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Meeting of Experts on Olive Oil
Production and Electroplating Industry

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MEETING OF EXPERTS ON ELECTROPLATING INDUSTRY PRESENTATIONS MADE BY THE SPEAKERS



Autonomous Government of Catalonia
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Centre for Cleaner Production Initiatives



UNEP



Ministry of the Environment
Spain

**THE ELECTROPLATING INDUSTRY
TYPICAL PROCESSES
GENERATED CONTAMINATION
PRESENT ALTERNATIVES**

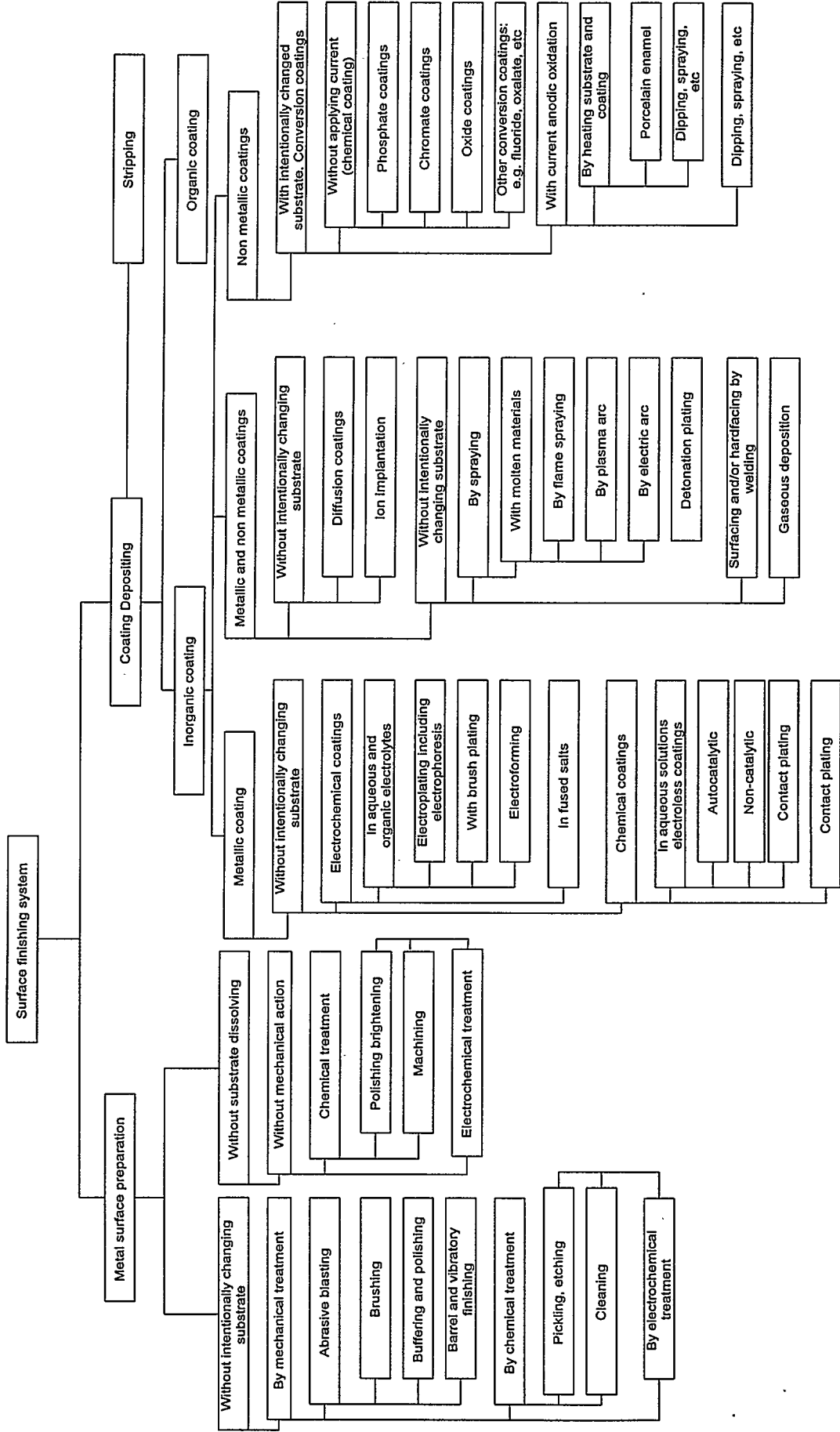
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A large fraction of the metal objects which we see in everyday life (screws, cans for food, kitchen utensils, car components, metal window frames, door handles, lamps, many electrical and electronic components, pens, spectacle frames, matches, jewelry, etc...) Have undergone a metal finishing process.

What does metal finishing mean? It is the name given to a wide range of processes carried out in order to modify the surface properties of a metal by deposition of a layer of another metal or different layers of different metals one on top the other and also in some cases by deposition of different alloys of two, three or more metals or by formation of an oxide film.

The origins of the industry lay in the desire to enhance the value of metal articles by improving their appearance, but in the modern times the importance of metal finishing for purely decorative reasons has decreased. The trend is now towards surface treatments which will impart corrosion resistance or particular physical or mechanical properties to the surface (for example heat or wear resistance, lubrication, solderability, electrical conductivity, etc.) and hence to make possible the use of cheaper substrate metals or plastics covered to give them essential metallic surface properties.

It should be emphasized that not all the surface finishing is carried out using electrochemical methods for the metal deposition as it can be seen in the following resume:



We are going to speak only of one part of the surface finishing known with the name of electroplating that comprises all the electrolytic metals deposition technology.

HISTORICAL REVISION OF THE ELECTROPLATING INDUSTRY IN SPAIN

Almost fifty ago, in 1949, there were approximately 300 companies in Spain dedicated to the electroplating. These companies were concentrated mainly in Catalonia and the Basque Country.

As you can see herebelow, the growth since then until now has been continuous.

<u>YEAR</u>	<u>STATUS</u>
1949	300 Companies
1960	550 "
1970	1.000 "
1995	2.500 "

Although there are not official figures concerning the turn-over level of this industrial segment, we can estimate that the annual turn-over is between 700 and 1.000 million dollars.

From these figures, it is easy to understand that it is an area comprised by a great number of small companies that until now it has been experimenting a continuous growth. However the strong pressure that every time more they are suffering in two very important aspects:

- 1) To meet technical specifications each time stronger, difficult to comply if there is not qualified technical personnel and control systems that the major part do not have.
- 2) To comply as well with the official regulations concerning the effluents, waste disposals and the industrial health and safety laws.

Makes us think that we can expect a significant reduction in the quantity of companies doing electroplating as a consequence of the concentration process of this activity in larger companies well prepared, that has been started a few years ago.

However we think that the business level in this sector will continue to grow in the future.

Before seeing the different electrodeposition processes that are used in this industry, I think it is of interest to describe a plating bath.

THE PLATING BATH

The plating bath is a water based solution containing a complex mixture of soluble species of the metal being plated has the desired quality and properties.

The function of each one of these components is:

I) The metal ion

The metal to be plated is present in the bath either as the simple hydrated ion or as a complex, normally in relatively high concentrations.

Generally we can say that the more high is the metallic concentration in the bath more high current density can be applied during the electrolysis and as higher this current density is higher will be the deposition speed.

II) Conducting salts

Various electrolytes are also added in high concentration to give the bath maximum conductivity. They also have an influence in controlling the pH of the solution.

III) Complexing agents

They are used when it is necessary to maintain in solution a metal in certain conditions that normally would be insoluble.

Its use is also necessary almost always when we want to plate an alloy in order to regulate the deposition conditions of the different metals forming the alloy to maintain the correct ratio between them.

Also they have an influence helping the dissolution of the anodes.

IV) Organic additives

A wide range of organic compounds are added in low quantities to the electroplating bath to modify the structure and properties of the plated metal or alloys.

These additives can be classified, depending on their function, as follows:

- Brighteners
- Levellers
- Structure modifiers
- Wetting agents

Combining adequately these type of additives allows to change the physical characteristics of an electroplated deposit, for example from the same type of electrolyte we can obtain semibright deposits with a very high corrosion resistance or full bright deposits with less corrosion resistance.

THE ELECTROPLATING PROCESSES

In principle, the electroplating process can be described as follows:

The substrate (cathode) negatively connected and the anode positively connected with the external source of electricity are immersed in the plating bath. When potential is applied under proper conditions, the metal ions are discharged at the cathode forming the deposit.

Although the quantity of metals and alloys that can be electroplated is very high, only some of them are used currently for the normal applications in the electroplating industry, these are:

Copper	Tin-Lead alloy
Nickel	Zinc-Cobalt/Zinc-Nickel/Zinc Iron alloy
Chromium	Nickel-Iron
Zinc	Gold and its alloys
Tin	Silver
Cadmium	Palladium and Palladium-Nickel
Brass	Rhodium
Bronze	Ruthenium
Tin-Cobalt/Tin-Nickel	

The adequate combinations of these processes allow us to obtain practically any finish. generally the treatment sequences include several processes.

Although there is not a standard classification in the electroplating sequences, we can say that there are three clear separate stages in plating:

- Pretreatment or surface preparation
- Intermediate deposits
- Final finish

Now we are going to see what includes each one of these stages.

PRETREATMENT

In this phase there are included all those necessary processes to obtain a surface completely clean and without oxidations to receive a metallic coating.

Many times it is said that in the preparation of metals for plating the most important consideration by far is the cleaning step. Perhaps it is not the most important but in the process can cause pores to be formed in plated surfaces, and they can give rise to poor adhesion, dullness and less corrosion resistance.

The selection of several systems available depend in principle of two factors:

The base metal:

The composition and physical properties of the basic metal influence the selection of the cleaning procedure. The condition of the basis metal is equally important. For example, a piece of metal with heat or welding scale requires much more processing than non oxidized cold rolled steel.

The soil:

The soil can broadly be defined as any substance on the surface of the metal that will hinder the metal plating process being performed. It is generally the result of an international application to the metal of a material to facilitate metal working.

Animal and vegetable ails, waxes, polishing compounds, oxide and metallic residues, etc., are the most normal.

In order to remove this soil, we use two types of cleaners:

- Solvent cleaners
- Alkaline cleaners

The solvents are used always as a first stage and they are used by different methods:

- Static immersion
- Immersion with ultrasonic agitation
- Spray
- Vapour phase

The two solvents most normally used are: trichloroethylene and perchlorethylene.

The alkaline cleaners are normally used in two stages:

The first one by simple immersion, named then soak cleaner or chemical cleaner followed always by a second electrolytic stage named then electrocleaner. the electrocleaners are always employed with current, either direct, reverse or periodic reverse. In electrocleaning, the usual wetting emulsifying and other physical and chemical actions of the alkaline cleaning solution are assisted by the solution agitation resulting from liberation of gases during electrolysis. The electrocleaner step has also a metal activation effect.

After the cleaning sequence it is done practically always an immersion in an acid solution that eliminates metal oxides. This is called acid dip.

A typical pretreatment system would be composed by the following stages:

- Precleaning with solvents
- Soak cleaning
- Electrocleaning
- Acid dip

Naturally with the rinses in water in between.

INTERMEDIATE DEPOSITS

The use of one or several intermediate deposits before the final finish is done mainly by three reasons:

- Improve the corrosion resistance
- Improve the final aspect
- Allow to plate some special metals (mainly zinc die-cast)

The most common metals used in this step are copper and nickel.

COPPER

Copper electrodeposits are used widely as underplates in multiple plate systems, as stop-offs for head transfer and in plating printed circuit boards. Although copper is relatively corrosion resistant, it tarnishes and stains rapidly when exposed to the atmosphere.

There are two types of electrolytes currently used in electroplating:

CYANIDE COPPER: Copper cyanide solutions with its accompanying health hazard and waste disposal problems, is still essential in many plating operations. Plating of zinc die-cast parts with cyanide copper offers the only practical method of applying a suitable undercoating.

The copper undercoating protects the zinc-casting from chemical attack by the acidic baths used for plating nickel.

ACID COPPER: These types of solutions allows to obtain copper of high brightness, good levelling and excellent ductility at a low cost.

They are used mainly in the plating on plastics, in the electronic industry and in the plating of zinc die-cast parts after the first layer plated in a cyanide copper solution.

NICKEL

Nickel plate, with or without an underlying copper, is one of the oldest protective-decorative electrodeposited metallic coating for steel, brass, zinc die-cast and other base metals. More recently, it has been applied to plastics. The importance of the nickel plating can be gauged by the estimated 60.000 tonnes of the nickel consumed each year in the western world. That represents more than 10% of the total nickel consumed in all the applications.

Virtually all nickel electrolytes are based on the Watts solution, which contains nickel sulphate, nickel chloride and boric acid. Nickel electroplating is the most versatile surface finishing processes available. The actual solutions allow to plate nickel deposits with very good levelling characteristics, what means that levels micro-roughness in the base metal, providing a smoother, brightener finish. With increased levelling in the nickel, the need for other expensive

substrate preparation work is reduced. Multilayer nickel plating such a duplex nickel are used to provide high corrosion resistance for parts that are subject to severe service conditions. Duplex nickel plating involves the deposition of two layers of nickel, one semibright and sulphur free, and one bright, before the application of the chromium finish.

ZINC

It is without doubt the more used metal in the electrodeposition field.

Approximately a 25% of the electrolytic plated surfaces are done with this metal.

It is a type of deposit that is slightly different from general scheme we saw before because it is used depositing it directly on iron and steel without any type of intermediate layer.

In spite that the zinc is an excellent rust retarder, the surface of steel coated with it does not remain bright and stain-free in service. To avoid staining and delay the formation of white corrosion products, practically all zinc deposits are given a thin protective film using one of the available chromate conversion finishing processes.

Initially only cyanide baths were available for its deposition. since the beginning of the 70's they have been substituted progressively by acid type baths and more recently by alkaline solutions without cyanide.

In the following figures, we can see the evolution that these baths have had:

	<u>1970</u>	<u>1990</u>	<u>2000 (outlook)</u>
Cyanide zinc	82 %	40%	20%
acid zinc	15 %	40%	35%
Alkaline zinc	3 %	20%	45 %

The basic zinc baths chemical compositions are:

	Zinc Metal	Sodium hydroxide	Sodium cyanide	Potassium chloride
Acid Zinc	22 - 37 g/l	-	-	185 - 225 g/l
Alkaline Zinc	6 - 20 g/l	75 - 160 g/l	-	-
Cyanide Zinc				
Low cyanide	8-12 g/l	75 - 90 g/l	12 - 19 g/l	-
Medium cyanide	13 - 19 g/l	75 - 90 g/l	26 - 45 g/l	-
High cyanide	26 - 34 g/l	75 - 90 g/l	82 - 105 g/l	-

FINAL FINISH

The final finish more used is the chromium.

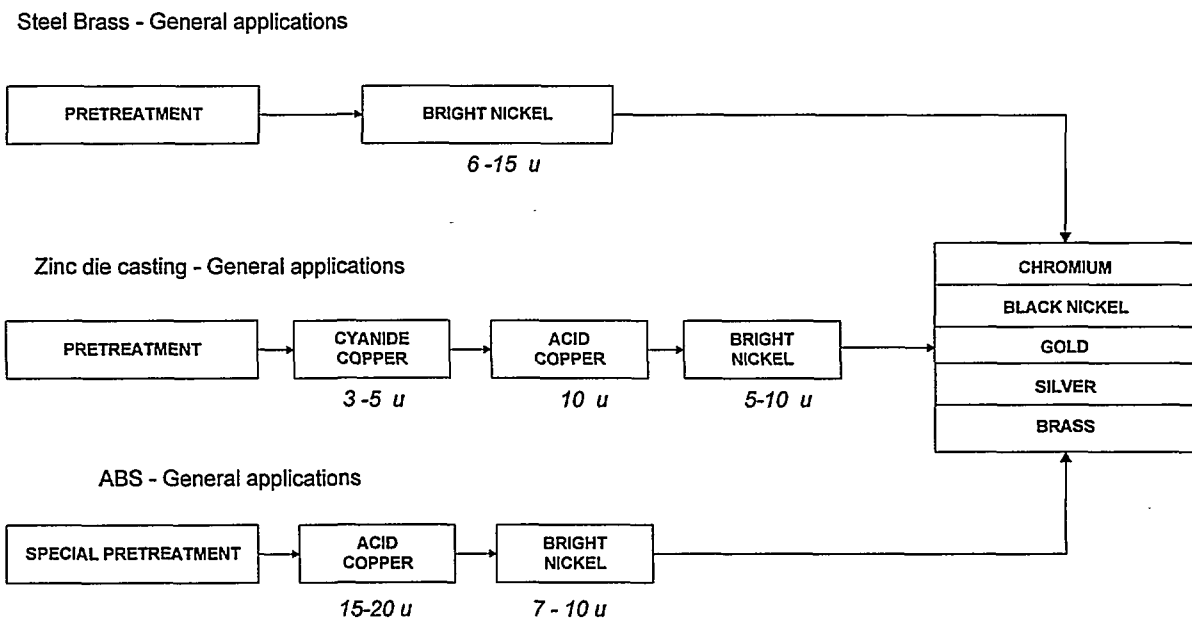
The most desirable properties of chromium as a metal coating are its inherent protective and decorative characteristics. The deposit's high reflectivity is retained in service because of chromium's excellent tarnish, corrosion, wear and scratch resistance. Chromium is almost exclusively plated over a bright nickel deposit. The traditional chromium deposit is product from an electroplating electrolyte containing hexavalent chromium ions and has a pleasing bluish-white decorative appearance.

The basic chemistry of these solutions is very simple: chromic acid as the source for metal along with small amounts of sulphates and fluorides to control the chromium deposition.

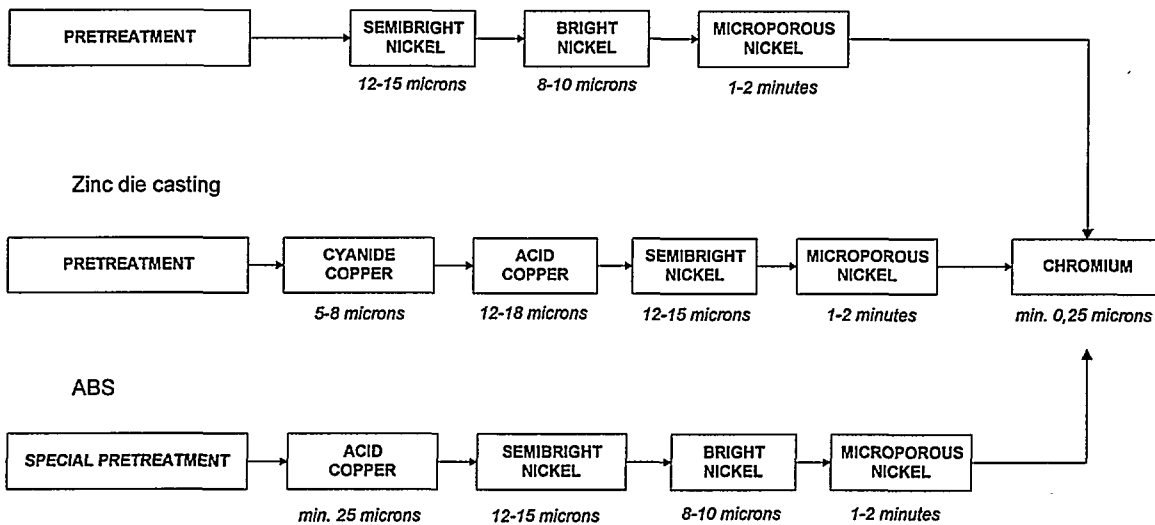
In spite of the high toxicity and high hazardous of the chromium bath, we must not forget that the hexavalent chromium has been identified as a carcinogen, continues being the most used white finish.

Other finishing purely decorative that are practically used always over a bright nickel deposit are: brass, gold, silver, black nickel and other precious metals as rhodium, palladium and ruthenium.

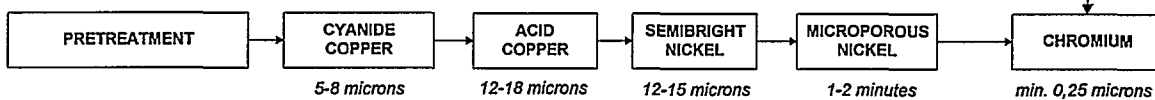
TYPICAL OPERATING SEQUENCES



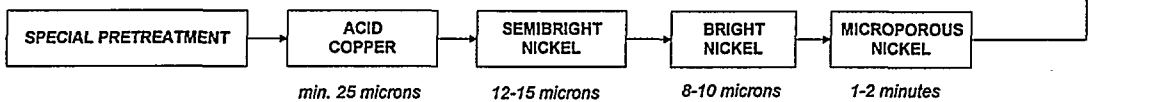
Steel Automotive / High corrosion resistance



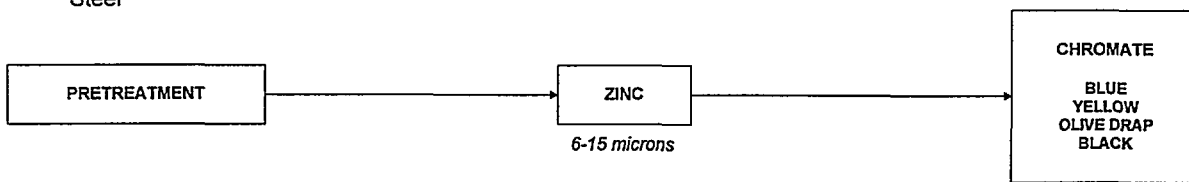
Zinc die casting



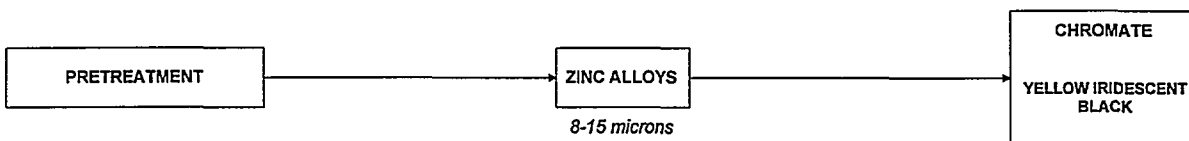
ABS



Steel



Steel



GENERATED CONTAMINATION

We can say that traditionally the keys in the development of new electrolytic processes have been to improve the technical performance of these in order to comply with the requirements every time higher and also reduce the cost of them.

To these factors they have been added recently two more that today we can consider the most important:

- Quality
- Environmental

The electroplating industry uses and stores large amounts of toxic, corrosive and flammable chemicals.

We can say that surely we only use a chemical compound that does not present any type of risk: the water.

A complete relation of all the contaminants that this industry uses would be very long because practically we should include to it all the ingredients used in the formulations of the plating solutions.

lets only analyse those that represent a large risk due to their toxicity or those that are used in big amounts:

- Acid
- Alkalis
- Cyanides
- Chromates
- Complexing agents
- Fluorides
- Metals
- Hydrocarbons
- Halocarbons

Now we are going to see in witch type of processes the contaminants are in:

ACIDS: solutions of mineral acids in concentrations that can go from 5 to 100 % in pickling baths, chemical polishing baths, phosphatising baths, etc. The acids more commonly used are: hydrochloric acid, sulphuric acid, nitric acid and phosphoric acid.

ALKALIS: The main source of this type of salts are solutions used for cleaning metals. Also the zinc alkaline processes contain a large amount of sodium hydroxide (quantities from 100 to 160 g/l are normal in these types of baths).

CYANIDES: Sodium cyanide has been used in the cleaner formulations in order to improve the performance of those solutions mainly when they work a low temperatures. Although they are used in some applications, its use today in these type of solutions has practically disappeared.

Sodium or potassium cyanide are the base for the alkaline copper baths. All the brass and bronze solutions are the base in cyanide.

In the precious metals field, these type of salts are also used for the gold and silver plating solutions.

Finally it has to be pointed out that the zinc electrodeposition field has been and continues being a large user of cyanide zinc plating baths.

CHROMATES: Soluble salts of hexavalent chromium are used in many sectors of the electroplating industry.

The most important are:

- Decorative and hard chromium plating.
- Chromate conversion coatings mainly as protection of the zinc deposits and its alloys, but also used to improve the corrosion resistance of the aluminium and the magnesium.
- Etching of plastic surfaces prior to electroplating in order to improve adhesion. This type of solutions contain normally 400 g/l of chromic acid with more than 300 g/l sulphuric acid.

As an example of the contamination that generated the chromium plating processes, we are going to analyse what happens using these systems.

As average we can consider that 1 m² of plated area takes-out 0,150 l of chromium solution. Considering that the average concentration of these baths is of 250 g/l of chromic or 130 g/l of hexavalent chromium this represents:

$$0,150 \text{ l} \times 130 \text{ g/l} = 19,5 \text{ g chromium consumed as a drag-out}$$

Considering that the medium thickness of a chromium deposit is 0,25 microns this represents that 1 m² of chromated pieces we have only deposited 1,75 g of chromium.

Taking into account that 1 g of chromic acid when it is reduced to trivalent chromium and precipitated as hydroxide generates approximately 3,1 g of sludge. We can see that each square metre of surface plated generates approx. 60 g of sludge in the effluent treatment plant. Of course there are different systems to minimize the losses by drag-out but many plants are working without any of them.

COMPLEXING AGENTS: The alkaline salts of the ethylenediaminetetraacetic acid, known normally as EDTA and nitrilotriacetic acid, known as NTA, together with other complexings as gluconates, secondary and tertiary amines, etc., are used in several cleaner formulations and in some copper and zinc baths formulations.

FLUORIDES: Small quantities of fluoride ion (normally between 0,2 and 0,9 g/l) are present in the majority of the formulation of decorative and hard chromium baths. Also we use relatively high amounts of fluorides together with mineral acids in different acid activators. As it is obvious, we will have all the metals.

METALS: Considering that we are talking about the metal deposition, it is clear that we will find as contaminants the same metals that we are plating, with some amounts of the metals treated that they are dissolved in the acid solutions.

HYDROCARBON: As indicated before, they are used for the precleaner of the pieces.

After this brief general analysis of the types of contaminations generated, we are going to proceed to a revision of the actual alternatives of this sector and of those that we expect will be available in a near future, in order to avoid or reduce the contamination level.

PRESENT AND SHORT/MEDIUM TERM ALTERNATIVES

CLEANERS: The elimination of the sodium cyanide in the alkaline cleaners formulations, substituting by other type of salts has been possible due to the optimization of the wetting agents systems.

It is not usual today to find plating shops that use cleaners containing cyanide.

- The development of alkaline cleaners more efficient and their combination with other physical means as ultrasonic, agitation systems of the cleaner as for example the eductors, etc., is doing possible the non-utilization of solvents prior the cleaning phase.

- The progressively introduction of the ultrafiltration technology and together with new cleaners formulations specially adapted to work with this technology, will permit to eliminate continuously the oils that the cleaners are retaining and that are the main cause that these type of solutions loose efficiency and have to be changed frequently (1-3 weeks generally). This will allow to increase the self life of the cleaners to several months and obtain by the other side of small volume of liquid highly concentrated in oils that can be treated conveniently by specialized companies.

CYANIDES:

COPPER CYANIDE BATH: There are already alkaline copper formulations that can substitute the cyanide solutions but only by a limited number of applications, Actually there is not a real substitute for these processes when coating zinc die-casting parts.

ZINC CYANIDE: As we have already seen, the cyanide solutions used to deposit zinc have been replaced by acid or alkaline solutions without cyanide. We can confirm that for any type of application it can be used solutions without cyanide with the same performance that with the

cyanide baths and if there are still large quantities of these solutions there are due to economic considerations mainly due to the cost of bath neutralizing but not as a lack of technological alternatives.

GOLD and SILVER CYANIDE: Although it exists in the market processes cyanide free for the gold and silver deposition since beginning of the 70's, until today they have not succeeded. But we can say there are available non toxic solutions to deposit these two metals.

CHROMATES:

Chromium Plating

If we can say that in the zinc plating, replacing the cyanide by acid or alkaline cyanide free baths has had an important success this has not happened with the hexavalent chromium bath.

In spite of that there available in the market chromium plating solutions based in trivalent chromium with a much lower toxicity than the conventional solutions and they are working at a low metal content, until 13 times less than the hexavalent chromium, its use has been until now very limited. We can say there is only one factor that has not allowed that these new baths grow as it was expected. The colour of the chromium deposit from a trivalent solution has not exactly the same bluish white appearance than the one obtained with the traditional hexavalent processes. Although all the research work that has been done until today in order to solve this cosmetic problem, we cannot expect a solution in a medium term.

Zinc Chromates

The situation in this area is different for each one the types of the chromates that we are using.

Blue Chromates

There are available solutions based on trivalent chromium with low toxicity and easier to neutralize than the conventional hexavalent blue chromates.

Yellow Chromates

Until now there are only available solutions based on hexavalent chromium. From some research programmes that are on going, we can expect a medium term solutions based in trivalent chromium.

Olive drap and black chromates

There are no alternative to the hexavalent chromium solutions and as far as I know we cannot expect any change in a medium term.

Etch solutions for plastics

A lot of work has been done trying to replace the chromic etch solutions without success. It seems difficult at this moment any other alternative to the chromic acid solutions for this specific application.

Before finishing I would like to say that if the 80's were characterized by the application of productivity concepts as a more significant driving force, without doubt the 90's have been oriented towards the quality, the application of the quality systems based on the standards ISO 9000. I think that on the next decade the most important booster of this industry will be the application of the Environmental management Systems as per the standards ISO 14000. This will enable to control and reduce the contamination that today is generating the electroplating industry.

**DEGREASING BATHS. MINIMIZATION.
NEW TECHNOLOGIES**

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NEW TECHNOLOGIES IN INDUSTRIAL DEGREASING AND WATER EMULSION OIL SEPARATION SYSTEM. A CLEAN PRODUCTION ALTERNATIVE

The pressure over disposal regulations, the trend to reduce and eventually to eliminate products damaging ozone, have motivated industry to evaluate and to search for other alternatives to degreasing and waste water operations.

In 1987, the Montreal Protocol, limited product production and consumption of products affecting ozone. Two of these substances, widely used in the finishing surfaces area, CFC-13 and III TCA, ought to disappear from the developed countries in the year 2000 and 2005 respectively.

But not only are these substances affecting the process of the degreasing products change but increasing demand for water is also compelling to have a much more efficient and stricter effluent treatment, therefore more expensive. Maximum values admitted in certain elements are diminishing constantly as well as chemical and biological demand values (BOD, COD).

A new philosophy resulting from the Paris Conference conclusions, PARCOM, as well as in the Barcelona Euromediterranean Conference, creates the necessity to modify products and systems, aqueous or solvent, according to a new design to meet these new necessities.

Although the interested users are waiting and pressing for the arrival to the market of a new miraculous product that can solve all these themes, the fact is that:

- In most cases direct replacement of a product by another one is not possible
- Only analysing the situation and investigating the alternative solutions may lead us to a system or degreasing process change.

In consequence, we will be changing the product at the same time that the method, system or working equipment.

SIDASA-UNITS COATING Group has quickly understood this fact taking advantage of its possibilities and its international implementation, which allows us to establish contacts and a tight collaboration with involved companies, either in chemical field or in the engineering field. SIDASA-UNITS COATING has succeeded after working meetings, lab and pilot test in several R+D, to achieve a level of knowledge that allows to give specific solutions, at industrial level, in the degreasing field and more specifically speaking in the surface treatment.

The systems below are the answer to three main and basic concepts:

- * **CHEMICAL PRODUCT CONSUMPTION REDUCTION**
Water as a basic product
- * **USE OF A LOW TOXICITY AND ECOLOGICAL LOW IMPACT PRODUCT**
Replacement of non-biodegradable chlorine solvents, nitrites, strong chelates, etc.

- * REDUCTION OF DISPOSAL VOLUME
The use of technological products making recycling easier.

These concepts combining products and installations:

- * PRODUCT
 - Aqueous
 - Solvent
- * INSTALLATION
 - Application system
 - Spray
 - Immersion
 - Recycling system
 - Membranes
 - Distillation
 - Vacuum evaporation

will allow us to choose a solution, perhaps not the perfect one, but surely meeting the environmental demand, degreasing and cleaning efficiency, without forgetting the positive economical aspects, and above all under a COMMITMENT TO PROGRESS.

TECHNOLOGICAL PROPOSAL

AQUEOUS PRODUCTS:

Aqueous solutions have high properties as cleaning agents. Water is the most suitable media to eliminate ionic products and combined with alkalis or surfactant, it achieves the capacity to saponify or even eliminate the non-polar ones.

The so called water-based "alkaline products", have been used for a long time, but due to the already mentioned environmental reasons they have been modified, eliminating all those compounds that can generate problems or interfere with the disposal treatment. They allow, thanks to its composition, to apply with satisfactory results oils separation technologies or procedures, (skimmers, mechanical filters, MF or UF membrane technologies), thus making the recycling of active matter possible, free and clean from any contamination or dirty which may have accumulated. To summarize, they are: aqueous alkaline or neutral degreasers enhancing degreaser's life and reducing disposal, and at the same time keeping a high and constant efficiency in the degreasing.

As the attached chart proves, our aqueous degreasers line KLEANEX new generation, meet almost all the surface treatment areas because they can be used, depending on its composition, in: electroplating (immersion), previous to phosphate-painting (immersion or spray), as an interoperation treatment KLEANEX POLICLEAN or in the metal industry as a preparation to thermal soldering treatment or as a final protection.

SOLVENT CLASS A3 DEGREASING PRODUCT

- Solvent line, the industrial cleaners on which we are now commenting, are hydrocarbons (Paraffins), n-iso, aliphatic cycle free from unsaturated matter, neutral products, inert to sensitive materials such as aluminium, painted or polished surfaces, most plastics and elastomers. It eliminates different types of dirt without chemical interactions, which makes it to be a system of wide application previous to thermal treatment such as: wetting, adhesion, organic alternative to chlorinate solvents. It is also suitable for use in electrodeposition galvanic lines if the installation allows it.

We are now pointing out four main characteristics related with the following stated areas:

- * Physical properties of the products
- * Environmental
- * Health and safety
- * Economical

WATER EMULSION OILS - SEPARATION SYSTEM

BACKGROUND

Aqueous cutting fluids used as emulsion or solution in several machining processes, mainly in the metal industry.

These products are used generally as lubricants coolers and in some cases, to drag out cuttings produced during the work.

As there are a lot of studies over this kind of products, we are going to comment in this report those outstanding aspects that justify the importance of the environmental problem produced by this type of disposal, which we could summarised as follows:

Amount:

Practically it does not exist any machining workshop that is not using this type of product.

The amount of "cutting oils" used this year in Spain is thousand of tons, with some particular cases of factories with disposal over 5 million litres per year (concentrated product and rinses).

Environmental hazard:

There are several classifications of these products, although taking into account the target of this report and simplifying it, is enough to know that mainly there are:

Emulsions:

- Oils (concentrations of 2,5 to 8%)
- Water
- Emulsifier
- Corrosion inhibitors
- Bactericide
- Fungicide
- Detergent
- Antifoaming
- Etc...

Solutions (synthetic products):

- Synthetic solution (1-14% concentration)
- Water
- Corrosion inhibitors
- Colouring
- Bactericide

- Paraffins
- Etc..

Pseudo-solutions (mixture of the preceding ones):

Depending on the work done we can add to the above mentioned several metal types, depending on the process in which the cutting fluid is used, such as zinc, iron, copper, cadmium, chrome, aluminium, nickel, etc...

All this, translated into disposal parameters, makes them to be classified as a toxic and hazardous disposal and therefore they should be treated correctly, since it is not possible to evacuate them directly.

The most outstanding parameters from this point of view are:

COD (Chemical oxygen demand)	Between 2000 and 2500 ppm
Oils and greases	Between 0,1 and 10%
Solid in suspension	Between 100 and 1500 ppm
Nitrites	Between 5 and 9000 ppm
Iron	Between 10 and 400 ppm
Aluminium	Between 0 and 150 ppm
Bore	Between 0 and 1500 ppm

All of them are, in general, above the allowed margins according to prevailing legislation.

POSSIBLE ALTERNATIVES

Undoubtedly manufacturers of these products are doing a great effort regarding the elimination of those compounds, which are more hazardous such as:

- * Chlorinated compounds
- * Nitrites
- * Phenols
- * Boron compounds
- * Etc.

Nevertheless, due to its own nature, and as long as there is not any system allowing to reuse cutting fluids, it is clear that it is necessary to treat them before disposal.

There are several alternatives usually used which we specify below:

Physic-chemical treatment:

It consists in adding to the cutting fluids, in appropriate installation, a certain number of products which neutralise them, precipitate or flocculate pollutant compounds, in a way that once decanted and separated from the sludge produced, the water remaining is the purest as possible.

Usually precipitants such as ferric chloride, together with calcium hydroxide and polyelectrolytes of several types are used.

Unfortunately, this method is quite inconvenient, it requires a lot of labour, producing a big amount of sludge and, what is worse, in many cases it does not succeed in reducing COD levels to established limits.

That is why it is increasingly less used as a treatment process.

Ultrafiltration:

The ultrafiltration process is based on a tangential ultrafiltration through membranes of several types and with a pore size of 0,02 and 0,01 μ .

These membranes can be organic (cellulose, polysulphone, PVDF, etc...) Or inorganic (coal, aluminium silicate, silicon carbide, etc...)

This system mainly consists, after eliminating metals in suspension and non emulsified oils, in passing the fluid through membranes with a flow and adequate pressure in a way that a concentrate product together with a permeate without oils is produced; the concentrate is moved back to the storage deposit, which is thrown away as disposal.

Once the oil reaches a determined concentration (usually between 40 and 50%) is moved back to a deposit to be collected by an authorised agent.

This system can be valid for some specific type of cutting fluids, but generally it can be said that although it takes out practically all the oils, usually it does not achieve required limits in COD, concerning dissolved metals and colorants.

Ultrafiltration complementary process:

As commented above since, ultrafiltration achieves an oil-free permeate, but does not meet prevailing legislation, other systems have been tested with the permeate coming from the ultrafiltration.

We are going to point out without detail the main ones:

Ozonisation:

Consisting in the oxidation of existing organic material through the injection of ozone.

This technique obtains good results in relation with COD reduction but on the other hand it can do nothing with the dissolved metals that the effluent contains.

Reverse osmosis:

Reverse osmosis is a similar ultrafiltration technique but with a difference as the membranes are semipermeate and allow smaller particles (below 100 Amstrong), to pass through.

There is no doubt that the fluid which passes through these membranes meets any legislation and it can even be reused in production processes, due to the high quality of the resulting water.

Nevertheless, even though the process is technically suitable, its practical application implies some problems such as:

- * Production of a second concentrate, besides the one produced in the ultrafiltration, with dyestuff, metals, inhibitors, etc... that were not held back in the mentioned equipment.
- * Obstructions difficult to clean in membranes due to dissolved metals (iron and aluminium) and especially to the various inhibitors which in many cases react producing a gradual flow lost until it is blocked without any possible regeneration.

Biological treatments:

Consisting in adding to the microfiltration technology a bioreactor system in which under suitable pH conditions, temperature, etc. colonies of specific bacteria are made to work to eliminate organic remains.

This is an interesting process, but it may create problems with dissolved metals and the influences that the changes and mixtures of cutting fluids on the biological treatment may have.

VACUUM EVAPORATION

This technique aims to make the water boil at 30 °C, by applying to the container a 0,9 bars depression approximately.

Through a heat pump, we succeed, with an single energetic source, in producing the boiling heat and the cold for the vapour condensation, obtaining water of a high purity.

The functional sketch is as follows:

Fluid enters the boiling chamber where it is heated by the coil with the hot compressed Freon coming from the compressor.

In this chamber, the existing water is vaporized at 30°C, due to the existing vacuum produced by the ejector and the pump.

Vapours go through the chimney until condensation chamber where it is cooled down through the coil with cold expanded Freon previously refrigerated in the exchanger.

The condensed water goes through the ejector to the distillation tank from which it goes out by the overflowing.

Due to the complexity of the factors that converge in the cutting fluids for its treatment, the use of the vacuum evaporation system has the following advantages:

- **All type of cutting fluids, even mixed, can be treated**
- **High concentrations of oils can be obtained**
- **Between 90 and 95% of existing water is eliminated**
- **It retains metals that may exist inside the concentrate**
- **It eliminates almost all-dyestuff**
- **It only requires a previous filtration to eliminate heavy particles**
- **It functions automatically at all stages even when unloading concentrated oils**
- **Without any emission of fumes of odours**
- **Since it boils a low temperature it has a relatively low cost.**

Taking into account the above mentioned characteristics and after having had the necessary laboratory experience, we installed in an important automotive industry an industrial plant with capacity to treat 12.000 litres cutting fluids per day, which described below.

PLANT DESCRIPTION

First stage of the project was the canalization of all the factory cutting fluids to a single deposit capable of storing all the volume that could be produced during the cleaning of deposit for concentrated oils was also foreseen.

The assembled plant following the storage deposit is made up of the following elements:

- Demulsified oils separator.
- Decanting system with sludge filtration.
- Concentrated decanting and evaporation system

We point out briefly the functioning of each system:

1. DEMULSIFIED OILS SEPARATOR

As a lot of cutting fluids can be mixed, part of the oil demulsifies and it floats on the surface.

As it does not have any sense to treat a concentrated product in the evaporator, it has been foreseen the use of an oil separator which through a special plastic flexible tube, drags our the oil which is on the surface towards the upper part of the equipment, where it is gathered and sent to the concentrated pit.

2. DECANTING SYSTEM WITH SLUDGE FILTRATION

To prevent sludge or metallic residues from reaching the evaporator, it has been foreseen a lamellae decanting system through which the product goes through at a small rate and where the mentioned residues stay.

The cleaned product arrives at a storage tank, from where evaporators suck up the material and the decanted sludge are suck up through the lower part of the filter.

EXAMPLE N 1

OIL SEPARATION USING RECOILS DS - BOLT MANUFACTURERS

The RECOIL DS is a fully automatic unit. It is utilized for the separation of oil-in-water emulsions, for the recycling of wash water, degreasing and phosphatising baths, and the microfiltration of liquids.

The RECOIL DS provides practical benefits in the:

Treatment of waste water:

- * Lower waste disposal cost due to an upgraded concentration of the impurities.
- * No auxiliary filter agent consumption (e.g. activated carbon, coagulants or flocculators, etc.)

Recycling of wash water and surface treatment media:

- * Reduction in expenditure on waste disposal due to the recycling of liquids from ultrasonic and metal component cleaning machines, degreasing and phosphatising baths and spray boots.
- * Improved quality of the cleaning process.
- * Cost savings resulting from the extended life of the cleaning solutions.

THE PROCESS:

In the RECOIL DS filtration process, the medium to be filtered is pumped through filter membranes at a high flow rate and defined pressure. Solid matter and impurities (e.g. oil) are retained. The permeate (filtrate) which has been separated out by the membrane, is collected in the module housing and then removed via the automatic back flushing units. It can then neither flow back to the working process or into the sewage system.

THE FUNCTION:

The heart of the RECOILS DS is a module with filter membranes. The membrane filter tubes consist of a porous body and the membrane itself, which is sinter fused onto the inside of the tube as a coating with a defined pore size (cut point).

The medium to be filtered is pumped in a cycle from the RECOIL DS container through the module and back again. The selected dimension of the pores is such that the dirt and oil are retained and only clean water can pass through the membranes.

THE BACK FLUSHING SYSTEM:

The fully automatic back-flushing system unit is a standard feature of the RECOIL DS. During back flushing a small amount of filtrate is pressed back through the filter membrane, against the filtration flow, by means of a brief pressure pulse. The returned filtrate cleans the inside of the membrane tube and thereby ensures the following:

- * Maximum efficiency and permanently high filtration performance.

- * Extremely long intervals between cleaning.
- * Reduced energy and maintenance costs.

GALVANIC LINE - BARREL ZINC PLATING (TWO LINES)

PROCESS:

- * Immersion degreasing
- * Electrolytic degreasing

TECHNICAL DATA:

Total production	25	Tn/day bulk
Immersion degreasing volume	4300	Litres
Electrolytic degreasing volume	4300	Litres

IMMERSION DEGREASING

Composition	KLEANEX FW 72 UF KLEANEX FW 72 W	50 g/l 3 g/l
Conductivity	40 μ s/cm	
Equipment	RECOIL DS 5 Connected to both lines	
UF flow		150 g/l
Average oil content functioning at 60%		1,5 g/l

ELECTROLYTIC DEGREASING

Composition	KLEANEX 81 UF KLEANEX 81 W	50 g/l 3 ml/l
Conductivity	175 µs/cm	
Equipment	RECOIL DS 2 Connected to both lines	
UF flow		100 l/hours
Average oil content functioning at 60%		1 g/l

ECONOMICAL ASPECTS

Preliminary remarks:

Work was done with a immersion and electrolytic degreaser (cyanide), and it was necessary to change it, due to the oil contamination and low efficiency, every 15 days.

Nowadays cyanide has been eliminated, working solutions have not to be changed (more than 10 months functioning), the only thing necessary is to go on taking away the oil concentrate from RECOIL DS every 4 weeks for the immersion one and every 8 weeks for the electrolytic one.

COST:

Based on a monthly production of 500 Tn degreased bulk

FORMELY:

Products	Immersion degreasing	1587	ECU
	Electrolytic degreasing	709	ECU
	Cyanide (including its disposal treatment)	<u>2250</u>	<u>ECU</u>
	TOTAL COST	4546	ECU

WITH NEW RECYCLING TECHNOLOGY:

Products	Immersion degreasing	950	ECU
	Electrolytic degreasing	1152	ECU
	Electrical energy	411	ECU
	RECOILS maintenance	<u>225</u>	<u>ECU</u>
	TOTAL COST	2738	ECU

TOTAL COST (*)

(*) Final neutralization in purifying plant not included.

MONTHLY SAVINGS:

4546 - 2738 = 1808 ECU

PRESENT COST:

2738 x 1/500000 = 0,876 ECU/Kg

RETURN ON RECOIL INVESTMENT:

TOTAL COST RECOIL DS = 53125 ECU

53125 / 1808 = 30 months

CONCLUSIONS:

We are not taking into account other very important points concerning saving such as:

- Reduction of labour in bath changing operations
- Less consumption of water due to recycling of working baths
- Less energy consumption in the initial heating
- Diminution of disposal volume
- Better functioning of the waste water treatment plant
- Best COD results

EXAMPLE 2

WATER EMULSION OIL SEPARATOR CUTTING FLUID PLANT

INITIAL PRODUCTS

Initial cutting fluid with a COD > 20000 and oil 5,01 gr/l

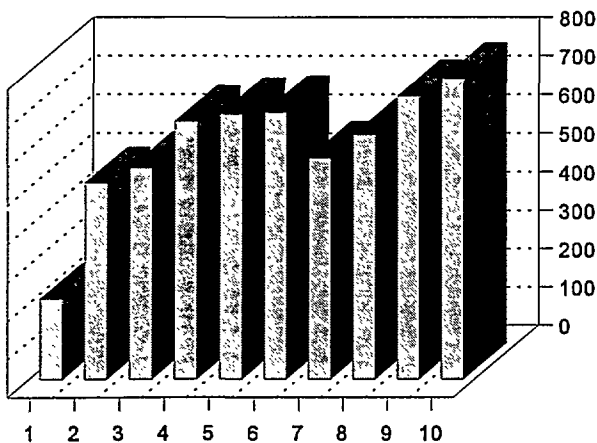
Results described below are the results of the experience and study made during 10 days, working 24 hours every day under the following premises:

FLOW- GRAPHICS:

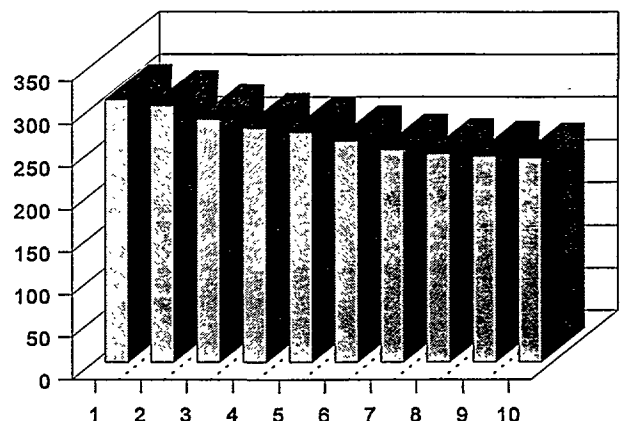
Made with average values for each day

Day	DISTILLED				CONC.
	Flow l/h	COD	pH	Grease + oil	Grease + oil
1	308	210	6,71	710	5,19
2	301	511			
3	285	550			133
4	275	670			
5	270	689			
6	260	694	7,46	543	
7	250	577			
8	245	636	8,36	616	445
9	242	735			
10	240	780	8,41	640	540

COD



FLOW



COD

Analysing 1 sample every day (the last of each working period)

pH AND CONDUCTIVITY

Measured in the samples where COD has been measured.

OIL AND GREASES

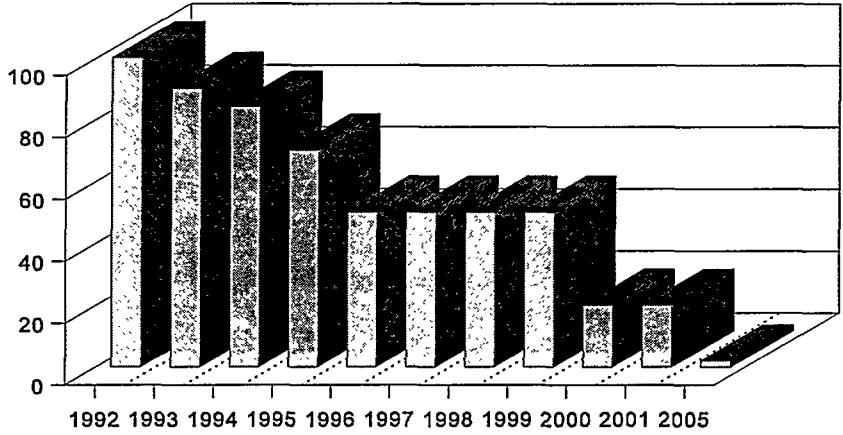
Four determination have been done, one at the beginning the other at the end and the two remaining in the middle of the process.

CONCLUSIONS:

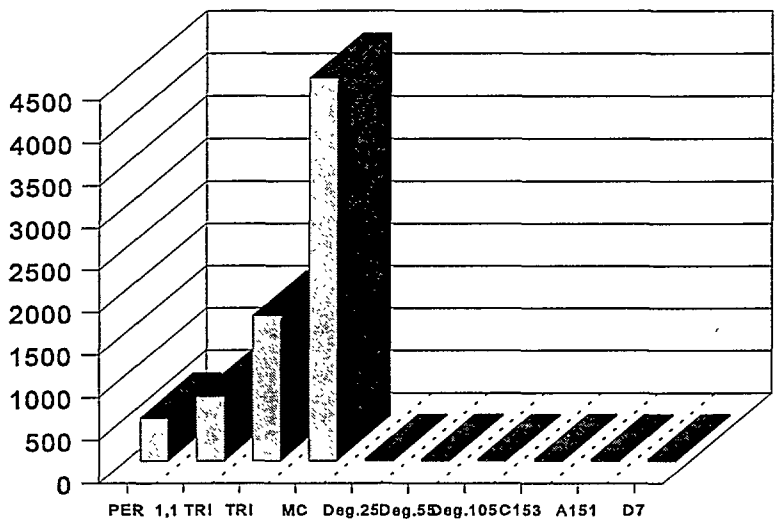
From all the above mentioned the following conclusions can be reached:

- a) Disposal characteristics, either in COD as in oil and greases, is kept around values meeting most of the standard and regulations concerning disposal directly to urban sewers.
- b) In reference to other systems it has not the problems of dissolving metals and solids in suspension in the concentrates.
- c) Although energetic cost is above other systems, maintenance simplicity and solidity of its compounds makes this system competitive, mostly for big flows.
- d) A much more higher oil concentration can be achieved, thus helping to reuse them.
- e) Very compact equipment thus not needing a lot of space.
- f) Summarizing, we think that using vacuum evaporation technique in the taladrine treatment, it is a big step in environment in a disposal minimization line which has a promising future.

Restriction production and consumption of TCA (III trichloroetano)



Hazard Index (HI) according TRGS 420 (Germany).
 HI= saturation concentration (mg/m3) at 20°C OEL



PRODUCT	APPLICATION						OBSERVATIONS
	Base metal	Spray	Immersion	Electrolytic	U.s	Observation	
KLEANEX AX UF	Fe	X	X			Good wetting power	
KLEANEX FW 72 UF	Fe		X			High oil dispersion	
KLEANEX 39 UF	Al, C	X	X			Without base metal attack	
KLEANEX 81 UF	Fe		X	X		High conductivity	
KLEANEX POLICLEAN 251	Universal	X	X		X	Interoperation degreasing	
KLEANEX POLICLEAN 246 NF	Universal	X	X		X	Interoperation degreasing	

PLANT DESCRIPTION

- * DEMULSIFIED OIL SEPARATOR**
- * DECANTING SYSTEM/SLUDGE FILTRATION**
- * CONCENTRATED DECANTING/EVAPORATION SYSTEM**

CHEMICAL PRODUCT CONSUMPTION REDUCTION

**USE OF A LOW TOXICITY AND ECOLOGICAL LOW IMPACT
PRODUCT**

REDUCTION OF DISPOSAL VOLUME

PRODUCT

- AQUEOUS

- SOLVENT

INSTALLATION

*** APPLICATION SYSTEM:**

- SPRAY

- IMMERSION

*** RECYCLING SYSTEM:**

- MEMBRANES

- DISTILLATION

- VACUUM EVAPORATION

**SOLVENT CLASS A-3
MAIN CHARACTERISTICS:**

- PHYSICAL PROPERTIES

- * LOW VAPOUR TECHNOLOGIES**
- * LOW EVAPORATION HEAT**
- * HIGH FLASH POINT**

- ENVIRONMENTAL

- * AIR LOW IMPACT**
- * WATER LOW IMPACT**

- HEALTH AND SAFETY

- * LOW TOXICITY**

- ECONOMICAL

- * LOW LIFE SOLUTIONS**

W/O EMULSION TYPE

CONTAINS:

- OIL (2,5 - 3%)
- WATER
- SURFACTANT
- CORROSION INHIBITOR
- BACTERICIDE
- FUNGICIDE
- DETERGENT
- ANTIFOAM ADDITIVE

W/O SYNTHETIC TYPE

CONTAINS:

*** SYNTHETIC POLYMER (1-14%)**

*** WATER**

*** CORROSION INHIBITOR**

*** DYE**

*** BACTERICIDE**

*** PARAFFINS**

W/O TYPICAL WASTE VALUES

* COD CHEMICAL OXYGEN	Between 2000 and 2500 ppm
* OILS AND GREASES	Between 0,1 and 10%
* SOLID IN SUSPENSION	Between 100 and 1500 ppm
* NITRITES	Between 5 and 9000 ppm
* IRON	Between 10 and 400 ppm
* ALUMINIUM	Between 0 and 150 ppm
* BORE	Between 0 and 1500 ppm

NEW TRENDS IN CUTTING OILS

PRODUCTS W/O FREE OF:

- * CHLORINATED COMPOUNDS**
- * NITRITES**
- * PHENOLS**
- * BORON COMPOUNDS**

VACUUM EVAPORATION

MAIN ADVANTAGES

- * ALL TYPE CUTTING FLUIDS CAN BE TREATED**
- * HIGH OIL CONCENTRATION DISCHARGES**
- * 90 - 95% WATER RECYCLING**
- * RETAINS METALS OF THE SOLUTION**
- * DYESTUFF ELIMINATES**
- * SINGLE PREVIOUS FILTRATION IS NECESSARY**
- * AUTOMATIC DISCHARGE CONCENTRATED OIL**
- * NO FLUX NO**
- * LOW COST**

BENEFITS OF RECOIL DS

- * REDUCTION OF LABOUR COST**
- * LESS WATER CONSUMPTION**
- * LESS ENERGY CONSUMPTION**
- * DIMINUTION OF DISPOSAL**
- * BETTER EFFICIENCY OF WWT PLANT**
- * BEST COD VALUES**

FORMERLY:

Products	Immersion degreasing	1587	ECU
	Electrolytic degreasing	709	ECU
	Cyanide (including its disposal treatment)	<u>2250</u>	<u>ECU</u>
	TOTAL COST	4546	ECU

WITH NEW RECYCLING TECHNOLOGY:

Products	Immersion degreasing	950	ECU
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	RECOILS maintenance	<u>225</u>	<u>ECU</u>
	TOTAL COST	2738	ECU

TOTAL COST (*)

(*) Final neutralization in purifying plant not included.

MONTHLY SAVINGS:

$$4546 - 2738 = 1808 \text{ ECU}$$

PRESENT COST:

$$2738 \times 1/500000 = 0,876 \text{ ECU/Kg}$$

RETURN ON RECOIL INVESTMENT:

$$\text{TOTAL COST RECOIL DS} = 53125 \text{ ECU}$$

$$\underline{53125 / 1808 = 30 \text{ months}}$$

CONCLUSIONS:

- * POSSIBILITY TO DISCHARGE DIRECTLY TO URBAN SEWERS.
(LOW COD OIL AND GREASE)**
- * NO HEAVY METALS OR SUSPENDED SOLID IN THE
CONCENTRATES**
- * LOW MAINTENANCE SYSTEMS. EASY TO CLEAN**
- * HIGH OIL CONCENTRATE. EASY TO REUSE THEM**
- * COMPACT EQUIPMENT**

WASTEWATER TREATMENT

*** PHYSICO-CHEMICAL**

*** UF ULTRAFILTRATION**

*** OZONIZATION**

*** R.O. REVERSE OSMOSIS**

*** BIOLOGICAL TREATMENT**

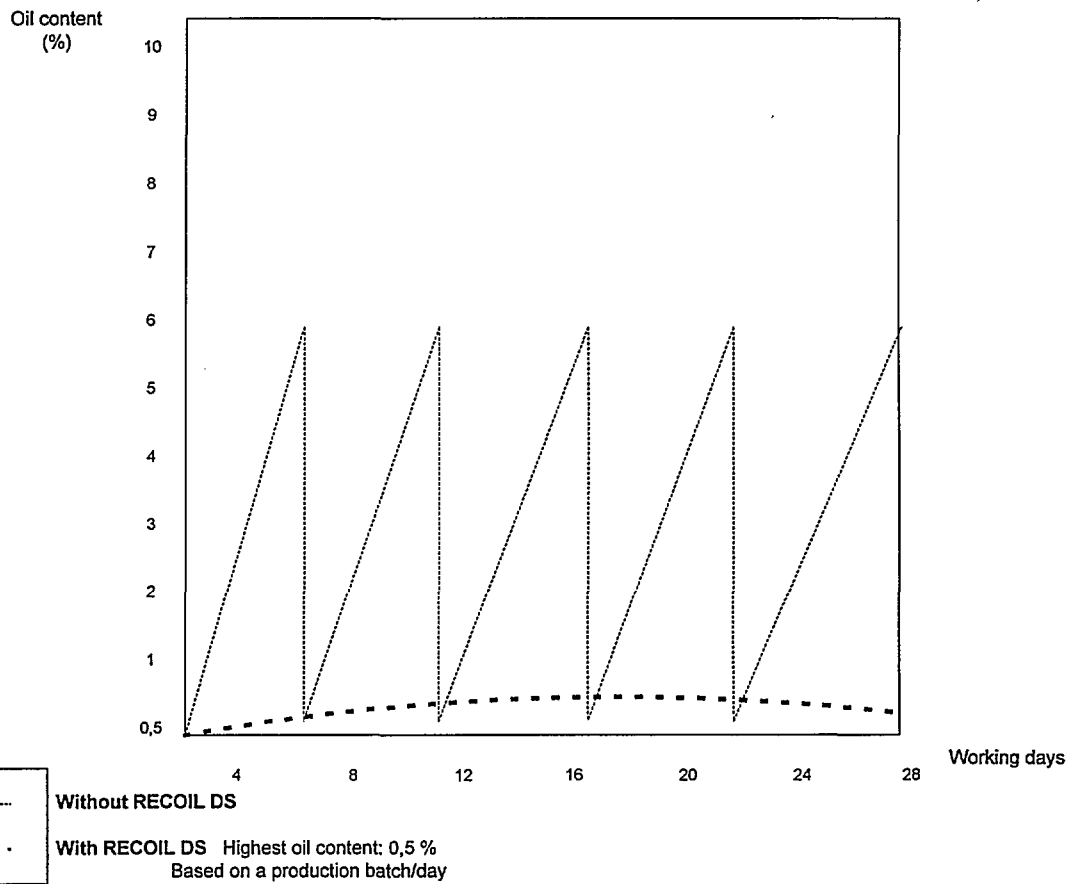
*** VACUUM EVAPORATOR**

RECOIL DS

Oil separation and degreasing solutions recovery

CHARACTERISTICS :

MODEL	AVERAGE FLOW (l/h)	SIZE (mm)
RECOIL-DS 1.4	40	1400x2000x600
RECOIL-DS 2.6	60	1400x2000x600
RECOIL-DS 5.15	150	2100x2200x1300
RECOIL-DS 10.30	300	2100x2200x1300
RECOIL-DS 15.45	450	3000x2300x1500
RECOIL-DS 40.70	700	3900x2300x1800



RECOIL DS

Oil separation and degreasing solutions recovery

The presence of oils in effluents is growing concern from the point of view of the environment, since their separation and disposal are both difficult and expensive.

The use of RECOIL-DS allows you to separate and to concentrate the polluting oils and greases that are present in the degreasing solutions thus keeping the solutions, at a high level of efficiency.

RECOIL-DS can be used for any kind of preliminary electroplating treatment: painting, pickling, etc.

ADVANTAGES

- Saving in degreasing products
- Constant quality of the degreasing operation
- Less polluting matter in the effluents.
- Lower chemical requirements in the purifying plant.
- Energy saving, thanks to the fact that it is unnecessary to heat the new baths.
- Labour saving, because fewer new baths are required.
- A smaller purifying plant and a lower quality of sludge.
- Automatic surfactants proportioning.

**REDUCTION OF DRIFTS. RECOVERING BATS. IMPROVING ON WASH AND RINSE
STAGES. REDUCTION OF WATER CONSUMPTION**

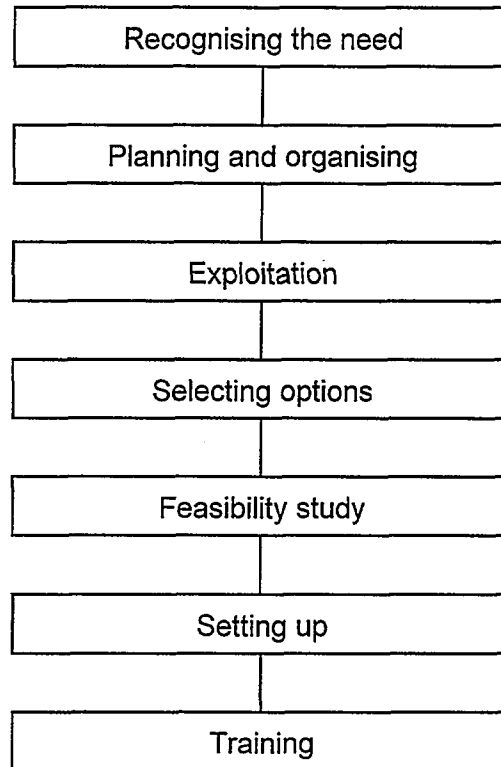
**Ramon Sans
Chemical Engineer Department
University Politechnics of Catalonia
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OPTIMISING THE PROCESS AND MINIMISING CONSUMPTION

PROGRAMME

- Introduction
- Stages for minimisation
- Goals
- *Economic consequences of minimisation*
- Experimental process
- Types of rinsing
- Application of tertiary treatment systems
- A practical example

STAGES IN SETTING UP A PROGRAMME IN A GENERAL WAY



INTRODUCTION

1993. The Single European Market caused companies from different countries to compete with each other, environmental regulations became stricter, and consequently companies had to make a considerable effort. This effort involved the incorporation of clean technology production processes, which, generally speaking, use less energy and raw materials, and the development of management techniques for these technologies.

So, we are committed to increasing production, without exhausting our resources, generating less waste and retrieving the effluents generated.

In order to fulfil these objectives, an ENVIRONMENT AUDIT will be required. The EPA (Environmental Protection Agency) has defined an ENVIRONMENT AUDIT as a systematic, documented, periodic and objective review of processes and environmental regulation procedures.

The “**process optimisation and waste minimisation programme**” could form part of this environment audit.

Traditional waste treatment methods base themselves on the treatment of already generated waste.

Industrial sinks provided an easy and inexpensive way out, but recent legislation has strengthened controls and reduced possibilities of use. This solution becomes more expensive by the day and will not contribute to a better environment. The alternative solution is to reduce waste or recycle. With adequate planning, companies can demonstrate their interest for the environment and can obtain more profitability from the process.

The aim of the “**process optimisation and waste minimisation programme**” involves any technique, facility or application of procedures that reduces environmental impact. At the same time it can improve management of the factories, make new activities profitable with regard to waste or raw materials, augment or improve energy and industrial reports and diminish factory production or management expenses in the medium term.

Most effluents produced by companies are the result of essential cleaning and rinsing:

- a) In the production process
- b) In manufactured parts
- c) In the reactors or elements in which the process is done
- d) In raw material, product or reagent conduction

For example:

- 1) Cleaning and reduction with sodium hydrosulphide in basic element after dark dyeing
- 2) Rinsing bits of cloth, after washing and neutralising
- 3) Rinsing electroplated parts, after an electrochemical dumping process
- 4) Washing and rinsing reactors after manufacturing a product
- 5) Washing and rinsing reception tank and conduits in milk product industries

These washing and rinsing processes are secondary to the production cycle. It is a process that lacks technical surveillance but produces the vast majority of wastewater generated, which is worrying.

Washing and rinsing is done to avoid any incompatibilities among processes, improve production, avoid pollution from products, etc.

From a point of view of quality, a good rinse can be achieved with a large flow of water. And, if one uses sufficient quantities of water for the concentration of pollutants not to exceed the legal level, one can always remain within legal limits. This type of solution to the problem needs to be forbidden because it is unacceptable from both a social and an environmental point of view.

It is necessary to define the number of rinses for each process and reuse the water to its maximum rinsing potential. Rinsing can in this way be measured and controlled perfectly (with the right quality), the concentration of pollutants in wastewater can be known (with no big increases in pollution) and, generally speaking, large amounts of water will be saved.

GOALS

- 1.- Keep rinsing contamination within the quality limits required for preceding processes.
 - 1.a No toxic industrial emissions into the environment
 - 1.b Avoid chemical incompatibilities
 - 1.c Increase the performance of each process

- 2.- Save rinsing water
 - 2.a Reducing water consumption to a minimum
 - 2.b Reducing waste to a minimum
 - 2.c Smaller sized treatment plants. Alternative cleaning processes (viable if water output requiring treatment is reduced)
 - 2.d Waste in accordance with current legislation

- 3.- Simplification of workers= tasks

FINANCIAL CONSEQUENCES

- Control of pollution caused by washing. Increase in quality of manufacturing process
- Decrease in clean water consumption
- Smaller treatment plant
- Possibility of retrieval of water and products
- Minimisation and control of waste

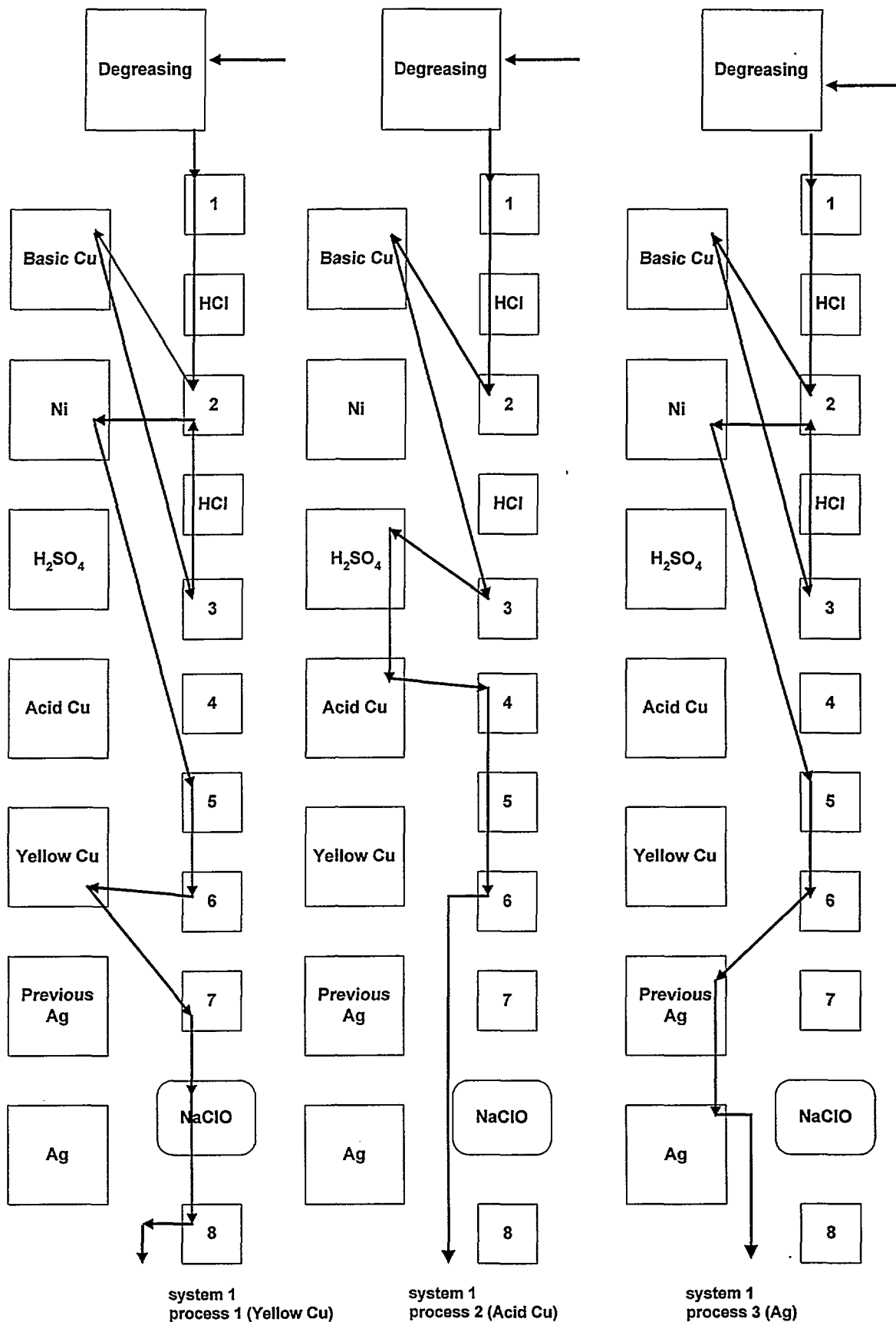
EXPERIMENTS

- 1.- Study of rinsing
- 2.- Working out surface washed
- 3.- Collecting samples
- 4.- Analysing pollutants
- 5.- Evaluating results
- 6.- Changing the washing system

RINSING CLASSIFICATIONS

- Not critical (750 ppm)
- Less critical (40 ppm)
- More critical (20 ppm)
- Very critical (5 ppm)

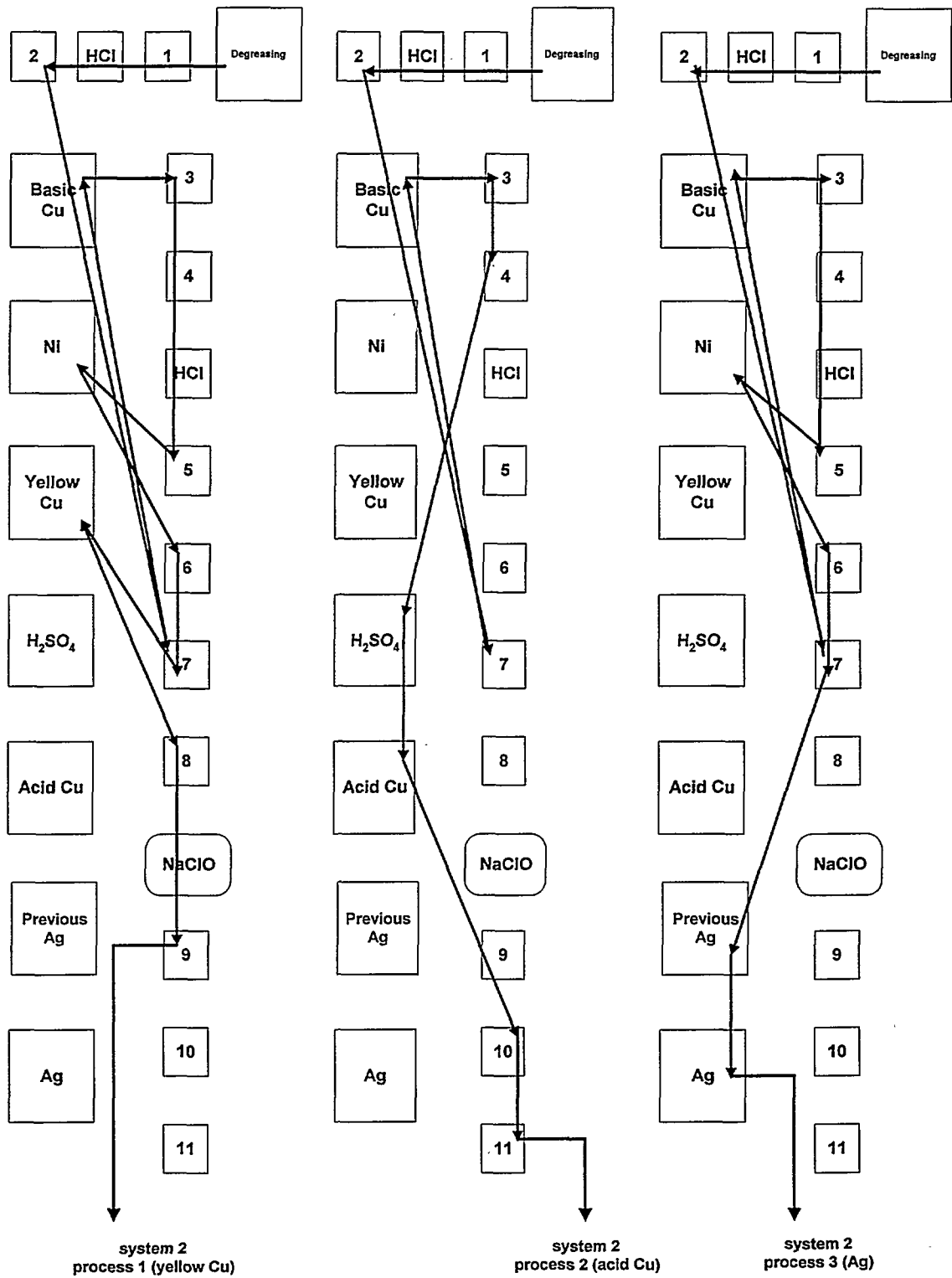
System 1



RESULT	pH	Si	Zn	CN	Cu	SO4	Cl	B	Ni	NaClO
1A	8,52	15,3	0							
1B	8,6	15,3	0							
1C	8,91	19,3	0							
2A	4,95		4,27							
2B	2,82		4,84							
2C	2,36		7,53							
3A	8,1			30	25,1					
3B	8,46			39,4	38,4					
3C	8,8			72,56	55,7					
4A	6,67				12,6	0	0			
4B	6,17				32,6	0	0			
5A	7,5							2,38	36,7	
5B	7,35							4,31	53,3	
5C	7							6,77	89,2	
6A	7,3								1,5	
6B	7,3								1,7	
6C	7,13								2,5	
7A	7,85		13,45	19,9	11,57					
7B	8,17		19,76	22	15,32					
7C	8,5		27,8	31,2	27,3					
8A	7,5		0		0					0
8B	7,5		0		0					0
8C	7,5		0		0					0

CONCLUSIONS: WATER CONSUMPTION

- Minimising water consumption cannot be contemplated whilst rinsing (according to the classification) is contaminated
- Rinses 2, 3 and 7 are ready only 3 hours after the start of the production process
- Rinses 2 and 6 use a lot of water and furthermore, 2 does not fulfil objectives
- Retrieval rinse in silver bath.

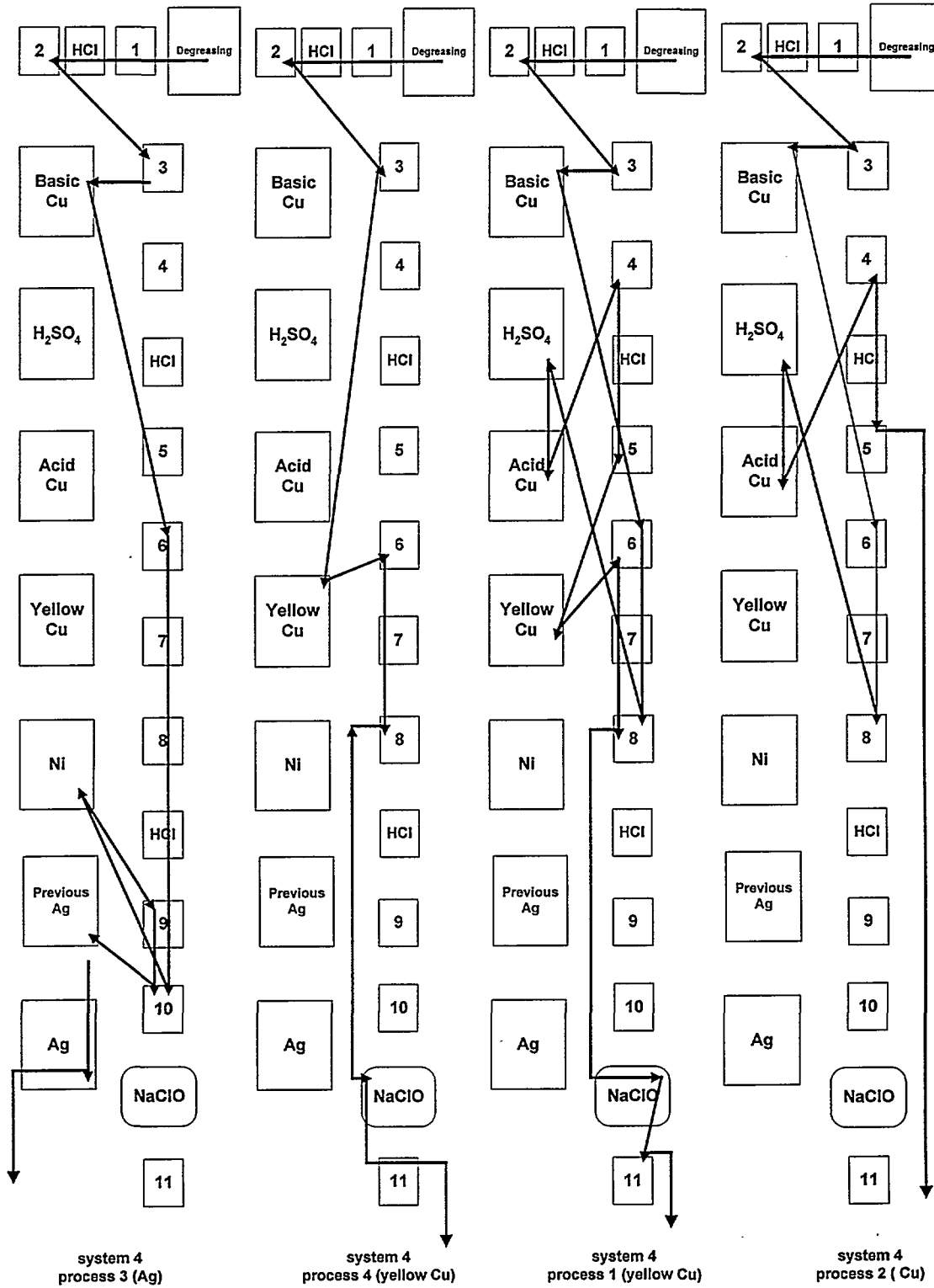


	surface	stored surface	pH	Zn	CN	Cu	B	Ni
1A	14500	14500	8,5	No				
1B	11000	25500	8,5	No				
1C	14000	39500	8,5	No				
2A	14500	14500	2,1	2.7				
2B	11000	25500	1,8	5.2				
2C	14000	39500	1.7	7.0				
3A	14500	14500	8,3		32.0	33.3		
3B	11000	25500	8,4		70.6	53.9		
3C	14500	39500	8.9		100.0,	90.6		
4A	14500	14500	7.3		2,8	4.8		
4B	11000	25500	7.5		3,1	5.1		
4C	14500	39500	7.8		3.2	5.4		
5A	14500	14500	2.2					
5B	5900	20300	1.8					
5C	4000	24300	1.7					
6A	12900	12900	7.1				4.7	62.0
6B	7600	20300	7.1				5.9	94.0
6C	4000	24300	6.9				8.3	107.4
7A	12900	12900	7.3					1.9
7B	7600	20300	7.3					2.1
7C	4000	24300	7,3					
8A	14500	14500	8.0	12.5	35.9	18.5		
8B	5200	19700	8.2	17.5	38.8	30.7		
8C	10700	30400	8.9	21.6	67.3	42.0		
9A	14500	14500	7.6					
9B	5200	19700	7.7					
9C	10700	30400	7.7					
10A	5100	5100	6.5		19.3			
10B	9900	15000	5.8		48.6			
10C	6200	21200	5.1		64.9			
11A	5100	5100	7.2					
11B	9900	15000	7.3					
11C	6200	21200	7.2					

CONCLUSIONS: WATER CONSUMPTION

- Pollution problems in rinsing processes 4, 5 and particularly 8 because it is continuous (higher water consumption)
- The path of parts that come from the alkaline Cu is too long. It has to be reduced

Footnote: The company replaced the brass bath with the bronze one.



RESULTS

	surface	pH	Zn	CN	Cu	B	Sn	Ni
1A	56000	9.8						
1B	86000	9.9						
2	142000	1.15	11.3					
3	142000	6.9						
4	14100	6.7			52.3			
5A	14100	7.3			2.2			
5B								
6	162900	10.3		340	54.5		30.4	
7	162900	8.0		20	34.3		6.0	
8	162900	7.8		0.9	1.2			
9	21900	5.7				9.8		384
10A	18000	7.4						1.85
10B	3900	7.4						
	142400	7.3						

CONCLUSIONS: WATER CONSUMPTION

- Rinses 2, 3, 4, 6, 7, 8, 9 and 10 can be kept up more than ten days
- Rinses 1, 5 and 10 must be renewed every 10 days

This is the first time that we have a rinsing system with concentrations of pollution in the cleaning water. These concentrations are within the limits of the rinsing classification. In other words, the process has been optimised as regards avoiding interference in baths.

With this system problems are avoided and consequently better results and quality are achieved. The process has been optimised and water consumption has been reduced from 2,372 l/day to 730 l/day.

Since some rinses have concentrations above what is permitted, system 4 will be modified to improve water replacement and save it.

RINSES	RESULTS
1A	pH 9.76
1B	pH 9.97
2	pH 1.15 Zn 11.3
3	pH 6.87
4	pH 6.70 Cu 52.3
5A	pH 7.35 Cu 2.22
6	pH 10.34 Cu 545 Sn 6.1 CN 20.1
7	pH 8.03 Cu 1.22 CN 0.94
8	pH 7.76 Cu 1.22 CN 0.94
9	pH 5.69 Ni 384 B 9.87
10A	pH 7.38
	Ni 1.85
10B	pH 7.36
11	pH 7.80

APPLICATION OF TECHNOLOGIES THAT ALLOW

- A) Water savings
- B) Retrieval of products
- C) Non-generation of waste

Evaporation: a+b

Replacement resin: a

Inverse osmosis: a + "b"

Ultra-microfiltration: a + "b"

Electrophoresis: "a" + b

Electrochemical store: "a" + b

Replacement resin + Electrochemical store: a + b + c

Inverse osmosis + electrochemical store: a + b + c

Ultramicrofiltration + electrochemical store: a + b + c

CONCLUSIONS

- Concentrations of less than the maximum level permitted in the classification in all washes
- Weak concentrations in some rinses, allowing unproblematic increased production relative to classification
- Movement of pieces in the rinses and the process is perfect, if we consider the use of each bath
- Weekly rinses
- Consumption is undoubtedly reduced to 75% from 11,350 l/sem to 2,800 l/sem
- Cleaning rinses 1, 5 and 10 is not necessary because they are renewed during the week. However, cleaning some rinses is necessary at the weekend.

**BATHS FORMULATION.
SUBSTITUTION AND RECOVERY OF RAW MATERIALS**

**J.A. Ortega
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McDermid Española
Barcelona (Spain)**

Modern technology would be unthinkable without components made from metal and plastics, Electroplating and electroless are the principal means by the metals and plastics are modified in order to make them fit for service.

The most important function of plating is to protect parts from corrosion and wear. Various institutes have estimated the annual loss to the economy of the countries caused by corrosion at \$ 150 billion in Europe. Electroplating and electroless techniques reduce dramatically this figures.

Lots of companies are active in the electroplating sector. The process used by these companies are developed by electroplating supply housed. They supply ready-formulated plating solutions and additives, along with plant and equipment, and products for pre-treatment and finishing.

All the electroplating supply houses are developing new products for use in electroplating-electroless processes.

The demands ever increasing are being made on electroplating supply houses:

- Environmental legislation and toxicological restrictions are becoming more severe.
- Health and safety regulations are becoming more stringent.
- Technical standards and standards for quality are increasing.
- Registration formalities for new formulations are becoming more and more complicates.
- Testing is becoming more expensive.
- Costs are trying to be reduced.

The electroplating-electroless industry supply houses have always the aim to develop products that are biodegradable, halogen-free, capable of being recycled or easy to dispose of, and do not form any metabolites or decomposition products.

The plating process has three separate stages in plating and coating.

- Pre-treatment
- Plating
 - Electrodeposition
 - Electroless
- Furnishing

PRE-TREATMENT

The actual plating process itself is preceded by a series of operations in which the substrate is ground and polished, degreased by several processes, and pickled to remove rust and seale. Parts also have to be rinsed between stages. The quality of plated surfaces depends to a large extent on the success of the pretreatment stage. Faults early on in the process can cause pores to the formed unplatted surfaces, find they can give rise to poor adhesion and dullness.

PRE-TREATMENT PROCESS

PROCESS	CHEMICAL REQUIRED
Buffing, polishing Pickling	Vaxes, emulsifiers HCl, H ₂ SO ₄ , H ₃ PO ₄ , etc. and corrosion inhibitors.
Cleaning and derusting	Na(OH), K(OH), PO ₄ ³⁻ , SiO ₃ ²⁻ , etc. surfactants, emulsifiers, chelating agents, dispersion agents.

PLATING

Electroplating is the process by which a layer of metal is applied to a metallic or non metallic substrate electrolytically or by chemical means. The term can also be extended to cover the application of passive layer of oxide and phosphate, and the whole range of cleaning polishing, colouring and finishing techniques, including pickling, degreasing and burnishing.

The aim of all these processes is to upgrade, by making them more resistant to corrosion, wear, abrasion and chemical attack, improving their hardness or conductivity, or enabling them to be soldered.

Modern electroplating have enabled valuable raw material to be saved, as well as eliminating the serious hazards to health posed by the repetitive, tedious task of polishing.

The advances that organic and inorganic additives have made possible have meant that they become indispensable in metal finishing processes.

ELECTRODEPOSITION PROCESSES

<u>PROCESS</u>	<u>CHEMICAL REQUIRED</u>
Electroplating metals, including nickel, zinc, copper, chromium, tin/lead, zinc/nickel, zinc/cobalt, zinc/iron, nickel/iron alloys, gold, gold alloys	Acetylene compounds, piridin derivates, thio compounds, unsaturated alkyl components, carbonyl compounds Nicotin and nicotin derivates, Iron Imidazole derivates surfactants, emulsifiers, dispersing agents, polyalkylene glycols. EO/PO blockcopolimers, β-naphthol compounds, etc.
Iridium Palladium, Palladium nickel alloy Rhodium Tin/nickel alloy	
Electroless plating of copper or nickel in plastics or metals.	Complexing agents, ammonia conditioning agents, reducing agents surfactants, heavy metals.
Chemical polishing of stainless steel	Acetylene compounds

Anodising aluminium

Acetylene compounds

The most important branches of the industry from the point of view of electroplating or electroless are listed below:

- Automobiles
- Building and construction
- Electrical industry
- Electronics
- Furniture
- PC

The most important electrodeposited metals in terms of their estimate share of the total area of plated production are:

Zinc	25%
Nickel	200%
Chromium	15%
Copper	15%
Other metals including precious metals	25%

World consumption of nickel and zinc in 1995 for electroplating:

Nickel	100.000 tones
Zinc	1.000.000 tones

Brightness provide an evenly distributed, high-gloss finish by inhibiting the growth of large crystals. They, or their decomposition products, often become an integral part of the metal deposit, which influences its physical properties.

The following properties can be controlled by means of brightness.

- Throwing power
- Levelling
- Brightness
- Corrosion resistance
- Hardness

- Ductility
- Tribology
- Internal stress
- Crystallinity
- Adhesion of metal
- Reactivity

The most important changes introduced on the last 10 years to meet the environmental, health and safety regulations has been the following,

ELECTROLYTIC NICKEL

The standard composition of the watts electrolyte is as follows:

Nickel sulphate	300 g/l
Nickel chloride	50-100 g/l
Boric acid	40-50 g/l
Anionic surfactant	0,2-0,5 g/l
Brightener	1-10 ml/l
pH	3-5
Temperature	55-65 °C

The metal salts for the make up of the nickel watts contain nickel sulphate and nickel chloride.

Concerning those nickel salts, the CEE work group has disposed the following rules:

Nickel sulphate

Xn (category 3) *

R22
R40
R 42/43
S22
S36/37

Nickel Chloride

Xn (category 3)*

R22
R25
R40
R 42/43
S22
S36/37

(*) To be suspected as a cancerous agent, since the recognition proofs as cancerous to persons and animals are insufficient or unsuitable. April 1997.

By that reason, the use of no air-agitated baths is still more strongly recommended, in order to fulfil the level of exposition to nickel, according with the following table:

- (a) Nickel as metals or its non-soluble compounds.
- (b) Nickel soluble compounds

Italy	(a) 0,1 mg/m ³	(b) 0,05 mg/m ³
UK	(a) 0,1 mg/m ³	(b) 0,05 mg/m ³
Germany	(b) 0,05 mg/m ³

Organic agents used in nickel electroplating baths belong to the families:

R - SO₃'
R - SO₂ - NH - R
R-S-R
R - C ≡ C - R
C₆H₅-N'- R - SO₃'

It appears in the USA market to be restricted the use of pyridine derivates compounds, as the pyridine (propyl or ethyl-) sulphobetaine, since the decomposition of that betaine makes that pyridine remains in the effluent from the rinses.

Nevertheless other compounds, as the acetylene derivates or the sulphonated compounds are fully able to replace the pyridine (propyl or ethyl) sulphobetaine.

ELECTROLYTIC CHROME

Usually the chrome is electroplated on a electrolytic nickel layer or by itself, for hard chrome purposes. The basis of a electroplating chrome bath formulations from the chromium trioxide CrO₃ is as follows.

CrO ₃	-- 200 to 500 g/l
Sulphate (SO ₄ ²⁻)	-- 1 to 4 g/l
Catalyst	-- proprietary according to the formulation
Working temperature	-- 30 to 50 °C

Catalysts used up to now were based on fluoride compounds, but the current techniques has developed other, based on Pyridine sulphate or on short - chain alkylsulphonates, which makes the chrome baths not to attack the basis material (steel or brass), thus increasing the useful life of the electroplating chrome baths.

Another possibility is the technological application of electroplating of chrome through its trivalent form, Cr^{3+} , although the appearance of the deposit is mainly different of the one achieved from the Cr^{6+} , being its application only able in a small proportion and for some special purposes.

Recently is under studies the possibility of replacing the chrome, as well in its hexavalent form Cr^{6+} , as in the trivalent one by two-metal or three metal alloys, which can offer similar features than the chrome as well in decorative as in corrosion resistance purposes.

ELECTROLYTIC ZINC

Zinc is one of the most important plated metals. It has many different applications, some of which are listed below.

- Fittings for mechanical, electrical and automotive engineering applications.
- Households equipment camping and sport goods, supermarket trolleys and shopping baskets, shielding, roof, racks, furniture.
- Bolts and fasteners.
- Plated wire, tubes and steel metal.
- Office equipment, lighting and electrical goods.

Zinc is relatively inexpensive, it can be plated from different types of electrolytes, and it is very resistant to corrosion. Its corrosion resistance can be further increased by chromation and or applying a silicate or organic coating, which also gives rise to other decorative an functional effects.

There are basically from different processes for plating zinc.

Alkaline	Cyanide
	Non - Cyanide
Acid	Ammonium
	Non - Ammonium

The most important criteria governing the choice of bath are listed below.

- Substrate
- Success of the pre-treatment process
- Bath control
- Current density
- Efficiency
- Throwing power
- Levelling
- Brightness
- Effluent treatment

The relative merits and drawbacks of acid and alkaline plating baths are shown in the table below:

<u>Characteristics</u>	<u>Acid</u>	<u>Alkaline</u>
Brightness	Excellent	High/excellent
Levelling	Very good	Moderate
Metal distribution	Poor	Excellent
Ductility	Satisfactory	Excellent
Efficiency	Very rich	Moderate
Cast Iron parts be plated	Yes	No
Bath control	Easy	Very Easy
Sensitive to impurities	Yes	No
Effluent treatment	Simple-ammonium free Complicate - ammonium	Simple (non cyanide) Complicate (cyanide)

The composition of typical alkaline zinc-plating solutions are shown below:

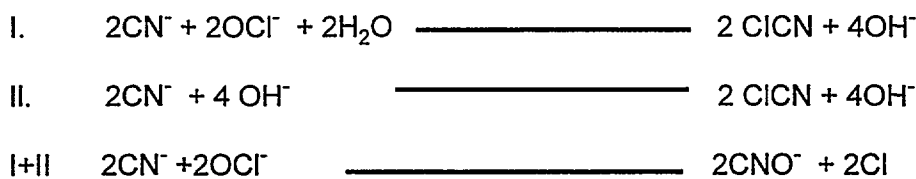
Components	Bath type (g/l)				
	High cyanide	Medium cyanide	Low cyanide	Trace cyanide	Non cyanide
Zn ²⁺	30-40	20-25	10	8	8-16
NaCN	90-130	40-60	20	8	-
NaOH	70-90	80-100	90	90	130-150
Carrier	-	-	-	-	10-20

Non cyanide baths are becoming increasingly more popular. They are less poisonous, but they are most quite as easy to control as cyanide baths, and they require more complex mixtures of brightener.

Components	Bath type (g/l)	
	Slightly acidic containing NH ₄ ⁺	Slightly acidic with no NH ₄ ⁺
Zn ₂ ⁺	20-25	20-50
NH ₄	10-60	-
Cl ⁻	100-125	100-140
H ₃ BO ₃	20-25	25-30
Brightener	1-2	1-2
Wetting Agent	30-40	30-40

The main problem that presents the Alkaline Cyanide baths is the needing of treatment of effluents by sodium hypochlorite.

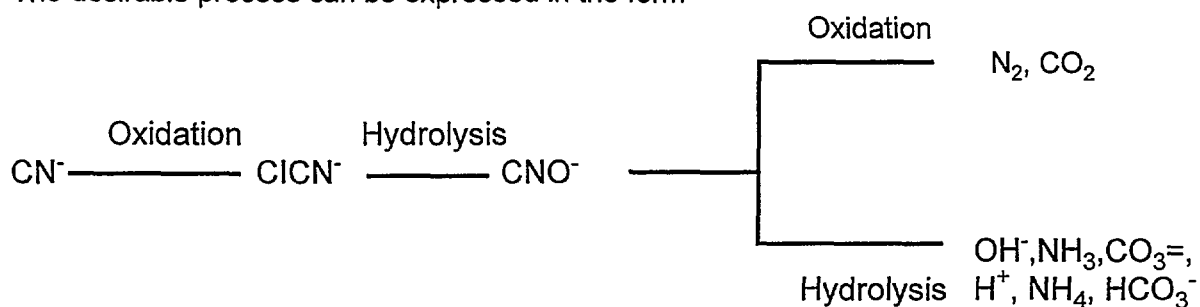
Reactions that takes form are as follows:



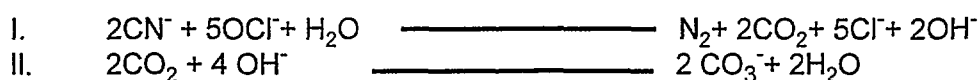
The cyanate thus formed can be oxidised or hydrolysed, according to the following reactions:



The desirable process can be expressed in the form



The desirable process is the full decomposition of cyanides to give N₂ and CO₂, as obtained by addition of the reactions I, II and III:



The main disadvantages of the cyanide treatment by Sodium Hypochlorite are:

- Chlorination of the aliphatics chains, both saturated and unsaturated



- Chlorination of alcohol, aldehydes, acids and aromatic rings, thus generating chlorophenols.

Likewise, the large amount of iron chloride Cl⁺, thus generated across the reaction may represent a serious problem in terms of disposal of effluents.

Other ways of treatment for the oxidation of cyanides are cleaner and involves the use of ozone, stream of oxygen gas, hydrogen peroxide and the acid of CARO (2 KHSO₅, KHSO₄, KSO₄) thus generating SO₄²⁻, which can be precipitates with calcium hydroxide.

Alkaline non-cyanide zinc baths can be easily treated by adjustment of the pH to 9,5 and precipitating metals by Ca(OH)₂.

Acid Zinc baths with ammonia implies that to form strong complexes with metals, being its treatment difficult and expensive.

Ammonia and ammonium salts form very stable complexes with zinc salts; to destroy them, Sodium Hypochlorite can be used, according to the reaction.



Acid zinc baths, ammonium free can be easily neutralised by adjustment of the pH and further treatment with Ca(OH)₂.

Concerning to the addition agents for Acid zinc baths, can be said that, at present, chlorinated compounds have been removed from the formulations.

An example could be the orthochlorobenzaldehyde that has been replaced by other cetonic compounds or aromatic aldehydes with no chlorine present in the ring.

Also nonilphenols as wetting agents has been fully removed and replaced by other mixed surfactants, as could be the following:

- Fatty alcohol ethoxylate
- B-naftol ethoxylate
- Sulphated alkyphenol ethoxylates
- Ethylhexyl sulphate
- Oxo alcohol ethoxylate
- Naphthalene sulphonic acid condensation product, sodium salt.

Chromic passivates, based on hexavalent chromium Cr⁶⁺, as finishing of zinc and its alloys, gives to them a cosmetic perfect appearance also with good features of corrosion resistance.

Automotive European industries are requiring for alternatives to the Cr⁶⁺ compounds to be less contaminant, what is compelling to the electroplating supply houses to develop new finishing processes that must be as reliable as the used before.

Nowadays is possible to use Cr³⁺ compounds instead of the Cr⁶⁺ ones, by giving on them a silicate complex layer that notwithstanding not totally avoiding the problems with the Cr⁶⁺, allows to largely limit them, since fulfils the VOLVO standard STD 513.102 that tolerates less than 0,3 µg/cm² of lixiviating hexavalent chromium.

In a very next future will be available new passivation processes, fully free of both hexavalent and trivalent chromium and giving mainly the same features.

Pb-Sn

In the Lead-Tin deposition baths the following salts have been replaced

Sn (BF ₄) ₂ . aq	Tin fluoborate
Pb (BF ₄) ₂ . aq	Lead fluoborate

to treat in waste as methansulphonic acid derivates H₃C-SO₂-OH which forms soluble salts with divalent lead and tin.

Methansulphonic acid is biodegradable and the characteristics of the deposit are practically the same than fluoborates.

Unfortunately there are some processes in which nowadays sodium or potassium cyanide has not been eliminated in formulations. These process are:

- Ag (silver)
- Brass
- Cu (monovalent)
- Bronze (whit, yellow)

Notwithstanding, we can say that efforts are being done in monovalent copper deposition in order to remove the cyanide, and in a short term, we will be able to have cyanide free industrial processes.

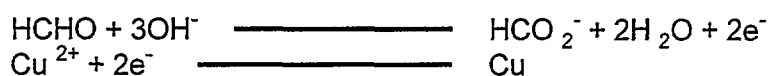
The rest of the above mentioned processes represent a small volume compared with the cyanide zinc baths which already have been completely replaced.

ELECTROLESS - PLATING

Electroless Copper

Substrates plated by electroless techniques have to be thoroughly cleaned and prepared in a number of separate stages. Electroless plating consists of reducing copper complexes with formaldehyde on surfaces catalysed with palladium or copper.

The plating reaction is shown in a simplified form bellow:



Typical electroless copper plating baths contain the following ingredients

<u>Ingredients</u>	<u>Function</u>
Copper Salts	Copper sulphate, copper chloride, etc.
Complexing agents	Complex compounds and cupric ions and impurities
Alkali hydroxides	Adjust pH
Formaldehyde	Reducing agent
Surfactants	Reduce surface tension
Nitrogen and sulphur compounds	Stabilisers

Those Electroless copper baths are being fully replaced through all European countries by processes involving metallization of the holes in the PCB by graphite-basis compounds, making them conductors and allowing to plate copper on them by electrolytic way with no technical problem at all.

This technological change has involved the total elimination of toxic compounds as:

- Copper
- Formaldehyde
- Complexing agent
- Sodium Hydroxide.

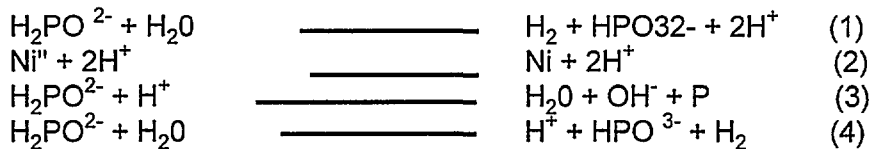
from sewage.

ELECTROLESS NICKEL

Typical electroless nickel plating. baths contain the following ingredients

<u>Ingredients</u>	<u>Function</u>
Nickel salts	Nickel sulphate, nickel chloride, nickel sulphonate.
Complexing agent	Hydroxyacids, amino acids
Sodium Hypophosphite , DMAB, sodium borohidrone	Reducing agent
Surfactants	Reduce surface tension
Acetylene derivates heavy metals	Stabilisers

The reactions which explain the electroless Ni deposition mechanism which is an Ni-P alloy, are the following:

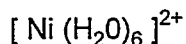


In reaction (1) the sodium hypophosphite decomposition catalytic reaction, produces monoatomic hydrogen which is able to reduce ionic nickel to metal (2). Part of hydrogen is able as well of reducing sodium hypophosphite forming phosphorus (3) . Reaction (4) is a secondary reaction which is produces in the chemical deposition of Ni-P and makes that process efficiency is quite low. 5 Kg of sodium hypophosphite are usually required to reduce 1 kg of nickel.

In order to maintain pH of the solution, the adjustment can be done with ammonia or potassium carbonate. The optimum pH values are 4,8-5 in industrial deposition baths and 8,5-9 in plating on plastic (ABS, ABSIPC) deposition baths.

At this point the problem of ammonia in waste treatment has been solved, as it forms complexes with nickel which are very difficult to treat.

Nickel forms in aqueous solution, the following complex with water:



With ammonia forms the complex:



The nickel blue ammonia complex is easy to treat by formulations as it forms compounds more solubles with hydroxyacids or aminoacids which complex it, but it presents the previously mentioned problem with waste treatment.

Nowadays we have replaced ammonia in electroless nickel formulations maintaining the same characteristics of the process, with ammonia.

SUBSTITUTION OF RAW MATERIALS

A very important chapter is the substitution of methylene chloride

CH₂Cl₂ (Dichloromethane) Xn R:40, S:23c-24/25-36/37

used in painting and varnish stripping. All the countries in the world have reduced its use as well as the exposition of workers due to its toxicity.

At present we can remove, methylene chloride (dichloride methane) from varnish or lacquer stripping formulations and use stripper products which contains esters of lactic acid, as ethyl lactate or butyl which together with other ingredients, work as well as the mentioned methylene chloride.

RAW MATERIAL RECOVERY

The main section in metal recovery is the one produced in the engraving of tracks in printed circuits boards, which can be 40 or 400 micrometers.

The liquid use to attack is formed by a cupro-ammoniacal solution which at certain temperature and by aspersion, removes copper from the tracks without undercoating.

At present we can recover copper from exhausted solutions and manufacture copper salts as copper sulphate, copper oxalate, etc.

After copper recovery eluate can be neutralised again, once formulation is adjusted and so on.

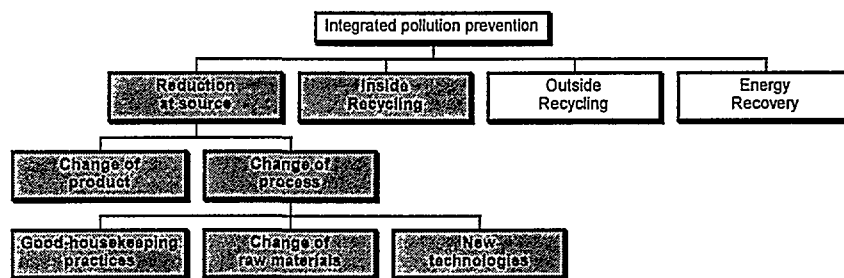
The previously existing problem, is been solved nowadays, as copper is totally recovered and the liquid is used again.

The same occurs in tin-lead stripping baths using oxygenated water or nitric acid. Tin and lead are removed and solution can be reformulated.

**GOOD-HOUSEKEEPING PRACTICES.
SEGREGATION OF WASTE STREAM**

**J.Ma Renau
Chemical Engineer
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What is Cleaner Production?

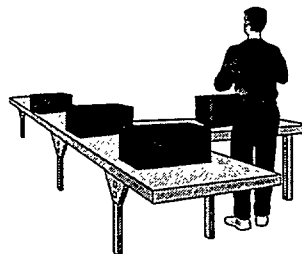


Good-housekeeping practices in the electroplating industry

Two levels to act on:



Managers



Employees

Managers

- * Listing chemical products according to different categories: their composition, dangerousness, flammability etc.
- * Negotiating with suppliers for parts to arrive in as clean a condition as possible and organise cleaning and degreasing procedures
- * Designing assembly for minimum dragging through baths
- * Modifying plant sewage output time to prevent bath losses through dragging
- * Attaching covers to joints to gather liquids that trickle from parts during transfer from one tank to another

Managers

- * Installing shaking system in cleaning baths to improve efficiency (mechanical, ultrasonic)
- * Modifying equipment design to facilitate periodic removal of oils from degreasing tanks.
- * Setting up preventive maintenance in factories
- * Using less toxic products
- * Reducing the concentration of products used in baths
- * Installing air shaking system in rinsing tanks

Managers

- * Analysing the optimum system for the rinsing process: number of stages, flow, tank volumes, etc.
- * Checking flow of water used in rinsing with flow meters
- * Putting in retrieval baths immediately after the process
- * Continuing good environmental practices training for workers
- * Keeping the plant clean: from soil, waste, dirt, etc.
- * Encouraging co-operate during routine and systematic inspections of the state of machines, barrels, valves, pumps, piping, and the company's general installations

Employés

- * Preventive cleaning of assembly and barrels
- * Slow extraction of assemblies and barrels to give time for draining and in order not to lose bath through dragging
- * Making sure that parts that can be filled with bath because of their shape are emptied
- * If working with barrels, rotate them for a few seconds to facilitate draining
- * Participating as much as possible in company training courses
- * Stopping dirt from forming or accumulating

Employés

- * Keeping packages in the right position, closed, in piles that are not too high, etc, in order to prevent them accidentally spilling and products being mixed
- * Cleaning up any accidental spillage in accordance with a specific procedure for the product spilt
- * Decanting liquids (pouring contents of a container into bath tanks) in such a way as to avoid spillages
- * Periodic checking of the quality of the baths (pH, T, C, etc.) to maintain efficacy and prolong useful life
- * Appropriate placing of parts in assembly in order to minimise drag

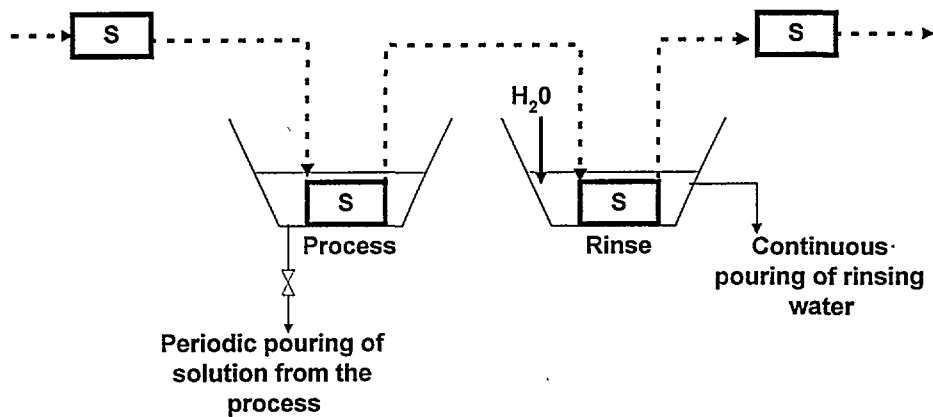
Main characteristics of effluents from the electroplating sector

- * Very toxic elements (heavy metals)
- * Relatively high concentrations

Most frequent polluting elements

- * Cyanides
- * Chromates
- * Nitrates and ammonium salts
- * Acids and strong bases
- * Heavy metals (Cu, Ni, Cr, Zn, Al, Fe, Sn, Pb)
- * Oils and greases
- * Surfactants and detergents

Simple diagram of process

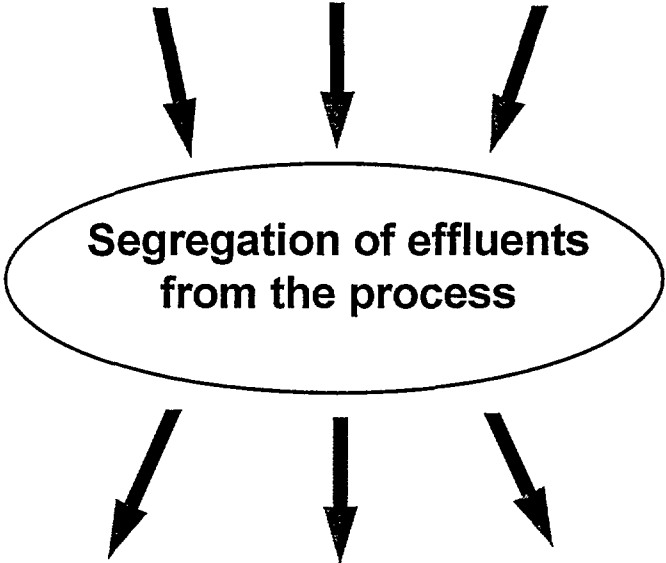


Classification of effluents from process

Depending on:

Concentration	Flow
-Concentrates (Used baths) -Diluted (Rinsing)	- Discontinuous - Continuous

Good-housekeeping practices



Thanks to the segregation....

You can decide:

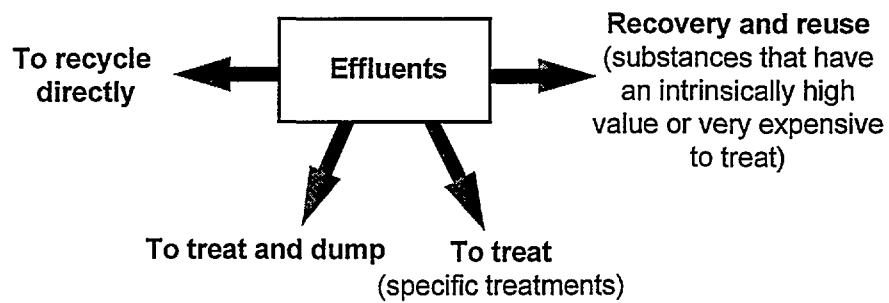
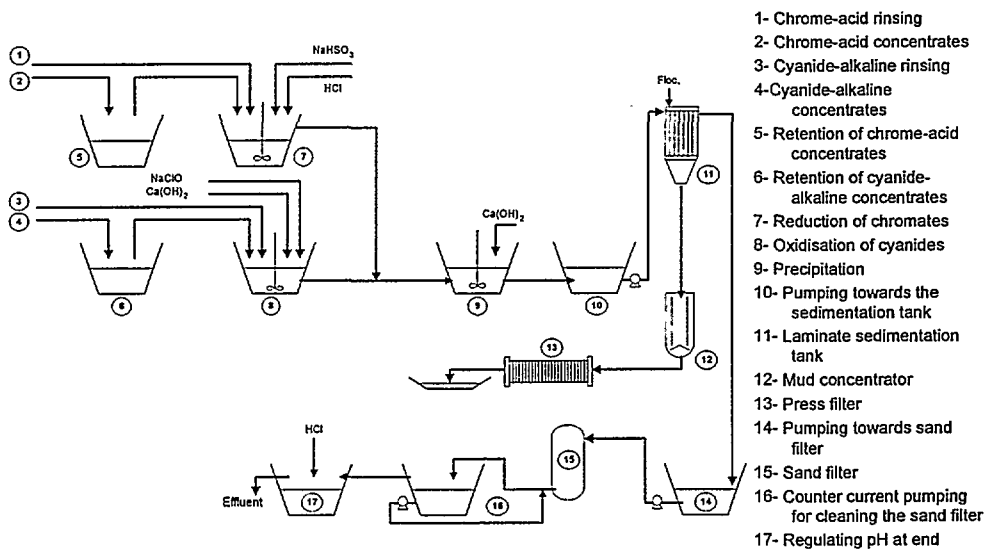


Diagram of a treatment plant



Treatment of effluents

It depends on:

- * Raw materials
- * Temperature
- * Concentration
- * pH
- * Time

to treat by chemical means all the substances present on the effluents of the electroplating.

Wastewater treatment plants

- *They are complexed as the effluents are also complexed.
- *Physico-chemical.

Main stages:

- Chemical treatment of specific pollutants
- Metal precipitation
- Sedimentation and treatment of sludges
- Filtration and adjustment of pH

**THE EXPERIENCE IN CATALONIA. WORKING GROUPS.
THE POLLUTION PREVENTION DIAGNOSIS**

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WORKING GROUPS WITH INDUSTRIAL COMPANIES

The Center for Cleaner Production Initiatives (CCPI) started out this kind of activity with Catalan industrial companies in 1995. Since that date, five different Working Groups have been formed and have carried out their activities in the following industrial sectors:

✓ **Surface treatment (Electroplating)**

Two different working groups with companies belonging to two different associations were formed. The first group initiated its activities in April 1995 and was formed by six companies. The second group initiated its activities in November 1995 and was formed by eleven companies.

✓ **Surface treatment (Paint Application)**

The group was formed by six different companies and carried out its activities from April 1996 to December 1996.

✓ **Paint manufacturing**

The group was formed by seven different companies and carried out its activities from September 1996 to June 1996.

✓ **Textile dyeing and finishing**

The group was formed by six different companies and carried out its activities from September 1996 to June 1996.

WHICH KIND OF ACTIVITIES ARE CARRIED OUT IN A WORKING GROUP?

Two main activities are basically stressed in a working group: the achievement of a *Pollution Prevention Diagnosis* to each of the participating companies and the holding of a series of periodical *meetings on pollution prevention options* for the industrial sector involved.

MEMBERS OF THE WORKING GROUP

The working group consists of, at least:

- ✓ One representative of each of the participating companies,
- ✓ one representative of the CCPI and

- ✓ an expert (either a single consultant or a consultancy company) specially hired to manage and execute the activities within the framework of the working group.

I would like to stop just for a minute here to remark the significance of the expert's figure in order to attain satisfactory results, both in the individual diagnosis and in the meetings.

It is absolutely necessary that the expert proves deep and real knowledge of the industrial sector involved and, specially, of the following:

- ✓ Industrial processes
- ✓ Raw materials used
- ✓ Technology and equipment involved and available
- ✓ Suppliers of raw materials, equipment and technology
- ✓ Environmental traits of the activities carried out
- ✓ Most frequent environmental trouble
- ✓ Pollution prevention options
- ✓ Etc.

The participating companies need to feel confident with the expert and know for certain that, if they share information about their processes with him, they will be able to improve their environmental performance while simultaneously increasing productivity and improving the quality of their products.

Too often we run into self-called environmental experts that may know about environmental laws and environmental auditing but have no experience on pollution prevention or industrial processes. I would say that the figure of the expert, together with the willingness of the participating industrial companies are the key factors to achieve satisfactory results from the group activities. Therefore, it is absolutely necessary to avoid situations such the one just mentioned.

THE ROLE OF THE CCPI IN THE WORKING GROUP

The CCPI has five main functions in the working group.

- ✓ Coordination of the different participating parties until the actual formation of the working group. This is, contacts and discussions with industrial associations, contacts with interested companies, explanation of the methodology and the different activities, selection of the expert, etc.
- ✓ Coordination and follow-up of the different tasks to be carried out in the framework of the working group.
- ✓ Financial support for the project.
- ✓ Review of the final reports.
- ✓ Dissemination of the project conclusions among Catalan industrial companies.

THE POLLUTION PREVENTION DIAGNOSIS

A Pollution Prevention Diagnosis is the assessment of an industrial facility to identify potential pollution prevention opportunities. The assessment is carried out by the expert, who will visit the company usually from three to five times in order to gather information about the following:

- ✓ Production processes - It is important to learn about the raw materials used, the manufactured products, the equipment available in the company, the technologies applied, the quality control carried out on both raw materials and products, etc.
- ✓ Way of working - It is also important to gather information on the written procedures that the company may already have to describe specific tasks such as cleaning, manufacturing or maintenance operations. But it is even more important to detect the lack of this kind of written information in order to recommend its implementation in the final report of the diagnosis.
- ✓ In-house organization - It is also interesting to learn about other activities such as inventory control, purchase management, environmental policy, environmental management systems, quality assurance systems, etc. All of them may affect the environmental performance of the company.
- ✓ Generated pollution - It is also important to identify the different waste streams (solid waste, waste waters, emissions) generated in the company and the focuses and quantities of such streams.

Once the information has been gathered and studied, a final report is written for each company, which should include, at least, the following or similar points:

- 1) Introduction
- 2) General description of the assessed facility
- 3) Description of the industrial processes, activities or areas assessed
- 4) Enumeration and description of the waste streams generated. Focuses, quantities and treatment or management.
- 5) Description of the recommended pollution prevention alternatives, including its technical and economical feasibility.

So far I have talked about what a pollution prevention diagnosis is. Let me remark, now, what it is not.

A pollution prevention diagnosis is not an environmental audit, since the assessed company usually has no environmental management system implemented.

A pollution prevention diagnosis does not pay attention to the legal situation of the assessed company regarding the meeting of legal environmental standards.

And, finally, a pollution prevention diagnosis should not translate into a general and vague final report. On the contrary, if we want it to be useful for the companies, it should quantify wastes, waste waters, emissions, investments, raw material savings, payback periods, etc.

As an example, the enclosed table shows some of the pollution prevention options identified in one of the participating companies, the suggested improvements and the estimated investments and payback periods. As you can see, the main targets of the suggested alternatives were:

- ✓ Reduction of water drag-out in rinsing operations.
- ✓ Substitution of electroplating baths using cyanide compounds.
- ✓ Correct maintenance of electroplating and degreasing baths to extend its working life.
- ✓ Optimization of rinsing operations to minimize water consumption and improve wastewater quality.

As you can see, the payback period of the estimated investments is under three years in most cases and is immediate in some of them.

We are also enclosing MedClean Fact Sheet #2, which shows the pollution prevention results attained by Industrias F. Sandoval by means of the adoption of good practices and process changes as a result of its participation in one of the working groups.

MEETINGS ON POLLUTION PREVENTION OPTIONS

A series of monthly meetings are held along a six month period, which is the forecasted duration of the working group's activities. The expert is responsible for the organization of the meetings, the selection of pollution prevention subjects related to the industrial sector involved and, if necessary, for the search of additional experts on these subjects who would participate in the meetings giving specific lectures.

Just as an example, I will mention now some of the subjects which were considered in the electroplating working groups:

- ✓ Methodology for the implementation of a pollution prevention program.
- ✓ Rinsing operations and water drag-out.
- ✓ Alternatives to halogenated solvents in degreasing operations.
- ✓ In-site recycling of degreasing baths.
- ✓ Electroplating baths with no cyanide compounds.
- ✓ Substitution of chromium (VI).
- ✓ Quality control of degreasing and electroplating baths.
- ✓ Pollution prevention success stories in the participating companies.
- ✓ Etc.

These meetings are not intended to be follow-up meetings for the individual pollution prevention diagnosis or forum of discussion of very specific and particular environmental problems which may affect any of the participating companies.

DOCUMENTATION AS A RESULT OF THE WORKING GROUP'S ACTIVITIES

As a result of the pollution prevention diagnosis and meetings, the expert should make a diagnosis final report for each company and a global final report.

We have already talked a little bit about the diagnosis final report, so let me now explain briefly which is the purpose of the global final report.

Since we assume that the expert has deep knowledge of both processes and environmental peculiarities of the industrial sector involved, we ask him to describe the most usual processes, the most frequent pollution prevention opportunities and the usually technically and economically feasible alternatives for the industrial sector. Therefore, the global, final report should not mention any particular company and should only include grouped data. This global final report is a good tool for the CCPI to learn more about the actual environmental situation of the sector as a whole.

The CCPI will get a copy of each diagnosis final report and a copy of the global final report. Each of the participating companies will get its own diagnosis final report and a copy of the global final report. The information contained in the diagnosis final reports is obviously confidential.

THE OPINION OF THE PARTICIPATING COMPANIES

Once we get to the end of the working group activities, a survey is handed out to the representatives of the participating companies. The target of such survey is to know their opinion about many subjects, such as the work of the hired expert, the results of the individual pollution prevention diagnosis, the technical level and interest of the meetings, etc.

And these are the results of the survey for both electroplating working groups:

- ✓ The fulfilment and the results of the pollution prevention diagnosis were considered positive.
- ✓ 50% of the participants would have liked the expert to spend more time in each company when gathering information for the diagnosis.
- ✓ The expert's work was considered good or very good by the participants.
- ✓ 70% of the participants intend to implement some of the improvements suggested in their diagnosis final reports.
- ✓ Their participation in the pollution prevention meetings was considered positive or very positive.

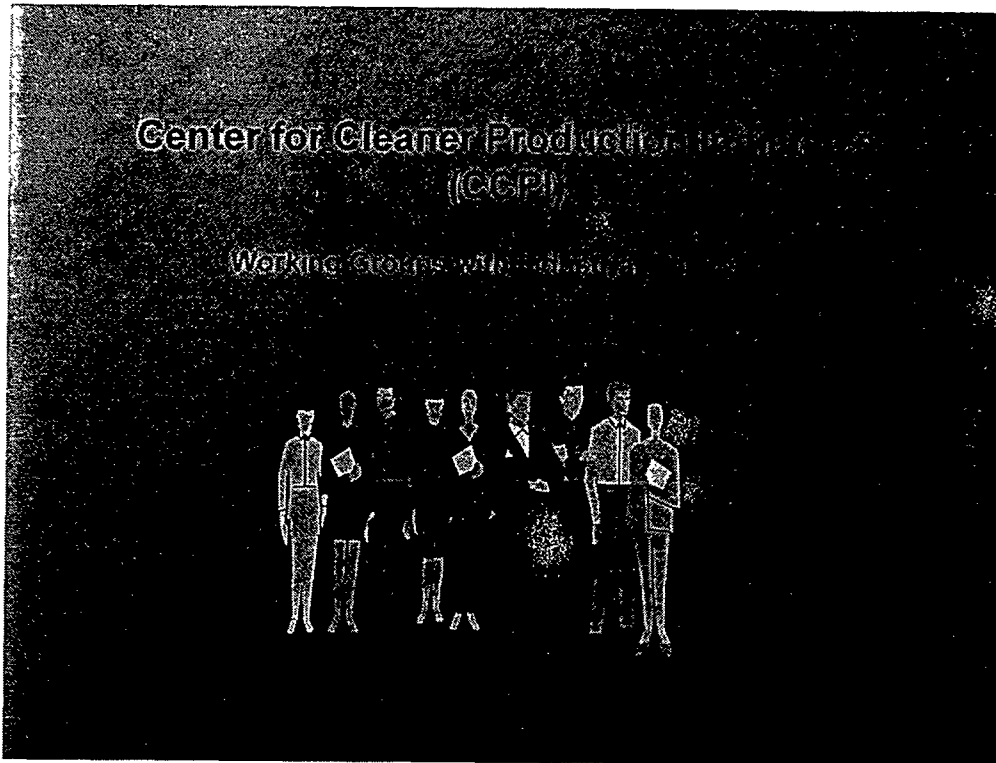
- ✓ The subjects that were chosen for the pollution prevention meetings were considered interesting or very interesting.
- ✓ The participants would have liked to talk about other subjects, too, during the meetings. Some of these subjects were: waste and wastewater management and treatment, occupational health and safety, state subsidies, etc.
- ✓ 20% of the participants would have liked to have more meetings.

CONCLUSIONS


From the CCPI point of view, there are some aspects of the described methodology that could certainly be improved in order to attain better results from the working group's tasks.

- ✓ It is very important in the initial stages and all along the project, to keep a very good communication between the participating companies, the expert and the CCPI. This is the only way to avoid misunderstandings and to redress the project if necessary.
- ✓ It is important for the correct operation of the group that the participating companies have similar environmental concerns, industrial processes and technological levels. If the group is not homogeneous enough, it is hard to keep up the participants' interest along the project.
- ✓ It is also essential to adapt the methodology to the technical level of the participating companies. The higher the level is, the more difficult the role of the expert turns since it becomes more and more complicated to identify pollution prevention options. In such cases, the selection of the expert is absolutely crucial for the good operation of the group.
- ✓ The attendance of the participating companies at the pollution prevention meetings is not as regular as we would like it to be. We believe there might be two different reasons for that. First of all, the selected subjects may not interest all the participants to the same extent. And also, the meetings are not interactive enough. Therefore, it is very important, first, to reach an agreement on the pollution prevention subjects for the meetings and, second, to encourage the active participation of all the group members.

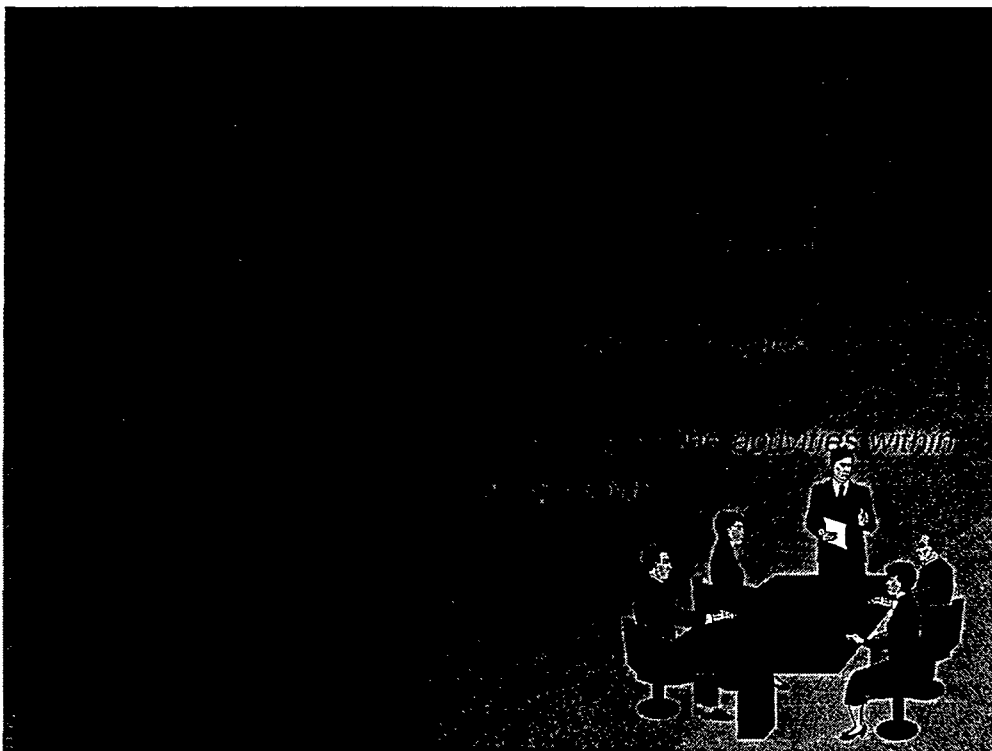
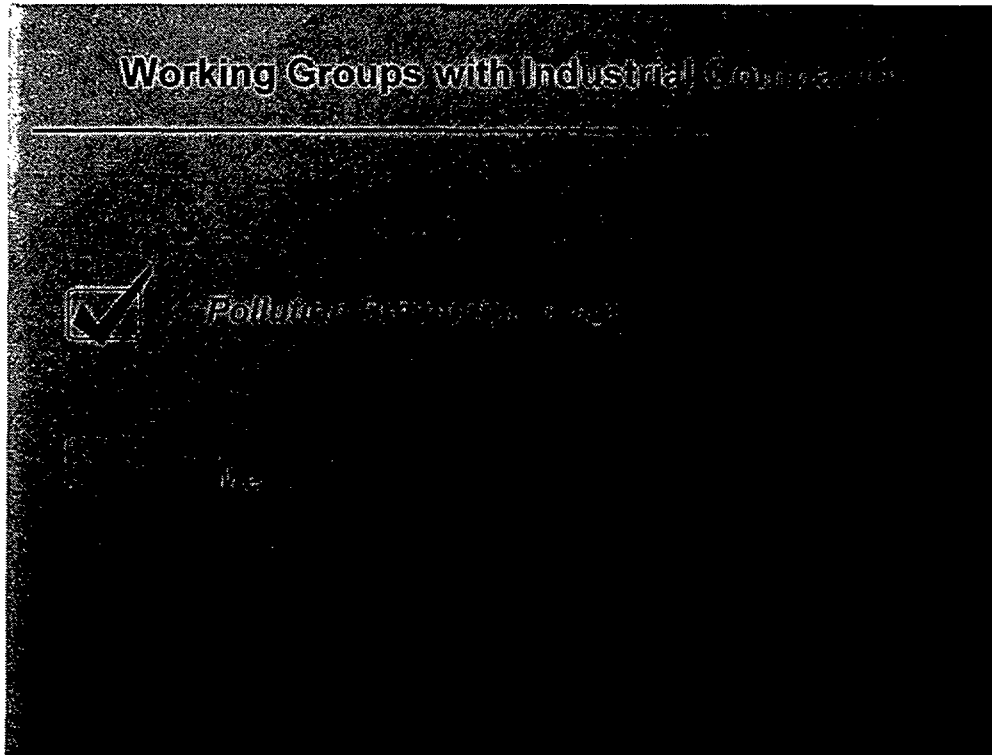
POLLUTION PREVENTION OPTIONS	SUGGESTED IMPROVEMENTS	ESTIMATED INVESTMENT (PTA)	ESTIMATED PAYBACK PERIOD (years)
Water drag-out	Application of professional and environmental good practices	0	non significant
	Flashing systems	non significant	non significant
	Reduction of salt concentration in electroplating baths	0	non significant
Electroplating baths	Increase of temperature in electroplating baths	200.000 (PTA/year)	0.5
	Use of acid copper instead of cyanide copper	0	non significant
	Filtration of tin baths	1.000.000	2.5
	Filtration of degreasing baths	600.000	1.5
Rinsing systems	Change of parallel double rinsing into cascade double rinsing	200.000	3
	Implementation of cascade double rinsing in the whole line	700.000	3
	Setup of new recovery baths	non significant*	non significant
	Set up of water recycling through ion exchange	4.000.000	2.5
TOTAL		6.500.000	1.8



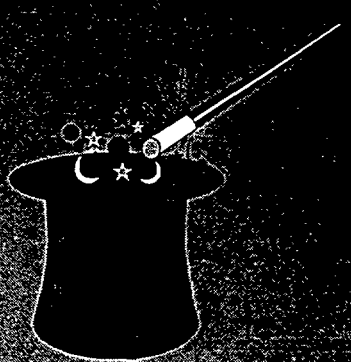
Working Groups with Industrial Firms

 **INDUSTRIAL SECTOR PARTICIPATION**

- Surface treatment - Electroplating (2)
- Surface treatment - Paint application
- Paint manufacturing
- Textile dyeing and finishing




Deep and real knowledge of the industrial sector:




- processes
- raw materials
- technology
- suppliers
- environmental traits
- etc.

Working Groups with Industry



THE ROLE OF UNEP

- *Coordination of the different participating parties until the actual formation of the Working Group*
- *Coordination and follow-up of the different tasks carried out by the Working Group*
- *Financial support for the project*
- *Review of the final reports*
- *Dissemination of the project conclusions among Catalan industrial companies*




*...of the industrial facility
...of the industrial facility
...of the industrial facility*

*...to be made
...to be made
...to be made*

**A POLLUTION PREVENTION
DIAGNOSIS IS NOT AN
ENVIRONMENTAL AUDIT**

Working Groups with Industrial Companies




POLLUTION PREVENTION

INFORMATION COMPILATION ABOUT THE FOLLOWING ASPECTS OF THE FACILITY:


- PRODUCTION PROCESSES** (raw materials, manufactured products, equipment, technologies, quality control, etc.)
- WAY OF WORKING** (written procedures, practices, habits, etc.)
- IN-HOUSE ORGANIZATION** (inventory control, purchase management, environmental management systems, etc.)
- GENERATED POLLUTION** (waste streams, generation focuses, quantities, present treatment or management, etc.)

Working Groups with Industrial Companies

 **MEETINGS ON POLLUTIVE SUBJECTS**

Meetings - Monthly Meetings
- Subject: ...
- ...

Working Groups with Industrial Companies

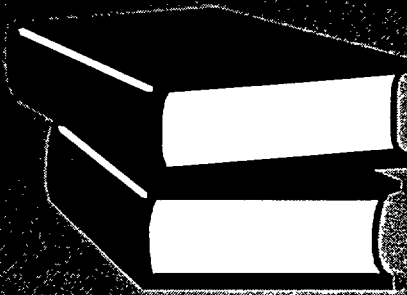
 **MEETINGS ON POLLUTIVE SUBJECTS**

SUBJECTS FOR THE ELECTROPLATING WORKING GROUPS

- Methodology for the implementation of a pollution prevention program
- Rinsing operations and water drag-out
- Alternatives to halogenated solvents in degreasing operations
- In-site recycling of degreasing baths
- Electroplating baths with no cyanide compounds
- Substitution of chromium (VI)
- Quality control of degreasing and electroplating baths
- Pollution prevention success stories in the participating companies
- Etc.

- Pollution Prevention Diagnosis final reports

- Global final report



Working Groups with Industrial Companies



GLOBAL FINAL REPORT

- List of the chosen subjects for the pollution prevention meetings.*
 - List of the experts that may have participated in the meetings.*
 - Records of the meetings.*
 - Working papers, etc.*
- Extrapolation of data for the involved industrial sector as a whole:*

General description of the Working Group

Generated pollution

Assessed waste streams

Identified pollution prevention options

Suggested alternatives

Estimated investments

Etc.

Working Groups with Industrial Companies



OPINION OF THE PARTICIPANTS
REGARDING THE MEETINGS
(Electroplating Works)

- Fulfillment and results of the Pollution Prevention Diagnosis were considered positive.
- 50% of the participants would have liked the expert to spend more time in each company.
- The expert's work was considered good or very good.
- 70% of the participants intend to implement some of the improvements suggested.

Working Groups with Industrial Companies



OPINION OF THE PARTICIPANTS
REGARDING THE MEETINGS
(Electroplating Works)

- Participation was considered positive or very positive.
- The subjects that were chosen were considered interesting or very interesting.
- The participants would have liked to talk about other subjects, too. (Waste and wastewater treatment and management, occupational health and safety, state subsidies, etc.).
- 20% of the participants would have liked to have more meetings.

Working Groups with Industrial Companies



CONCLUSIONS

- Good communication between the participating parties
- Homogenous group
- Working Group methodology adapted to the technical level of the participating companies
- Agreement on pollution prevention subjects and interactive meetings

