CETS **European Committee for Surface Treatment**

Integrated Pollution Prevention and Control (IPPC)

Reference Document on best available techniques
**Surface Treatment of metals and plastic materials
using electrolytic or chemical process**
(volume of treatment vats > 30 m^3)

June 2001

BAT Reference Document : June 2001

SURFACE TREATMENT OF METALS AND PLASTIC MATERIALS USING ELECTROLYTIC OR CHEMICAL PROCESS
(volume of treatment vats > 30 m³)

Best Available Techniques Reference Document
**Surface treatment of metals and plastic materials
using electrolytic or chemical process**
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1   GENERAL INFORMATION

Introduction

Surface engineering and finishing plays an important environmental role. It enables low-cost, easily produced substrates to be used for mass production, and gives those substrates special surface properties. These extend the life of components and retrospectively conserve our resources and the environment.
People's requirements become ever more demanding and products are required to last longer perform better, faster and more efficiently than ever before. Surface engineering is helping to meet that demand.
For example, electroplating produces thin layers of just a few microns onto base materials using valuable resources sparingly. These very thin deposits give the base material properties such as vastly improved corrosion and wear resistance, and produce a surface appearance to meet people's demands.

To judge the electroplating branch and the impact of chemical and electrochemical surface treatment on both the economy and the environment, the following figures might be of interest :

1.1   Surface protection

1 kg of zinc protects 1 tonne of screws against corrosion; 100 mg of gold protect 5 000 electrical contacts, and in addition provide special low resistance properties; In modern cars 2 to 3 thousand items are electroplated; in Airbus planes, this figure increases to about 2 million. The electroplating of steel coinage with copper, brass or nickel is widespread. Low denomination euro coinage, such as the UK penny pieces, are made from steel blanks plated with 30 μm copper, and then minted.

Approximately 1 tonne of Iron is required to make a car; approximately 70 tonnes of Carbon Dioxide is produced to make a car.
Surface engineering has extended the life of the car from about 10 years to 20 years and improved its efficiency in terms of fuel consumption and raw materials.
Therefore, this has more than halved the quantity of Carbon Dioxide produced during the manufacture and use of cars.
Car manufacturers have been able to significantly increase their warranty periods due to improvements in corrosion protection that have also resulted in car components maintaining their original appearance by the use of alloy plating such as Zinc/Iron, Zinc/Nickel, Zinc/Cobalt and Tin/Zinc. These alloys require as little as a third of the thickness of the alloy compared to just Zinc to give much better performance.

Losses from corrosion on steel parts cost 218 billion euros per day in Europe. This is equivalent to 1 € per day and per habitant.
Galvanising screws saves over 0.8 tonnes of Carbon Dioxide per tonne of screws, as well as reducing the use of Iron.

Advanced electronics and electrical systems are indispensable in today's automobile industry. They account for about 20% of the cost of a new car, and this is increasing.
Without circuit boards most modern electronic equipment would not exist.

Tin/Lead was used on 100% of printed circuit boards. 30% has now been replaced by Tin due to the Lead being banned on printed circuit boards in 2003.

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The use of coloured lacquers to produce a desired appearance on some household items such as locks, fans lamp stands etc. has reduced the need to use some metals such as Gold, Brass, Bronze etc. to produce the required coloured finish.

Without Hard Chromium plating (used to make hard wearing, low frictional, corrosion resistant surfaces) :
- plane under-carriages would not work, nor the various wing movement gearboxes,

- mines would have to go back to wooden pit-props (they creak with the strain),

- steel rolling mills would consume 10 times more rolling mill oil and the life of the rolls would be reduced by 85%. Aluminium mills would suffer similar problems,

- hospital equipment used for delicate operations would be very difficult to perform,

- steel cans would become very expensive as Tin-Free-Steel cans would not be cost effective to make,

- plastic would stick to the moulding tools,

- ship's engines would stop due to poor movement of their piston rings,

- re-build and repair of old equipment would not be possible.

1.2   The industry

More than 10,000 jobs and 8,300 in-house plating shops employ about 440,000 people in Europe. These figures include manufacturers of printed circuit boards.

1.3   Environmental aspects

Job and in-house shops together produced less than 1% of the total hazardous waste in Europe.
Through consistent and increased application of existing prevention techniques, a further reduction of hazardous waste from plating shops can be expected.

1.4   Best available techniques

The following paper is applicable to installations with a volume of treatment vats larger than 30 m³ as defined in article 2.6 of Annex I of the IPPC-directive 96/61/EC. It indicates a modular system of process integrated best available techniques for pollution prevention and control.
They are related to the main process steps of chemical and electrochemical surface treatment of metals and plastics and may be applied alternatively or cumulatively.

All mentioned techniques have proven their reliability as well as their economical and ecological efficiency through application over a longer period of time.
They are subjects of development and modification, and revision will be necessary every five years.
Optimal operation may result from automatic process control and trained personnel.
Annex 2 gives a survey on limits for Surface treatment wastewater in some EU countries.

1.5   Definitions

"Treatment vat" shall mean the process tank, assigned for the explicitly intended surface treatment of metal and plastic, using a chemical or an electrochemical process.

"Explicitly intended" shall refer to the process step serving the main purpose of the line.

"Surface treatment" shall mean the removal, conversion and deposition of layers.

Treatment vats for instance are, in a :
- pickling line the pickling tank(s),
- passivating line the passivating tank(s),
- phosphating line the phosphating tank(s),
- anodising line the anodising tank(s),
- cataphoretic coating line the tank(s) containing the lacquer dispersion,
- zinc plating line the zinc plating tank(s),
- copper plating line the copper plating tank(s),
- line for copper-nickel-chromium plating the respective plating tanks.

"Treatment vats" shall not mean the process tanks preceding and following the explicitly intended surface treatment as well as the rinse tanks; therefore eg tanks for soak clean, pickling, acid dip, passivation and rinsing within a zinc plating line shall not be treatment vats.

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2. APPLIED PROCESSES AND TECHNIQUES

2.1 Pre-Treatment

The main pre-treatment methods found in metal finishing are:
- degreasing,
- pickling,
- electrolytic activation (electrolytic degreasing),
- conditioning of plastics

These treatment steps are usually employed to remove heavy greases, oil and oxides (pickling) and to prepare the surface of the items prior to metal finishing.
Chemicals used are hazardous for health and environment (strong bases or acids).

2.1.1 Degreasing

2.1.1.1 Chlorinated Solvents

A reliable degreasing method is the application of *stabilised Trichloroethylene and perchloroethylene*: components are clean and dry after only one operation. The disadvantage of this method is the potential risk for both the operators and the surrounding environment. Modern totally closed degreasing plants are secure and waste very little solvent. In general they are not integrated in plating lines.

Environmental considerations:
Emission of liquid and vapour to the environment has strictly to be prevented. Stabilisation of both products is necessary to prevent uncontrolled decomposition.

2.1.1.2 Water based Degreasing

Water, the most common solvent has always been used in cleaning. The cleaned items can remain wet if the subsequent treatment is a non-organic coating e.g. plating.
The cleaning effect is improved by adding sodium hydroxide, carbonate, silicates, phosphates, complexing and wetting agents and in many cases emulsifiers.
The wetting agent helps to lift the grease and oil from the surface.
In case of non-emulsifying degreasing, oil or grease are removed as droplets, which can easily be separated from the degreasing solution.
Aqueous alkaline degreasing is in most plating lines the first step of surface processing.

Environmental considerations:
Process tanks operate at 50-90°C and therefore have to be equipped with fume extraction to remove water vapour.
Aqueous degreasers have replaced the major proportion of solvent degreasers. Lifetime of solution can be extended by continuous removal of oil and grease by eg skimming, micro filtration or gravity separation. Drag-out recovery is possible through balancing drag-out and evaporation losses by rinse water. Effluents are easily treated in normal wastewater treatment plants.

2.1.2 Pickling

2.1.2.1 Pickling of Metal

Pickling of metal is necessary to remove scale, oxides and other corrosion products from the surface. Inorganic acids as hydrochloric, sulphuric acid and mixtures of these are in use for pickling of heavy metals, depending on the base material and its surface condition. Fluoride containing solutions are necessary for reliably pickling certain alloys.

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Pickling solutions for aluminium are mainly based on sodium hydroxide, fluorides are added when necessary. Also acidic solutions are in use (eg nitric acid or a mixture of chromic acid and sulphuric acids).

Zincate treatment of aluminium is necessary for good adhesion prior to electroless or electrolytic metal plating. The solution is based on sodium hydroxide, containing zincates (<20 g/l).

Environmental considerations:
Process tanks have to be equipped with fume extraction to remove generated aerosols and hydrochloric acid gas.

Regeneration of pickling solutions in most cases fails due to economic reasons. Lifetime is mainly determined by drag-in of rinse water and drag-out of acid. In some cases, counter current operation in 2 or 3 stages is helpful in reducing acid consumption. Effluents can easily be treated in normal wastewater treatment plants.

2.1.2.2 Pickling of Plastic

Pickling of plastic is a precondition for sufficient metal adhesion. The aqueous solution is a mixture of chromic acid (380 g/l), sulphuric acid (380 g/l) and wetting agent. Applied to ABS type plastic surfaces it oxidises and dissolves the butadiene component, thus generating a micro rough surface.

Environmental considerations:
Process tanks have to be equipped with fume extraction to remove small amounts of generated aerosols and acid gases.

The solution lifetime can be extended by membrane electrolysis to oxidise Cr^{3+} to Cr^{6+}. Effluents can easily be treated in a similar manner to other hexavalent chromium containing solutions in wastewater treatment plants.

2.1.3   Electrolytic activating (electrolytic degreasing)

Pickling of metals is often followed by electrolytic activation to remove the rest of unwanted residues from the surface. The basic composition of the solution is similar to alkaline degreasers. The chemical concentration is generally twice as high. Wetting agents are left out to prevent foaming, however, cyanides or other complexing agents may be added to improve the activation of steel items. For normal applications, cyanide and chelator free electrolytes are sufficient.

Environmental considerations:
Process tanks have to be equipped with fume extraction to capture vigorously generated aerosols.

Lifetime is mainly determined by dilution through drag-in of rinse water and drag-out of process solution. Effluents are treated as alkaline or cyanide solutions in wastewater treatment plants.

2.1.4   Conditioning of Plastics

This process step is inevitable in surface treatment of plastic and printed circuit boards. It provides wetability of the surface as prerequisite for voidless covering and good adhesion of metal layers.

The process solution contains sulphuric acid (<20% by volume.) or sodium hydroxide and carbonate (<10% by volume), water soluble organic biodegradable solvents (alcohol, glycol derivatives).

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Environmental considerations:
Effluents have to be treated in wastewater treatment plants.

2.2   Main treatment

2.2.1   Copper plating

Copper plating is very common for many items in daily use: from coins, buttons or zippers with patina on haberdashery to printed circuit boards in television sets, mobile phones etc.
Parts can be plated on jigs or in plating barrels.

2.2.1.1 Cyanide Copper
Cyanide copper low temperature electrolytes are necessary for strike plating on steel and zinc die casts to prevent spontaneous cementation of copper and poor adhesion of the subsequent metal deposit. This type of solution is based on copper cyanide and sodium cyanide with a copper concentration of 15 - 20 g/l. Copper strike layers are usually not thicker than 2-3 µm.
Thicker layers (6-8 µm) are achieved with potassium cyanide and potassium hydroxide based high performance electrolytes at a metal content of 25-50 g/l, mainly for barrel plating and others. Potassium carbonate is generated during processing. It disturbs bright copper deposition and causes roughness at concentrations beyond 90 g/l.
Another high performance electrolyte is based on copper cyanide and sodium cyanide with potassium-sodium-tartrate, providing higher current densities, enhanced brightness of layers and reduced tendency to anode passivation. Metal content is 40-60 g/l.

Environmental considerations:
Process tanks have to be equipped with fume extraction to remove generated aerosols. Sodium based solutions can be regenerated by batch or continuous precipitation of sodium carbonate. Potassium based electrolytes have to be discarded as soon as the content of potassium carbonate exceeds 90 g/l. Effluent is treated in normal wastewater treatment plants, with cyanide oxidation stage.

2.2.1.2 Acid Copper
Due to their excellent levelling capability, acid copper electrolytes based on copper sulphate and sulphuric acid are used to make polishing and buffing redundant prior to decorative bright nickel and chromium plating on chair frames, bathroom fittings, wirework etc.
Normal copper content is 50-60 g/l, sulphuric acid 60-90 g/l.
Another important technical application of acid copper electrolytes is for through-hole, panel and pattern plating of printed circuit boards (PCB) and multilayers (ML). Sulphuric acid enhances the conductivity, the macro throwing power and provides fine crystalline and ductile layers. In such electrolytes the concentration of sulphuric acid is in the range of 180-200 g/l, the copper concentration is 20 g/l.

Environmental considerations:
Process tanks have to be equipped with fume extraction to remove aerosols generated by air agitation of the plating solution.
Effluents are treated in normal wastewater treatment plants

2.2.1.3 Pyrophosphate Copper
Pyrophosphate copper electrolytes are based on copper pyrophosphate (110 g/l) and potassium pyrophosphate (400 g/l). Additives are citric acid (10 g/) and ammonia (3 g/l): They are used for special technical applications as shielding on heat treated parts, as drawing aid for wires, and other thick bright layers that need little or no polishing, to prevent hydrogen embrittlement and as intermediate layer below nickel and silver [nn].

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Pyrophosphate electrolytes are also used for through-hole and panel plating of printed circuit boards and multilayers, but are now substituted mainly by acid copper electrolytes.

Environmental considerations:
Fume extraction is recommended at process tanks.
Pyrophosphate is continuously decomposed by hydrolysis. Lifetime of process solution is shortened, and appropriate regeneration means are not available. Effluents have to be treated with lime. Due to the ammonia content, separate treatment from other metal containing effluents is required.

2.2.1.4 Electroless Copper
Electroless copper plating is still a key process for through-hole plating of printed circuit boards and multilayers as well as metalisation of plastics. Copper deposition starts on metal nuclei as palladium and continues autocatalytically, thus providing an initial conductive layer. The deposition rate is 5-8 µm/h. The solution has a copper content of 2-5 g/l, sodium hydroxide (15-20 g/l), chelators as EDTA or similar (10-15 g/l) or tartrates (5-10 g/l) and reducing agents, e. g. formaldehyde (3-5 g/l).
Main properties of the copper layers are uniform thickness of layer, fine crystalline, ductile layers with low internal stress. Copper layers are applied on small items as buttons, fashion jewellery but also on plastic housings for shielding, and through hole plating of printed circuit boards.

Environmental considerations:
Fume extraction for the process tanks is necessary to remove gases (formaldehyde and others).
Lifetime limitation through reaction products. There is a trend to the replacement of EDTA as a chelator. The effluent has to be treated separately.

2.2.2   Nickel Plating

2.2.2.1   Nickel plating - Watts Type
Nickel deposits are to be found on decoratively plated items such as screws, nuts, clips on ball pens, cutlery, trays, bathroom and furniture fittings and items inside and outside of motor vehicles, simultaneously providing excellent corrosion resistance to any base material, on copper layers and below final chromium layers and as barrier layers below silver or gold layers.
Nickel electrolytes are based on nickel sulphate (240-310 g/l), nickel chloride (35-50 g/l) and boric acid (30-45 g/l). The organic content depends on the expected function of the nickel deposit and varies from small amount of organic semibrightener (<1ml/l) and wetting agent (<1 ml/l) for the semibright type to primary and secondary brighteners (10-20 ml/l) and wetting agent (<10 ml/l) for the bright type.
The properties of the organic content are influenced by quantity, quality and mixture of primary and secondary brighteners, which significantly influence the properties as ductility, levelling, brightness and hardness as well as internal stress. Air and/or workload agitation allow the application of enhanced current density. The process tanks operate at 50 - 70°C.

Environmental considerations :
Fume extraction is recommended to remove water vapour.
Regular activated carbon treatment is generally sufficient to provide unlimited lifetime of the plating solution.
Since aerosols escaping from air agitated nickel plating solutions are considered as being carcinogenic, fume extraction on the process tanks is necessary. A mist eliminator is often employed.

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A steady increase of nickel content is observed when drag-out recovery is implemented to reduce electrolyte losses. The installation of membrane anodes with individual DC supply is the appropriate means to keep nickel concentration at a constant level. Removal of decomposition products of organic additives by adsorber polymers provides extended lifetime of plating solution. Closed loop operation is therefore achievable, thus reducing effluent and effluent treatment to almost zero.

2.2.2.2 Sulphamate Nickel

Sulphamate nickel based electrolytes, having a nickel content of 60-140 g/l, thus allowing higher current densities (10-120 A/dm²) and corresponding higher deposition rates of high ductile layers. The chloride content is kept low (1,5-3 g/l) but is necessary to promote anode solubility.

Since it is more expensive than a Watts electrolyte, a sulphamate electrolyte is mainly used, but not limited to, to deposit thick nickel layers (> 2000 µm) for technical applications, eg electro-forming and plating of printing cylinders, or high speed nickel plating in reel to reel applications at current densities of up to 120 A/dm². Another application is the deposition of barrier layers of nickel on copper below final tin or gold layers, e. g. on connectors and printed circuit boards.

Environmental consideration :
Fume extraction is recommended to remove water vapour.
Continuous electrolytic cleaning is necessary, to keep metal contamination at lowest possible level. As continuously generated ammonia reduces ductility, the life of plating solution is limited. Due to the ammonia, the effluent should be treated separately in a normal waste water treatment plant.

2.2.2.3 Satin Nickel (decorative matt nickel)

Satin nickel electrolytes are similar to the Watts type, but the nickel content is >100 g/l. The satin effect is generated by organic additives (cationic or non-ionic surfactants) that disturb the regular build-up of the nickel layer.

Dull satin nickel layer has gained importance in many industrial areas. It is applied on decorative parts inside motorcars as well as on bathroom and furniture fittings.

Environmental considerations: As for bright nickel.

2.2.2.4 Nickel strike

Nickel strike electrolytes are based on nickel sulphate (70 g/l) and sulphuric acid (100 g/l) or on nickel chloride (60 g/l) and hydrochloric acid (100 g/l) and operated at ambient temperatures. Nickel strike deposits are applied for activating passive nickel surfaces and stainless steel prior to further metal plating.

Environmental considerations:
Fume extraction on the process tank is necessary to capture aerosols generated as a result of a poor current efficiency. Effluents to be treated in normal wastewater treatment plants.

2.2.2.5 Electroless Nickel for Plastics

Similar to electroless copper, electroless nickel solutions are used for generating a first conductive metal layer on plastic surfaces prior to further electrolytic metal (copper, nickel) deposition.

Process solutions contain nickel sulphate or nickel chloride (nickel 2-5 g/l), reducing agents eg sodium hypophosphite (5-20 g/l), dimethylaminoborane (>10 g/l) and optionally chelating compounds, as e. g. organic acids. Both, weakly acidic (pH 3-6, sulphuric acid) or alkaline solutions (pH 8-10, sodium hydroxide or ammonia hydroxide) are in use.

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Environmental considerations:
Fume extraction is recommended for alkaline or high temperature processes. Normal effluent treatment to remove metals, except effluents containing chelators, which have to be treated separately.

2.2.2.6 Electroless nickel for metals
Electroless nickel electrolytes are based on nickel sulphate and nickel chloride (Nickel 2-10 g/l).
Sodium hypophosphite (10-50 g/l) is the most often used reducing agent, besides $NaBH_4$ and dimethylaminoborane. Besides these, solutions contain chelators (organic carboxylic acids 10-50 g/l) and buffers as sodium hydroxide and sodium carbonate. Cadmium may be present in some formulations.
Autocatalytically deposited nickel-alloy layers contain 2-15% phosphorus.

Their significant properties are :
- uniform thickness of deposit, no matter the size and shape of items to be plated,
- resistance against wear and abrasion,
- corrosion resistance,
- good adhesion on base material.

Application for
- data storage devices as rigid memory discs,
- components for chemical and oil and gas industry,
- machinery, wiring and automotive industries.

Environmental considerations:
Fume extraction at process tanks including mist elimination to remove nickel containing aerosols.
Short solution life (6-8 MTO) due to the formation of reaction by-products. Process performance also deteriorates. Frequent discarding of used solutions. Separation of metal from effluents precipitation, plate-out or ion-exchange. Extended normal wastewater treatment.

2.2.2.7 Nickel composite plating
Nickel composite coatings have a small niche market for special applications. Electrolytes contain hard particle as silicon carbides, diamond and aluminium oxide or soft particles as PTFE, graphite and molybdenum sulphide to either increase hardness and wear resistance or reduce friction.
The composition of the process solutions, process properties and environmental impact are similar to Watts type electrolytes.

2.2.3 Chromium plating

Chromium plating has found a wide usage both as decorative surface finish (Bright chromium plating) and functional coating (Hard chromium plating), because of its typical high hardness and wear resistance properties. The first application is usually applied on very levelled and bright surfaces, generally on bright nickel undercoats, deposit thickness is generally in the range 0.2-0.4 µm, with a treatment time from 2 to 5 minutes. The finish has a typical white-blue colour and has a very high resistance to tarnishing.
The second application (hard chromium plating), better known as "hard chrome", consists of heavy deposits, applied on particular components (drive shafts, hydraulic cylinders, pins, valves, etc) to make them highly resistant to any mechanical and wear damage. These high

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thickness coatings have hardness values from 750 up to 1100 Hv, very limited porosity and high corrosion and wear resistance.

2.2.3.1 Bright chromium plating

Bright chromium plating electrolytes are based on chromic acid (180 -350 g/l) and a catalyst, containing sulphate (1.8-3 g/l) or fluoride ions (< 10% of the concentration of the chromic acid). Chromium coating properties are determined by the characteristics of the nickel underlayer, by the CrO3/catalyst ratio and by the operating temperature (20 - 38 °C).
When a high corrosion protection is required chromium coating can be made micro-cracked or micro-porous using special techniques.

Environmental considerations:
Process tanks, due to the toxicity of the chromic acid, must be equipped with fume extraction to remove aerosols generated by cathodic hydrogen evolution. The usage of a special fume suppressant (controlled foaming) is a measure to reduce the amount of aerosol. Extracted vapours must be treated through a suitable mist eliminator and the wash liquor must then be treated in the normal effluent treatment plant.

2.2.3.2 Hard chromium plating

Hard chromium plating electrolytes are based on chromic acid (180 - 350 g/l) and on one of the following catalysts:
sulphate ions (1.8 – 3.5 g/l)
mixed sulphate and fluoride ions (< 10% of the content of the chromic acid)
mixed proprietary fluoride free (20% of the content of the chromic acid)
Catalyst choice is fundamental to the efficiency of the electrolyte (from 16-17% for the sulphate one to 25-27% for the mixed proprietary fluoride free type)
The type of the catalyst used and the operating temperature have a great influence both on the physical properties (cracked, microcracked and crack free coatings) and on the chemical and mechanical properties, eg the corrosion and wear resistance, the mechanical workability, etc.

Environmental considerations:
Process tanks, due to the toxicity of the chromic acid, must be equipped with fume extraction to remove aerosols generated by the cathodic hydrogen evolution. The amount of the aerosol can be reduced using a special fume suppressant (foaming). Extracted vapours must be treated through a suitable mist eliminator. Wash liquor is generally concentrated and recycled to the process tank. Rinse water coming from the rinse section subsequent to the chromium plating tank, due to the very long plating times and to the high process temperature (50 - 60°C), is usually reused to replenish the level of the process tank, therefore hard chromium plating plants do not generally have a Cr^{6+} effluent.

2.2.4 Zinc and zinc alloy plating

Zinc and zinc alloy coatings provide corrosion resistance to any kind of iron and steel items, as sheet, wire, screws, washers, nuts, bolts, housings, shopping trolleys and construction frames in household machines and many other kind of application.
Zinc layers, being 6–18 μm thick only with varying conversion coatings (see 2.3 Post treatment) are sufficient to protect parts for their whole lifetime.
Zinc plating has been in existence for a hundred years, so that several different electrolyte compositions are in use, some of which are listed below.

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2.2.4.1 Alkaline cyanide zinc

Compositions of zinc oxide (10-30 g zinc/l), sodium hydroxide (80-120 g/l) and sodium cyanide (5-100 g/l) are easy to operate electrolytes working at pH-values close to 14, using both soluble and insoluble anodes.

Environmental considerations:
The tendency is towards decreasing the cyanide content due to environmental and safety reasons.
Fume extraction of the process tanks to remove developing aerosols is often employed. Mist elimination is recommended.

2.2.4.2 Alkaline zinc, cyanide-free

These process solutions contain zinc oxide (5-15 g zinc/l) and sodium hydroxide or potassium hydroxide (100-150 g/l). Their weakness is lack of stabilising cyanide.

Common application and properties of cyanide and non-cyanide electrolytes:
- mainly applied for technical corrosion resistant layers,
- good metal distribution, better for non-cyanide electrolytes,
- current efficiency near 50%, decreasing with increasing current density,
- low conductivity of the plating solution, thus a higher voltage (6-8 V for jig plating, 10-15 V for barrel plating) and higher energy demand is needed.

2.2.4.3 Weak acidic zinc

Acidic zinc electrolytes are mainly used to deposit bright decorative layers on eg furniture frames, wire and shopping trolleys, providing corrosion resistance of layers comparable with those from alkaline-type electrolytes.
They contain zinc chloride (30-55 g zinc/l), potassium and sodium chloride (130-180 g Cl⁻/l), boric acid (10-40 g/l) and wetting agent.
Only soluble anodes are used.
Properties:
- bright, decorative layer,
- acceptable to poor metal distribution, but better with warm electrolytes
- current efficiency 100%,
- good conductivity of the plating solution providing a low energy demand.

Environmental considerations:
Plating tanks should be equipped with fume extraction hoods to remove chloride containing mists thus preventing corrosion of plating equipment. Mist elimination for the extracted air is recommended.
Effluents are treated in normal wastewater treatment plants.

2.2.4.4 Zinc alloy plating

Zinc alloy coatings provide extended active corrosion resistance and are mainly used for automotive applications.
The main zinc alloys deposited are:
- zinc-nickel (<15% Ni), from acid (ammonium chloride based) or alkaline cyanide-free electrolytes,
- zinc-iron (<1% Fe), from alkaline cyanide-free electrolytes,
- zinc-cobalt (<3% Co), from acid or alkaline cyanide-free electrolytes.

Environmental considerations:
Plating tanks should be equipped with fume extraction hoods to capture aerosols or ammonium chloride gases. Mist elimination for the extracted air is recommended.
Alkaline cyanide-free effluents are treated in normal wastewater treatment plants.

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Carbonate is removed by freezing. Treatment of effluents from ammonium chloride based electrolytes is difficult and has to be effected separately. Recovery of drag-out close to 100% (closed-loop operation) facilitates effluent treatment.

2.2.5 Tin and Tin Alloy plating

Tin plated metal is widely used because of its unique properties. Plated tin coatings are non-toxic, ductile, resistant to corrosion, easy to coat with a high throwing and good distribution properties, making it possible to plate complex shapes items with a uniform thickness compared with hot tin dipping methods.
Main applications are PC boards, electrical connectors, chassis, etc. It is also used for kitchen tools as well as for decoration sets.

Several different electrolytes are available, eg acid stannous sulphate, acid tin fluoborate, alkaline sodium or potassium stannate and more recently the stannous organic acid base (methane sulphonate acid MSA Type) system.
The sulphate bath containing stannous sulphate, sulphuric acid and addition agents (antioxidants for stannous tin, plus grain refiner) is the most popular, for its high current efficiency, in rack and barrel applications.
Tin lead plating is the most commonly tin plated alloy used as solder in different alloy ratios (60/40, 90/10, 95/5) traditionally use stannous, tin and lead fluoborate and additives with fluoboric acid.
Non-fluoboric tin lead electrolytes are now available as organic acid base (MSA) methane sulphonate acid systems. The stability, low sludge formation, deposit properties and the structure of the deposit ensures the market acceptance, in reel- to-reel machines, as well as in barrel.

Environmental considerations:
Process tanks have to be equipped with fume extraction to remove aerosols generated during the electrolysis.
Effluents are treated in normal wastewater treatment plant.
Fluoborate bath effluent should be pre-treated separately to a normal wastewater treatment plant.

2.2.6 Copper alloy plating

2.2.6.1 Brass
Copper cyanide and zinc cyanide dissolution are widely used to deposit copper and zinc alloys for decorative purposes.
They are alkaline electrolytes containing between 8-15 g/l copper and 5-30 g/l zinc (depending on the formulation used). The total sodium cyanide content can vary from 70-90 g/l and working pH around 10.
The deposited alloy contains 65-80% of copper and the colour is light yellow.
It can be used as a flash over a bright substrate or if heavier deposits are used then several finishes can be obtained through a subsequent chemical colouring of the deposit.

2.2.6.2 Bronze
Cyanide bronze alloy is used as a decorative plating process. The metal concentration in this stannate and cyanide based electrolyte is 4-10 g/l of stannate, 4-20g/l copper, and some zinc 1-4 g/l zinc with 6-10 g/l potassium cyanide. It is used in two different colours; white or yellow bronze.

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It is now being used as substitute for nickel in jewellery as a "nickel free" coating to avoid skin allergy effects.
Lead used in low concentration, as a brightener in some electrolytes will be banned in the future.

Environmental considerations:
Process tanks have to be equipped with fume extraction to remove generated aerosols.
Solutions have to be discarded as soon as the carbonate level exceeds 40 g/l.
Effluent treatment in normal wastewater treatment plants with a cyanide oxidation step.

2.2.7 Precious Metal plating

Silver and gold have been deposited electrolyticaly since the first half of the nineteenth century. More recently, processes for the so-called platinum metals as palladium, rhodium, ruthenium and platinum have been developed.
Thin layers of less than 1µm make a wide range of items appear valuable without being costly. They also provide stain and corrosion resistance.
Other outstanding technical properties as eg conductivity, hardness and wear resistance have lead to a growing application in the electric and electronic industries.

2.2.7.1 Silver
The majority of silver electrolytes is based on potassium-silver cyanide (potassiumdicyano-argentate). A silver content of 30-65 g/l and a free potassium cyanide 100-160 g/l with potassium carbonate (15-120 g/l) is necessary for good plating performance. However, a potassium carbonate concentration over 20g/l makes it necessary to discarded the electrolytes.
Attempts to replace cyanide by eg thiosulphate failed due to poor stability of the complex.

Silver plating of cutlery and hollowware is one of the oldest decorative applications. Bright silver deposits are to be found on fashion jewellery as well as on candlesticks.
Due to its outstanding conductivity and other mechanical and chemical properties, silver layers are to be found on many components of electrical and electronic devices. Silver-palladium layers on connectors as substitute for gold have recently became more important.

Environmental considerations:
Plating tanks should be equipped with fume extraction hoods to remove cyanide fume.
Drag-out should be recovered.
Residues of silver to be recovered from rinse water through electrolysis or ion exchange. Recovery of silver from spent electrolytes may be achieved through precipitation with zinc powder.
Cyanide has to be oxidised prior to normal effluent treatment in wastewater treatment plants.

2.2.7.2 Gold
Alkaline cyanide gold electrolytes, based on potassium-gold cyanide (potassiumdicyano-aurate) with a gold content of 2-20 g/l and free potassium cyanide (5-30 g/l) have been the first electrolytes.
Cyanide complexes of other metals eg copper or silver added to the base electrolyte, allow for the deposition of gold of various colours. High molecular organic as well as inorganic additives are used as brighteners for decorative layers.
Very pure gold deposits can also be achieved from neutral electrolytes, based on potassium-gold cyanide. Traces of arsenic, thallium, lead and bismuth provide the fine grain structure needed for electronic devices and printed circuit boards.

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Hard gold layers are plated from weak acidic based potassium gold cyanide, and from strong acid electrolytes, based on potassiumtetracyanoaurate, with a gold content of 7-8 g/l. The important alloying metals are cobalt, nickel, iron, indium and tin.

Due to the good wear resistance of the deposits, acid electrolytes are used for plating connectors, printed circuit boards, pencils, tableware, buttons, fashion jewellery, spectacle frames, bed frames, many other items in daily use.

Alkaline cyanide free gold electrolytes based on the gold-sulphite complex $Au(SO_3)_2$ with copper (0-2%) and palladium (3-9%) as alloying metals, provide rosé and white layers of high hardness and ductility on fashion jewellery and spectacle frames, frequently as a base layer followed by rhodium.

Environmental considerations:

Drag-out recovery and gold recovery with electrochemical reactions on ion exchangers from the rinse water is economically viable.

Permanent chelators have been substituted in most cases by biodegradable ones.

The lifetime of alkaline cyanide electrolytes is determined by the carbonate content.

Effluent treatment similar to other electroplating rinse streams in normal wastewater treatment plants.

2.2.7.3 Palladium

The most common formulation is based on palladium (II) chloride (10-20 g Pd/l), containing ammonia. Alloying metals are nickel, cobalt and silver.

Layers of Palladium-nickel alloy (75-80% Pd/25-20% Ni) are hard and of white colour with good corrosion resistance. They are suitable for spectacle frames and writing utensils.

Pure palladium deposits are also used to substitute nickel as a diffusion barrier below a final gold flash on spectacle frames, fashion jewellery and buttons.

Sandwich layers of nickel, palladium or palladium/nickel alloy and gold flash have proved their applicability on printed circuits and connectors as substitute for hard gold layers.

Environmental considerations:

Tanks for ammonia containing electrolytes should be equipped with fume extraction hoods to capture ammonia, escaping from the plating electrolyte.

Besides drag-out recovery, electrolytic palladium recovery as well as recovery through ion exchange from rinses are normal. Effluents may be treated in normal wastewater treatment plants.

2.2.7.4 Rhodium

Electrolytes are based on rhodium (III) sulphate or rhodium(III) phosphate, with a rhodium content of 2.5-20 g/l depending on their application for decorative (thickness of layer 0.05-0.5 µm) and for technical purposes (thickness of layers 0.5->8 µm), where selenium and sulphites are added to prevent cracking.

Due to their silvery white colour, very thin rhodium deposits on silver are used to prevent staining. Their hardness and wear resistance properties are suitable for technical application on eg reed-contacts and heavy duty connectors. Rhodium is also applied on reflectors for optical equipment and devices for spacecraft.

Environmental considerations:

Tanks for sulphuric acid containing electrolytes should be equipped with fume extraction hoods to remove fume.

Besides drag-out recovery, electrolytic rhodium recovery as well as recovery through ion exchange from rinses are normal. Effluents may be treated in normal wastewater treatment plants.

2.2.7.5 Platinum

Acid electrolytes are based on chloride, sulphate, nitrate and nitrite complexes of platinum, alkaline electrolytes on phosphate, ammonia and sodium hydroxide complexes, with metal

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contents of 6-40 g/l. Thin platinum layers are applied for decorative purposes, thicker layers on electrical devices and in equipment for the chemical industry. Non-soluble platinised titanium anodes and anode baskets are well known and in common use in electroplating.

Environmental considerations:
Besides drag-out recovery, electrolytic platinum recovery as well as recovery through ion exchange from rinses are normal. Effluents may be treated in normal wastewater treatment plants.

2.2.8 Electrolytic oxidisation of aluminium

The anodising of metals is an electrolytic surface oxidation process. Aluminium is the most important material to be anodised.
On a smaller scale, magnesium, titanium, tantalum and niobium are also anodised.
The aluminium work piece to be treated is made anodic. During the anodising process the negatively charged anion migrates to the anode where it is discharged with a loss of one or more electrons. The aluminium reacts with the oxygen of the anion and a layer of aluminium oxide forms on the surface.
Sulphuric and chromic acid electrolytes are usually used.

2.2.8.1 Sulphuric acid anodising
On most aluminium alloys a colourless, transparent aluminium oxide is formed, but alloys containing high manganese and silicon levels tend to give greyish or brownish coloured layers. The anodising voltage is in the range of 17-22V and the temperature of the electrolyte 18-20 ^{o}C . The electrolyte concentration is 160-185 g/l H_2SO_4 A film thickness of 5-25 µm is used for decorative and protective sulphuric acid anodising for example architectural anodising. Sulphuric acid anodised coatings are often coloured by special colouring processes. The oxide coating is sealed to obtain improved corrosion resistance.
In hard anodising, a film thickness of 25-250 µm is obtained.
The electrolyte is operated at -3 ^{0}C - 0 ^{0}C. Processes with oxalic acid and sulphuric acid with organic additions are also in use for hard anodising. The hard anodising layer is normally not sealed. In this state, it can be impregnated with lubricants.

2.2.8.2 Chromic acid anodising
Most aluminium alloys from a light to dark grey aluminium oxide film. The electrolyte consists of a solution containing 30-100 g of chromic acid per litre. The temperature is within the range of 38-42 ^{o}C for the most aluminium alloys. The voltage cycle used depends on the alloy treated and must be closely followed to avoid etching**.**
The coating is thin averaging 2-5 µm and is relatively soft. Its corrosion resistance is good. The coating is normally not sealed.

Environmental considerations:
Process tanks have to be equipped with fume extraction to remove generated aerosols and gases. The regeneration of anodising baths through the use of a retardation process extends the electrolyte life by reducing its aluminium content. Effluent may be treated in normal wastewater treatment plants.

2.2.9 Electrophoretic coatings

Organic coatings may be applied from aqueous media to a conductive substrate by a process known as electrophoresis. Upon application of a direct current, charged paint polymer will migrate electrophoretically to the electrode of opposite charge, become insoluble, and form an insulating film that limits further deposition. When negative charged polymers deposit on the

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anode, the process is termed anionic or anodic electrocoating or anaphoresis. When positively charged polymers deposit on the cathode, is referred to as cationic or cathodic electrocoating (cathaphoresis)

Freshly coated work (anodic or cathodic) are transferred to a counterflow deionised water rinse system and then by a conterflow ultrafiltrate rinse, followed by a final deionised water rinse.
The work is then cured in an oven, usually for 15-30 minutes at 150-200ºC, depending on the resin system.

Compared with conventional paint systems, the advantages of electrophoresis are as follows:
- A very uniform coverage, including the edges and corners,
- The deposit in blind holes etc is good,
- The film is deposited at a very high solids content, eliminating problems of sagging and vapour washing in blind sections,
- Coatings may be formulated with a low organic solvent content, thus enhancing safety and environmental friendliness.

Utilization of paint is high, normally over 95%. Fully automated systems are usual.
This advantage confirms its use for decorative clear topcoats, and as a functional pigmented corrosion resistant coating.

Environmental considerations:
Process tanks have to be equipped with fume extraction to remove generated aerosol.
Effluents need to be treated in wastewater treatment plants. Solid paint residues (resin pigment) from the cleaning of filters must be discharged separately and treated as an organic residue.

2.3   Post treatment

2.3.1   Conversion coatings

Conversion coatings are applied and used to enhance corrosion protection on various metal surfaces, including electroplated zinc and cadmium, zinc die castings, aluminium, magnesium and magnesium alloys, copper, brass and bronze, nickel, silver and stainless steel.
Additionally, these coatings also improve bonding between metal surfaces and paint.

2.3.1.1 Chromate (Cr^{6+}) conversion coatings
Conversion coating processes have been introduced since 1936, and conventional processes are all based on the use of acid and oxidising solutions, the oxidant being hexavalent chromium (Cr^{6+}).
The protection mechanism is based on the local dissolution of the Cr^{6+} present at the surface of the film, the local supply of chromate solution works as local inhibitor of any corrosive action on the exposed metal surface.

2.3.1.1.1 Chromate (Cr^{6+}) conversion coatings on electroplated zinc Layers
Coatings are applied by chemical reaction in appropriate aqueous solutions.
Numerous proprietary conversion coating processes are available today, all of them are capable of producing decorative and protective films, ranging in colour from clear through to iridescent-yellow to brass, brown, olive drab and black.

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Environmental considerations:
Effluents are treated as hexavalent chromium containing solutions in normal waste water treatment plants.

2.3.1.1.2 Chromate(Cr^{6+}) conversion coatings on aluminium

Chromate or phospho-chromate conversion films, ranging from clear to yellow can be produced on aluminium, the film colour depending on immersion time, pH, solution concentration and, to some extent, on the composition of the alloy to be treated.
The accepted uses of chromate coatings on aluminium include aircraft, electronics, missiles and some other appliances. Particularly interesting for electronic applications is the ability of the treatment to provide corrosion resistance without excessive loss of conductivity.
Chromate treatments of aluminium have the typical environmental problems associated with the use of Cr^{6+}. This is the reason that has driven the industry to develop new more environmental friendly processes.

Environmental considerations:
Effluents are treated as hexavalent chromium containing solutions in normal wastewater treatment plants.

2.3.1.1.3 Chromate (Cr^{6+}) conversion coatings on copper, brass and bronze

Chromate solutions to treat copper and copper alloys are prepared with proprietary materials. The treatment is used not only to produce passivity, but also to provide an effective chemical surface polishing. Chromate bright dipping solutions are preferred because of their non-fuming nature.
Chromate treatments on copper and copper alloys are used both as final finish and as a whole or partial substitute for buffing prior to nickel or chromium plating. The passivity obtained is effective in reducing corrosion and sulphide tarnishing.

Environmental considerations:
Effluent treatment does present additional problems due to the dissolution of copper into the process bath.

2.3.1.1.4 Chromate (Cr^{6+}) conversion coatings on magnesium and its alloys

Because of their corrosion characteristics chromate treatment is still the only normal available method to treat magnesium and magnesium alloys. This treatment often is applied at the raw material source, in order to ensure good storage characteristics. Chromate treatment is also used to prepare magnesium and magnesium alloys to the subsequent plating, particularly to the nickel electroless plating.
There are two typical process methods in use:
-       the first one, known as pickling, is mainly used to protect parts during storage and shipment,
-       the second one, known as dichromate treatment, provides maximum corrosion protection and the adhesion properties for paint.

Environmental considerations:
Effluents to be treated as hexavalent chromium containing solutions in normal waste water treatment plants.

2.3.1.2 Trivalent chromium (Cr^{3+}) conversion coatings on zinc

Trivalent chromium (Cr^{3+}) conversion coating processes were first developed about 20 years ago as a more environmentally acceptable alternative to hexavalent chromium (Cr^{6+}) conversion coating processes for use on mainly electroplated zinc. The conversion coating

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products and treatment baths do not contain hexavalent chromium, and therefore they do not have the environmental or health problems associated with hexavalent chromium.

Used trivalent chromium conversion coating processes typically produce clear or blue conversion coatings only. Recently, trivalent chromium passivates producing a higher film thickness and greater corrosion resistance have been developed that perform well against iridescent hexavalent chromium passivation. The thickest conversion coatings (olive drab and black) that give greater corrosion protection for zinc are only achieved using hexavalent chromium conversion coating processes.

Compared to hexavalent chromium conversion coating processes, the trivalent chromium conversion coating is normally more corrosion resistant, freshly prepared passivation solutions do not require a running in period, the colour and performance of the processes are more uniform throughout their useful life and the working life of the passivation solution is normally at least twice that of conventional hexavalent chromium, resulting in less solution dumps.

Trivalent chromium based blue coating processes can produce the appearance traditionally associated with hexavalent processes over acid, cyanide or alkaline non-cyanide zinc plating systems but require more process control to gain the benefit of extended bath life.

This extended bath life is now limited by impurity content rather than consumption of the active chromium compounds.

Environmental considerations:
Reduction of Cr^{6+} to Cr^{3+} during effluent treatment is eliminated when trivalent chromium processes are used and sent to normal wastewater treatment plant.

2.3.1.3 Metal colouring

It is possible to obtain a wide range of shades and colours over different metals by heat treatment, chemical dip or electrolytic treatment.

It is used for brass, copper and steel parts. The most used system is chemical dipping. The results obtained will depend more on the practice of the operation and process parameters than on the formula used.

At the beginning sulphide and polysulphide solutions in alkaline media using sodium, ammonium or barium salts from room to high temperature were used.

It is now more usual to use solutions containing metallic ions (copper, selenium, molybdenum etc) in an acid media and at room temperature.

Small articles may be coloured in bulk, then relieved by tumbling with abrasive media. All sulphide treated parts require wet or dry scratch-brushing and must be protected by a good top coat of clear lacquer.

Environmental considerations:
Effluents may need to be pre-treated separately prior to normal wastewater treatment.

2.3.2 Top Coatings

Chromate conversion films are porous and adsorbent in nature, their thickness is very limited, thus their protective action can be further improved applying a subsequent top coating film, either of organic (e.g. methacrylate), inorganic (e.g. metasilicate) and/or mixed inorganic-organic nature.

Moreover top coatings have two additional functions: a self healing effect, providing protection against local mechanical scratches due to improper handling during processing, and a substantial reduction in the quantity of Cr^{6+} leaching out from the treated surface.

Top coatings are applied immediately after chromate or trivalent chromium conversion coatings, by dipping in an appropriate proprietary medium.

Top coating protection is mainly due to the physical barrier of the coating itself.

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Environmental considerations:
Effluents have to be pre-treated separately before normal wastewater treatment.

2.3.3 Colouring and sealing aluminium

Anodised aluminium, sulphuric acid anodising, can be coloured in many shades and colours. A normal post-treatment of decorative and protective sulphuric acid anodised coatings is sealing to obtain better corrosion protection.

2.3.3.1 Colouring of anodised coatings
Colouring of anodised coatings is carried out in several ways :

- Immersion colouring by adsorption
Colouring by adsorption is the most widely used colouring method. By immersion of the anodised aluminium in a water based dye solution, the pores in the oxide layer adsorb dye. For colouring, a thickness of the oxide film of not less than 10 µm is required. For good corrosion and weather resistance, 20 µm is required. The colouring process is followed by a sealing process to obtain a good durability.

- Electrolytic colouring
Electrolytic colouring is a process, whereby metal is electrodeposited in the bottom of the pores of the oxide film. By immersion of the anodised part in an acid solution containing metal salts and applying an alternating current, metal oxides will be deposited in the porous structure in a thickness of 1 – 5 µm. The film obtains a colour characteristic of the metal salts used. The metal salts most commonly used are tin, nickel, cobalt and copper.

- Interference colouring
A special approach to colour anodised surfaces is the interference colouring based on the electrolytic colouring principle. The appearing colour is produced by the interference effects between two light scattering layers : the electrochemically deposited metal layer at the bottom of pores and the aluminium oxide/aluminium interface beneath.

- Integral colouring
With integral colouring, the aluminium oxide layer is coloured itself during the anodising process. Colouring occurs either by anodising in a solution of special organic acids or by normal anodising in sulphuric acid of special aluminium alloys containing components not being oxidized like Al-Si or Al-Fe-Mn. The oxide layer appears with a colour ranging from light bronze, through dark bronze to black, depending on the layer thickness.

2.3.3.2 Sealing
Sulphuric acid anodising is normally followed by a sealing process. Sealing improves the corrosion and stain resistance of the oxide layers. It also prevents organic dyes from leaching out and improves the light fastness. Sealing may be carried out in hot or cold processes.

- Hot sealing
With hot sealing, the pores in the oxide layer are closed as the oxide is hydrated to boehmite. The conversion to boehmite is accompanied by an increased volume that closes the pores. The sealing process is carried out by dipping the anodised parts in boiling or hot (minimum 98°C) deionised water for 3 minutes per µm thickness. Sealing with steam has the same effect as with boiling water.

- Cold sealing

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Sealing methods at lower temperatures have been developed. There are so-called mid-temperature (about 60°C), and room temperature sealing products are also available. The latter is not based on the hydrothermal conversion of aluminium oxide for closing the pores, but by the use of nickel salts eg fluoride or silicate. There is some concern about long term properties such as light fastness and corrosion resistance in the European market.

Environmental considerations:
Process tanks in immersion colouring or electrolytic colouring have to be equipped with fume extraction to remove generated aerosols. In hot sealing process tanks have to be equipped with lids with low extraction to remove the generated vapour of water.
Some organic colouring dye and cold sealing solutions must be treated separately before discharging sending them to the wastewater treatment plant.

2.3.4 Drying for barrelled and racked components

Centrifugal drying for small components e.g. those surface treated in barrel plants, is effective and energy efficient. The drying of rack surface treated components is generally carried out in a tank type hot air drier at the end of surface treatment plant. In this system, hot air is evenly recirculated from top to bottom of the tank at the temperature of 60-80°C. Hot air escaping from the top of the drier tank is such that such equipment is thermally inefficient.
There is a growing use of localised hot air drying by means of nozzles or "air knives" that is more energy efficient.
After all wet processing operations have been completed, the components need to be quickly and effectively dried in order to avoid the occurrence of staining and corrosion.
The simplest method of drying components is by immersion in hot water. After adequate rinsing, the components are immersed for a few seconds in hot water and then allowed to dry-off in the atmosphere.
The water temperature needs to be carefully controlled. The temperature must be limited to 60°C for plated plastic components in order to avoid deformation. Zinc plated and passivated components also are limited to 60°C to avoid dehydration and loss of corrosion protection of the passivate film. Chrome plated components can be dried at up to 90°C. Deionised water is usually used to prevent drying stains. Some plants use a continuous trickle feed of deionised water, the water overflow is then used to provide a feed for the preceding cascade rinsing system.
The disadvantage of hot water drying is the high energy loss from the tank surface. It is however common practice in manual surface treatment shops.
Drying in automated jig plants is generally accomplished with hot air. Barrel plants use centrifugal drying or hot air drying depending upon the life of the component. Centrifugal drying is energy efficient.

2.4   Rinsing

Appropriate rinsing is necessary between all steps of surface processing containing different chemicals to prevent unacceptable contamination of process solutions. Rinse water may vary in quality, depending on the process requirements:

-    Normal tap or well water,
-    recycled rinse water, continuously cleaned through ion exchange,
-    de-ionised water.
-    Recycled trade effluent

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Numerous rinsing techniques have been developed, to reduce water consumption to the ecological and economic reasonable minimum, needed to achieve the requisite cleanliness of the surface.
For applied rinsing techniques see section 4.4 "Drag-out recovery".
Discharged rinse water, containing process chemicals, has to be treated in wastewater treatment plants (see below).

2.5 Wastewater treatment

2.5.1 Introduction

The environmental benefits of surface treatment are maximised with judicious selection of immersion and spray processes with appropriate rinsing of treated components. Various technologies are available for the appropriate utilisation of process solutions to make best use of the water required for such purposes but, nevertheless, leaving a quantity of spent materials for subsequent discharge including wastewater.
In assessing possible technologies it is essential to address health and environmental impacts at the local and wider level, to reduce a benign discharge which causes environmental pressure elsewhere is unsound, eg soluble aluminium in waste water from an anodising plant may be ideal for flocculation in a local sewage treatment plant, sulphate may be desirable as a nutrient for the microbes in an organic treatment plant. Clearly prior removal of these components would be wasteful and environmentally unsound in respect of the chemicals used for their removal, the effect of the environment of their production, and of the need to make yet other chemicals for the sewage treatment plant

In seeking to select the most appropriate means of wastewater treatment one properly has to address :
Regulatory discharge requirements, which should address the following :
    -The processes practised which give rise to the wastewater
    -The size of the plant, volume and composition of the wastewater
    -The fate/use of the wastewater discharge
    -The composition of other streams discharging to the same water course or foul sewer
    -Wider environmental impacts of adopting any particular process

Additional information:
In terms of health aspects the level of information on the effects of solutes in water is incomplete. We do know that certain components are beneficial e.g. calcium and magnesium, and even fluoride, which is frequently added to drinking water as the sodium salt. All life forms are a complex myriad of chemical and electrochemical reactions and certain elements and ions regarded as toxic are nevertheless essential to life e.g. chromium is required to hydrolyse sugars and phosphate is essential to bone development. Paracelsus (1493 - 1541) recognised "all things are poison and none without poison. Only the dose determines that a thing is not a poison"

2.5.2 Treatment Fundamentals

It is important to recognise that wastewater contains spent reagents and if it is to be treated either :

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The water must be removed from the spent reagents. The spent reagents must be removed from the water. In the latter case this would ordinarily be affected by the addition of another species even if that other species is a hydronium or hydroxide ion.
The removal of water may be effected
- by evaporation, with or without condensation of the water vapour, yielding a residual sludge.
- by reverse osmosis, the latter process essentially providing a purified, but not pure, water and yielding a wastewater, which is more concentrated in those impurities.
The residual concentrate may in turn be reduced to a solid by, if the addition of other reagents is to be avoided, evaporation of the remaining water.

Both processes are capital and operating cost intensive. To vaporise 1 l of water requires:
  - Energy to evaporate water, latent heat of vaporisation is 2589 kJ/kg at 1 bar (a)
  - Energy required to raise the water to the boiling point.
An existing installation operates a reverse osmosis plant, with appropriate pre-filters to treat 20 m3/hr with a 80% recovery costs circa $\in$ 150,000 and the operating costs are circa $\in$ 1.50/m3.
Both processes can only be assessed on a case-by-case basis.
The removal of components from wastewater streams, affected by component variation or phase change which are effected by exchange processes (including precipitation) are discussed in the next section.

2.5.3   Treatment Options

Within the waste streams arising from surface engineering processes any or all of the following categories of constituents may be present:
  - Metal ions e.g. sodium and zinc
  - Simple and complex anions e.g. chloride and cyanide
  - Immobile/Volatile organic e.g. trichoroethylene
  - Miscible organics e.g. sequestering agents
  - Particulate material e.g. powders
It may be preferable to segregate the wastewater streams for individual treatment or to operate whole plant treatment on a mixed waste stream or streams. The decision will depend on regulatory requirements and/or the economics of either route.
The wastewater stream may be treated on a batch basis or continuously and the elected course will depend on regulatory and/or economics though whichever route is selected the most suitable underlying treatment process is likely to be the same.
In some installations the spent process waters are segregated (and may or may not be separately treated). The following sets out potential means of controlling these constituents:

2.5.3.1 Metal Ions
The univalent ions, in surface engineering almost exclusively sodium and potassium, are not considered to present any hazard and their means of control is therefore not addressed.
The removal of other ions may be achieved selectively, to ultimately produce the metal or a metal precipitate rich in the metal in question, or collectively. Apart from the precious metals collective control is both cheaper and environmentally more sound within the surface engineering industry. However, any final selected approach will need to reflect the wider environmental impact, the practicality, and the desirability of recovering the removed metal.

 - High Oxidation State Metals
Whether separate or collective metal ion control is selected multi-oxidation state ions are best first reduced, except where removal is effected by plating out e.g.:

$$4\ Na_2Cr_2O_7 + 3\ Na_2S_2O_3 + 13\ H_2SO_4\ ----->\ 4\ Cr_2(SO_4)_3 + 7\ Na_2SO_4\ + 13\ H_2O$$

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For metal concentrations above circa 3 meq/l removal precipitation as the hydroxide is preferred.

- Precipitation
The multivalent metal ions are most conveniently removed by precipitation as the hydroxide and concentrations of individual metals well below 1 mg/l are achievable in theory. As the transition metals are amphoteric there is a minimum solubility requiring careful pH selection and control (see below)
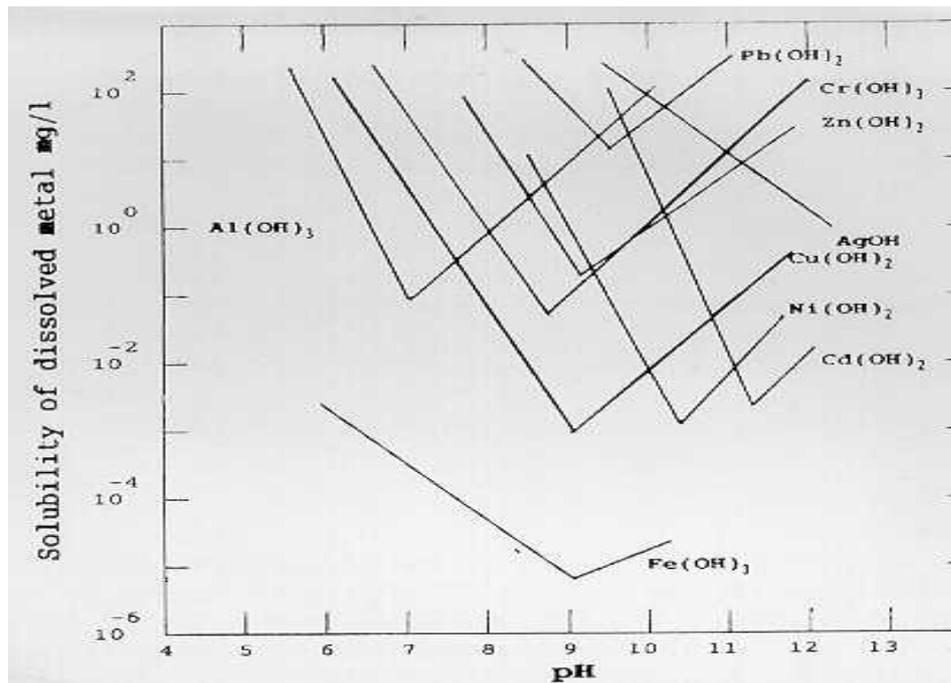
Where simultaneous removals of several ions to very low levels are required segregated treatment streams may be preferable over sequential pH adjustments with intervening solids removal stages. If a high pH is required, a post solids removal pH reduction to the permitted discharge range will be required.

The precipitated metals may be separated by settling, the use of an anionic settling aid is beneficial, with the supernatant polished by filtration using sand, mixed media, cartridge or pressure leaf filters. For small discharges direct filtration of the suspension may be more cost effective. The fine hydroxide precipitates are not readily separated by enhanced gravitational means and centrifuge/hydrocyclone based separators are not recommended.
For residual metal ion concentrations below that achievable by hydroxide addition alone insoluble sulphide based salts may be used in conjunction with, or post hydroxide addition, and dithio-carbamate (DDC) is one of a range of suitable materials which are capable of reducing the concentration of soluble transition metals to below 0.1 mg/l

The success of precipitation processes is, however, dependent on the reaction between the soluble metal ion and hydroxide. Complexed metals present particular challenges. Waste water streams containing the complexant cyanide may be easily be treated with sodium hypochlorite using redox control though sequestering agents present in a number of cleaners

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and proprietary electrolytes are considerably less easy to overcome. Where complexing agents are a problem metal precipitation may be possible with the use of calcium hydroxide in place of sodium hydroxide or by the addition of calcium or magnesium chlorides. Extensive prior digestion (30+ minutes) with strong oxidising agents has been found to be beneficial in reducing the effect of sequestering agents but will oxidise chromium and manganese requiring reduction prior to precipitation if these metals are present. Alternative organic removal treatments, eg activated carbon and non-ionic resins, prior to precipitation may be environmentally sound, and microbiological oxidation of organics remains a theoretical possibility.

Where metal recycling is environmentally or economically sound or where it is required under appropriate legislation it may be preferable to precipitate the metals arising from different metal plating lines in segregated streams, where multiple processes are operated, rather than on a whole plant basis.

- Plating Out

Transition metals can be removed from wastewater streams by plating out on high surface area electrodes in metal recovery cells. However, at concentrations below about 10 mg/l the metal deposition becomes very inefficient with 10 to 100 times the theoretical energy requirement actually needed for metal deposition.

This approach has found some application when combined with ion exchange as a means to concentrate metal ions but here the chemical requirement for metal ion capture is generally 3 to 4 times the theoretical requirement and this inefficiency poses a considerable environmental and cost penalty.

Electrochemical ion exchange may offer improved scope though has not yet been developed for application in the treatment of wastewater arising from surface engineering operations

- Ion Exchange

Direct ion exchange treatment of wastewater provides a means of concentrating multivalent cations for subsequent treatment on column regeneration. This approach, whilst of possible interest in concentrating metals for plating out, is both grossly energy inefficient and requires extensive chemical dosing presenting environmental challenges in their manufacture.

- Reverse Osmosis

Reverse osmosis, effectively filtration of ions through a membrane at high pressure, provides an alternative means of concentrating impurity metals in a retentate for subsequent removal. However, this approach is capital intensive, energy demanding and any solids, together with organics, have to be removed prior to reverse osmosis plants.

2.5.3.2 Simple and complex anions e.g. chloride and cyanide

In many cases the residual levels of anions will be below the level that could be considered to have an environmental impact. However, where treatment is required specific ion dependent technologies are likely to be the most appropriate viz. :

- Ammonia

If recovery by steam stripping is not economic ammonia may be oxidised to nitrogen and water with sodium hypochlorite. Any excess hypochlorite can be reduced using sodium sulphite.

- Cyanide

This may be oxidised by, for example sodium hypochlorite, to carbon dioxide and nitrogen. Any excess hypochlorite can be reduced using sodium sulphite.

- Fluoride

This is most conveniently precipitated out, as calcium fluoride at a pH above 7, the solubility of calcium fluoride at pH 11.2 is 15 mg/l.

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- Phosphate
This is most conveniently precipitated out as calcium hydroxide phosphate, the solubility is less than 5 mg/l at pHs above 10.
- Sulphate
This is most conveniently precipitated out as calcium sulphate, the solubility product is 2 g/l
- Sulphide
This may be precipitated out as elemental sulphur on oxidation with hydrogen peroxide or iron III salts, if control is not otherwise achieved with the multivalent cations present in most wastewater streams.
- Pre-concentration
In some cases pre-concentration of the ions may be desirable and ion exchange or reverse osmosis may be adopted, as outlined above, prior to treatment as discussed here.

2.5.3.3 Immiscible/Volatile Organics e.g. trichoroethylene
Immiscible/volatile organics may first be reduced to their solubility limit by liquid/liquid phase separation.
When levels below the solubility limit is required two options exist:
Air stripping, with removal from the air, eg by activated carbon, to circa 1 mg/l and final polishing by passing the wastewater through activated carbon.
Oxidation to carbon dioxide (and halogen acid in the case of halogenated organics) using UV irradiation and hydrogen peroxide addition.

2.5.3.4 Miscible Organics e.g. sequestering agents
Sequestering agents and other organics in wastewater raise the COD and sequestering agents contribute to the difficulty in removing metals by complexing them, see above. The concentration of miscible organics may be reduced by oxidation by hypochlorite, by UV irradiation and hydrogen peroxide addition (typically 30 minutes), or their deleterious effects reduced by the addition of a benign metal salt e.g. calcium chloride/hydroxide.

2.5.3.5 Particulate Material
Particulate may be removed by settling or filtration, see above.

2.5.4 Batch or continuous treatment

Batch treatment offers the advantage of ensuring that treated water is within the authorised discharge requirements and offsets the need for continuous control. It is, however, wasteful in terms of the plant requirements to effect such treatment.

2.5.5 Usable metal containing waste streams

The concentration of metals for recycling, either directly or after further treatment, may be economically viable.
The capture of precious metals eg platinum, gold, silver, rhodium, ruthenium may be achieved from waste water from such plating lines by electrochemical recovery or by ion exchange with sale of the loaded resin to specialist recyclers or the concentrated regeneration liquor stream. The retention of other ions from wastewater streams may be affected individually or as a composite of many metals. Apart from the precious metals there is unlikely to be any general economic case for such recovery as the costs and environmental impact of recovery is likely to exceed that relating to primary extraction. Indeed for by-product metals, eg cadmium, production already exceeds demand. Conversely, there may be useful outlets for sludge for direct use in other industries. Where recycling is, nevertheless, required specialist recycling operators will need to be found.

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2.5.6   Sludge dewatering

Most wastewater treatment involves the precipitation of undesirable components and their removal by settling and or filtration. The removed solids, e.g. settler underflow or filter backwash, are conveniently further concentrated by pressure filtration in a filter press to produce a solid cake usually sent to secure landfill. Dependant on final disposal and destination, minimising the water content may be desirable and in some cases filter press treatment of metal sludge can give a final cake with 30-35% solids at pressures above 15 bar.

2.5.7   Sludge drying

Fees for sludge disposal are calculated as euro/ton. At first sight, it seems to be sensible to save money by simply reducing the weight by 65-70% through producing a dry cake. However this requires 450 kWh of thermal energy per tonne and unless waste heat is available, this additional step is hardly attractive. Not to mention that drying of sludge creates a powdery waste harder to handle than a solid cake. It is also reported that dried sludge still containing residues of oxidising components as H_2O_2, NaOCl or persulphates, tend to heat up through exothermal reactions when stored in big-bags and eventually incinerate.

2.5.8   Final cleaning

Whatever wastewater treatment technologies are adopted the treated water will contain small to trace amounts of the treated components and a significantly higher concentration of benign materials arising from the treatment reagents used. Dependent on local requirements a further treatment may be required to reduce the discharge levels further eg:
Passing the treated water through a fine (sand) filter (circa 5 µm) to remove residual particulate material. Passing the treated water through a carbon bed to remove organic material. Passing the treated water through a chelating, crown or thiol cation exchange resin bed to selectively remove multivalent ions.

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3.   PRESENT CONSUMPTION/EMISSION LEVELS

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

3.1   Input materials

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

Zinc plating (all processes)	: 70-90%
Nickel plating (without recycle)	: 80-85%
Nickel plating (with recycle)	: 95%
Autocatalytic nickel plating	: 95% (excluding spent baths)
Copper (cyanide)	: 80%
Tin and tin alloys	: 95%
Chromium plating (without recycle)	: 15%
Chromium plating (with recycle)	: 96%
Gold and precious metal	: 98%
Silver	: 95%
Cadmium	: 99%
Electrophoretic coatings	: 98%

The data demonstrate generally low materials efficiencies except where financial (eg :gold, silver) or environmental (cadmium) regulatory pressures are paramount.
The vast bulk of the material losses leave the plating shop as solid waste, for disposal by a licensed waste disposal contractor.

3.2   Utilities

The utilities used in surface treatment are natural gas (or fuel oil), electricity and water. Electricity is used in the form of direct current for the electrochemical processes. Gas and/or electricity is used for process heating, depending on availability and cost. Electricity is also used for process cooling and fume extraction. Gas and/or electricity is used for the drying of surface treated work.
Water is used directly for rinsing purposes, or as make-up to recirculation water rinse systems. To a much lesser extent, it is required for making-up evaporation losses from process tanks if the recovery of drag-out is not feasible, and the washing of filtration and heat exchange equipment.

3.2.1 Energy

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

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

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

3.2.2   Water

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

Output	: 6 barrels/h
Barrel length	: 1200 mm
Throughput	: circa 500 kg/h depending on the components
Plating electrolyte	: acid zinc, 33 g/l zinc
Plating stages	: 5
Zinc anode usage	: 20-25 tonnes/year
Plating time	: 45 min
Cascade rinsing	
- post first stage cleaning	: 4 stages (with return of drag-out)
- post acid pickle	: 3 stages
- post electroclean	: 3 stages
- post plate	: 5 stages (with forced evaporation and drag-out return)
- post passivate	: 2 stages
Overall rinse water usage	: 600-1000 l/h

3.2.3   Gaseous emissions

The fume extraction system is exhausted to the external atmosphere. The loss of input materials whether or not mist eliminators, or gas scrubbers are used is negligible. Recovery for waste minimisation is therefore unnecessary except for chromium plating electrolytes on health and safety grounds. Routine measurements of the stock gas generally show they are zero.

3.2.4   Aqueous effluent

An aqueous effluent is discharged to the municipal drainage system or controlled waterways after metals and other contaminants are removed. The quality of the effluent is controlled by national or local regulations. Metal and chemical losses are generally low and recovery technology is uneconomic.
Typical consent limits most European countries are in Annex 2.

3.2.5   Solid Waste

By far the largest source of waste from surface treatment plant is solid waste in the form of sludge or filter cake from the effluent treatment plant. For most surface treatment shops the waste is filter cake from a batch pressure filter containing 60-70% water, depending upon the maximum filtration pressure. At this water content, the filter cake has a dry appearance and is easily friable.
The solid waste contains metals in the hydroxide form, together with small quantities of insoluble inorganic salts, organic compounds and general soil. Precious metals are recycled internally.
Filter cake can be dried to a lower content to reduce transport and disposal costs. It does however become dusty at a water content of less than 40%.
Filter cake is of no use to surface treatment shops as recovery technology for the metals is far too expensive and technically challenging for the relatively small quantity involved. Specialist

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waste handling companies may however be able to recover metals, e.g. nickel, copper, tin or even zinc on an economic basis. Potentially a more significant application may be its use in the building industry as a filler for brick making and similar products.

Some particles if dried too much can pose a risk due to the presence of organic materials that may provoke the burning of finely divided metals.

4.   CANDIDATES FOR BEST AVAILABLE TECHNIQUES

4.1.   Corrosion prevention

Most metal surfaces oxidise when exposed to oxygen in the atmosphere. Some quickly eg aluminium, others more slowly. Oxidation occurs only with exposure to oxygen; humidity and temperature are factors, these determining how quickly this process takes place. Oxidation time is dependent on the type of material and the conditions under which the material is stored.

4.1.1   Storage

Components stored in a humid environment can suffer corrosion. To avoid this, components may be treated with corrosion prevention materials.

Ferrous components do not corrode in an atmosphere with less than 50% humidity, dehumidifying can therefore be an alternative to using corrosion prevention oil.

Corrosion can even occur when components are transported in cold weather and delivered to a warm location. Moisture condensates on cold components and quickly damages polished ferrous and zinc surfaces. A warm transport method and storage in a low humidity environment can eliminate these problems.

By eliminating or shortening storage between operations e.g. between manufacture and surface treatment, the need for temporary corrosion prevention treatment can be avoided.

4.1.2   Oil and grease

Oil or grease is often used to minimise tool wear. Eg when pressing sheet steel, drilling operations and drawing operations.

By changing the production method the use of oil can be minimised or eliminated. Eg pressing with plastic film or drilling with compressed air-cooling.

Choice of Oil/Grease:

If oil and or grease must be used either during manufacture or in storage then timing becomes significant with respect to cleaning the components at a later date.

Long storage times especially during warm weather complicate cleaning.

Pure mineral oils are generally easier to remove compared with emulsions and vegetable-based products. Vegetable based oils and grease are often promoted as being environmentally friendly products, however these can be very difficult to remove especially if the product has been stored during a warm weather period.

A thick layer of grease prevents metal surfaces from atmospheric contact. Military equipment is often stored for long periods in humid conditions without corrosion attack thanks to grease and oil conservation. The disadvantage of this method is that items have to be cleaned before processing.

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4.2   Pre-cleaning

The choice of cleaning method begins early in the production process. Degreasing operations prior to surface treatment can often be simplified by manufacturing and storing components in the correct way.

4.2.1   Mechanical pre-cleaning
Excessive oil and grease should be removed mechanically whenever possible before other pre-treatment like chemical degreasing.
The majority of oil deposits on small components can be removed by centrifugal force, providing the components can withstand the mechanical load without distortion, e.g. screws, bolts, nuts and nails.
Removed oil can in most cases be recycled after filtering.
Cleaning is often improved with warming-up, so decreasing the viscosity of the oil.

4.2.2   Other techniques
Large components can be cleaned manually with cloth or paper wipers. From sheet metal and wire components the majority of oil can be removed by passing through a divider that can be mechanical or in air-knife form.
Clean hot water (80-90° C) without chemicals can remove the majority of oil and grease. This method is used mainly in the car industry when cleaning pressed sheet steel.
Using a high-pressure water jet further improves the effect.

4.3   Reduction of drag-out

4.3.1   Preliminary remarks

In electroplating and metal chemistry, impacts on the environment mainly result from
− rinsing processes to remove the adherent process solutions from the surfaces of the articles,
− spent process solutions which cannot be regenerated and must be discarded, and
− cleaning operations, spilling, wiping up, repair work etc.
Due to the adherence of liquids to solid surfaces, the articles have to be rinsed after every treatment step and, therefore, losses of chemicals, operating costs and environmental problems arise from drag-out. Because of that, a reduction of drag-out is the most effective primary measure for the protection of the environment.
A reduction of losses of chemicals resulting from drag-out can be achieved in many different ways, which are outlined below:

4.3.2   Rack Plating

The major surfaces of the articles should be arranged in a vertical position at the racks to allow the adhering solution to run down to the bottom edge.
The longer dimensions of the articles should be arranged rather horizontal and somewhat inclined to allow the adhering solution to run down to improve drainage.
The lower edge of all articles should be tilted to allow the droplets to increase so they will drip down above the process tank.
When lifted out from the process solution, the racks should be tilted in such a way that big droplets can be formed faster, which will drip down from the lowest point of the suspended articles.
Above the process tank, a sufficient drainage time should be provided to allow the adhering liquid to run together and to form droplets, which will drip off from the articles.

By slow withdrawal of the racks from the process solution, the drag-out volume can be decreased considerably. Therefore, slow withdrawal and a sufficient drainage time above the process tank, followed by a fast transfer of the racks from one tank to the next, can significantly minimise drag-out.

Withdrawal and dwell times

	Minimum time-seconds	
Process	Withdrawal	Dwell
Plating	10	10
Cleaning/pickling	8	7
Passivation	10	10
Seals/lacquers	10	5

In some circumstances excessive drainage time may affect the quality of treated surface.

Cup-shaped recesses should be avoided, and racks should be inclined, therefore, so in this way process solution cannot be ladled out into the rinse water.
Dripping of process solution on other articles arranged lower on the rack has to be considered by suitable racking and positioning of the work pieces.
An automatically or manually inserted draining pan below the racks will collect the drippings and prevent contamination of subsequent tanks and solutions.
Drag-out by racks can be reduced by inclined supporting arms to avoid horizontal surfaces from which the adherent solution cannot sufficiently run off.
The insulation of the racks should show a smooth surface or even have hydrophobic properties.

No trapping of solution in fissures or cracks of a damaged insulation should occur.

K. G. Soderberg (Proceedings of the American Electroplaters' Society 24 (1936) pp. 233 – 249) developed the following equation:

$$W = 0{,}02\, A \cdot \sqrt{\frac{a \cdot p}{t \cdot d}}$$

where **W** is the volume withdrawn in cm³, **A** is the surface area of the article in cm², **a** is the vertical length of the article in cm, **p** is the dynamic viscosity of the process solution in Poise (1 Poise = 0.1 Pascalsecond), **t** is the withdrawal time in seconds and **d** is the density of the process solution.

The surface roughness of the articles was found to have no effect on the volume of drag-out.

In the absence of actual drag-out measurements eg by chemical or volumetric analysis, the following typical data are used for rack plating :

Flat surfaces   : 0.1 l/m2

Contoured surfaces   : 0.2 l/m2

Cup shapes   : 1 l/m2

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4.3.3 Barrel Plating

The plastic material of the barrel should have a smooth surface without worn areas, forming recesses or bulges around the holes.

The bores should have a sufficient cross section to minimise capillary effects, and the thickness of the plates of the cylinder should be as small as possible, just thick enough to meet the mechanical requirements.

The total perforation of the body of the barrel should be as high as possible to allow the drag-out to drop back easily into the process tank, apart from the fact that in this way the whole plating process is effectively improved.

A further reduction of drag-out has been achieved by the application of draining ledges within the barrels to allow the draining liquid to flow together and to run out after rotating the barrel.

A further reduction of drag-out can be attained by intermittent rotation of the barrel above the process tank (angle of rotation about 90 degree, stop for at least 10 seconds, next sequence of intermittent rotation, etc.).

In a barrel, the position of the major surfaces of the articles is horizontal, and that is the reason why inclined lifting of the barrels from the tanks should be seriously considered The suspension and hoisting systems should be adapted to this requirement. In conventional systems this particular possibility is difficult to realise

The inclined barrel is to be withdrawn from the liquid slowly to decrease the drag-out effectively, and afterwards a sufficient draining time should guarantee that the volumes of liquid dragged over into the subsequent tanks is a minimum.

Withdrawal and dwell times

Process	Minimum time-seconds		
	Withdrawal	Dwell	Stationary Periods (*)
Plating	5	24	3 x 8
Cleaning/pickling	5	24	3 x 8
Passivation	5	16	2 x 8
Seals	5	24	3 x 8

(*) Barrel is rotated two or three times through 90° with an 8 second dwell period in between.

Consider forced "blow-off" for larger plants.

In reducing the length of the bores in the plates of the cylinder body of the barrel. The application of mesh plugs instead of holes has proven successful. In this way, the drag-out can be decreased, and the voltage drop at the perforation is effectively reduced.

In the absence of actual drag-out measurements e.g. by chemical or volumetric analysis, the following typical data for barrel plating of flat components used for design purposes :

760 mm barrel	: 1.0 l/barrel
1100 mm barrel	: 1.5 l/barrel
1200 mm barrel	: 2.0 l/barrel

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Data for zinc barrel plating :

Diameter : barrel 380 mm – 8 mm holes

	760 mm barrel	1200 mm
Flat and contoured surfaces	1 – 2 l/barrel	2 – 3 l/barrel
Cup shapes	2 – 4 l/barrel	3 – 6 l/barrel

Diameter : barrel 380 mm - 2 mm holes

	760 mm barrel	1200 mm
Flat and contoured surfaces	2 – 4 l/barrel	3 – 5 l/barrel
Cup shapes	3 – 6 l/barrel	4 – 8 l/barrel

4.3.4 Properties of Process Solutions – Effect on Drag-out

The drag-out also depends on the properties of the process solutions. It is proven that drag-out is reduced by raising the temperature of the process solution. This parameter is connected with the viscosity of the solution.
Lowering the concentrations of the process solutions will effectively reduce the drag-out.
The addition of wetting agents to the process solution (reduced surface tension) also reduces the drag-out.
To avoid excessively increased concentrations, a constant composition by regeneration of the process solution as well as the selection of appropriate process solutions is an important step in the reduction of drag-out.

4.3.5 Transition from Draining to Rinsing

Rinsing is not to be discussed here. But there is a close connection between minimised drag-out and the following rinsing steps. Therefore, this interrelation shall be concisely outlined:
In barrel plating, sucking off or blowing off a considerable part of the drag-out above the process tank is a successfully proven measure to reduce losses of process solutions. This treatment can be combined with a pre-rinse, using water from the first static rinse to return a further part of the drag-out.
When racks are being removed from a tank of heated solution, it is a good practice to drench it with a fog spray while it is still over the processing tank. This effects a reduction in drag-out loss, and the water used compensates for evaporation. For the purpose of removing solution adherent or trapped in recesses, combined water and air jets may be used above the process tank and within an empty tank, respectively. Sloping drain boards of plastic material should be provided at the exit end of each tank. In effect, these extend the draining period for the workpieces and return as much of the drippings as possible to the tank of origin.

Conclusion

Drag-out depends on a large variety of parameters and, therefore, a reduction of this main reason for impact on the environment connected with electroplating can only be achieved in a close co-operation of all persons involved. For this reason a thorough understanding of the complex interrelations of many parameters needs to be transferred to the operational staff to improve the situation successfully.

4.4. Drag-out Recovery

4.4.1 Preliminary remarks

The chapter above outlines how drag-out by different means can be *reduced*. *Elimination* of drag-out however is impossible.
Drag-out of process solution and drag-in of rinse water leads to continuous dilution and drop of chemical concentration.
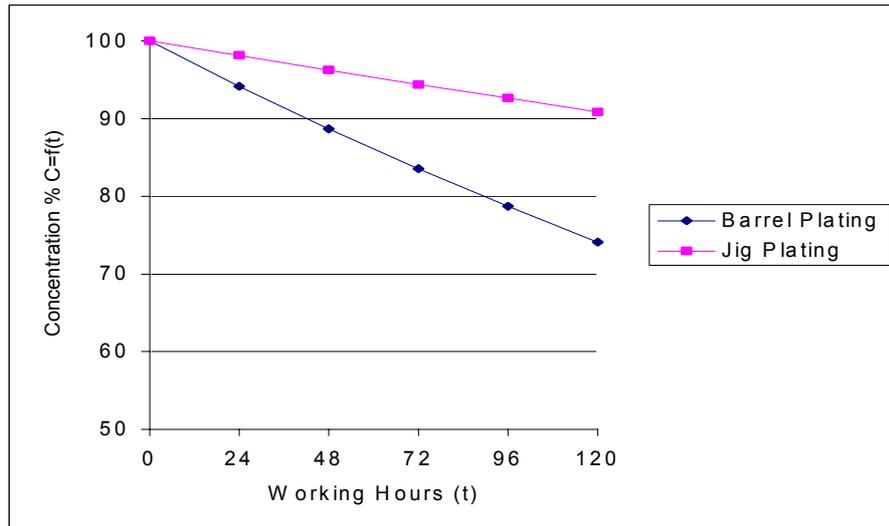

Fig. 1 - Drop of chemical concentration in process solution due to drag-in
of rinse water and drag-out of process solution without replenishing

$$C_{0n} = [V/(V+D)]^n * C_0 \qquad < 1 >$$

C_0.... Concentration of chemicals in process solution at start of operation,
C_{0n}.. Concentration of chemicals in process solution after n work loads,
D...... Quantity of drag-in/drag-out per work load (barrel or flight bar),
V...... Volume of process solution,
n...... Number of workloads processed.
References:

Barrel Plating

Throughput:	10 barrels per hour.
Drag-in/-out:	1.5 litres per barrel, 15 litres per hour
Process solution:	medium cyanide zinc
Total volume:	6 m³
Processing temperature:	ambient

Jig Plating

Throughput:	15 flight bars per hour (25 m² of surface area to be plated)
Drag-in/-out:	0.4 litres per flight bar, 6 litres per hour.
Process solution:	bright nickel, air agitated
Total volume:	7.5 m³
Processing temperature:	60 °C

Drag-out in many cases is useful as a means for regeneration of process solution, as it continuously removes process disturbing residues of degraded brighteners and other organic additives, disregarding that other valuable inorganic components are carried out simultaneously. It is better however to reduce or remove contaminants by properly designed techniques in situ.

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Recovery of the inorganic chemicals not only reduces the impact of chemical or electrochemical processes on the environment but also saves cost for chemicals necessary to replenish the process solutions.

4.4.2. Prerequisite for drag-out recovery

A prerequisite for economic recovery of drag-out is the need for water to equalise evaporation losses from process solution, either caused by natural evaporation due to elevated processing temperature (e. g. electroless [>80°C] and electrolytic [>55°C] nickel, phosphating [>90°C]), see Figure 2, or cooling of the process solution by evaporation (eg cyanide zinc for barrel plating [<25°C], bright [40°C] and hard [60°C] chromium), to maintain a constant processing temperature. The evaporation of 1 litre of water requires approximately 1.4 kWh.
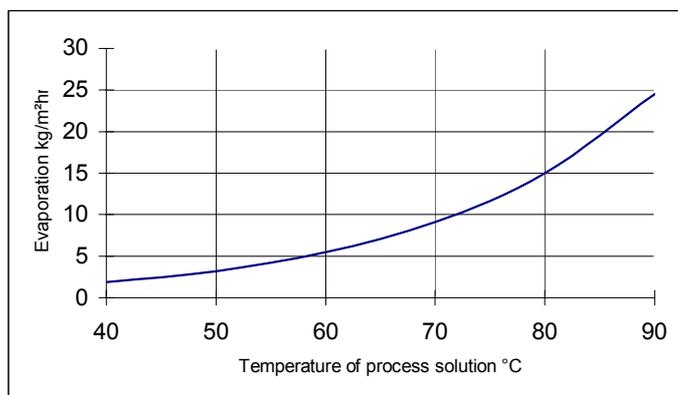

Fig. 2 - Specific water evaporation "e" from process solutions,
with fume extraction at process tank

The evaporation losses in operating parameters in the previous example can be calculated as follows:

Barrel Plating

Plating energy/barrel	2.5	kWh
Plating energy total	25	kWh
Water evaporation equivalent (E)	35	litres/hr

Jig Plating

Surface area of plating solution	6	m²
Water evaporation at 60°C	5.5	litres/m²hr
Water evaporation (E)	33	litres/hr

Equivalent quantities of rinse water with diluted process solution can be added into the process tank. The recovery rate is directly related to the concentration of process chemicals in rinse water, and this again depends on the chosen rinse technique. A choice of appropriate techniques is outlined below.

Even if there is no significant evaporation there is still an energy free technique for drag-out recovery as shown next.

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4.4.3 "Eco" rinse

Drag-out from process solutions working at ambient temperature (but not limited to) can be recovered through a single rinse station in which the workload is dipped before and after being processed. Figure 3 shows the sequence of workload transport schematically.
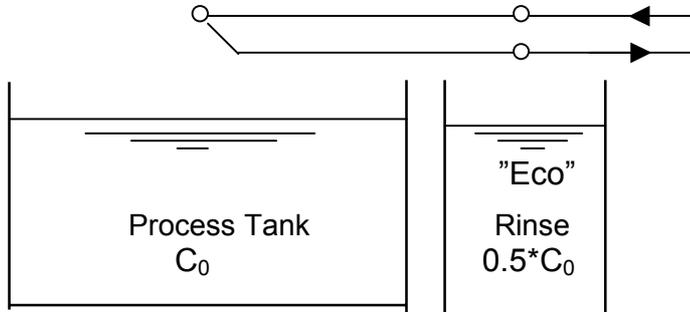
Fig. 3 - Drag-out recovery through "Eco" rinse

The "Eco" rinse station can be made up with diluted process solution from the very beginning or filled with deionised water only. In this case it will take some time until the final concentration of $0,5*C_0$ will be reached. The solution has to be changed only when the tank itself and/or the tank walls have to be cleaned. During normal operation no water has to be added assuming that drag-in is equivalent to drag-out.

Drag-out recovery rate (jig and barrel plating): approx. 50%

"Eco" rinsing is the best available technique from an ecological point of view where more effort cannot be justified due to technical or economic reasons.

4.4.4 Multiple rinse techniques for drag-out recovery

Due to comparatively high water consumption, dual stage rinsing can be excluded as technique for drag-out recovery. Only 3-5 rinses can be considered as appropriate. Combinations of static with flow rinses may be sensible.
The achievable recovery rate is, at a given volume of evaporation losses directly related to the concentration of process chemicals in rinse station 1.

4.4.4.1 Multiple counter flow rinse

The rinse criterion R achievable with counter flow rinsing can be calculated as

$$R = C_0/C_n = (q^{(n+1)}-1) / (q-1) \qquad <2>$$
$$q = W/D \qquad <3>$$

C_0 ......   Concentration of chemicals in process solution
C_n ......   Concentration of process chemicals in last n^{th} rinse station
D ....   Quantity of drag-out,
n ....   Number of counter flow rinses
R ....   Rinse criterion
W ......   Quantity of rinse water to achieve R at a given D,

A triple counter flow recovery rinse is shown in figure 4.
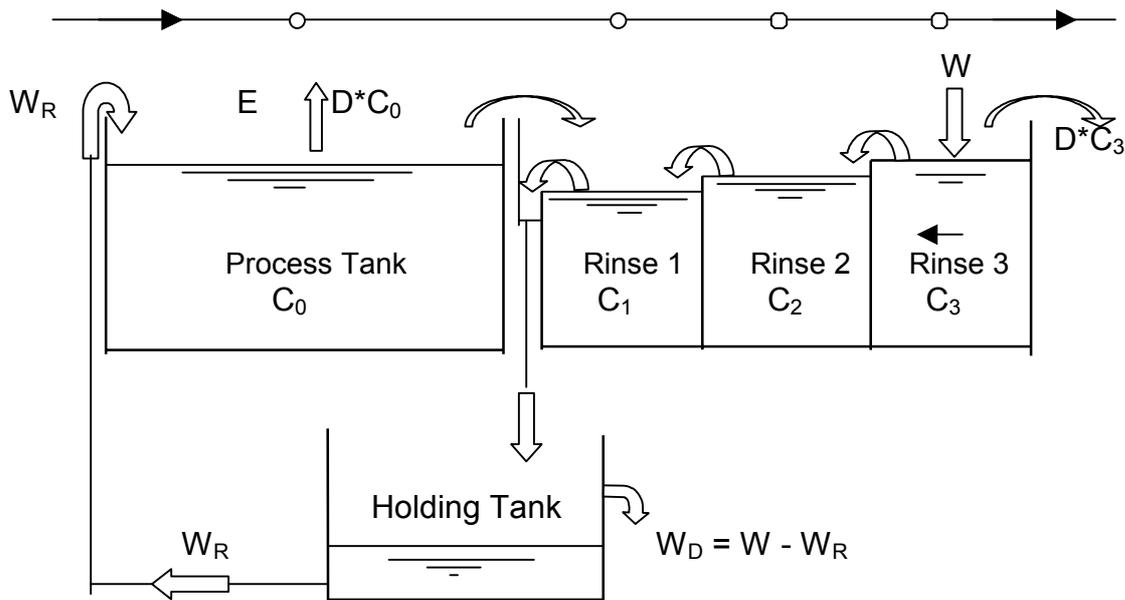
Fig. 4 - Recovery of drag-out with triple counter flow rinse

In cases where E >= W, drag-out recovery rate

$$Rc_R = 1 - C_3 / C_0 \qquad <4>$$

In cases where $E = W_R < W$, drag-out recovery rate is reduced to

$$Rc_R = (1 – C_3)*W_R / W \qquad <5>$$

C_0 ....   Concentration of chemicals in process solution,
C_3 ....   Concentration of process chemicals in rinse station 3,
E ......   Evaporation losses,
Rc_R...   Recovery rate of drag-out,
W .....   Quantity of rinse water,
W_D ..   Quantity of rinse water to be discharged
W_R ...   Quantity of rinse water available for drag-out recovery.

Figure 5 shows the specific water consumption of triple and quadruple counter flow rinses in litres per litre drag-out.
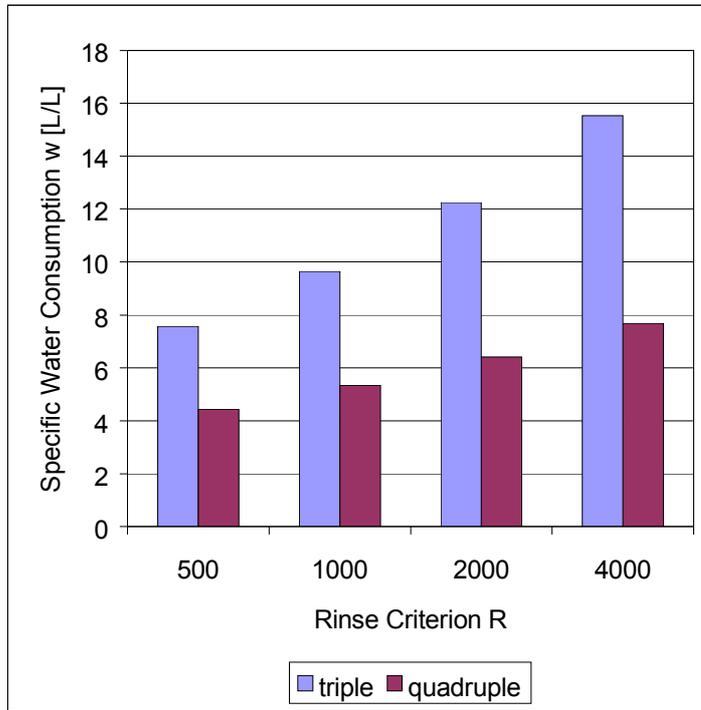

Fig. 5 - Specific water consumption "w" of triple and quadruple counter flow rinses

4.4.4.2 Multiple static rinse

Multiple static rinsing instead of counter flow rinsing allows for reduced water consumption. Figure 6 shows the arrangement of tanks and the process sequence of a triple static rinse.
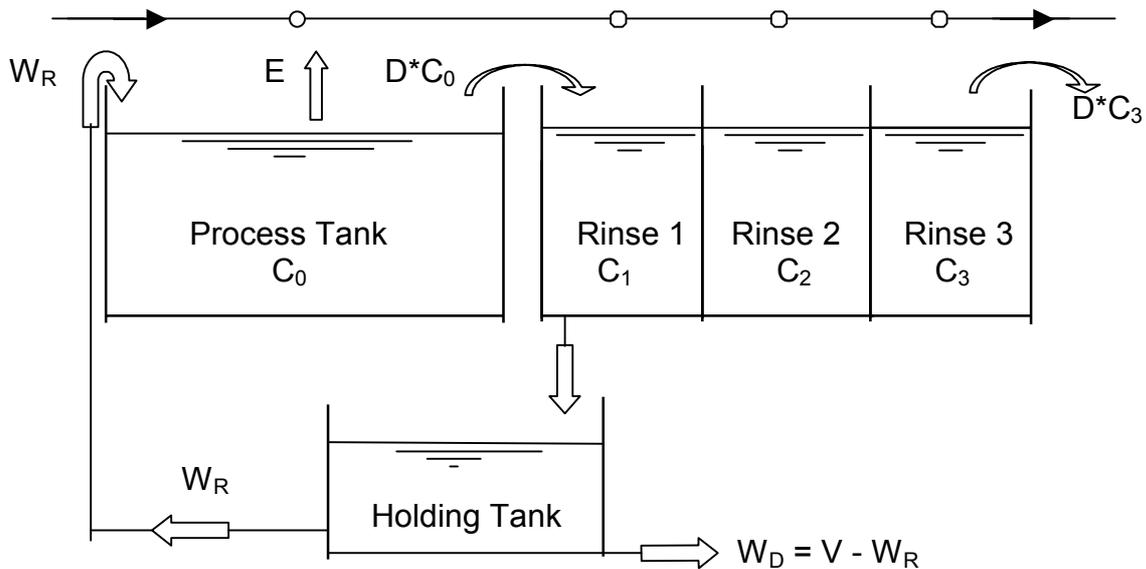

Fig. 6   Recovery of drag-out with triple static rinse

Instead of continuous inflow and overflow, rinse 1 is discharged into holding tank only when C_3 has reached its set value. Rinse water from tank 2 than is pumped into tank 1 and water from tank 3 into tank 2. After tank 3 has been filled with fresh water, processing can be continued.
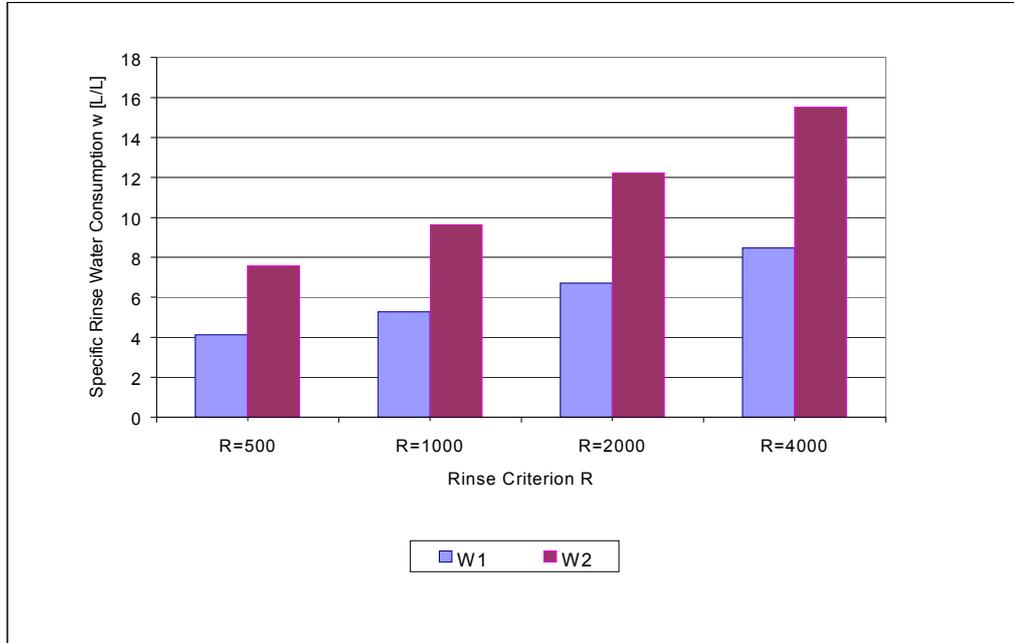

Fig. 7 - Specific water consumption in litre per litre of drag-out :
w_1 triple static vs. w_2 triple counter flow rinse
(Values for w_1 valid when all three tanks are filled with fresh water)

As Figure 7 shows, savings of water compared with counter flow rinsing are substantial: approx. 45%, when all rinse tanks are filled with fresh water, approx. 40%, when water from tank 2 has been filled into tank 1 a. s. o., as it is done at normal operation.

The concentration of process chemicals in static rinses 1, 2, 3 can be calculated with the following equations:

$$C_{1n} = (1-q^n)*C_0 \qquad \qquad <6>$$

$$C_{2n} = [1-(n+1)*q^n + n*q^{(n+1)}]*C_0 \qquad \qquad <7>$$

$$C_{3n} = [1-(1/2)*(n+1)(n+2)*q^n +n*(n+2)*q^{(n+1)} - (n/2)(n+1)*q^{(n+2)}]*C_0 \qquad <8>$$

$$q = V/(V+D) \qquad \qquad <9>$$

$C_{1,2,3n}$.. Concentration of process chemicals in rinse station 1, 2, 3 after n workloads rinsed,
D ...... Quantity of drag-out,
n .... Number of workloads rinsed,
V ...... Volume of water per rinse station.

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4.4.4.3 Dual static rinse followed by final flow rinse with recirculated water

At comparatively high drag-out rates, even triple counter flow or static rinses might not be sufficient for satisfactory drag-out recovery. A modified triple rinse is shown in figure 8.
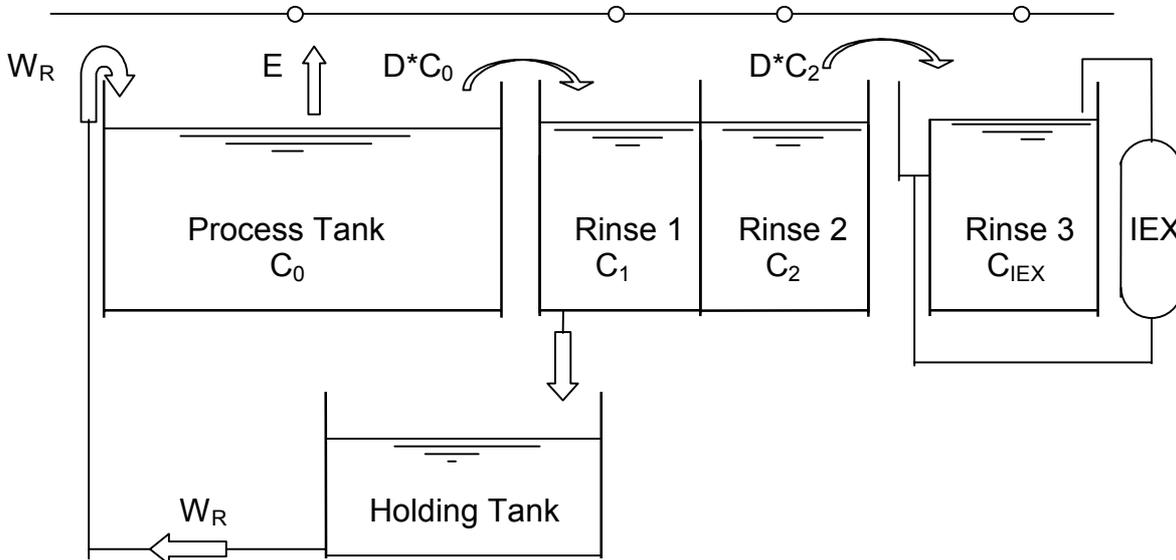

Fig. 8 - Dual static rinse followed by single flow rinse with recirculated water,
continuously purified in ion exchangers.

Rinse 1 should be discharged into holding tank after a period of time depending on the mode of operation of the line. In the outlined reference this would be after 3 shifts or 240 rinsed barrels (Figure 9).
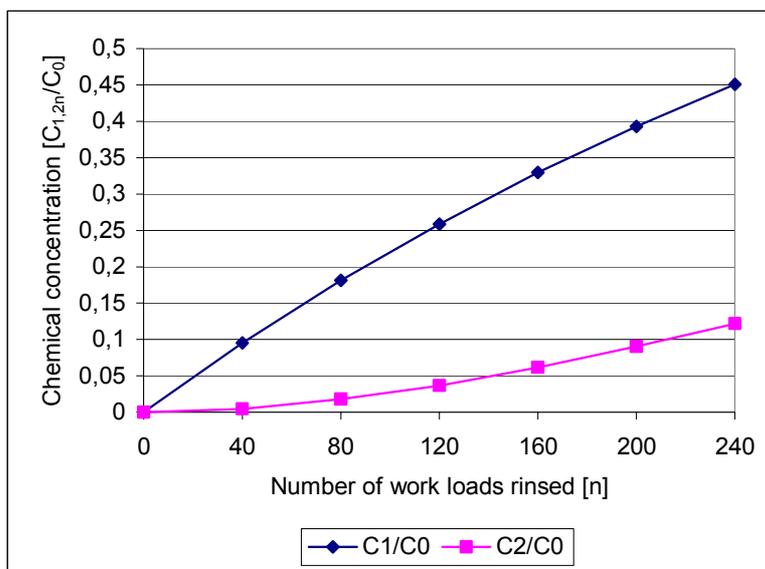

Fig. 9 - Increase of chemical concentration C_1 and C_2 related to number of rinsed barrels
(see reference "Barrel Plating", Volume of rinse 1, V_{R1} = 600 L)

This technique allows for concentrations $C_2 <= 0.2*C_0$, equalling an average value of approx. $0.095*C_0$, starting from 0 and ending at $0.2*C_0$. The area below curve C_2/C_0 is equivalent to the

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quantity of chemicals loaded on the ion exchangers. The flow rate of recirculated water has to be designed as high as the ion concentration must not exceed 2 mVal per litre.

Final rinse in recirculated water provides a sufficiently high rinse criterion R at low water consumption (approx. 5% of flow rate).

4.4.5   Drag-out recovery rates

Table 1 shows drag-out recovery rates achievable with different multiple rinse techniques, taking the respective values of the reference lines as basis. The rinse criterion after both main processing steps – medium cyanide zinc barrel plating, bright nickel jig plating – should be at least R>=1000.

Rinse technique	Medium cyanide zinc barrel	Bright nickel, jig
Triple counter flow rinse [1]	<24%	<57%
Triple static rinse [2]	>40%	>95%
Dual static rinse plus flow rinse [3]	>90%	>98%

Table 1 - Achievable recovery rates

1) This technique does not provide satisfactory recovery rates in barrel plant, since $W_D>3*W_R$. Taking into consideration that no major additional investment is necessary, a rate of 57% in jig plant seems attractive.

2) The necessity of changing rinse water already after less than 8 hours operation in barrel plating plant makes this technique difficult to apply, whereas in jig plant the rinse water has to be changed not earlier than after 56 hours operation and the recovery rate of >95% can be attained again without major additional investment.

3) If a high drag-out recovery is required, this technique is mandatory in barrel plating. Changing of rinse water is required after 24 hours operation. Prerequisite is the installation of an appropriate ion exchanger plant or a counterflow rinse system to minimise the use of water.

4.4.6   Enhancing drag-out recovery rate

Where the quantity of water needed for proper rinsing exceeds evaporation losses, and recovery rates >90% are expected, the surplus water has to be extracted from rinse water. The concentrate is used as replenisher for the process solution whilst the condensate can be reutilised as rinse water.

Techniques for this purpose in use are e. g.:
- AE, atmospheric evaporation
- VE, vacuum evaporation,
- ED, electro dialysis, and
- RO, reverse osmosis.

Any of these requires additional energy, which means cost, which may be off-set by savings in cooling energy and drag-out recovery. The most appropriate one has to be selected with regard to the chemical content of rinse water to be processed.

The principle of rinse water extraction and chemical concentration is shown in figure 10.
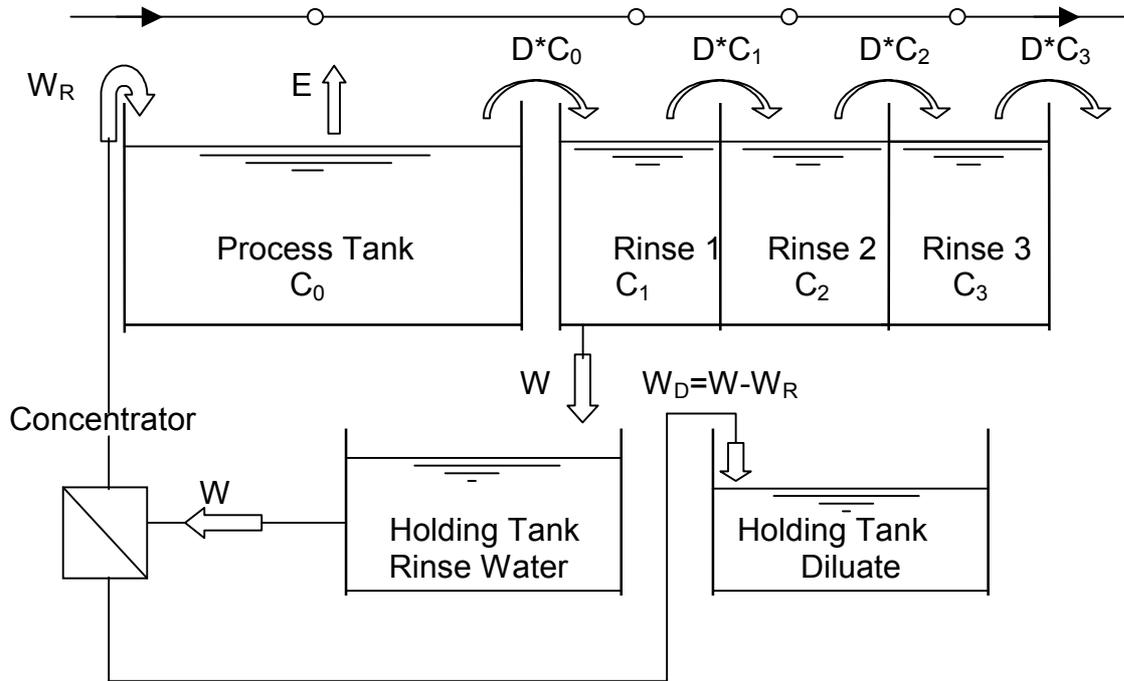

Fig. 10 - Rinse water and chemical recovery through concentration

Another sensible possibility to increase recovery rates above 50% is to add an "Eco" rinse tank (see 4.4.3). As this alone already provides 50 % recovery of drag-out, the total rate can be found when 50% of the values in table 1 are added to 50, e.g. triple static rinse in barrel plating:

$Rc_{R\ total} = 50\% + 0.5*40\% = 70\%,$

equivalent to an increase of 75% and a reduction of rinse water by>20%.

Conclusion
Drag-out recovery in many applications is a sensible means to reduce the impact of electroplating processes on the environment. Since not only valuable components but also degraded additives are recovered, which – if allowed to accumulate - will eventually disturb process operation, it is necessary to consider purification of the process solution. Techniques for regeneration are subject of the next chapter.

N. B.: All formulas mentioned in this chapter provide exact results from a theoretical point of view, which do not exactly concur with practical experience. This is caused by (but not limited to) such simple parameters as varying quantities of drag-out for different workloads, different rinsing efficiency due to differing shape of processed components or changing concentrations of wetting agents.

4.5   Energy saving

Energy saving measures and systems involve the design of operating tools or of equipment devices capable to :
- determine a sensible reduction of the air extraction,
- minimise the energy used to heat process solutions,
- minimise the energy used to cool process solution.

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4.5.1 Reduction of the volume of extracted air

Electroplating processes generate vapour of water, acidic fumes and aerosols. Therefore respective tanks have to be equipped with a suitable system of air extraction to protect the internal environment of the plating shop and the workers.
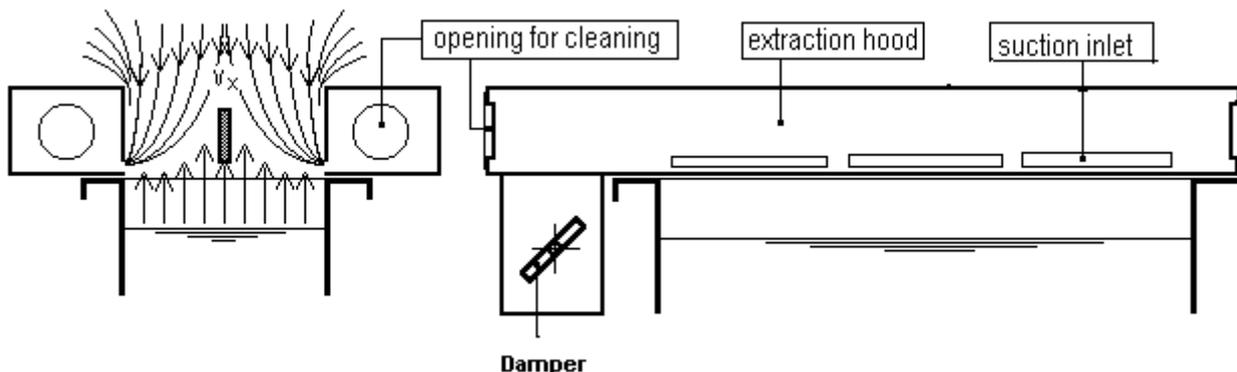

Fig. 11 - Fume extraction on top of treatment tank

The most common system uses extraction hoods located laterally to the entrance area for plating jigs on flight bars and plating barrels above processing vats.
The efficiency of air extraction is determined by the minimal air velocity v_x necessary to capture the up-rising vapour, fumes or aerosols at the most distant point from the extraction hood.
Values for v_x differ between 0.2 m³/s capture velocity for moderate water vapours and 0.5 m³/s for aerosols from hard chromium plating solutions.
The volume of air to be extracted depends on the free surface area of the processing solution.

It can be calculated by the following equations :
-       Single-sided extraction (W<0.5 m) $V = 2\,v_x\,L\,W\,(W/L)^{0.2}$ <10>
-       Double-sided extraction (W>0.5 m) $V = 2\,v_x\,L\,W\,(W/2L)^{0.2}$ <11>

V.....   volume of extracted air
v_x.....   minimal air velocity at point x
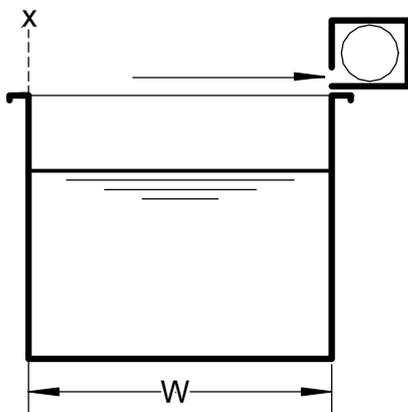L......   length of extraction area
W....   width of extraction area
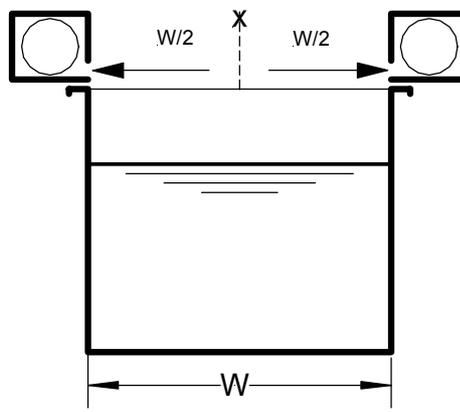

Fig. 12 Single-sided extraction (W<0.5 m)   Fig. 13 Double-sided extraction (W>0.5 m)

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Air extraction needs energy twice: for the fan motor drive and for the warming-up of in-coming air in periods with outside temperatures below approx. 12 ^{0}C. A reduction in the volume of extracted air is therefore desirable.

4.5.1.1 Reduction of free surface area above tanks

The following figures 14 and 15 show different means for reducing air and thus energy consumption.
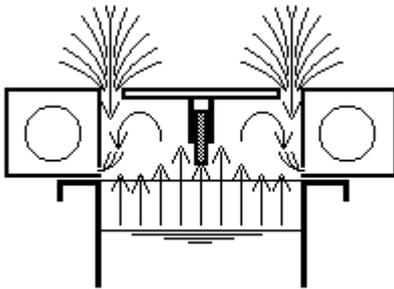

Fig. 14   Lid protecting free surface area, fixed to and moved with the flight bar
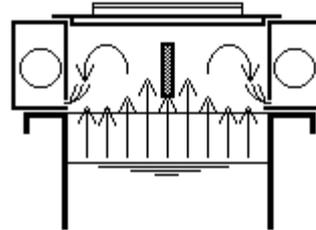
Fig. 15   Lid protecting free surface area above extraction hood, movable by transporter

Figure 14 : Since hazardous fumes or aerosols are generated mainly during processing, lids fixed to and moved with the flight bar are a suitable means for reducing the volume of extracted air by 60-75 % of the normal rate without reduction of surface area.

Figure 15 : These lids cover all process stations where vapour, fumes or aerosols are generated at any time except during loading and unloading of the stations. The reduction in extraction rate increases may be more than 90 % (Patent DE 35 30 322). A major advantage of this system is that these lids need no drive at the station itself since they are moved simultaneously with the drip tray of the transporter.

Lids hinged to the tank, driven individually and automatically opening and closing when jigs and barrels enter and leave the processing tank are another appropriate but more expensive design. Usually this system is combined with a device designed to automatically increase the volume of extracted air when lids are opened. A reduction in extraction rate of up to 90 % may be achieved.

4.5.1.2 Push - Pull System

An alternative method, known as "Push-Pull System" has been introduced. This method is basically designed to create an airflow over the surface of the processing bath. It works with a blowing tube and a sucking hood opposite. The surface of the processing solution must not have any frame or obstacle to the airflow. Therefore its application remains quite limited.

4.5.1.3 Enclosure of the Plating line

In recent times, the complete segregation of the process plant has been implemented. The plating line is installed inside an enclosure, while all plant operation, the plant management system, and the loading/unloading stations are located outside.

Since a substantial amount of extracted air is still necessary to prevent corrosion of the equipment within the enclosure, an energy saving higher than the above mentioned figures cannot be expected.

4.5.2   Energy recovery from extracted air

This potential energy saving measure is limited to installations of very large volume and size. The capital investment and operating costs are very high. As savings from energy recovery are only a fraction of these costs, a feasibility study including economic considerations is mandatory prior to installation.

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4.5.3 Heating of process solutions

Energy saving may be achieved by a reduction in the process temperature; it depends mainly on the innovation coming from the R & D activity of the proprietary process suppliers.

Energy losses from the surface area of heated process solutions related to processing temperatures are shown in the following table.

It demonstrates that the highest energy loss from the solution surface with air extraction and with liquid agitation. Air extraction above the surface of process solutions enhances evaporation and thus the energy loss. It is recommended that lids be used to minimise the volume of extracted air.

Energy losses at the surface of hot process solutions

Processing Temperature [°C]	*without* liquid agitation, *without* air extraction [W/m²]	*without* liquid agitation, *with* air extraction [W/m²]	*with* liquid agitation, *with* air extraction [W/m²]
30	352	559	839
35	530	837	1.209
40	757	1.196	1.677
45	1.048	1.635	2.268
50	1.426	2.198	3.012
55	1.922	2.910	3.949
60	2.587	3.815	5.129
65	3.505	4.973	6.621
70	4.824	6.469	8.521
75	6.844	8.436	10.974
80	10.279	11.096	14.212
85	17.386	17.386	21.188
90	41.412	41.412	46.023

Process solutions may be heated by energy coming from process steps generating energy.

Water from the cooling circuit of various process solutions is collected in a central vat and cooled through a suitable heat pump. The gain in energy may be used to heat process solutions with process temperatures up to 65 °C, or to heat up water for other purposes.

Since the capital investment is very high, the use of this approach is doubtful.

4.5.4 Air agitation

Compressed air for the agitation of process fluids should never be used except for the smallest tanks. Air for agitation should always be provided by a low pressure blower. The energy saving is substantial.

An option to air for agitation is the use of hydraulic turbulence from a pumped system with eductor nozzles placed at the bottom of the tank. Although the energy required is greater than that needed for traditional air or cathode rod agitation, the energy loss through evaporation of water in air agitated tanks off-sets the higher energy usage of hydraulic turbulence. Hydraulic turbulence is higher than air agitation. This results in improved plating quality, reduction of rejects, and optimisation of proprietary additives consumption.

4.5.5 Cooling of process solutions

Atmospheric evaporators are widely used to remove excessive energy by evaporating water from the process solution and maintaining the process temperature at the desired level.

Evaporators are idle and costs are lowest, if processing temperature is allowed for being as high as necessary to remove any plating energy by natural evaporation on solution surface.

Any kWh removed by evaporation is equivalent to 1.4 litres of water which can be balanced by rinse water, containing process chemicals, thus enabling drag-out recovery.

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4.5.6   DC supply

Energy savings can be attained through:
-    reduction of voltage drop in conductors and connectors.
-    Regular maintenance of rectifiers and contacts in the electrical supply system,
-    installation of modern rectifiers having a better conversion factor than older types.
-    Increasing of conductivity of process solutions through additives, e. g. sulphuric acid in acid copper baths, and by maintenance of solutions, such as lowering the iron and the trivalent chromium content in hard chromium baths.
-    Modified wave forms (eg pulse, reverse) may improve metal deposits.

Altogether, an energy saving in DC supply of 10-20 % may be expected.

4.6   Modification of process solutions

Using less hazardous chemicals in an existing process or reducing chemical concentrations can be alternatives in surface finishing, but only if :
-    Quality and performance are at least the same the existing products or processes ;
-    Waste generated by the substitute solutions lead to a global reduction of both the amount and the toxicity after an efficient waste treatment.
-    Costs involved in the alternative solution have to be economically acceptable.

Cases where these criteria are respected do not often occur. In most cases it is impossible to find a single and acceptable alternative. Substitute solutions do not usually have as wide a range of application as existing solution.

Other barriers to the use of substitute processes or less concentrated solutions in metal finishing solutions are :
-    customer requests frequently involve particular surface treatments where the processes are fixed and precisely defined,
-    secondary effects (corrosion phenomenon on the work or jigs, poor knowledge of the compounds used, waste treatments difficulties etc),
-    modification of the coating and work characteristics,
-    uncertain process security and reliability.

Nevertheless for a few applications, and in specific situations, there are viable options.

4.6.1   Substitution of complexing agents (chelators)

In newly developed degreasing solutions strong chelators are replaced by weaker and biodegradable ones.

4.6.2   Substitution of cyanide

Some surface finishing electrolytes use cyanide compounds (stainless steel degreasing, zinc, copper, cadmium or gold plating, nickel stripping etc). There is no European regulation that limits the use of cyanide. Nevertheless the trend is to reduce and/or avoid the use of cyanide compounds in surface finishing bath formulations.

The reason: despite it is rather easy to control cyanide wastewater treatment to reduce toxicity in accordance with national discharge requirements, AOX might be generated through chemical oxidation with sodium hypochlorite.

In limited applications, the only acceptable cyanide alternatives concerned non-cyanide zinc (or copper) plating replacement by non-cyanide or acid electrolytes.

Limits for cyanide substitutions are :
-    poor degreasing ability of cyanide free electrolytic degreasing electrolyte;
-    maintenance and skill level required (bath control, bath analysis etc);
-    new environment risks (often underestimated) caused by cyanide substitutes (complexing agents used generate COD pollution);

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- modification of the coating characteristics;
- cost.

4.6.3 Substitution of hexavalent chromium

Hexavalent chromium chemicals, such as chromic acid, are frequently used in surface finishing. The main applications are :
- Decorative chromium plating
- Hard chromium plating
- Chromic acid anodising
- Chromate conversion coatings

Because of environmental and health concerns, European directives are planned to limit the use of hexavalent chromium (e.g. automotive industries, electronic industries).

Hexavalent chromium has been classified as carcinogenic by inhalation; in addition chromate films do contain hexavalent chromium and may release some of it during the handling and the usage of the finished product.

Therefore the labelling of proprietary solutions and/or proprietary solid compounds containing hexavalent chromium do have to show the risk designation "R 49", as required for products classified as toxic and carcinogenic. This is the driving force for innovative hexavalent chromium free and other competitive technologies.

With reference to existing conversion processes, the colour of the finishes and the level of their corrosion protection is directly in relation to their thickness and to their hexavalent chromium content.

4.6.3.1 Trivalent Chromium processes

New processes, based on trivalent chromium, would have to be included into the list of the best available techniques, provided they will meet the requirement and the specifications of the final OEM (Original Equipment Manufacturer).

The protection mechanism of the trivalent chromium conversion coatings is not yet well known, their behaviour seems to indicate that the protection is mainly due to the physical barrier of the coating itself, since the coating is not sensible to any subsequent thermal shock.

Up to now the upper limit of the corrosion protection achievable with these processes is limited to the protection level provided by the equivalent clear blue and yellow iridescent finishes based on hexavalent chromium. They are not yet capable of replacing the conventional brown, olive drab and black finishes.

The unwanted properties of hexavalent chromium also initiated significant research and development concerning hexavalent chromium free electrolytes for metal deposition. At this time, the only acceptable use for hexavalent chromium free (trivalent) electrolytes baths is for decorative plating.

Other hard chromium plating substitutes as nickel-tungsten-silicon carbide composite are still in the research phase. For specific applications, an alternative could be an electroless nickel coating.

4.6.3.2 Chromium free processes

Chromium free solutions on market are not yet fully able to provide zinc and aluminium corrosion protection equivalent to chromate conversion coatings. Chromium free processes are based on treatment with a composite organic-zirconium fluoride solution, on treatment with titanium fluoride, or, on treatment with organic silicon derivatives (silanes).

These new processes still have some limitations with regard to the level of corrosion protection and the required bonding capability with any subsequent polymeric layer applied for functional and/or decorative purposes.

4.6.3.3 Health and environmental considerations

Any zinc-plated part is usually post-treated with a suitable chromate conversion process. When the process used is based on hexavalent chromium the finish varies aesthetically in colour, technically in its intrinsic corrosion protection and environmentally for its typical hexavalent chromium release.

The following table shows the results of the above classification, base on several statistical industrial determinations.

Electroplated coating	Chromate conversion coating Finish colour process type		Cr^{6+} release
Zinc	Clear-blue	Cr^{6+}	$0.05 – 0.1\ \mu g/cm^2$
	Clear-blue	Cr^{3+}	$0.0\ \mu g/cm^2$
	Yellow-Tropical	Cr^{6+}	$0.3 – 0.6\ \mu g/cm^2$
	Green	Cr^{6+}	$0.7 – 0.9\ \mu g/cm^2$
	Black	Cr^{6+}	$0.7 – 1.0\ \mu g/cm^2$
	Yellow-Tropical Followed by a top coat layer	Cr^{6+}	$0.1 – 0.2\ \mu g/cm^2$
	Black Followed by a top coat layer	Cr^{6+}	$0.02 – 0.1\ \mu g/cm^2$

The simple application of a suitable top coating layer on the chromate conversion coating is sufficient to prevent release of chromium VI.

It is obvious that the chromium VI release is a function of the quality of the rinses following the post-treatment: rinses have to be designed to avoid any residue of the chromate conversion solution remain adsorbed on the surface of the treated parts.

4.7   Regeneration of Process Solutions

A precondition for consistent high quality electrochemical surface treatment is a uniform composition of all process solutions involved. Since disturbing contaminants eg conversion or decomposition products accumulate during processing, batch or continuous maintenance and regeneration are necessary, especially when the rejuvenating function of drag-out is eliminated through drag-out recovery.

The following table shows significant disturbing pollutants related to most important process solutions.

No.	Process Solution	Disturbing Pollutants	Remarks	Regeneration means	Remarks
01	Soak Cleaner	Sludge Oil, liquid grease, metal slivers	dragged in with the work	Sludge: decanting of process solution, discarding of sludge to waste water treatment. - Skimmer, - Gravity separation - Bio-degradation [1] - Ultrafiltration of static rinse water prior to balance drag-out and evaporation losses of treatment solution.	1) emerging technique See 6.1.1
02	Pickling of Metals	Dissolved metal		- Retardation	Big volumes only
03	Pickling of Plastics	Dissolved resin	balance	Reoxydation through	

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No.	Process Solution	Disturbing Pollutants	Remarks	Regeneration means	Remarks
		reduced oxidising agent	situation	electrodialysis	
04	Desmear of Multilayers	Dissolved resin Cr6 and O4--		-Electrolytic re-oxidation	
05	Electrolytic Cleaner	Dissolved metal, oil, grease	Use overflow compartment	-Skimmer	
06	Cyanide Copper	Redundant copper, decomposition products of organic additives carbonates		- Insoluble anodes with individual DC supply - Active carbon treatment -Dilution of solution	
07	Acid Copper	Redundant copper, decomposition products of organic additives		-Dilution of solution -Active carbon treatment	
08	Electroless Copper	Decomposition products		Feed and bleed	
09	Dull nickel, Watt's type	Redundant nickel, by-metals		- Membrane anodes with individual DC supply - Selective plating cathode at low current densities	
10	Bright Nickel, Watt's Type	Redundant nickel, decomposition products of organic additives, by metals as Zn, Cu, Fe		Membrane anodes with individual DC supply -active carbon treatment -electrodialysis -adsorber resin treatment [2] -selective plating cathode at low current densities	2)emerging technique See 6.2.1.1
No.	Process Solution	Disturbing Pollutants	Remarks	Regeneration means	Remarks
11	Sulphamate Nickel	Decomposition products of surfactants		- Active carbon treatment	
12	Electroless Nickel for Plastics	Orthophosphite, sulphate, sodium Palladium		Replace after lifetime3)	3)emerging techniques See 6.2.1.2
13	Electroless Nickel for Metals	Orthophosphite, sulphate, sodium		Replace after lifetime3)	3)emerging techniques See 6.2.1.2
14	Bright Chromium and Hard Chromium	Cr^{3+}, by-metals, dissolved from plated items		- Static rinse water recirculated over cation exchanger prior to balance evaporation losses of treatment solution	
15	Alkaline Zinc	Carbonates		Crystallisation of carbonate by low temperature treatment	In batch and/or continuously
16	Cyanide Zinc	Redundant zinc, decomposition products carbonates		Insoluble anodes Crystallisation of carbonate by low temperature treatment	In batch and/or continuously
17	Acid Zinc	Redundant zinc, decomposition products of organic additives, by-metal (iron)		- Membrane anodes with individual DC supply - Active carbon treatment - H_2O_2 treatment with lot of air - Low pH treatment	
18	Zinc - Nickel (alkaline)	Carbonates		Crystallisation of carbonate by low temperature	
19	Zinc – Iron	Carbonate		Crystallisation of carbonate by low temperature	
20	Passivation	Conversion products of		Feed and bleed	

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No.	Process Solution	Disturbing Pollutants	Remarks	Regeneration means	Remarks
		passivated zinc and zinc alloys, sulphate, by-metals			
21	Aluminium Oxidation (sulphuric)	Dissolved aluminium		-Retardation[4]	4)see 4.7.3
22	Aluminium Oxidation (chromic acid)	Dissolved aluminium, Cr^{3+}		-Feed and bleed -Correct anode--cathode ratio	
23	Electrolytic Colouring	Sn^{4+} Aluminium enrichment	Filtration not appropriated	- Feed and bleed - R.O.	
24	Inorganic Colouring	Drag in of sulphate and phosphate Iron hydroxide Free ferri-ammoniumoxalate	Affects colour	- Feed and bleed based on colour - Filtration - Reduction with H_2O_2	
25	Organic Colouring	Numerous pollutants		- Difficult regeneration	
26	Silver	Decomposition products, potassium carbonate	Based on potassium	- Feed and bleed	
27	Static Rinses	Metal hydroxides, depending on pH, surfactants and algae		Filtration	
28	Running Rinses	Dissociated chemicals		Elimination by ion exchange	

4.7.1 Regeneration techniques

The following examples illustrate what can be achieved in the electroplating plants through the use of regeneration techniques.

4.7.2.1 Separation of oil and grease from alkaline cleaners

Over a long period a de-greasing plant becomes contaminated with oil and grease. Removal of these contaminants enhances efficiency and extends the life of the cleaners, consequently reducing environmental pollution.

Mechanical separation by skimmers is the simplest and cheapest method of removing floating oil from the cleaner surface.

Gravity oil separators working in bypass are another suitable means of separating oil/grease from degreasing solutions: small globules of oil accumulate and coalesce to larger globules with a greater tendency to float to the surface and are then removed.

Separating emulsified oil is more difficult. Chemical decomposition is the easiest way. A chemical is added which breaks down the wetting agent system and releases the oil, at the same time destroying the de-greasing effect.

An alternative to chemical decomposition is filtering. Water, salt solutions and oil are all different sizes, oil is largest. By choosing a filter with pores smaller than oil but larger than water and dissolved salt, the oil can be separated.

Micro or ultra filtering requires higher pressure to pass the water and salt solutions through the filter. The permeate is returned to the cleaner and the retentate is collected as waste or for incineration.

Unfortunately a proportion of the wetting agent is removed during this process and must be complemented so the degreasing plant can recover its effectiveness. The success of cost effectiveness of this technique is based on the likelihood of finding the membrane for the wide range of pollutants often seen in degreasing bath. Most of the equipment is installed in in-house shops.

Gravity separation for removing the majority of oil/grease from the cleaner together with ultra filtration at the following rinse station has multiple advantages:

- improved process reliability,
- extended life time of the cleaner,
- reduced size of ultra-filtration and
- prevention of drag-in of residues of oil/grease into following process steps

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The same processes used for alkaline cleaners can be applied for electrolytic cleaners taking into account that the quantity of oil is only marginal compared with soak cleaning.

4.7.2.2 Electrodialysis

Electrodialysis is a suitable means to recover eg ductility of nickel deposits by removing organic decomposition products from nickel electrolytes. It is also used to extend the lifetime of electroless nickel plating solutions.

4.7.3 Retardation

Retardation is an ion separation technique and used for the regeneration of various ionic solutions (e.g. acid pickling and anodising).

When pumping a metal containing solution up-stream through an ion resin, the major proportion of free acid diffuses into the resin, whereas metal ions pass through. In a second step, when water is pumped downstream through the resin, the acid is set free again. The recovered acid can be reused. A depletion rate between 40 to 60 % can be achieved, depending on the type of acid and metal.

The efficiency of retardation decreases in the following sequence :

$HCl > HNO_3 > HClO_4 > H_2SO_4 > (HF)_n > H_3PO_4 >$ tartaric acid

4.7.4 Crystallisation of carbonates and metal sulphates

Metal salts are generated during pickling of metal surfaces. Sodium carbonate is produced by chemical reactions with CO_2 in the air during alkaline and alkaline cyanide electrolyte plating.

The salts affect process operation above a certain concentration level. They can be crystallised and removed from electrolytes at temperatures <5°C.

Iron salts eg can be used as precipitation aid in waste water treatment plants. Sodium carbonate is useful for make-up of electrolytic cleaners.

4.7.5 Activated carbon treatment

Organic decomposition products tend to disturb electrolytic metal deposition or the properties of the metal deposit itself. The major proportion of such products can be extracted from electrolytes through activated carbon treatment.

The quantity of active carbon needed depends on the quantity of products to be removed. Up to10g/l are necessary.

Activated carbon is mixed into the electrolyte and removed by filtration after a suitable reaction time.

Sometimes a combination of normal filter and filter with active carbon cartridges in bypass is used to continuously remove both, solid contaminants and soluble organic decomposition products from electrolytes.

A disadvantage of this method is the fact that not only contaminants but also additives such as brighteners and wetting agents are removed simultaneously.

4.7.6 Electrolytic purification at low current densities

Some metallic contaminants can be removed selectively from electrolytes at current densities from 0.05 to 0.3 A/dm². The efficiency of this selective cleaning can be enhanced with increased electrolyte throughput.

Similar to activated carbon treatment not only by-metals but also organic additives are removed. Therefore electrolytic purification should be reduced to a minimum.

4.7.7 Purification of metallic contamination by ion exchange

Ion exchange serves to selectively remove unwanted metal ions (cations) from aqueous solutions. Cation exchange resins with special properties as eg resistance against oxidants are in use.

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This technique is applied in bypass for the regeneration of eg phosphoric acid pickling and chromium plating electrolytes. Cleaning of passivating solutions is also possible as long as no chemicals such as trivalent chromium or silver are not present.

Eluates deriving from ion exchange column regeneration have to be treated in wastewater plants.

4.7.8   Membrane electrolysis for re-oxidation of by-products

Chromium/sulphuric acid pickling of ABS plastic items oxidises and dissolves the butadiene component of the blend, simultaneously generating trivalent chromium. Both, the organic decomposition product and the trivalent chromium are going to disturb the process beyond a tolerable concentration level.

Ceramic Membrane electrolysis is the appropriate reliable means to continuously regenerate process solution.

4.8   Recovery of precious metals out of rinses

Metal recovery is inevitably linked to the whole question of its cost effectiveness. Usually, only the recovery of precious metals and silver is economically attractive. Other metals recovery or recycling could become only indirectly attractive because of its inherent potential to produce indirect savings, eg on reduced disposal costs. This is the reason that the recovery of precious metals from effluent in the surface treatment industry is one of the oldest forms of recycling.

Precious metals in concentrated solution are usually recovered electrolytically, while more dilute solutions, sometimes with no more than a few mg/litre, are treated by adsorption of the metal content on ion exchange resins.

Improvements in the design of electrolytic reactors continue to lower the concentration at which direct electrolytic recovery becomes economically viable.

Electrolysis, in fact, is the true recovery process, while ion exchange provides only a concentration of the metal in the resin, the subsequent recovery being possible by the resin incineration or by the metal release in dissolved form, but at higher concentration. Further advantages of the electrolytic recovery over the ion exchange method are :

a) it does not produce any increase of the dissolved salt concentration,

b) the presence of other metals in similar concentrations does not affect the rate of removal of the desired species.

Noble metals, because of their electropositive character, are more readily electrodeposited than non-noble ones. Gold and silver have been recovered electrolytically for well over 50 years.

Finally, an alternative recovery treatment method is the cementation with metallic zinc powder; zinc excess is subsequently dissolved with hydrochloric acid. This method, even if very rarely used, has been applied to recover silver and gold.

4.8.1   Electrolytic recovery

Precious metals electrolytic recovery requires the electrolytic reactor to be able to reduce the metal concentration down to a very low concentration (1 ppm or less). The current efficiency at this level is very low. In general a simple flat plate cathode would be sufficient, but when high current efficiencies are required, sophisticated cathode design is needed (rotating tube cell, graphite fibre cathode). In all cases, including those involving anodic oxidation, the anode must be of the "insoluble" type.

Cathodes are usually sheets, foil or particles, in general of the same metal to be recovered, but also of stainless steel or other metals, which allow either a mechanical parting of the deposit from the cathode blank, or its removal by anodic dissolution. Iron, stainless steel, porous carbon, graphite particles, glass or plastic metallized beads, metallized fabrics are all examples of the common materials used. Cathode material selection is largely determined by

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the nature of the treatment, which follows the metal deposition. In any case maximising both the cathode surface area and the diffusion process are the most important means to enhance the efficiency of the electrolytic reactor.

Anodic material includes: graphite, lead, lead alloys with antimony, silver or tin, stainless steel, cast iron, ferrosilicon and the valve metals (titanium, tantalum, tungsten, niobium) coated with noble metals (platinum iridium) or with noble metal oxides (iridium, ruthenium oxides).

Anodic material selection is usually a compromise based on:

➢ overvoltage behaviour for the particular reaction on a given material,

➢ anode corrosion, mechanical properties and form in which the material is available,

➢ price.

Operating conditions vary as a function of the metal to be recovered; for gold the recommended conditions are: pH minimum 10, cell voltage 8V, current density 20 Amp/dm^2, temperature > 60 °C, anode - cathode gap from 8 to 16 cm.

4.8.2 Ion exchange recovery

For gold and precious metals the principle of the method is based on the rinse water treatment with strong basic type of anionic ion exchange resins, in the OH$^-$ or in the Cl$^-$ form, indifferently for alkaline cyanide or chloride based effluent rinses, followed by incineration. Ion exchange resins are quoted as having a useful capacity of 100 g Au /litre of resin.

Typically the equipment consists of two ion exchange resin columns in series, with the front unit taking the main load, while the downstream column takes any excess. Each resin column should contains around 4 litres, or more, of ion exchange resin

The final metal recovery is made by incineration in an oxygen-rich atmosphere at 500 - 600 °C. Metals are found with the residual ash. Recovery is about 95% efficient.

When a very large volume of rinse water is used, an interesting option is the treatment of the static rinse, following the precious metal plating tank, through the resin column in a close loop. This ensures such a low gold concentration in the static rinse, that further drag out losses into the following cascade rinses may be neglected.

Silver recovery, instead, requires using weak basic anionic ion exchange resins, followed by regeneration and subsequent electrolytic recovery of the regenerate. Typically resin capacity is in the range of 50 – 75 g of Ag / litre of resin. An interesting option is the use of ion exchange units built into a recirculation rinse loop with periodical regeneration. Silver is than recovered by electrolysis from the concentrate.

Palladium used in the PCB industry is recovered from chloride containing acid solutions (pH about 2), where it is present as chloro-complex, using strongly basic ion exchange resins. The same process readily allows its separation from copper. The typical resin capacity (same type of resin as used for gold) varies from 30 to 50 g of Pd per litre of resin.

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5.   BEST AVAILABLE TECHNIQUES

The processes illustrated in chapter 2 are in use by an estimated 18,000 sites in Europe. Every plant is specialised and uses only a few of these processes. The result is a great number of different units, which cannot be compared with each other.

It is not possible to conclude that a single production process can be applied to this group. The choice of process is highly dependent on the required physical and chemical characteristics of the final product.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques.

Best Available Techniques are influenced by a number of factors and a methodology of examining the techniques is needed. The approach that has been used is given below.

- o First of all the choice of process depends strongly on the products that are made, in particular their size and additives needed and regeneration capacity.

- o Secondly, the process should be suitable for use with the best gas collection and abatement systems that are available. The fume collection and abatement processes used will depend on the characteristics of the main processes, for example some processes are easier to seal.

- o Finally, the water and waste issues have been taken into account, in particular the minimisation of wastes and the potential to reuse residues and water within the process or by other processes.

- o Energy used by the processes is also a factor that is taken into account in the choice of processes.

The choice of BAT in a general sense is therefore complicated and depends on the above factors. The varying requirements mean that BAT is influenced mainly by the desired products and their properties.

The following points summarise the recommended methodology that has been used in this work:

- o Is the process industrially proven and reliable ?

- o Are there limitations in the feed material that can be processed ?

- o The type of feed and other materials contained in it influences process selection for particular products.

- o Are there production level constraints? - eg a proven upper limit or a minimum throughput required to be economic.

- o Can latest and efficient collection and abatement techniques be applied to the process ?

- o Can the process and abatement combinations achieve the lowest emission levels ? The achievable emissions are reported later.

- o Are there other aspects such as safety that are related to processes ?

The processes vary in the throughput that can be achieved, the materials that are used and the products that can be made and so the process stages that are described are techniques to consider when forming the basis of BAT.

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The level will also vary with time depending on the condition of the equipment, its maintenance and the process control of the abatement plant. The operation of the source process will also influence performance as there are likely to be variations in temperature, gas volume and even the characteristics of the material throughout a process or batch. The achievable emissions are therefore only a basis from which actual plant performance can be judged. Process dynamics and other site specific issues need to be taken into account at a local level.

The examples given in the section on techniques to consider in the determination of BAT give the concentrations associated with some existing processes.

5.1. Multiple Rinse

The conclusions for the Best Available Techniques of the rinsing processes are shown in section 2.4 of this document and are applicable to the materials in this chapter.

5.2. Drag-out Recovery (see 4.4.)

5.3. Regeneration of the Process Solutions (see 4.7.)

5.4. Energy Saving (see 4.5.)

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6. EMERGING TECHNIQUES

6.1 Chemical Processes

6.1.1 Degreasing Systems with Bio-Regeneration
Together with oil and grease on the surface of parts micro organisms are brought into degreasing solutions. After oil and grease being emulsified micro organisms are capable of degrading the oil and grease through metabolism when life conditions as eg pH-value and temperature are controlled optimally.
Ecological and economic advantages are:
- constant regeneration efficiency
- greatly extended lifetime of the degreasing solution and consequently reduced costs
for discharge and treatment of the used and make-up of the new degreasing solution,
- reduced amount of sludge and organic contamination in waste water.
Bio-regeneration is continuously operated as an integrated closed-loop system as shown in figure 1.
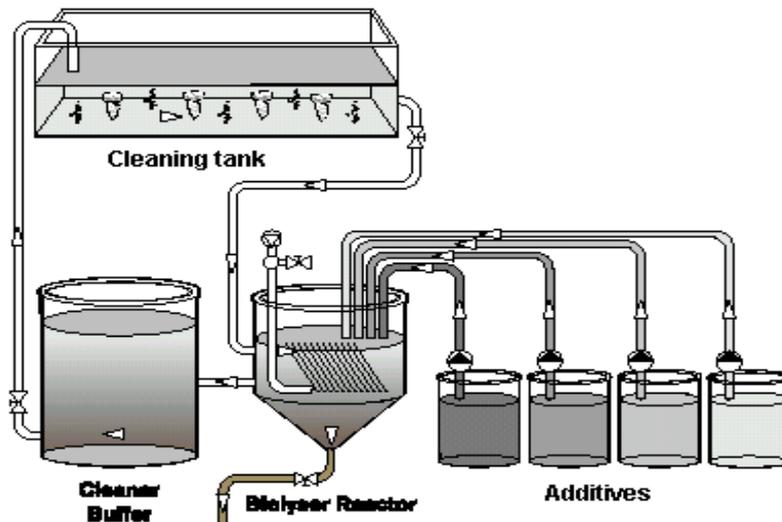

Fig. 1 - Bio-regeneration in closed-loop system.

6.1.2 Regeneration of Pickling Solutions for Plastics
To provide means for best adhesion of a metal layer, plastic surfaces have to be pickled properly.
Appropriate solutions contain $KMnO_x$ and CrO_3 . The oxidants Mn^{7+} and Cr^{6+} are reduced, the generated Mn^{6+} and Cr^{3+} can be reoxidised electrochemically to achieve a greatly extended lifetime of pickling solutions.

6.1.3 Reduced Emissions through Regeneration of Electrolytes
A precondition for reduced emissions of surface treatment processes are electrolytes that can be regenerated. When developing new electrolytes several measures need to be considered :
- Simple chemical composition,
- to be analysed by simple means as eg by conductivity, pH- and photo meter.
Conductivity of chromium electrolytes is a criterion for the concentration of metal ions including Cr^{3+} .

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- The pH-value serves to judge the activity, and photometric measurement provides the concentration of metal ions in solutions for electroless metal deposition. These parameters influence the stability of the process positively and extend the meantime between two cycles of treatment vat cleaning.
- The concentration of complexing agents should be held at lowest possible level to minimise the production of decomposition products.
- Decomposition products should not disturb metal deposition or easily be removable. Recently developed regeneration units use so-called adsorber resins for the removal of decomposition products.
- Regeneration of treating solutions again is the prerequisite for drag-out recovery and closed-loop processes (c.f. also chapters 2.1.2 and 2.2.3.1)

6.1.4   Substitution of nickel
Due to allergy concerns, a European directive limits the use of nickel for articles in contact with skin.
For decorative applications, brass, palladium or tin alloys baths are already available.
Limits for nickel substitutions are:
- new environment risks (cyanide or fluoride formulations)
- maintenance and skill level required (bath control, bath analysis etc);
- cost (precious metals)

6.1.5   Zinc Alloys
In recent years, under the incentive of higher standards in the automotive industry, several investigations have been carried out to prepare new types of zinc coatings with high corrosion protection. For this purpose, attention was focused on electrodeposited coating of zinc alloys.
Coatings of zinc alloyed with nickel, iron, cobalt etc are recognised as having a corrosion protection of up to several times that of zinc alone. An improvement of two or three hundred percent. Added to this is the fact that the alloy can be deposited with only slight modification to existing plating equipment, leading to a product cost that is at least equal to that commonly obtained with conventional zinc.
For these reasons zinc alloys has been adopted by some automotive manufacturers and are being tested as a replacement for cadmium deposits in the aerospace industry.

6.1.6   Alternative coatings on copper and copper alloys
- The "anti-tarnishing copper surface treatment", particularly used to protect and maintain the solderability of various electronics products. This treatment is usually made by immersion in vertical and on horizontal continuous processing plants, the process solution is an aqueous medium containing organic derivatives of the benzotriazole family.
- The "Black oxide process", used to convert the copper surface of the printed circuit innerlayers, in the fabrication of multilayers PCB. The same process can be used for the surface preparation of solar heat exchangers. The process is usually applied by immersion in vertical or in horizontal continuous processing plants, the process solution is an aqueous alkaline solution based on sodium hypo chloride (NaOCl)

6.2 Equipment

6.2.1 Improved Regeneration Systems

6.2.1.1 Adsorber Systems
Adsorber polymer units together with membrane anodes are already in use for the regeneration of eg electrolytic nickel solutions as shown in figs. 2 and 3. A column containing adsorber resin removes continuously decomposition products from the electrolyte, allowing uniform high quality of metal deposition, simultaneously making active carbon treatment superfluous. Increasing metal concentration, caused by different electrolytic efficiency at

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cathode and anode or by drag-out recovery, can be prevented by using insoluble membrane anodes.
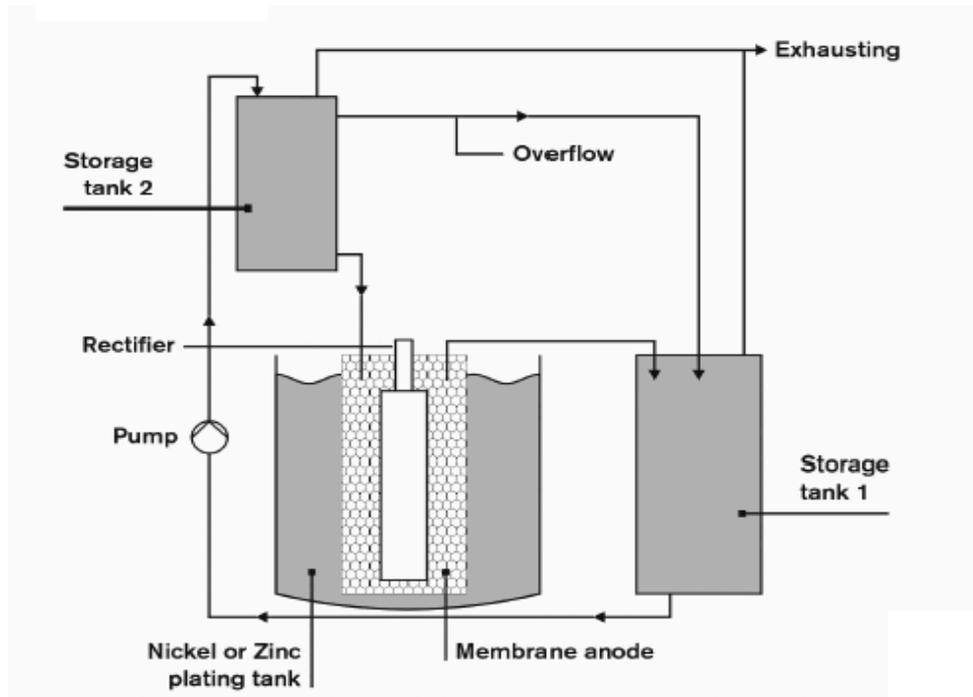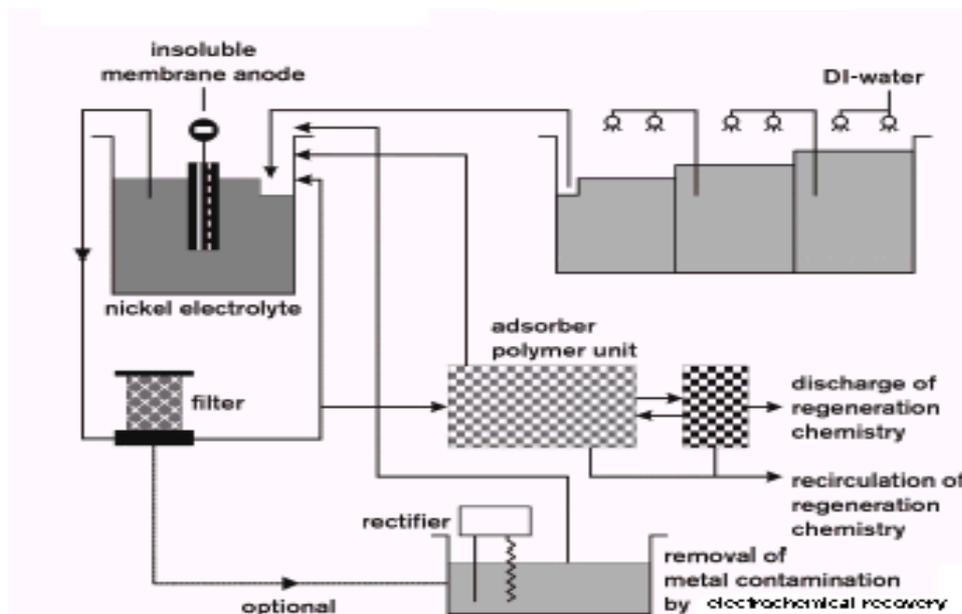

Fig. 2 - Membrane Anode - Anolyte - System

Fig. 3 - Nickel Plating System

6.2.1.2 Lifetime extension of electroless nickel plating solutions

Hypophosphite is used as reductive agent in electroless nickel processes. The amount of deposited nickel and hypophosphite have to be replenished as Ni-sulphate, Ni-hypophosphite

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or Na-hypophosphite. During nickel deposition hypophosphite is oxidised to orthophosphite. The increasing concentration of decomposition products as sulphate and orthophosphite limits the lifetime of electroless nickel solution to usually 6 - 10 metal turnovers.
Batch and continuous processes for regeneration of electroless nickel electrolytes with or without integrated nickel recycling module are available to remove decomposition products through :
- precipitation with e. g. Ca- and Mg- compounds,
- ion exchange,
- electrodialysis together with partial regeneration of decomposition products.

Advantages of these systems :
- constant deposition speed and quality,
- possibility for complete drag-out recovery from rinse water,
- lifetime extension : 3 to 5 times,
- Significant reduction of effort and cost for discharge and treatment of spent solutions.

6.2.2 Production-Integrated Single-Purpose Lines
Single-purpose lines can be in-line integrated into the production process with automatic load and unload of items to be surface-treated.
Besides major advantages as e g:
- smaller lines and corresponding installation space,
- minimised effort for transportation and handling,
- less damage of surface of items,
- reduced bound capital for material and storage,
- improved occupational safety,
- enhanced quality through process and item monitoring,
important other features with environmental impact can be achieved. This shall be instanced by a line for hard chromium plating of piston rods for shock absorbers. The line is enclosed and integrated into the production sequence. The transfer speed within the line is adjusted to the manufacturing speed of preceding and following mechanical process steps.
Advantages are:
- temporary corrosion protection obsolete,
- saving of chemicals through reduced number of process steps,
- reduced amount of drag-out,
- total recovery of drag-out,
- waste water free operation possible,
- energy saving through low amount of extracted air,
- reduced emission rate.

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Fig. 4 - Production Integrated Hard Chromium Plater
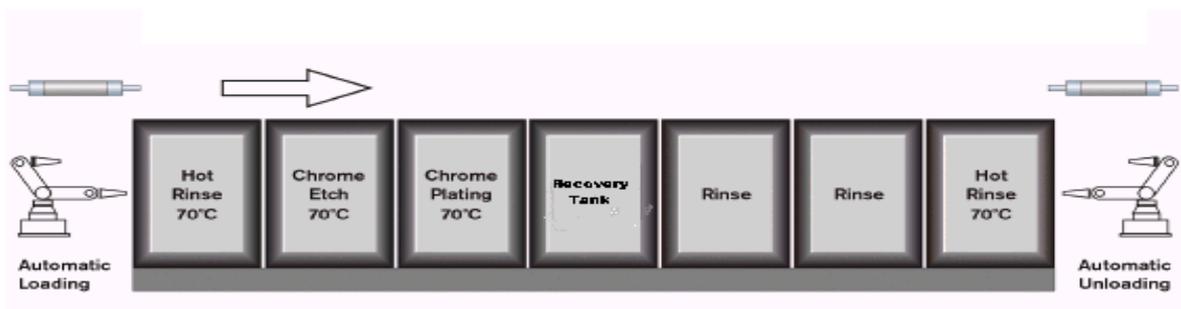
Fig. 5 - Hard Chromium Technology:
Closed Loop Process for Chrome Rinse Water Evaporation.

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6.2.3 Hard chromium plating

Recovery and purification system by ion exchange and vacuum evaporation
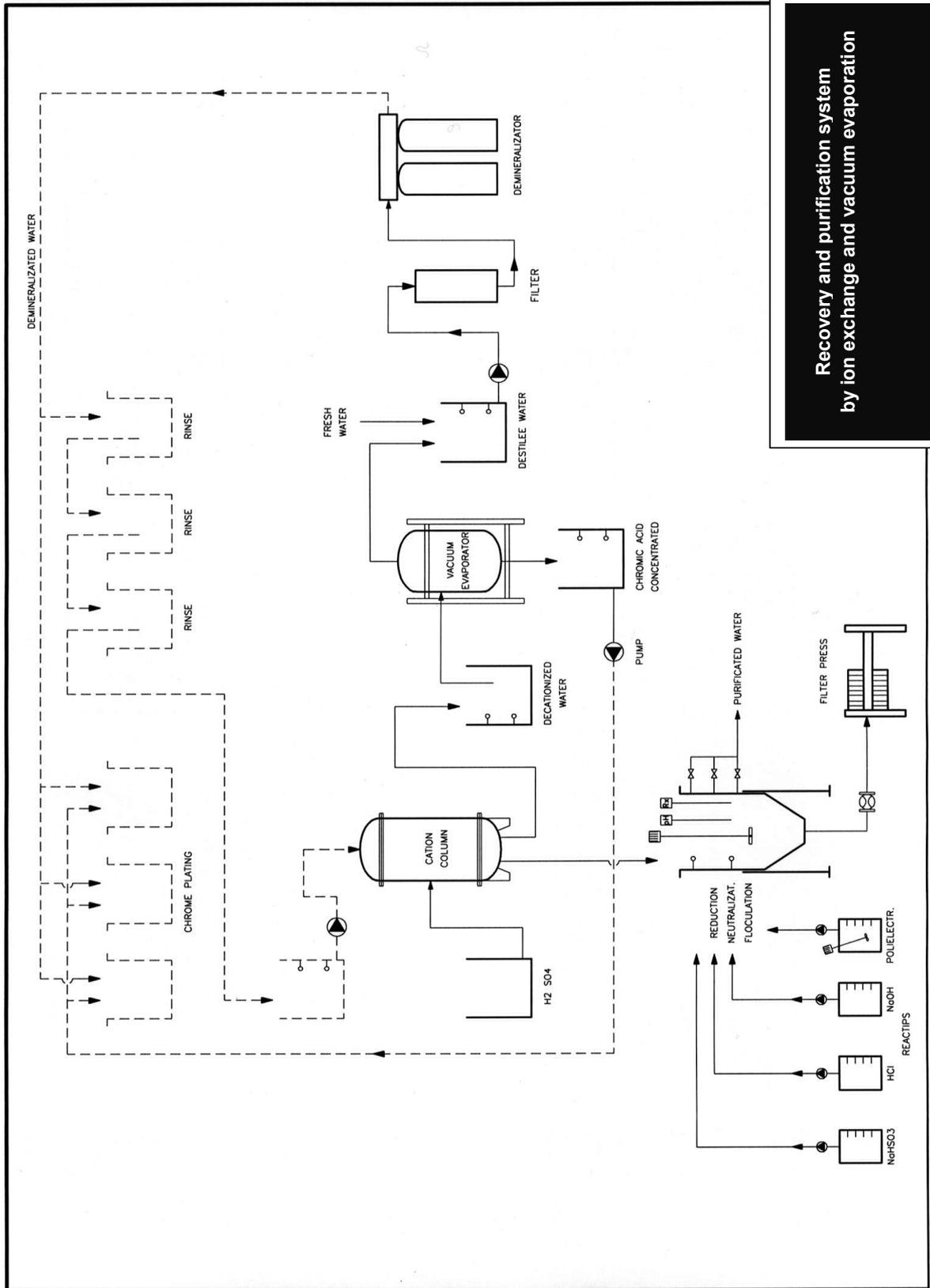
Recovery and purification system
by ion exchange and vacuum evaporation

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7.   CONCLUSIONS AND RECOMMENDATIONS
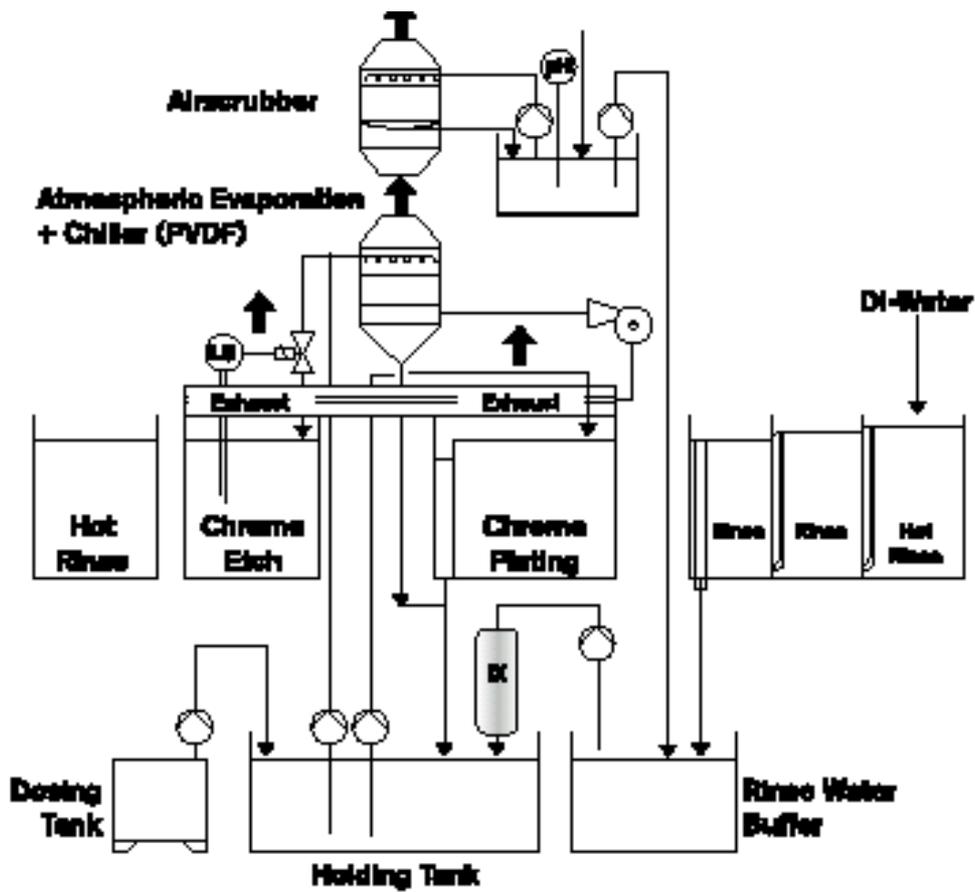
The Best Available Techniques that are included in the document, whilst not yet widely employed throughout the European Union, are based on sound production experience and may be regarded as effective tools that do not incur excessive cost. Indeed, the key BATs may well represent opportunities yielding an overall cost benefit, especially for new installations.   These BATs are generally related to waste minimisation and/or recycling within the battery limits of the process plant.

Historically, the largest loss of pollutants to the external environment was, and is, sludge or more commonly, filter cake from the effluent treatment plant. Sludge or filter cake mass discharge is proportional to the losses of process chemicals, plating metals and proprietary additives caused by drag-out from the several process operations that are required for electrolytic and autocatalytic plating, anodising etc that fall within the IPPC definition of surface treatment.
Losses in mass terms to the atmosphere and to the municipal sewer are normally extremely small in relation to the industry's solid waste.

The key BATs therefore address the solid waste challenge through:

1. The use of the lowest possible concentration of process chemicals in the several process operations.

2. The minimisation of drag-out from the process operations.

3. The return of drag-out from whence it came.

4. Recovery of process chemicals, and especially plating metals from "spent" process operations.

There are also BATs which are designed to minimise the use of water through cascade rinsing or the internal recycling of water. It should be noted however that water reduction through recycling may not be as effective as cascade rinsing in enabling the return of drag-out from whence it came.

Other BATs address the need for energy reduction through the selection of processes with a higher plating efficiency and those which are designed for low temperature operation, or are capable of operating at thermally stable conditions where significant energy inputs for cooling or heating are unnecessary.

The recent development of aqueous biological cleaning systems as a potential replacement for conventional alkaline cleaners as a BAT for the in-house reduction of oils and greases is to be noted. There is an element of energy reduction as well.

The most important longer term challenge for the surface treatment industry is the disposal of solid wastes. Even after the implementation of BATs for the reduction of drag-out and its return upstream, there remains a significant disposal challenge, albeit less than 1% of all manufacturing industry's special waste. Internal recycle or recovery of filtercake on an individual scale necessarily involves costly capital and operating costs, a high energy usage, and complex control management. Indeed in most cases, the appropriate technology may not be available or fully proven. It should also be noted that such technologies may incur their own environmental problems. An attractive approach is to develop a use for the solid waste.

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Some development work has been carried out on the use of surface treatment waste in the building materials industry.

Finally, the thirty cubic metre threshold requires formal definition at the European level. The definition in the draft BAT Reference Document excludes certain "non-process" volumes, eg pre-treatment and post-treatment tanks in a zinc plating line.
In the meantime, the UK regulatory authority has decided that the volume of all process tanks, but excluding running rinse tanks, in a surface treatment line forms the basis for the thirty cubic metre threshold value.

Annexes

1.   Bibliography

2.   Limits for surface treatment waste water in Europe (values in mg/l) - Detailed figures on the sector

3.   Existing national and international legislation for the sector

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Annex 1

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Annex 2

Limits for surface treatment waste water in Europe (values in mg/l)

	Belgium	France (*)	Germany	UK/ Thames Water Region (†)	Italy	Nether-lands	Spain/ Catalonia
Ag	0.1		0.1			0.1	
Al	10.0	5.0	3.0		1.0		20
Cd	0.6	0.2	0.2	0.2	0.02	0.2	0.5
CN free		0.1	0.2		0.5	0.2	1.0
CrVI	0.5	0.1	0.1		0.2	0.1	0.5
Cr total	5.0	0.3	0.5	2.0	2.0	0.5	3.0
Cu	4.0	2.0	0.5	2.0	0.1	0.5	3.0
F	10.0	15.0	50		6.0		12
Fe	20.0	5.0	3.0		2.0		5
Hg		0.1			0.005	0.05	0.1
Ni	3.0	5.0	0.5	2.0	2.0	0.5	5.0
NO2		1.0					
P	2.0	10	2		10.0	15	5.0
Pb	1.0	1.0	0.5		0.2		1.0
Sn	2.0	2.0	2.0		10.0	2.0	5.0
Zn	7.0	5.0	2.0	5.0	0.5	0.5	10.0
COD	300	150	400	5000	160 as O_2		1500
EDT			0			0	0
HC<Total		5.0	0.1		5.0	0.1	0.1
Vox			1.0	Nil	1.0	0.1	0.1
Settleable solids				50			
Total load of salts		No limits regionally partly for sulphates	No limits	No limits	Cl^- 1200 SO_4 1000 SO_3 1 S^{--} 1	No limits	
Total load of heavy metals		15	No limits	25		50kg/year /factory, 20kg/year /metal	

COD : Chemical Oxygen Demand
HC : Hydrocarbons
Vox : Volatile Organic halogens

(*) France : Water consumption : 8 litres per square metre of treated surface
(†) UK : There are no national limits. Each Water Service plc sets its own limits based on local conditions. There are ten local Water Service plcs.

SURFACE TREATMENT OF METALS AND PLASTIC MATERIALS USING ELECTROLYTIC OR CHEMICAL PROCESS
(volume of treatment vats > 30 m³)

ANNEX 3

Existing national and international legislation for the sector

(i) Air

Regulation:
88/3322/EEC EC regulations on CFCs and Halons that deplete the ozone layer
94/309/EEC   Directive concerning substances that deplete the ozone layer

Directives:
80/779/EEC   Directive on air quality limit values for sulphur dioxide and suspended
             particulates
84/360/EEC   Directive on the combating of air pollutants from industrial plants
85/203/EEC   Directive on air quality standards for nitrogen oxide
96/61/EC   Directive concerning Integrated Pollution Prevention Control (IPPC)
96/82/EC   Seveso II Directive

International agreements, protocols, etc.:
The Helsinki Convention 1985 (endorsed by EU member states)
The Sofia Protocol (1991)
UNECE Convention (1983) on Air Pollution
Kyoto Conference on Global Warming 1997

(ii) Water

Directives:
76/464/EEC   Directive on pollution caused by discharge of certain dangerous substances
             into aquatic environment
80/68/EEC   Directive on the protection of groundwater against pollution caused by certain
             dangerous substances
80/778/EEC   Directive on quality of water intended for human consumption
96/61/EC   Directive concerning Integrated Pollution Prevention Control (IPPC)
96/82/EC   Seveso II Directive
98/83/EC   Directive on quality of water intended for human consumption

(iii) Waste

Directives:
75/442/EEC   Directive on waste (Framework) (91/156/EEC as amended)
78/319/EEC   Directive on toxic and dangerous waste
84/631/EEC   Directive on the trans-frontier shipment of hazardous waste
91/156/EEC   Directive on waste (Framework)
94/62/EEC   Directive on packaging and packaging waste
96/61/EC   Directive concerning Integrated Pollution Prevention Control (IPPC)
99/31/EC   Directive on the landfill of waste

*************************END*************************