment: approx. 19.5 days.

DESCRIPTION OF MINIMISATION ALTERNATIVES

Waste flow analysed: alkali solutions with oil residues

Minimisation alternative: reuse of the solution through the introduction of a predegreasing process.

Minimisation options: implementation of two predegreasing tanks, one for each bath.

Other flows affected: Waste water to be treated.

Raw materials affected: Degreasing by ultrasonic and electrolytic degreasing.

Processes or products affected: Preparation of the metal surface to be coated electrolytically.

Possible economic saving in the use of raw materials and auxiliary materials: Reduction of 25% in the consumption of salts and water for degreasing preparation.

Possible pollution reduction: Reduction of 25% in the volume of aqueous alkaline solution containing oil.

Technical justification for each option:

Comparison of technology: Moderate use is made of this method in the sector. It actually involves degreasing using two tanks (the first being more diluted) instead of one, as is the case at present.

Effect on process or product quality: the introduction of an initial degreasing bath improves the operation and gives better results as far as oil and grease elimination is concerned. There is thus an improvement in the quality of the process.

Space requirements: Each predegreasing tank obviously extends the plating line as new process tanks are added.

Implementation time: Assembly time is approximately one day.

Requirements for use: There are no specific conditions as far as use is concerned and quite simply the usual operations for degreasing are used.

Economic justification for each option (in €):

Expenditure:

- *Equipment:* 2 tanks x 901.52€ each =1,803.04€.
- *Installation:* 1 operator x 1 day x 8 h x 15.03 €/h = 120.20€.
- *Engineering*
- *Service*
- *Set-up*
- *Value of equipment at end of useful life*
- *Training*
- *Raw materials*
- *Waste management*
- *Operation*
- *Maintenance*

- Others
- **TOTAL INVESTMENT: 1,923.24€**

Income:

- Sale of existing equipment
- Increase in selling price of the product
- Increase in production
- Sale and/or revaluation of by-products
- Saving of raw materials and auxiliary materials: 25% of 450.76 €/year in ultrasonic + 25% of 681.55 €/year in electrolyte = 1,112.69 €/year + 170.39 €/year = 283.08 €/year; 25% of 2,100 l. of water for ultrasonic at 1.37 €/m³ + 25% of 8,400 l. of electrolyte at 1.37 €/m³ = 0.72 €/year + 2.88 €/year = 3.60 €/year; 283.08 €/year + 3.60 €/year = 286.68 €/year.
- Economic saving as result of waste management: 10.500 l. of waste alkaline solution/year x 25% = 2,625 l.; 2.625 l. x 0.27 €/l = 709.95 €/year.
- **TOTAL: 996.62 €/year.**

Period of return on investment: approx. 1.9 years.

DESCRIPTION OF MINIMISATION ALTERNATIVES

Waste flow analysed: acid solution containing dissolved metals.

Minimisation alternative: reuse of the solution through the introduction of a pre-pickling process.

Minimisation options: Addition of a pre-pickling tank.

Other flows affected: waste water to be treated.

Raw materials affected: Acid pickling.

Processes or products affected: Preparation of the metal surface to be coated electrolytically.

Possible economic saving in the use of raw materials and auxiliary materials: Reduction of 25% in the consumption of salts and water for degreasing preparation.

Possible pollution reduction: 25% reduction in the volume of acid solution containing metals.

Technical justification for each option:

Comparison of technology: Moderate use is made of this method in the sector. It actually involves degreasing using two tanks (the first being more diluted) instead of one, as is the case at present.

Effect on process or product quality: the introduction of an initial degreasing bath improves the operation and gives better results as far as oil and grease elimination is concerned. There is thus an improvement in the quality of the process.

Space requirements: Each predegreasing tank obviously extends the plating line as new process tanks are added.

Implementation time: Assembly time is approximately one day.

Requirements for use: There are no specific conditions as far as use is concerned and quite simply the usual operations for degreasing are used.

Economic justification for each option (in €):

Expenditure

- *Equipment:* 1 tank x 901.52€ = 901.52€.
- *Installation:* 1 operator x ½ day x 8 h x 15.03 €/h = 60.01€.
- *Engineering*
- *Service*
- *Set-up*
- *Value of equipment at end of useful life*
- *Training*
- *Raw materials*
- *Waste management*
- *Operation*
- *Maintenance*
- *Others*
- ***TOTAL INVESTMENT: 961.62€***

Income

- *Sale of existing equipment:*
- *Increase in selling price of the product:*
- *Increase in production:*
- *Sale and/or revaluation of by-products:*
- *Saving of raw materials and auxiliary materials:* 25% of 315 l. of hydrochloric acid = 78.75 l.; 78.75 l. x 0.09 €/l = 7.10 €/year; 25% of 3,150 l. of water at 1.37 €/m³ = 1.08 €/year; 7.10 €/year + 1.08 €/year = 8.18 €/year.
- *Economic saving as result of waste management:* 25% of the solution remains as an aqueous acid waste containing metal = 3,150 l./year x 25% = 787.5 l./year of waste; 787.5 l x 0.15 €/l = 118.32 €/year.
- ***TOTAL: 126.50 €/year.***

Period of return on investment: approx. 7.6 years.

DESCRIPTION OF MINIMISATION ALTERNATIVES

Waste flow analysed: Acid solution containing dissolved metals.

Minimisation alternative: Replacement of the pickling solution by hydrochloric acid.

Minimisation options: Use of sulphuric acid for pickling ferrous parts.

Other flows affected: Waste water to be treated.

Raw materials affected: Acid pickling.

Processes or products affected: Preparation of the metal surface to be coated electrolytically.

Possible economic saving in the use of raw materials and auxiliary materials: Reduction of 15% in the consumption of salts and water for degreasing preparation.

Possible pollution reduction: Reduction of 15% in the volume of acid solution containing metals.

Technical justification for each option:

Comparison of technology: While both have a very similar pickling effect (as can be seen from this report), the replacement of hydrochloric acid by sulphuric acid offers the advantage of being able to control the degree to which the acid attacks the iron through the temperature of the bath, which extends the useful life of the bath.

Effect on process or product quality: Replacing one acid for another means that the operation can be improved as a result of being able to control the degree to which the acid attacks the iron. There is thus an improvement in the quality of the process.

Space requirements: The same pickling tank can be used for both acids.

Implementation time: Around ½ day to change from one bath to the other. Besides the changeover, a few days are needed in order to establish the *modus operandi* with the new bath.

Requirements for use: For the system to be effective, a thermometer needs to be installed to control the working temperature of the acid. Once the necessary checks have been made to determine the degree to which the acid is to attack the iron, the working temperature interval of the bath needs to be set and, if necessary, it needs to be heated or cooled as required.

Economic justification for each option (in €.):

Expenditure:

- *Equipment*
- *Installation:* 1 operator x ½ day x 8 h x 15.03 €/h = 60.01€.
- *Engineering*
- *Service*
- *Set-up:* 1 operator x 1 day x 8 h x 15.03 €/h = 120.20€.
- *Value of equipment at end of useful life*
- *Training*

- Raw materials
- Waste management
- Operation
- Maintenance
- Others
- **TOTAL INVESTMENT: 180.3€.**

Income:

- Sale of existing equipment
- Increase in selling price of the product
- Increase in production
- Sale and/or revaluation of by-products
- Saving of raw materials and auxiliary materials: 15% of 315 l. of hydrochloric acid = 47.25 l.; 47.25 l x 0.09 €/l. = 4.26 €/year; 15% of 3,150 l. of water at 1.37 €/m³ = 0.65 €/year; 4.26 €/year + 0.65 €/year = 4.91 €/year.
- Economic saving as result of waste management: 15% of the solution remains as an aqueous acid waste containing metal = 3,150 l./year x 15% = 472.5 l./year of waste; 472.5 l. x 0.15 €/l. = 70.99 €/year.
- **TOTAL: 75.90 €/year.**

Period of return on investment: approx. 2,4 years.

DESCRIPTION OF MINIMISATION ALTERNATIVES

Waste flow analysed: waste water generated in the rinsing process.

Minimisation alternative: Reuse of part of the rinsing water.

Minimisation options: Use the rinsing water from pickling as a rinse for electrolytic degreasing (**skip technique**).

Other flows affected: Waste water to be treated.

Raw materials affected: None.

Processes or products affected: None.

Possible economic saving in the use of raw materials and auxiliary materials: Saving in the consumption of water at the electrolytic degreasing position.

Possible pollution reduction: Reduction in the treatment of pickling water.

Technical justification for each option:

Comparison of technology: Moderate use is made of this method in the sector. As has already been explained, there is no drawback with this given that the parts go on to the acid pickling tank after having been rinsed with this reused water.

Effect on process or product quality: No significant effect.

Space requirements: None.

Implementation time: Around ½ day for assembling the piping.

Requirements for use: Once it has been established how it works, the usual operations for degreasing as in any rinse are used.

Economic justification for each option (in €):

Expenditure:

- *Equipment*
- *Installation:* 1 operator x ½ day x 8 h x 15.003 €/h = 60.01€.
- *Engineering*
- *Service:* 120.02€ in PVC piping.
- *Set-up*
- *Value of equipment at end of useful life*
- *Training*
- *Raw materials*
- *Waste management*
- *Operation*
- *Maintenance*
- *Others*
- **TOTAL: 180.03€.**

Income:

- *Sale of existing equipment*
- *Increase in selling price of the product*
- *Increase in production*
- *Sale and/or revaluation of by-products*
- *Saving of raw materials and auxiliary materials:* 280 l/h of rinsing water from electrolytic degreasing x 1,760 h/year = 493m³/year; 493m³ at 1.33 €/m³ = 675.86 €/year.
- *Economic saving as result of waste management:* 493m³ x 0.90 €/m³ waste water treatment, transportation and management of sludge = 444.45 €/m³.
- **TOTAL: 1120.30 €/year.**

Period of return on investment: approx. 2 months.

COMPANY B:

Type: A medium-sized company that specialises in the anodising of hard aluminium on automatic lines.

General description:

Number workers: 49 *Job time hours day:* 24 *Working shifts:* 3

Activity: rectification and hard anodising of aluminium.

Type of installation: automatic lines.

Production: 25 million aluminium parts for the automobile sector.

Main pollutants produced:

Waste water:

- Characterisation: continuous diluted and concentrated batch effluents with
 - very alkaline or acid pH, according to the concentrate
 - presence of oil, detergents, etc.
 - presence of heavy metals, such as aluminium
 - presence of hexavalent chromium
 - other compounds present as soluble salts are sulphates, chlorides and nitrates.
- Discharge regime: around 10.5m³/day, in batches

Industrial waste:

- Characterisation:
 - Hazardous:
 - ⇒ waste water and depleted concentrated bath solutions
 - ⇒ waste water sludge
 - ⇒ acid and alkaline solutions containing oil
 - Non-hazardous:
 - ⇒ General waste (without selective collection)

Current management of the pollutants produced:

Waste water: physico-chemical treatment consisting of the reduction of hexavalent chromium to trivalent chromium using sodium bisulphite, neutralisation with calcium hydroxide, flocculation with anionic polyelectrolyte, sedimentation, concentration and press filtering of sludge.

Industrial waste: apart from waste water and depleted concentrated bath solutions that are treated in the company itself, the remaining waste generated by the company is managed externally through authorised companies.

Current cost of waste management:

Through losses of raw materials and water: 1,502.53 €/year

Waste water: 11,118.72€/year

Industrial waste: 32,454.65 €/year

DESCRIPTION OF MINIMISATION ALTERNATIVES

Waste flow analysed: polluted rinsing water.

Minimisation alternative: reduction in the consumption of rinsing water.

Minimisation options: Installation of delayed electrovalves at each rinsing position.

Other flows affected: generation of waste water and treatment sludge.

Raw materials affected: none.

Processes or products affected: none.

Possible economic saving in the use of raw materials and auxiliary materials: saving in the consumption of rinsing water:

Process bath or component	Single rinse usual (l/h) volume	Single rinse volume (l/h) with electrovalves	Reduction in the consumption of water (l/h) ¹¹	Total economic saving (€/year)
Degreasing	485	291	194	779.05
Pickling	485	291	194	779.05
Anodising	1,940	1,164	776	3,116.20
Sealing	970	582	388	1,504.01
TOTALS	3,880	2,328	1,552	6,232.40

Table 13

Possible pollution reduction: The same reduction needs to be applied for each rinsing position, given that all rinsing water ends up as waste:

$$1,552 \text{ l/h} \times 5,760 \text{ h/year} \times 0.01 \text{ €/l.} = 123,573.47 \text{ €/year}$$

Technical justification for each option:

Comparison of technology: The installing of time delayed electrovalves makes it possible to regulate the real consumption needs for rinsing water; on the other hand, it offers all types of advantage concerning the control and regulation of rinsing water volume and there is no technical difficulty involved in the process.

Effect on process or product quality: No negative effect provided that the dilution ratio at each rinsing position is respected.

Space requirements: No space requirements are necessary in the plating line in order to install delayed electrovalves.

Implementation time: Around ten hours for the entire set of tanks.

Requirements for use: None in particular; only the rinsing volume needs to be regulated with the valve on the device.

¹¹ Reduction by 40% of the volume of water at each rinsing position.

Economic justification for each option (in €):

Expenditure:

- *Equipment:* 300.51€ each x 4 rinsing tanks = 1,202.02€.
- *Installation:* 10 h x 15.03 €/h = 150.25€.
- *Engineering:*
- *Service:*
- *Set-up:*
- *Value of equipment at end of useful life:*
- *Training:*
- *Raw materials:*
- *Waste management:*
- *Operation:*
- *Maintenance:*
- **TOTAL: 1,352.28€.**

Income:

- *Sale of existing equipment:*
- *Increase in selling price of the product:*
- *Increase in production:*
- *Sale and/or revaluation of by-products:*
- *Saving of raw materials and auxiliary materials:* 6,232.40 €/year
- *Economic saving as result of waste management:* 123,573.47 €/year
- **TOTAL: 129,805.87 €/year.**

Period of return on investment: Approx. 4 days.

DESCRIPTION OF MINIMISATION ALTERNATIVES

Waste flow analysed: Alkaline solutions containing oil residues.

Minimisation alternative: Reuse of the solution by way of ultrafiltration

Minimisation options: Installation of two sets of ultrafiltration equipment, one on each degreasing bath

Other flows affected: Waste water from degreasing treatment rinsing and sludge.

Raw materials affected: Ultrasonic and chemical degreasing.

Processes or products affected: Preparation of the metal surface to be anodised electrolytically

Possible economic saving in the use of raw materials and auxiliary materials: Reduction of 95% in the consumption of salts and water for preparing degreasing.

Possible pollution reduction: Reduction of 95% in the volume of aqueous alkaline solution containing oil.

Technical justification for each option:

Comparison of technology: Membrane ultrafiltration technology has been successfully tested and used by companies in the sector. It is necessary, however, to carry out prior tests with real samples of the pollutant in order to establish the technical viability of the system and in any case to determine the most appropriate type of membrane for each specific application.

Effect on process or product quality: As ultrafiltration acts continuously on the degreasing bath, the solution can be constantly maintained in optimum working conditions. There is therefore an improvement in the quality of the process.

Space requirements: The two sets of ultrafiltration equipment needed by the company require approximately 6m².

Implementation time: From the time when the order is made, it can take two months for the equipment to arrive because it has to be imported; 2 to 4 days are needed for assembly and around 5 days more for tests and set-up; altogether it can take between 2 to 3 months.

Requirements for use: membrane technology needs certain controls and maintenance to keep it in good condition; the manufacturer's recommendations thus need to be strictly followed.

Economic justification for each option (in €):

Expenditure:

- *Equipment:* 2 sets of equipment x 24,040.48€ each = 48,080.97€.
- *Installation:* (included in the price of the equipment).
- *Engineering*
- *Service*
- *Set-up:* (included in the price of the equipment).
- *Value of equipment at end of useful life¹²:* 9,616.19€.
- *Training*
- *Raw materials:* cleaning products for the membranes = 240.40 €/year.
- *Waste management:* 5% of the solution remains as oil residues = 28,350 l. ultrasonic/year + 28,350 l. chemical/year = 56,700 l./year of degreasing solution; 56,700 l. x 5% = 2,835 l./year of oil residue; 2,835 l. x 0.10 €/l. = 283.35 €/year.
- *Operation:* 901.52 €/year (labour and electricity).
- *Maintenance:* 601.01 €/year labour.
- *Others:*
- ***TOTAL INVESTMENT: 38,464,77€.***
- ***TOTAL COST OF THE OPERATION: 2,026.29 €/year.***

¹² Based on a five year amortisation.

Income:

- Sale of existing equipment
- Increase in selling price of the product
- Increase in production
- Sale and/or revaluation of by-products:
- Saving of raw materials and auxiliary materials:
 - 95% of degreasing: $7,212.15 \text{ €/year} \times 95\% = 6,851.54 \text{ €/year}$;
 - 95% of the water for preparing degreasing: $(28.35\text{m}^3 \text{ (ultrasonic tank)} + 28.35\text{m}^3 \text{ (chemical tank)}) - 1.5\text{m}^3 \text{ (the part in purchased salts)} = 55.2\text{m}^3$; $55.2\text{m}^3 \times 95\% = 52.44\text{m}^3$ at $0.7 \text{ €/m}^3 = 36.56 \text{ €/year}$.
- Economic saving as result of waste management: $(28.35\text{m}^3 \text{ (ultrasonic tank)} + 28.35\text{m}^3 \text{ (chemical tank)}) \times 95\% \text{ saving} = 53.86\text{m}^3$ of waste alkaline solution /year; $53,860 \text{ kg} \times 0.10 \text{ €/kg} = 5,383.22 \text{ €/year}$.
- **TOTAL: 12,271.31 €/year.**

Period of return on investment: Approx. 3.7 years.

DESCRIPTION OF MINIMISATION ALTERNATIVES

Waste flow analysed: alkaline solutions containing oil residues.

Minimisation alternative: reuse of the solution by installing sealed recovery tanks.

Minimisation options: Installation of two tanks, one for each degreasing bath.

Other flows affected: waste water to be treated.

Raw materials affected: ultrasonic and chemical degreasing.

Processes or products affected: preparation of the metal surface.

Possible economic saving in the use of raw materials and auxiliary materials: reduction of 70% in salt and water drag-out from degreasing.

Process bath	Loss due to drag-out	Saving by recovery (70%)
Degreasing	670,46 l	469,32 l
Process bath water	21.67m ³	15.17m ³
Water from subsequent rinses ¹³	485 l/h	388 l/h
TOTAL	1,570.09 €/year	

Table 14

¹³ In this case, the saving in water is from the reduction of the rinsing volume to 1/5 without recovery.

Possible pollution reduction: reduction of the volume of water to be treated:

388 l/h of rinsing water saved x 5,760 h/year x 0.1 €/l of treated water 30,893.37 €/year

(469,32 l degreasing/year + (15.17m³ of process bath water x 1000 l/1.m³)) x 0.1 €/l = 218.18 €/year

TOTAL: 31,109.55 €/year.

Technical justification for each option:

Comparison of technology: As this matter is dealt with on different occasions throughout this report, please refer to the corresponding chapters.

Effect on process or product quality: The means are available to filter oil from the bath; if this is not the case, the alternative is not recommended.

Space requirements: As the lines are automatic, the current functions are transformed by each recovery tank, so the space requirements are therefore the same.

Implementation time: Assembly takes approximately one day.

Requirements for use: There are no specific conditions as far as use is concerned and quite simply the usual operations for degreasing are used. Analytical control of the bath does need to be increased, however, to prevent any possible contamination with oil.

Economic justification for each option (in €):

Expenditure:

- *Equipment*
- *Installation:* 1 operator x 1 day x 8 h x 15.03 €/h = 120.20€.
- *Engineering*
- *Service*
- *Set-up*
- *Value of equipment at end of useful life*
- *Training*
- *Raw materials*
- *Waste management*
- *Operation:* ½ h/day to return the recovery into each bath x 220 days/year x 15.03 €/h = 1,652.78 €/year.
- *Maintenance*
- *Others*
- **TOTAL INVESTMENT: 120.20€.**
- **TOTAL COST OF THE OPERATION: 1,652.78 €/year**

Income:

- *Sale of existing equipment:*
- *Increase in selling price of the product:*
- *Increase in production:*

- Sale and/or revaluation of by-products:
- Saving of raw materials and auxiliary materials: 1,570.09 €/year ;
- Economic saving as result of waste management: 31,109.55 €/year
- **TOTAL: 32,679.64 €/year.**

Period of return on investment: approx. 2 days.

DESCRIPTION OF MINIMISATION ALTERNATIVES

Waste flow analysed: acid solutions containing metal from the anodising process.

Minimisation alternative: total reuse of the anodising bath.

Minimisation options: Installation of ion delay equipment.

Other flows affected: waste water to be treated.

Raw materials affected: sulphuric acid from anodising.

Processes or products affected: none.

Possible economic saving in the use of raw materials and auxiliary materials: 90% saving approximately in the consumption of sulphuric acid and water in the anode bath.

Possible pollution reduction: 90% reduction in the volume of acid water containing metal to be treated.

Technical justification for each option:

Effect on process or product quality: With a low level of dissolved aluminium, there is an improvement in the behaviour of the bath.

Space requirements: about 1m²

Implementation time: around two days to assemble the piping.

Requirements for use: once it has been established how it operates, there are no specific conditions as far as use is concerned apart from periodic cleaning of the equipment.

Economic justification for each option (in €):

Expenditure:

- *Equipment:* One set of equipment for the three anode baths: 36,060.73€.
- *Installation:* Included in the price of the equipment.
- *Engineering*
- *Service:* 300.51€ in PVC piping.
- *Set-up*

- *Value of equipment at end of useful life¹⁴*: 721.21€.
- *Training*
- *Raw materials*
- *Waste management*
- *Operation*: 90152 €/year (counting the water and energy to carry out the regeneration process).
- *Maintenance*: 30051 €/year.
- *Others*
- **TOTAL: 29,149.09€.**
- **TOTAL OPERATING COSTS: 1,202.02 €/year.**

Income:

- *Sale of existing equipment*
- *Increase in selling price of the product*
- *Increase in production*
- *Sale and/or revaluation of by-products*
- *Saving of raw materials and auxiliary materials*: 90% saving in the purchase of sulphuric acid: 22,020 l/year x 90% = 19,818 l/year; 19,818 l/year x 0.22 €/l = 42,872.89 €/year; 42.84m³/year of water x 90% = 38.55m³/year; 38.55m³/year x 0.70 €/m³ = 26.88 €/year.
- *Economic saving as result of waste management*: 22,020 l of acid + 42,840 l of water = 64,860 l/year; 64,860 l/year x 90% saving = 58,374 l/year; 58,374 l/year x 0.01 €/l = 806.92 €/year.
- **TOTAL: 5,121.70 €/year.**

Period of return on investment: approx. 7.4 years.

DESCRIPTION OF MINIMISATION ALTERNATIVES

Waste flow analysed: rinsing waste water.

Minimisation alternative: reuse of rinsing water from the anode and sealing baths.

Minimisation options: installation of an ion exchange resin unit.

Other flows affected: treatment sludge from waste water.

Raw materials affected: none.

Processes or products affected: rinsing stages of the anodising and sealing processes.

¹⁴ Based on a five year amortisation.

Possible economic saving in the use of raw materials and auxiliary materials: 80% reduction in water consumption in these rinsing positions:

Process bath or component	Minimum single flow rinse (l/h)	Reduction 80% water consumption (l/h)	Total economic saving (€/year)
Anodising	1,940	1,552	6,232.40
Sealing	970	776	3,116.20
TOTAL	2,910	2,328	9,348.60

Table 15

Possible pollution reduction: 80% reduction in the volume of water to be treated at these rinsing positions.

Technical justification for each option:

Comparison of technology: water recycling technology based on ion exchange resins has been successfully introduced in numerous companies in the sector.

Effect on process or product quality: rinsing water that contains resins has a very low conductivity, which benefits the rinsing process of parts. There is thus an improvement in the quality of the process.

Space requirements: water recycling equipment adapted to the needs of the company requires approximately 2 to 3m².

Implementation time: Once the equipment is built (which can take around one month), 1 to 2 days are necessary for assembly and 2 to 3 days more for tests and set-up.

Requirements for use: As resin technology is very sturdy, there are few maintenance and control requirements; however, avoid organic substances, such as surfactants, oil, etc., from coming in contact with the resin, and concentrated baths, especially the anode bath, as this would lead to the immediate breakdown of the resin.

Economic justification for each option (in €):

Expenditure:

- *Equipment:* self-regenerating equipment of 500 l. of resin, consisting of active carbon, medium strong cationic resin and medium weak anionic resin: 33,055.67€.
- *Installation:* included in the price of the equipment.
- *Engineering*
- *Service:* water piping to the rinsing tanks for recycling: 450.76 €.
- *Set-up:* included in the price of the equipment.

- *Value of equipment at end of useful life:*¹⁵ 6,611.13 €.
- *Training*
- *Raw materials:* resin regeneration products = 120.20 €/year.
- *Waste management:* 10 l. of resin per litre are generated as waste water to be treated in regeneration: 10 l. x 500 l. of resin x 2 bottles = 10,000 l.; 10,000 l. x 0.01 €/l. waste water treatment, transportation and management of sludge = 138.23 €/year.
- *Operation:* 300.51 €/year (labour and electricity).
- *Maintenance:* 240.40 €/year labour.
- *Others*
- **TOTAL INVESTMENT: 26,895.29€.**
- **TOTAL OPERATING COSTS: 799.35 €/year.**

Income:

- *Sale of existing equipment*
- *Increase in selling price of the product*
- *Increase in production*
- *Sale and/or revaluation of by-products*
- *Saving of raw materials and auxiliary materials:* ion exchange recycling equipment gives an 80% reduction in water consumption at each rinsing position involved: 9,348.60 €/year (see adjacent table).
- *Economic saving as result of waste management:* 2,328 l/h x 5,760 h/year = 13,409,280 l/year; 13,409,280 l/year x 0.01 €/l x waste water treatment, transportation and management of sludge = 185,360.21 €/year.
- **TOTAL: 194,708.81 €/year.**

Period of return on investment: approx. 52 days.

¹⁵ Based on a five year amortisation.

7. CONCLUSIONS

At a time when the goal of protecting the environment through man's daily activities has become a vital need in society, large waste flows are being generated by industrial premises that are not always managed in the way that best ensures high levels of quality in terms of working conditions and the environment.

The entrepreneur who makes the decision to undertake an industrial project not only has to take aspects of production into account but also the comprehensive factors of input and output of materials and energy. His activities will in no way be isolated from those of everybody else. In fact, the situation will be quite the opposite, and he will find himself forming part of an “ecosystem” which lives according to the individual actions of each member of it.

The surface treatment industry consumes a wide variety of raw materials, together with large quantities of water in relation to the size of the industrial premises. It thus generates large amounts of waste element compounds that, if badly managed, endanger the functioning of the very system itself.

Up until a few years ago, the producer of electroplated products used to consider the large consumption of materials and water as being vital for the good finish of the product. Costs were not, in fact, excessively high for production economies so a good final product was thus assured. 'End-of-pipe' purification treatment systems were deemed to be the best solution for the environment.

These determining factors have given rise to badly designed electroplating process plants that are ill-adapted to the present or future needs of companies. Moreover, the general view on correct environmental management has been just partial, and might still be. This view only included the installation corresponding to the physicochemical treatment of waste water as a prolongation of the production line as well as the handling of industrial waste and emissions into the atmosphere according to environmental legislation. And this, without considering the possibility of reducing such residual flows; at the end, waste is just raw material and energy resources that have not been transformed into a finished product, but must be managed as waste flow.

This document aims at presenting guidelines that might optimise production processes in order for companies to integrate environmental issues in the management of their businesses. That is, reducing waste flows in a manner consistent with production requirements, and as a result, *eco-efficiently*.

Due to the fact that drag-out is the most significant source of the loss of raw materials and water, and that which causes most waste water and waste, a large proportion of the alternatives that are dealt with in this research study are based on drag-out reduction and recovery. The main goal of both the chapter on reduction at source and the one on recovery and recycling concerns the occurrence of drag-out in the electroplating plant.

In the section on pollution reduction at source, the substitution of raw materials and processes, together with the extension of the operating life of baths and the reduction of drag-out, are the main points. The introduction of improvements to the systems of rinsing and washing (counter-current overflow rinses, sealed recovery or ECO rinses, etc.) is also covered. With regard to recovery and recycling at source, aspects such as raw materials' recovery (degreasing, pickling and contributing products), the reuse of water (using ionic exchange resin equipment and reverse osmosis) and the recovery of drag-out (by electrolysis, electrodialysis, reverse osmosis, ultrafiltration, evaporation and ionic exchange) are dealt with. Besides relatively simple and inexpensive solutions, other more elaborate possibilities with increasingly large investment requirements are analysed. Due to the importance and the particular characteristics of the subject, the section on good housekeeping techniques has deservedly been given a chapter of its own, together with the chapter on the alternatives for treating effluents.

It can thus be asserted that there is a large variety and number of solutions available to the industry that are also very variable in terms of cost, both in the economising of water and raw materials, and reductions in the generation of waste flows.

It is therefore advisable to carry out a prior study to establish what the most adequate options are in each case. This study essentially needs to define the very best systems for reducing consumption by assigning the different process structures, the recovery equipment and the systems of purification.

In short, it is a matter of *rationalising* an industrial activity that is highly satisfying professionally speaking and one that faces numerous challenges of all kinds.

8. SOME REAL EXAMPLES FOR THE PROPOSED ALTERNATIVES

Below, specific examples are shown for companies on the Mediterranean that have implemented one or more minimisation alternatives. These examples are excerpts from the Med Clean case studies published by the Regional Activity Centre for Cleaner Production:

Medclean 2. Cleaner production in an electroplating bath sector company by means of the adoption of good practices and process changes. Industrias F. Sandoval, S.L. (Spain).

Medclean 5. Minimisation of waste in a chemical nickel-plating process. Electroless Hoard Coat, S.A. (Spain).

Medclean 11. Cleaner production application in a sanitary fittings producing plant. Eczacibasi Yapi Gereçleri. (Turkey).

Medclean 15. Cleaner production in an aviation industry. Israel aviation industry (Israel).

Medclean 16. Cleaner production in a surface treatment sector company. Zincats Industrials Canovelles, S.L. (Spain).

Medclean 19. Cleaner production in the sector of metal finishing within the electronics industry. ST Microelectronics (Malta).

Medclean 22. Reduction of drag-out in the chromium plating. Manuel Muños Clarós, S.L. (Spain).

Medclean 30. Elimination of trichloroethylene in the production of metal parts. Sasonia de Corte Fino, S.A. (Spain).

9. REFERENCES

ADEME. *Étude technique et économique de l'utilisation des solvants dans huit secteurs industriels.* Agence de l'Environnement et de la Maîtrise de l'Énergie. France. 1995.

AMETLLER, J. *Depuración de efluentes producidos por instalaciones de tratamiento de superficies.* Institut de Tecnologia i Modelització Ambiental. Terrassa. June 1993.

BARA, J-C. *Traitement de surface. Environnement et compétitivité.* Paris. 1988.

BREUIL, J.N. *Traitement de surface. Depollution a la source.* Cahiers Techniques de la Direction de la Prévention des Pollutions. Ministère de l'Environnement. Paris. 1986.

CORDERES, J. *Estudi i sistematització de les tecnologies de prevenció de la contaminació i producció neta en el sector de banys galvanics.* Unpublished. Barcelona, 1999.

DEPARTAMENT DE MEDI AMBIENT. Generalitat de Catalunya. *Galvanotècnia i Medi Ambient. Guia pràctica per a una correcta gestió medioambiental a les empreses de galvanotècnia.* Barcelona, 1st and 2nd editions 1992 and 1994.

HARTINGER, L. Handbook of effluent treatment and recycling for the metal finishing industry. Finishing Publications, Ltd. Wiltshire. 2nd edition. 1994.

KUSHNER, J.B. *Water and waste control for the plating shop.* Gardner Publications, Inc. Ohio. 1976.

NOYES DATA CORPORATION. Hazardous waste reduction in the metal finishing industry. PCR Environmental Management, Inc. California. 1989.

OECD. *Managing wastes containing cyanides: guidance document.* Organisation for Economic Co-operation and Development. Paris. 1992

UNEP. *Environmental management in the electronics industry. Semiconductor manufacture and assembly.* Technical Report n° 23. United Nations Publication. 1st edition. 1994.

U.S. ENVIRONMENTAL PROTECTION AGENCY. *Guides to pollution prevention. The metal finishing industry.* Ohio. 1992.

10. ENTITIES AND INDIVIDUALS THAT HAVE COLLABORATED IN THE PREPARATION OF THIS REPORT

- AMBIOMA CONSULT, S.L. (BIOMA)
- EDELAMP, S.A.
- ENTHONE-OMI (ESPAÑA), SA
- ESPAÑOLA DE ELECTRÓLISIS, S.L. (FORPEZ)
- INDUSTRIA GALVÁNICA SAMA, S.A.
- MACDERMID, SA
- SIDASA, SA
- TRELLEBORG AUTOMOTIVE SPAIN, S.A.
- 3 M (ESPAÑA), SA
- USF (ESPAÑA), SA
- Mr. Carles Ventura
- Mr. José A. Ortega

11. USEFUL WEBSITES RELATED WITH THE PROJECT

<http://www.gencat.es/mediamb/>: web site of the Ministry of the Environment of the Catalan Government

<http://www.cema-sa.org>: web site of the Centre for the Company and the Environment***.

<http://www.epa.gov/>: U.S. Environmental Protection Agency

<http://www.cygnus-group.com:9011>: waste reduction with special attention being paid to reduction and recycling at source.

<http://www.euler.berkeley.edu/green/cgdm.html>: information research on clean production.

<http://www.acs.org>: The American Chemical Society.

<http://www.envirolink.org>: An important source of environmental information with numerous Internet links.

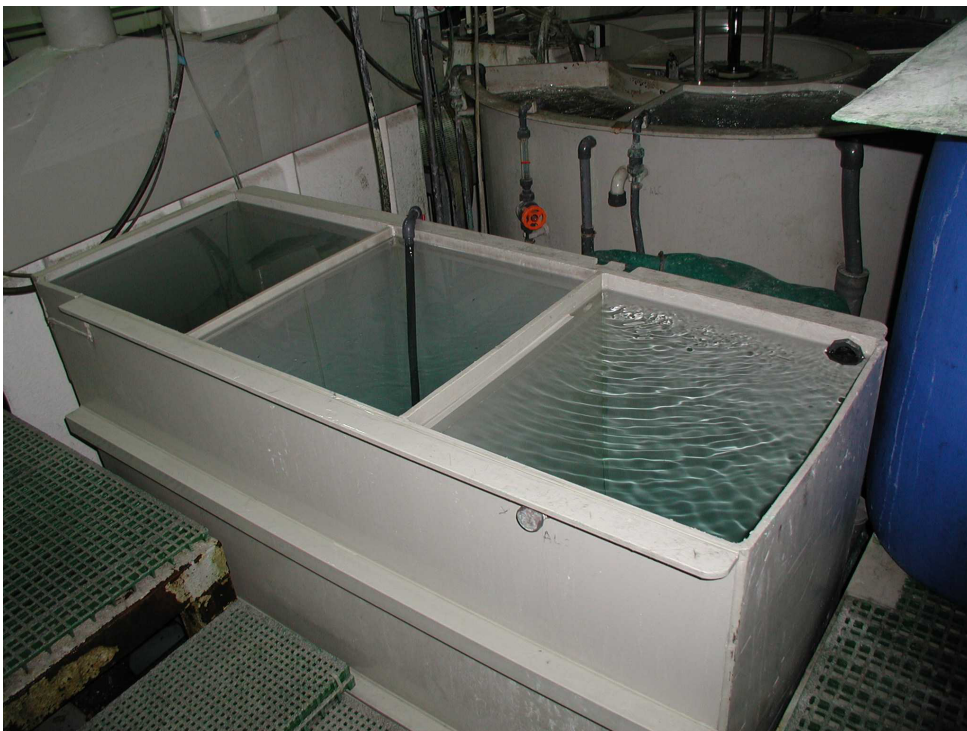
12. PHOTOGRAPHIES ON MINIMISATION ALTERNATIVES



1 – Recycling equipment for water used for washing with ion-exchange resins.



2 - Automated washing installation with programmable robot.



3 – Double forced-flow rinsing, against the direction of the flow.



4 – Vacuum-drying equipment.



5 - Frame-hanging line in the nickel baths.



6 – Reverse osmosis process for mains water.



7 – Demineralisation process for mains water.



8 – Installation for the oxidation of cyanides, before the evaporation of the wastewater.



9 – Blade sedimentator for concentrating the pollutants before the evaporation process.



10 – Baths filtration equipment.



11 – Fume extraction systems for the nickel baths.



12 – General view of the corridor with collection trays for dripping to the floor.