Integrated Pollution Prevention and Control

Draft Reference Document on
Best Available Techniques for the Surface Treatment of
Metals and Plastics

Draft August 2003
This document is one of a series of foreseen documents as below (at the time of writing, not all documents have been drafted):

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EXECUTIVE SUMMARY
Preface

1. Status of this document


This document is a working draft of the European IPPC Bureau. It is not an official publication of the European Communities and does not necessarily reflect the position of the European Commission.

2. Relevant legal obligations of the IPPC Directive and the definition of BAT

In order to help the reader understand the legal context in which this document has been drafted, some of the most relevant provisions of the IPPC Directive, including the definition of the term “best available techniques”, are described in this preface. This description is inevitably incomplete and is given for information only. It has no legal value and does not in any way alter or prejudice the actual provisions of the Directive.

The purpose of the Directive is to achieve integrated prevention and control of pollution arising from the activities listed in its Annex I, leading to a high level of protection of the environment as a whole. The legal basis of the Directive relates to environmental protection. Its implementation should also take account of other Community objectives such as the competitiveness of the Community’s industry thereby contributing to sustainable development.

More specifically, it provides for a permitting system for certain categories of industrial installations requiring both operators and regulators to take an integrated, overall look at the polluting and consuming potential of the installation. The overall aim of such an integrated approach must be to improve the management and control of industrial processes so as to ensure a high level of protection for the environment as a whole. Central to this approach is the general principle given in Article 3 that operators should take all appropriate preventative measures against pollution, in particular through the application of best available techniques enabling them to improve their environmental performance.

The term “best available techniques” is defined in Article 2(11) of the Directive as “the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole.” Article 2(11) goes on to clarify further this definition as follows:

“techniques” includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned;

“available” techniques are those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator;

“best” means most effective in achieving a high general level of protection of the environment as a whole.

Furthermore, Annex IV of the Directive contains a list of “considerations to be taken into account generally or in specific cases when determining best available techniques ... bearing in
mind the likely costs and benefits of a measure and the principles of precaution and prevention”. These considerations include the information published by the Commission pursuant to Article 16(2).

Competent authorities responsible for issuing permits are required to take account of the general principles set out in Article 3 when determining the conditions of the permit. These conditions must include emission limit values, supplemented or replaced where appropriate by equivalent parameters or technical measures. According to Article 9(4) of the Directive, these emission limit values, equivalent parameters and technical measures must, without prejudice to compliance with environmental quality standards, be based on the best available techniques, without prescribing the use of any technique or specific technology, but taking into account the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In all circumstances, the conditions of the permit must include provisions on the minimisation of long-distance or transboundary pollution and must ensure a high level of protection for the environment as a whole.

Member States have the obligation, according to Article 11 of the Directive, to ensure that competent authorities follow or are informed of developments in best available techniques.

3. Objective of this Document

Article 16(2) of the Directive requires the Commission to organise “an exchange of information between Member States and the industries concerned on best available techniques, associated monitoring and developments in them”, and to publish the results of the exchange.

The purpose of the information exchange is given in recital 25 of the Directive, which states that “the development and exchange of information at Community level about best available techniques will help to redress the technological imbalances in the Community, will promote the world-wide dissemination of limit values and techniques used in the Community and will help the Member States in the efficient implementation of this Directive.”

The Commission (Environment DG) established an information exchange forum (IEF) to assist the work under Article 16(2) and a number of technical working groups have been established under the umbrella of the IEF. Both IEF and the technical working groups include representation from Member States and industry as required in Article 16(2).

The aim of this series of documents is to reflect accurately the exchange of information which has taken place as required by Article 16(2) and to provide reference information for the permitting authority to take into account when determining permit conditions. By providing relevant information concerning best available techniques, these documents should act as valuable tools to drive environmental performance.

4. Information Sources

This document represents a summary of information collected from a number of sources, including in particular the expertise of the groups established to assist the Commission in its work, and verified by the Commission services. All contributions are gratefully acknowledged.

5. How to understand and use this document

The information provided in this document is intended to be used as an input to the determination of BAT in specific cases. When determining BAT and setting BAT-based permit conditions, account should always be taken of the overall goal to achieve a high level of protection for the environment as a whole.

The rest of this section describes the type of information that is provided in each section of the document.
Chapters 1 and 2 provide general information on the industrial sector concerned and on the industrial processes used within the sector. Chapter 3 provides data and information concerning current emission and consumption levels reflecting the situation in existing installations at the time of writing.

Chapter 4 describes in more detail the emission reduction and other techniques that are considered to be most relevant for determining BAT and BAT-based permit conditions. This information includes the consumption and emission levels considered achievable by using the technique, some idea of the costs and the cross-media issues associated with the technique, and the extent to which the technique is applicable to the range of installations requiring IPPC permits, for example new, existing, large or small installations. Techniques that are generally seen as obsolete are not included.

Chapter 5 presents the techniques and the emission and consumption levels that are considered to be compatible with BAT in a general sense. The purpose is thus to provide general indications regarding the emission and consumption levels that can be considered as an appropriate reference point to assist in the determination of BAT-based permit conditions or for the establishment of general binding rules under Article 9(8). It should be stressed, however, that this document does not propose emission limit values. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also needs to be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and levels presented in chapter 5 will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document is fully taken into account by permitting authorities.

Since the best available techniques change over time, this document will be reviewed and updated as appropriate. All comments and suggestions should be made to the European IPPC Bureau at the Institute for Prospective Technological Studies at the following address:

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Best Available Techniques Reference Document on the Surface Treatment of Metals and Plastics

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SCOPE

The scope of this document is based on Section 2.6 of Annex 1 of the IPPC Directive 96/61/EC: ‘Installations for the surface treatment of metals and plastics using an electrolytic or chemical process where the volume of the treatment vats exceeds 30m3’.

The interpretation of ‘where the volume of the treatment vats exceeds 30m3’ is important in deciding whether a specific installation requires an IPPC permit. This document does not address this issue of interpretation. It does include descriptions of activities that may be carried out at volumes below this threshold, because many installations carry out more than one activity. As point 2 of Annex 1 of the Directive notes: ‘Where one operator carries out several activities falling under the same subheading in the same installation or on the same site, the capacities of such activities are added together’.

This document does not deal with:

- hardening (with the exception of hydrogen de-embrittlement, where it is carried out in conjunction with electroplating)
- other physical surface treatments such as vapour deposition of metals
- hot-dip galvanising and the bulk pickling of iron and steels are discussed in the Reference Document on Best Available Techniques in the Ferrous Metals Processing Industry
- surface treatment processes are discussed in the Reference Document on Best Available Techniques for Surface Treatment Using Solvents (solvent degreasing is also briefly discussed in this document as a degreasing option)
- electropainting (electrophoretic painting) is discussed in the Reference Document on Best Available Techniques for Surface Treatment Using Solvents.
1 GENERAL INFORMATION ON THE SURFACE TREATMENT OF METALS AND PLASTICS

Treating the surfaces of metals

The surface treatment of and by metals dates back to early man using gold decoratively before 4000 BC. Gold and silver plating (including their deposit from amalgams) was well-known by the 13th century AD, and tin plating of iron was carried out in Bohemia in AD 1200. In the mid-19th century, the electrodeposition of metals was discovered enabling new possibilities, which are still being extended [Cramb, #4; Hook, 2003 #5; 2003 #41].

The surface properties of metals are typically changed for:

- decoration
- improved hardness (to maintain cutting edges and resistance to damage and wear)
- prevention of corrosion.

Two further commercial areas of application have emerged since the 1960s:

- in microelectronics, especially with the advent of telecommunications and microprocessor controls in many common appliances. These demand mass-produced components with high conductivity capable of carrying very small electrical currents. This is achieved by applying precious metal plating on cheaper substrates
- in printing, where aluminium is usually the substrate of choice for lithographic plates. The aluminium is first treated by electrochemical graining and anodic oxidation (anodising) prior to photosensitive treatments.

Treating the surfaces of plastics

Plastics are now widely used in their own right and not only to replace metals. However, although they can be easily formed, may be flexible or rigid, and are corrosion resistant and insulating, they lack other desirable properties. This has led to demands to change the surface properties of these new materials for:

- decoration, to achieve a high-value, metal-like appearance similar to gold, brass, and chromium
- reflectivity, similar to chromium
- durability, as plastics are generally softer than metals
- electrical conductivity, usually in selected areas.

These requirements are met by depositing layers of metals on the surface of the plastic.

Printed circuit boards are a specific case, where intricate electronic circuits are manufactured using metals on the surface of a plastic – usually resin or glass fibre board but also plastic films. A complicated series of processes removes and adds successive layers of metals as circuits to connect small holes. The inside surface of these holes are also coated with metal during the processes to enable electronic components to be subsequently soldered into them.
1.1 Industries using surface treatments

The surface treatment of metals and plastics does not itself form a distinct vertical industry sector. Surface treatments do not create products; they change the surface properties of previously formed components or products for subsequent use. Printed circuit boards might be considered products but are components manufactured for use in other products, and are made by a considerable number of inter-dependant manufacturing stages. The surface treatment of metals and plastics is therefore largely a service to many industries and examples of key customers are given below: Table 1.1 sets out examples of key treatments and their uses.

- automotive
- aerospace
- information systems
- telecommunications
- heavy engineering
- construction (building)
- bathroom fittings
- hardware
- furniture
- printing
- domestic appliances
- jewellery, spectacles and ornaments
- food and drink containers
- clothing
- coinage
- medical
<table>
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<td>Zinc plating and chromium passivation</td>
<td>Steel</td>
<td>Fastenings (nuts, bolts, screws, nails, specialist design, etc.) for construction,</td>
<td>• corrosion protection</td>
</tr>
<tr>
<td></td>
<td></td>
<td>automotive, furniture.</td>
<td>• decoration</td>
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<td>Automobile brake system components, windscreen washer system components.</td>
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<td>Chassis and casings for domestic goods (TVs, Hi-fis, videos, washing machines,</td>
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<td>fridges).</td>
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<tr>
<td>Hard chromium plating</td>
<td>Steel</td>
<td>Heavy duty engines (marine, etc.).</td>
<td>• durability</td>
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<td></td>
<td>Rolling mill bearings (steel and non-ferrous metal).</td>
<td>• prevention of sticking</td>
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<td>Rollers (in paper mills).</td>
<td>• micro-smooth surface</td>
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<td>Aerospace undercarriage and control components.</td>
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<td>Medical equipment</td>
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<tr>
<td>Chromium plating</td>
<td>Steel coil</td>
<td>Food, domestic and commercial products packaging (cans)</td>
<td>• corrosion protection</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• decoration</td>
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<tr>
<td>Nickel, autocatalytic plating (for subsequent</td>
<td>Plastic</td>
<td>Bathroom fittings. Furniture fittings.</td>
<td>• Decoration.</td>
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<td>chromium plating)</td>
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<td>Automotive trim.</td>
<td></td>
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<tr>
<td>Nickel, electrolytic</td>
<td>Steel</td>
<td>Coins (all EU currencies)</td>
<td>• Corrosion protection</td>
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<tr>
<td></td>
<td></td>
<td>fittings (screws, etc.)</td>
<td>• Decoration.</td>
</tr>
<tr>
<td>Copper and copper alloy (brass) plating</td>
<td>Steel</td>
<td>Coins (all EU currencies).</td>
<td>• Decoration.</td>
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<tr>
<td>Cadmium plating</td>
<td>Steel</td>
<td>Aerospace fittings</td>
<td>• corrosion prevention</td>
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<td></td>
<td></td>
<td></td>
<td>• prevention of sticking</td>
</tr>
<tr>
<td>Gold plating</td>
<td>Copper, printed</td>
<td>Connectors and wires for telecommunications and IS hardware</td>
<td>• corrosion prevention</td>
</tr>
<tr>
<td></td>
<td>circuit boards</td>
<td></td>
<td>• high conductivity</td>
</tr>
<tr>
<td>Precious metal plating (gold, silver, iridium,</td>
<td>Steel, copper,</td>
<td>Jewellery, ornaments (hollowware), spectacle frames.</td>
<td>• decoration, corrosion prevention</td>
</tr>
<tr>
<td>platinum)</td>
<td>brass, alloys</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anodising</td>
<td>Aluminium</td>
<td>Automobile bodies and panels.</td>
<td>• corrosion protection</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aerospace wing and fuselage panels.</td>
<td>• decoration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Building door and window frames, cladding panels.</td>
<td>(with or without colour)</td>
</tr>
<tr>
<td>Hard anodising</td>
<td>Aluminium</td>
<td>Bearing surfaces in turbine compressor housings for automotive engines</td>
<td>• durability</td>
</tr>
<tr>
<td>Phosphating</td>
<td>Steel and other</td>
<td>Nuts, bolts, screws, tubes.</td>
<td>• corrosion protection</td>
</tr>
<tr>
<td></td>
<td>metals</td>
<td>Engine pinions, camshafts, pistons, gears, valves.</td>
<td>• durability (surface lubrication</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cold forming of wires, tubes, etc.</td>
<td>for cold drawing, or forming)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Food and domestic goods packaging. Automotive body panels, domestic electrical</td>
<td>• overcomes surface irregularities</td>
</tr>
<tr>
<td></td>
<td></td>
<td>goods, etc.</td>
<td>• adhesion of paints</td>
</tr>
<tr>
<td>Printed circuit boards (tin and copper plating,</td>
<td>Copper on plastics</td>
<td>Control systems for aerospace, automotive products (engine management, braking,</td>
<td>• circuit systems</td>
</tr>
<tr>
<td>etching etc)</td>
<td></td>
<td>etc), telecommunications and IS, domestic goods.</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1: Examples of key treatments and examples of their uses
1.2 Industry structure and economic background

1.2.1 Type and size of installations

The surface treatment of metals and plastics discussed in this document is carried out in more than 18300 installations (both IPPC and non-IPPC) in Europe, ranging from small private companies to facilities owned by multinational corporations. The large majority are small or medium enterprises (SMEs, [61, EC, 2002]); in Germany the typical number of employees is between 10 and 80. Altogether, the surface treatment of metals and plastics employs about 440000 people in Europe. These figures include manufacturers of printed circuit boards. More than 10000 (55 %) are specialist surface treatment installations (known as job or jobbing shops). The remaining 8300 (45 %) are surface treatment shops within another installation typically also an SME. The majority of jobbing shops serve more than one industry (see those listed in Table 1.1). There is no installation typical of the whole range of activities, and even though there are strong similarities between sites engaged in the same activities, no two sites will be identical [3, CETS, 2002, 104, ÜBA, 2003]. For gathering economic statistics, electroplating, plating, polishing, anodising and colouring are classified under the Standard Industrial Classification (SIC) code 3471, but this includes establishments engaged in all types of metal finishing. Companies that both manufacture and finish (surface treat) products are classified according to the products they make. For data on sources of emissions, the industry is classed under general purpose manufacturing processes (for emissions, NOSE-P 105.01 [2, EC, 2000]. These groupings make the extraction of data for specific surface treatments or for the whole sector difficult as they cannot be differentiated readily from the other engineering activities.

Surface treatment is positioned between initial workpiece or substrate manufacture and final product assembly, completion and packaging. Treatment (both in jobbing shops and many in-house workshops) often has low priority in the production chain, although there are exceptions. This can result in insufficient attention to correct and up to date specifications, insufficient attention given in product design to minimise and reduce consumptions, as well as a lack of investment.

Surface treatment is carried out after the primary metal or plastic has been formed into workpieces or shaped substrates, such as nuts, bolts, pressed or moulded components, sheets, or coils. They may even be sub-assemblies made of several components, often of different materials. These components and sub-assemblies can be complex shapes which have been pressed, cast and/or machined. In coil processing the substrate used on the largest scale is steel and can vary from wires to steel strip 2008 mm wide. In smaller scale reel-to-reel applications, copper, brass or other alloys are also coated. Printed circuit boards are made from plastic or glass fibre boards which are already laminated (usually with copper) or plastic films.

Process lines are usually modular, and small lines can be easily assembled as a series of tanks. However, large automated lines and the modules in those installations handling steel coil on a large scale, or large components such as parts of aircraft wings, are typically specialist, large and capital intensive.

Most installations, particularly the jobbing shops, will operate multiple lines side by side. This assists in increase capacity and reliability of delivery, and allows the installation to offer different treatments (jig, coil or small scale coil, see Chapter 2) for different products and prices and/or to offer different finishes. In these cases, point 2 of Annex 1 to the IPPC directive should be noted: “Where one operator carries out several activities falling under the same subheading in the same installation or on the same site, the capacities of such activities are added together” [1, EC, 1996]
1.2.2 Equipment lifetime

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

1.2.3 Technical characteristics of installations

Due to the modular nature of the process lines, some techniques can be installed or changed relatively quickly and cheaply. For instance, some process solutions are changed on a regular basis, others are expensive with a long life and change is an investment decision. Some techniques may require alterations or extensions to production lines. Although the modular nature facilitates such changes, in many cases other factors will affect the ease of change, such as the limits of transporter mechanisms and control systems, and the space available in the installation. In-house operations tend to be for specific products. Introducing changes for these and for plants handling larger products such as steel coil coating, aerospace parts or automotive bodies may be more technically difficult and/or involve higher capital costs.

Because of over-capacity in the sector, it is rare for totally new plants to be built. In existing installations, it is more common to replace modules or lines.

1.2.4 Market structure

1.2.4.1 Competition

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

While this industry serves several major manufacturing areas, there is a high concentration of customers in some areas (such as the automotive industry) with highly competitive markets, and surface treatment over-capacity. Very few jobbing shops are large enough to serve more than three or four industry types or provide more than three finish options, with most company business strategies focused on specialising in certain finish types. There are some limited opportunities to differentiate the business by providing specialist treatment finishes and/or by specialist quality standards, or for vertical integration such as manufacturing the components to be treated. The in-house installation is the complete vertical integration of the business. The large-scale production lines depend on large volumes of very specific surface finish, such as one type of coating for steel coil, and typically opportunities for diversification or new markets are extremely limited.

1.2.4.2 Extent of the market

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

1.2.4.3 Substitutes

Substitutes in this context [88, EIPPCB] means alternative, competing ways for the customer to achieve the desired result, and not the substitution of chemicals or other processes described in Section 4.9. Alternatives are readily available for many of the surface treatments of metals and plastics. The customer may change because of price or for design reasons. This type of substitution can take three forms:

- a different surface treatment system. For example, electrolytic or chemical treatments compete with surface treatments by solvent-painting: painted car door handles have largely replaced chrome-plated ones; lithographic printing from aluminium plates can be replaced by laser or ink jet for small runs

- component manufacture from a different material. The customer may redesign the products or components from alternative materials, reducing the need for surface treatment. For example, paint or foodstuffs can be sold in plastic containers instead of metal cans; lithographic plates can be produced with different substrates such as plastics

- a combination of the above. Car light reflectors can now be moulded from plastic with vapour deposition of a metal, instead of copper/nickel/chrome plating of a steel pressing.

Figure 1.1 and Figure 1.2 show an example activity where customers can switch between anodising and other coatings, according to design trends, customer specification requirements and cost.

1.2.5 Summary of general economic situation

Opportunities to pass any increased costs to customers are limited because of:

- the large number of surface treatment installations competing for a decreasing number of customers
- the decline of engineering businesses in Europe
- the increasing substitution options (as described above).

1.3 Specific industry activities

1.3.1 Anodising of aluminium architectural panels and profiles

The surface treatment of aluminium predominantly for construction use as architectural profiles is carried out in more than 460 plants across 13 EU and 6 non-EU countries. Again, these are mainly small or medium enterprises. [9, ESTAL, 2002]
Figure 1.1: Total production of coatings for aluminium
(Source: ESTAL)

Figure 1.1 shows the total production for both anodising and other coatings for aluminium profiles in Europe.

Figure 1.2: Total European aluminium surface finishing of architectural profiles
(Source: ESTAL)

Figure 1.2 shows the European production of anodising by batch (jig line, see Chapter 2), other coatings by batch, and other coatings on coils from 1996 to 2000.

Figure 1.3 shows the production of the leading four European countries for anodising of profiles from 1996 to 2000.
1.3.2 Large scale continuous coating of steel

There are four types of electrolytic treatment systems applied to steel coil: tin plate, chromium (ECCS, electrolytic chrome coated steel), zinc or zinc/ nickel alloy and lead. [19, Eurofer, 2003 January]. (No data provided on other processes)

Electrolytic tin plate and electrolytic chromium coated steel (ECCS)

The main application for the substrate from this process is packaging. The production of continuous electrolytic tin plate and electrolytic chromium (ECCS) in EU-15 was 4800 kt in 2000. The trend in production for both tinplate and ECCS is shown in Figure 1.4 and by country in Table 1.2.

---

Figure 1.3: Leading anodising countries in Europe
(Source: ESTAL)

Figure 1.4: Steel for packaging (tin plate and ECCS) production in EU-15 (in kt)
(Source: APEAL)

1 APEAL: - The Association of European Producers of Steel for Packaging – a federation of four multinational producers of steel packaging for Europe across 7 countries. This represents some 90 % of the total European production of steel for packing and hence of Tinplate and ECCS lines.
<table>
<thead>
<tr>
<th>Country</th>
<th>Production (kt) tin plate in 2000</th>
<th>Production (kt) ECCS in 2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Belgium</td>
<td>281</td>
<td>12</td>
</tr>
<tr>
<td>Denmark</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Finland</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>France</td>
<td>886</td>
<td>207</td>
</tr>
<tr>
<td>Germany</td>
<td>802</td>
<td>147</td>
</tr>
<tr>
<td>Greece</td>
<td>69</td>
<td>-</td>
</tr>
<tr>
<td>Ireland</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Italy</td>
<td>283</td>
<td>67</td>
</tr>
<tr>
<td>Luxembourg</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Netherlands</td>
<td>612</td>
<td>51</td>
</tr>
<tr>
<td>Portugal</td>
<td>76</td>
<td>-</td>
</tr>
<tr>
<td>Sweden</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Spain</td>
<td>494</td>
<td>61</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>588</td>
<td>147</td>
</tr>
<tr>
<td>Totals</td>
<td>4091</td>
<td>692</td>
</tr>
</tbody>
</table>

Table 1.2: Production tonnages for the year 2000 for both tin plate and ECCS by country in EU15
Source EUROFER STATS

Tin plate and ECCS activities annual turnover is in the order of 3 EUR billion and employs directly and indirectly 15000 people.

There are installations in 9 EU Member States. The number of continuous coil production lines in EU member states operating, under construction and planned is shown in Table 1.3.

<table>
<thead>
<tr>
<th>Country</th>
<th>No of tin plate lines</th>
<th>No of ECCS lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Belgium</td>
<td>Unknown</td>
<td>Unknown</td>
</tr>
<tr>
<td>Denmark</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Finland</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>France</td>
<td>Unknown</td>
<td>Unknown</td>
</tr>
<tr>
<td>Germany</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Greece</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Ireland</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Italy</td>
<td>Unknown</td>
<td>Unknown</td>
</tr>
<tr>
<td>Luxembourg</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Netherlands</td>
<td>4</td>
<td>2 including tinning</td>
</tr>
<tr>
<td>Portugal</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Sweden</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Spain</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 1.3: Number of continuous tin plate and ECCS lines in EU-15

Figure 1.5 shows the share of tin plate and ECCS consumption by industries in the EU. Of an average annual production close to 5 million tonnes of this type of steel packaging, the human and pet food segments represent the main application with a 48 % share, followed by the general line (paint cans, industrial cans etc.).
Continuous electrolytic zinc/ zinc nickel (Zn/ZnNi) coating of steel

Since the 1970s, the production of zinc- or zinc alloy-coated steel sheet has increased significantly, particularly for the car industry. This is in response to the demand for longer car lifetime to fulfil anti-corrosion guarantees.

The production of continuous electrolytic Zn/ZnNi coating steel was 5.37 Mt in 2001. The evolution of the production in the EU-15 is shown in Table 1.1, below.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Germany</td>
<td>1400</td>
<td>1413</td>
<td>1567</td>
<td>1565</td>
<td>1632</td>
<td>1796</td>
<td>1828</td>
<td>1899</td>
<td>2001</td>
<td>1989</td>
</tr>
<tr>
<td>France</td>
<td>601</td>
<td>619</td>
<td>755</td>
<td>761</td>
<td>819</td>
<td>906</td>
<td>967</td>
<td>943</td>
<td>1071</td>
<td>957</td>
</tr>
<tr>
<td>Italy</td>
<td>374</td>
<td>393</td>
<td>507</td>
<td>559</td>
<td>420</td>
<td>452</td>
<td>479</td>
<td>361</td>
<td>484</td>
<td>384</td>
</tr>
<tr>
<td>Netherlands</td>
<td>234</td>
<td>271</td>
<td>524</td>
<td>599</td>
<td>447</td>
<td>705</td>
<td>871</td>
<td>863</td>
<td>922</td>
<td>794</td>
</tr>
<tr>
<td>Luxembourg</td>
<td>192</td>
<td>185</td>
<td>216</td>
<td>191</td>
<td>195</td>
<td>227</td>
<td>223</td>
<td>207</td>
<td>266</td>
<td>336</td>
</tr>
<tr>
<td>UK</td>
<td>343</td>
<td>370</td>
<td>415</td>
<td>450</td>
<td>470</td>
<td>511</td>
<td>526</td>
<td>486</td>
<td>462</td>
<td>261</td>
</tr>
<tr>
<td>Ireland</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Denmark</td>
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</tr>
<tr>
<td>Greece</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Portugal</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spain</td>
<td>133</td>
<td>151</td>
<td>180</td>
<td>179</td>
<td>187</td>
<td>168</td>
<td>262</td>
<td>251</td>
<td>266</td>
<td>284</td>
</tr>
<tr>
<td>Sweden</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Finland</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Austria</td>
<td>273</td>
<td>280</td>
<td>307</td>
<td>340</td>
<td>333</td>
<td>354</td>
<td>366</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td>3278</td>
<td>3401</td>
<td>4164</td>
<td>4578</td>
<td>4449</td>
<td>5071</td>
<td>5496</td>
<td>5344</td>
<td>5825</td>
<td>5372</td>
</tr>
</tbody>
</table>

Table 1.4: Production of continuous zinc/ zinc-nickel coating steel in EU-15 (x kt)

Continuous electrolytic lead coating of steel

There is only one continuous lead coating plant, in Austria. This plant will lose key European automotive customers and is due to close by 2005 - 6 because of other European legislation controlling the amount of lead in end-of-life vehicles [99, EC, 2000].

Other continuous electrolytic coating of steel

No data provided
1.3.3 Coil and sheet anodising for lithographic (offset) printing plates

[38, Ullman's, 2002/3] Lithographic or offset printing uses an intermediate roller to transfer ink from a plate to paper. It requires plate-making that is simple, quick, and economical. Aluminium is the usual substrate of choice. There are two types of plates:

- presensitised (PS) plates (manufactured with a photosensitised finish). Current world sales are about $180 \times 10^6$ m$^2$
- wipe-on plates which are not precoated and are coated by the printer as required. They are still being used in some countries, mainly the United States and Eastern Europe. Worldwide consumption amounts to about $30 \times 10^6$ m$^2$.

1.3.4 Printed circuit boards

No data provided

1.4 Key environmental issues

1.4.1 Overall

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

Surface treatments have traditionally been associated with large water usage creating a wet working environment, although many installations have moved away from this way of working. The chemicals used have the potential to cause environmental harm particularly to surface waters, groundwaters and soil. Metals removed from waste waters end up in solid wastes and, together with some used process solutions, may need special management for recovery or disposal. The industry can discharge fumes and dust to air, as well as generating noise. The sector is a significant user of electricity, water and non-renewable resources (metals). The following issues are crucial:

- minimisation of the consumption of raw materials, energy and water
- minimisations of emissions by process management and pollution control
- minimisation of waste production and its management
- improvement of chemical safety and reduction of environmental accidents.

The measures to achieve better environmental performance are frequently complex and have to be assessed in respect to their potential impacts on the product and other processes (both pre- and post-treatment), the age and type of installation as well as the benefits to the environment as a whole. Best available techniques will be balanced against these criteria and therefore include changes within process units as well as end-of-pipe abatement techniques.

Sophisticated process and treatment techniques play an important part in achieving improved environmental performance. Competent operation and regular maintenance are as essential as the choice of technology. Important considerations therefore include good management and working decisions and practices, good process and site design, education of the workforce on environmental and process performance, workplace safety and accident prevention, and finally, monitoring of the process and environmental performance.
1.4.2 Water

The activities covered in the scope of this document predominantly use aqueous solutions as the medium, therefore the management of water, its pathways and targets - the protection of surface water, groundwater and soils - are central themes. Both in-process techniques and end-of-pipe processes can affect the type and quantity of solid and liquid wastes produced (sometimes negatively), as well as changing the quality of waste waters.

Process waters are often treated in on-site waste water treatment plants. The discharge is then usually to municipal (urban) waste water (sewage) treatment plants, or if the effluent is treated to a suitable standard, directly to surface waters. This is the principal route for chronic pollution and can be caused by poor process controls and/or inadequate end-of-pipe controls. This may be due to poor management and maintenance, or lack of investment.

Although the industry has improved both its practice and infrastructure in many areas, it is still the source of a significant number of environmental accidents, [44, France, 2003]. For the Ile de France, from 1992 to 2002, 1.2% of all serious industrial water pollution incidents were attributable to this sector, rising to 5% for “near misses”. Thames Water plc in the UK has identified the sector as posing high risk to sewage operations [18, Tempany, 2002] The impacts can include the loss of biological sewage treatment processes, disruption of sewage sludge management, as well as damaging water resources for drinking water use and aquatic ecosystems.

Poor housekeeping or accidents in handling and storing solutions, including the failure of storage containers and process tanks, cause acute polluting discharges to surface waters, as well as both chronic and acute pollution events affecting groundwaters and soils. The batch discharge of used process solutions without inadequate treatment or which overload treatment facilities is also a cause of surface water pollution.

Water usage is also an important issue. The largest proportion of water intake is used in rinsing between process stages and then discharged. In some sites, significant amounts of water are used in cooling. There are no water losses in the processed workpieces or substrates, although there may be insignificant amounts in wastes. There are some losses in evaporation from drying components, hot solutions in open tanks and from some recovery processes. Some water is used in making fresh process solutions (make up); the service life of these solutions varies according to the activity and throughput.

1.4.3 Energy

Electricity is consumed in electrolytic and other electrochemical reactions (inter alia, electroplating and anodic oxidation). Electricity is also used to operate the process plant and equipment such as pumps, transporter equipment, other motors and compressors. It may also be used for supplementary vat heating (by immersion heaters) as well as space heating and lighting in the installation.

When electricity is transformed down from high voltage equipment, there can be losses known as 'funny energy'. Energy can also be lost when drawing from more than one phase, as well as in DC (direct current) supplies to the treatment lines. Energy is lost, too, as heat when electric current is passed through the treatment solutions: some process chemistries are less energy efficient than others.

Energy is also consumed in raising the temperature of the process baths, in drying components and for other heating activities. Losses occur from evaporation and as radiant heat from equipment. Some process chemistries require more heat energy than others. Energy is also used in drying workpieces or substrate and in extracting process fumes. Cooling can consume significant amounts of water in open flow or some cooling towers, and electricity is consumed by sealed refrigerating systems.
1.4.4 Substances of concern

Due to the wide range of process activities, the range of substances used and emitted by the industry is substantial. Table 1.5 identifies key substances used and the media they may affect when emitted. As most substances are used in aqueous solutions, they will be found in process waste waters as well as in-plant leakages and spills. Very little is known of the breakdown products in the processes.

<table>
<thead>
<tr>
<th>Principal substances of concern</th>
<th>Medium affected</th>
<th>Other issues to be considered</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water</td>
<td>Soil</td>
</tr>
<tr>
<td><strong>Metals:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Copper</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Nickel</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Chromium</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Tin</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Lead</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Cadmium</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Silver</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Iron</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Aluminium</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td><strong>Non-metals:</strong></td>
<td></td>
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</tr>
<tr>
<td>Cyanides</td>
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<td>✔</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>AOX (absorbable organic halogens)</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Peroxides</td>
<td>✔</td>
<td></td>
</tr>
<tr>
<td><strong>Surfactants:</strong></td>
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<td></td>
</tr>
<tr>
<td>Dispersing agents, emulsifiers,</td>
<td>✔</td>
<td></td>
</tr>
<tr>
<td>detergents, wetting agents (including nonyl and other alkyl phenyl ethoxylates brightening agents (brighteners)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Complexing agents</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDTA</td>
<td>✔</td>
<td></td>
</tr>
<tr>
<td>Tartrate, EDDS, NTA, gluconate,</td>
<td>✔</td>
<td></td>
</tr>
<tr>
<td>Quadrole</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium dithionite</td>
<td>✔</td>
<td></td>
</tr>
<tr>
<td><strong>Acids and alkalis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrochloric, nitric, phosphoric,</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>hydrofluoric, acetic</td>
<td></td>
<td></td>
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<tr>
<td>Sodium and potassium hydroxides,</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>lime</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Other ions</strong></td>
<td></td>
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</tr>
<tr>
<td></td>
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</tr>
<tr>
<td><strong>Solvents</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichloroethylene (TRI)</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Tetrachloroethylene (PER)</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Trichlorotrifluoroethane (CFC-113)</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td><strong>Gases</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorine</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td><strong>Dusts</strong></td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td><strong>Wastes</strong></td>
<td>✔</td>
<td>✔</td>
</tr>
</tbody>
</table>

Table 1.5: Key substances of concern and media potentially affected
Chapter 1

Process discharge problems with metals, cyanides, surfactants, complexing agents, acids, alkalis and their salts can be addressed by substituting processes and/or chemicals, and managing processes and rinsing systems to reduce the amount of chemicals dragged out of the solution on the substrates being treated. End-of-pipe treatment may also be applied.

1.4.4.1 Metals

The main impact of metals is as soluble salts. Metals are conservative materials, that is, they cannot be created or destroyed: they are neither created nor destroyed in the treatment processes or in waste water treatment. Their form may be changed and/or managed so they are not readily access environmental pathways but their disposal means that the metals still remain in part of the environment. Options exist for maximising their in-process recovery and recycling as well as for external recovery. They can also be separated in end-of-pipe systems into sludge. Metals not removed from the effluent accumulate in sewage sludge or in aquatic ecosystems. Management routes for municipal waste water treatment sludges vary in all Member States and are strongly dependent on the acceptability of applying the sludges to agricultural land. The metal content is a key determining factor.

Hexavalent chromium has adverse health effects, causing skin irritation and certain cancers. Aerosols are generated from the electroplating process solution by cathodic hydrogen evolution (see Section 2.5.3). Workplace health and safety regulations usually require measures to meet maximum allowable concentrations (MACs). Hexavalent chromium is also soluble at a wide range of pHs contributing to high aquatic toxicity. Its solubility means that for precipitation in waste water treatment, it must first be reduced to trivalent chromium.

Nickel sulphate is currently classed under Directive 67/548/EEC as a category 3 carcinogen2.

1.4.4.2 Cyanides

Cyanides are well-known hazardous substances but are still essential in some processes. As well as their inherent toxicity, cyanides give off cyanide gas in acid conditions. Cyanides can cause problems in effluent treatment by strongly complexing some metals, such as nickel, and this interferes with both the easy oxidation of the cyanide and the separation by precipitation of the metal (see complexing agents, below).

1.4.4.3 Hypochlorite, chlorine and AOX

Hypochlorite and chlorine are used in the oxidation of cyanide in effluent treatment plants. There are concerns that they are capable of reacting with organic substances to form AOX (absorbable organic halogens) [104, ÜBA, 2003]. Chlorine is the only gas likely to be used in surface treatment installations, and is not widely used. Hypochlorite can release chlorine in certain conditions, such as low pH.

1.4.4.4 Surfactants

Surfactants are widely used in many of the processes, such as in degreasing, in wetting surfaces and assisting other process such as etching, and as brighteners by promoting finely-divided metal deposition. Some surfactants have low degradability in aquatic systems, and the by-products of degradation may have adverse effects. Nonyl phenyl ethoxylate (NPE) is cited as being used in the industry [38, Ullman's, 2002/3]. For metal working, with effect from 17 July 2003, NPE and nonylphenol are banned except for uses in “controlled systems where the washing liquid is recycled or incinerated” [30, EC, 2003]

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2 R40: possible risk of irreversible effects. R42/43; may cause sensitisation by inhalation and skin contact.
1.4.4.5 Complexing agents

Complexing agents (complexons) including cyanides and EDTA retain metals as complexes and by preventing the adsorption the metal onto sediments or suspended sediments carry the soluble metals through effluent treatment systems and into sewage and aquatic systems. EDTA is both a strong complexing agent and has low biodegradability. Excess uncomplexed EDTA carried into aquatic systems may remobilise metals from sediments with high metals loads [22, Fraunhofer, 2002].

1.4.4.6 Acids and alkalis

Acids and alkalis are commonly used industrial chemicals and their discharge without neutralisation may affect sewers or receiving water courses. Spillage and leakage can also contaminate soils. When used in hot solutions the resulting fumes may cause problems in the workplace or locally when extracted. Hydrochloric acid is the most commonly used acid and its fumes can also cause corrosion damage inside the installation, affecting equipment controls. Specific problems occur with nitric acid, as it can release NOx when in contact with metals. This is local environmental and workplace health issue, as most installations are not significant NOx emitters.

1.4.4.7 Other ions

Chlorides, sulphates, phosphates and other salts are the necessary anions in treatment solutions and are not usually a problem when discharged to municipal waste water treatment plants. However, they may occasionally cause salinity problems, and phosphates contribute to eutrophication, especially if discharged directly to surface waters.

1.4.4.8 Solvents

Solvents are used for degreasing incoming components. 1, 1, 1-trichlorethane used to be widely used, but is being phased out under controls as an ozone layer damaging substance. The heavier solvents trichloroethylene and tetrachloroethylene can cause problems including accumulation in and leakage from sewerage systems [70, Ellis, 2001]. This can cause health and safety problems to maintenance workers and pollution problems to groundwater. Organic solvents have health and safety effects in use and the degree of control depends on the substance.

1.4.4.9 Dusts

Dusts are generated from linishing and polishing where these occur as directly related activities. They are usually a mixture of particles of abrasives with the abraded substrate. They may have internal health and safety impacts, but may also cause nuisance when extracted.

1.4.4.10 Wastes

Much of the waste produced from process activities is likely to be classed as hazardous [92, EC, 1991, 100, EC, 2000] The industry produces in the order of 300000 tonnes of hazardous waste a year in Europe\(^3\) - approximately 16 tonnes a year per installation. Liquid wastes are spent process solutions that cannot be treated or discharged, and solid wastes are largely sludges from waste water treatment plants and treatments of process solutions. Metals may be recovered from

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\(^3\) This derived from an industry estimate of <1% of hazardous waste in Europe and the Eurostat figures form hazardous waste management in the EU.
both solid and liquid wastes. Other solid wastes include broken equipment such as jigs, which may contain recoverable, materials and packaging for workpieces and used chemicals.

1.4.5 Other emissions

1.4.5.1 Noise

Surface treatment is not a major noise emitting industry. However, some activities do generate significant noise. The loading and unloading of loose components during delivery in stillages and loading for processing in barrels can give non-continuous peaks. Linishing and polishing generate continuous levels. Both may have associated in-house health effects.

1.4.5.2 Odour

Again, odour is not a major factor for this industry. However, odour can be associated with some activities, particularly acid fumes and especially when stripping metal layers. The impact will depend on the type and size of activity carried out, the design and operation of any extraction system (e.g. chimney height) and the proximity of receptors, such as housing.
2 APPLIED PROCESSES AND TECHNIQUES

General description of activities

The surface treatments of plastics and metals described in this document are mostly water-based and the installations carry out activities sequentially, usually in process lines made up of a series of vats or activities. Figure 2.1. shows a simplified process workflow of a typical process line. All lines (except some simple iron phosphating lines, see Section 2.5.18) contain more than one treatment or activity type, usually with rinsing vats in between. Some activities are waterless, such as drying and for printed circuit boards, drilling. The volume of an individual vat can range from a few litres for precious metal coating, to 500 m³ or more for some installations processing automotive and aerospace workpieces. Historically the surface treatment industry has been characterised by the large volumes of water used in processing, and these were often visible running across process area floors: this is no longer usual.

Figure 2.1: A simplified process line workflow diagram

A common feature of surface treatment installations is the large number and complex mix of processes and activities carried out in an installation, particularly in jobbing shops (Figure 2.2). Figure 2.6 shows a section through a typical jig plating process line with multiple processes and activities (note the activities are not carried out in numeric order because of transporter programming).

The size and complexity of the installation, the core activities and associated activities are dictated by:

- the type of surface treatments to be carried out
- the quality standards being worked to
- the type, size and amount of workpieces (substrates) to be treated
- the transport systems required to handle the workpieces.

These all also impact on the pollution potential from the installation.

After the activities described here, subsequent operations may be performed on the workpiece or substrate such as pressing, forming, bending, crimping, drilling, welding, soldering, etc. These subsequent operations, as well as the final use of the treated product, will be critical factors in determining the specification and type of surface treatment to be applied.
The manufacture of printed circuit boards is the most complex, and can involve over 40 activities.

Despite this complexity and the range of activities described in this chapter, all workpieces or substrates pass along a common route of activities, described in Figure 2.3. The first activity on-site is the delivery and storage (Section 2.1) of incoming workpieces, substrates and raw materials. Workpieces or components are loaded onto the appropriate transport systems (see Section 2.2) prior to pre-treatment, such as degreasing. Most workpieces or substrates are given more than one pre-treatment (see Section 2.3), and some of these may be prior to loading to a process line. The workpieces or substrates are then surface treated with one or more of the activities described in core processes. Rinsing, Section 2.4, is usually carried out between processing steps, whether pre-treatment and/or core processing. Treatment is followed by after-treatments such as drying, Section 2.6, and the workpieces or substrates are stored and dispatched (described in Section 2.1, together with incoming goods).

All the core treatment processes and other activities have historically been developed for jig lines. Indeed, jig lines still carry out the widest range of activities. The treatments are therefore described generically for jig lines, with specific issues for barrel and coil processing and printed circuit boards described subsequently: barrel processing in Section 2.7, coil processing – reel to reel in Section 2.8, coil processing for large scale steel coils in Section 2.9, coil and sheet processing for aluminium lithographic plates in Section 2.10, and printed circuit boards in Section 2.11.

There are also utility inputs - energy and water - to surface treatment installations (described in Section 2.12), as well as the use of abatement techniques for the treatment of water, waste and air emissions (see Section 2.13).
Electrolytic processes

An electrolytic process needs:

- a solution of electrolytes, i.e. capable of carrying a current
- at least two electron conductors (electrodes) and the ability to form a circuit
- a current – usually direct current (DC), although the voltage can be AC or reversing DC in specific cases.

The electrolytic process requires the electrolyte to complete an electric circuit between the electrodes. When the electrodes are connected to a source of direct current (DC) one, the cathode, becomes negatively (−) charged while the other, the anode, becomes positively (+) charged. The positive ions (cations) in the electrolyte will move toward the cathode and the negatively charged ions (anions) toward the anode. This migration of ions through the electrolyte constitutes the electric current in that part of the circuit. The migration of electrons into the anode, through the wiring and an electric power supply (supplied by rectifiers), and then back to the cathode constitutes the current in the external circuit. Electrolysis therefore converts electrical energy into chemical energy [11, Tempany, 2002, 34, Brett, 2002, 35, Columbia, 2002, 36, IUPAC, 1997].

Chemical energy in electrolytic reactions is associated with changes in the oxidation state in part of the circuit (in the electrolyte, at the anodes or at the interface) and can be manifested as some or all of the following:

- the dissolution of metal ions into electrolyte
- the deposit of metal from the electrolyte
- some layer conversion coatings, e.g. anodising, change the oxidation state at the anode surface (see Section 2.5.15)
- the release of gases. In the circuits discussed here, hydrogen and/or oxygen are the gases usually released.
Chapter 2

Electrolytic cells and reactions

When the workpiece or substrate (in this example, the strip to be plated) is connected to the circuit in the electrodeposition cell, the cations (in the example, Zn\(^{2+}\) and H\(^+\)) move towards the cathode (-ve). The metal is deposited while hydrogen is generated as a secondary cathodic reaction. The cations (e.g. SO\(_4^{2-}\)) move towards the anode (+ve). See Figure 2.4. [11, Tempany, 2002, 19, Eurofer, 2003 January, 39, 1993].

As example, the electrolysis in a zinc sulphate base electrolyte with an insoluble anode proceeds as:

As example, the electrolysis in a zinc sulphate base electrolyte with an insoluble anode proceeds as:

\[
\begin{align*}
\text{Cathode reactions (strip)}: \\
\text{Zinc depositing:} & \quad Zn^{2+} + 2e^- \rightarrow Zn \downarrow \\
\text{Generation of hydrogen:} & \quad 2H^+ + 2e^- \rightarrow H_2 \uparrow
\end{align*}
\]

\[
\begin{align*}
\text{Anode reactions:} & \quad 2 SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \\
\text{Decomposition of } S_2O_8^{2-}: & \quad 2 S_2O_8^{2-} \rightarrow 2 SO_4^{2-} + 2 SO_3 + O_2 \uparrow \\
\text{Synthesis of } H_2SO_4: & \quad SO_3 + H_2O \rightarrow H_2SO_4 \\
\text{Electrolysis of } H_2O: & \quad 2 H_2O \rightarrow 4 H^+ + O_2 \uparrow + 4e^- 
\end{align*}
\]

The choice, design and sizing of the other line components and associated activities are dependant on the choice of the electrolytic cell and its components. The choice of an electrolytic cell depends on:

- the industrial applications the producer intends to supply
- the layer type and thickness required (deposit and/ or conversion) and of the throughput capacity required
- the type of substrates (workpieces) to be treated
- the transport type required to move them: jig, barrel or coil.
Electrolytic cells may be classified in function by four main parameters:

- electrolytic cell geometry
- current density
- types of electrolyte bath (described for each process, below)
- anode types.

Two families of anodes are available:

- soluble anodes which have two functions: to provide metal ions to the electrolyte bath and to repel the positive ions towards the substrate (forming the cathode). The anodes are consumed during the process and need to be replaced regularly to maintain the solution strength. They are fixed on a supporting rail which carries the current to them.

- insoluble anodes have only one function: to repel the positive ions towards the steel strip (cathode). They are constructed of current carrying materials that do not take part in the solution reaction. They are used in electrochemical processes where the anode material does not take part in the process, such as electrolytic degreasing. Where there is deposition of material, process solution strength is maintained by additions as make-up, often from a separate feed tank, e.g. a zinc dissolution tank.

### 2.1 Delivery and storage – workpieces and consumable raw materials

#### 2.1.1 Incoming workpiece and/or substrates to be treated

The workpiece and/or substrates to be treated are delivered in different ways according to size, substrate material, quality and cost, and whether they are intended for in-house treatment or for external shipment to another site or a subcontractor. Jig treatment is most costly, and workpieces may be packed in bulk in stillages for cheaper steel components but are more carefully packaged for more valuable workpieces: from layering in stillages with protective inter-layers (to protect against physical damage and/or corrosion) to high-value components such as aluminium alloy aircraft wing sections being individually packed in robust boxes. Handling of workpieces can be mechanically or by hand. Barrel plating tends to be cheaper, where the quality of the finish is less critical and substrate is robust. Workpieces are usually transported loose in stillages and emptied mechanically. For coils, the external initial layers protect the rest of the coil. While small coils (in reel-to-reel processing) can be moved by hand, large-scale coils (because of their weight) need specialist equipment, such as air flotation rafts and overhead cranes.

**Environmental considerations**

The amount and type of packing used and the minimisation of loss of materials by damage to workpieces or substrate.

#### 2.1.2 Consumable raw materials

Raw material inputs will vary according to the installation and will depend on the chemistry the various processes carried out and the workpiece or substrate condition, shapes and surface area throughput. Larger sites will receive some liquid chemicals in bulk by tanker, most IPPC sites will receive at least some chemicals in IBC (Intermediate Bulk Containers) and all will receive liquids in sizes from 2.5 litres to 210 litre containers. Bulk liquid storage is in bulk tanks or in IBC containers, with smaller quantities being stored ‘as delivered’ and used from the delivery containers.
Large-scale solids deliveries may be by bulk tanker, but are more usually in the form of tonne bags. Most commonly, 25 kg sacks or drums are used for powders, pellets and flakes. Storage of bulk solids may be in silos, or in tonne bags.

Metals for deposition are usually delivered as anode bars or anode balls, but may be in proprietary solutions for chemical treatments (including autocatalytic processes) or precious metal plating.

Smaller quantities of chemicals are used in laboratories and for replenishing costly ingredients, such as in gold solutions or some trace components of process solutions.

The largest amount of chemicals in an installation are usually stored in use in the process line vats and the containment of these chemicals, the use of chemicals in maintaining the solutions and leakage issues are analogous to those for the incoming raw materials.

A description of the storage and handling of chemicals is given in [23, EIPPCB, 2002].

Key issues are:

- acids and cyanides should not be stored together or used in proximity because of the risk of generating free cyanide gas
- flammables and oxidising agents should not be stored together because of the fire risk
- chemicals which are spontaneously combustible when damp should be stored in dry conditions and not with oxidising agents because of the risk of fire
- spillages and leakages of chemicals can contaminate soil and water environments
- corrosive chemicals and fumes from their handling and use can cause corrosion of storage vessels, pipework, delivery systems and control systems.

2.2 Loading for processing

When workpieces are in a suitable state for the core treatments, they are loaded for processing processed using one of the three transport types described below [104, ÜBA, 2003]:

- Jigs or racks - frames carrying the workpieces singly or in groups
- Barrels - plastic cylinders holding many workpieces
- Coil - coils or reels of substrate working on a continuous basis.

Jigs - Jigs provide both physical support for handling as well as electrical contact. Jigs may be used all sizes of components from small, such as jewellery and small precision engineered components, to large installations handling parts of aircraft and automotive bodies. Small components are placed by hand on jigs (frames). The s are hung, usually being clipped onto springs forming part of the jig or are wired on using copper wire to carry the current. Jigs are hung on flight bars which are used both to move the jigs through the core process steps and (where the processes depend on electrical current) provide the electrical contact. The flight bars sit in V-shaped cradles at each process vat, which are also contactors for the vats using electrical current. For very large components, the jig may be a large platform or frame without a separate flight bar.
Flight bars can be moved by two types of mechanism:

- transporters, which are hoists travelling on rails running the length of the process line. This is the most flexible type of system and can be programmed for various finish options, with different dwell times in different vats, or operated manually.

- beams, where the flight bars are hung on a beam. The beam moves up and down at present intervals. In the up position, the flight bars are moved to the next process vat position. However, the only way of varying the process time in different vats is to change the tank length.

In process lines with low throughput, jigs may also be moved by hand.

**Barrels**

Barrel lines tend to be used for high-volume, lower-cost work such as nuts and bolts, and can only achieve lower quality finishes than jigs. Barrels are usually hexagonal or octagonal plastic drums, with many holes in the long panels allowing access for the process liquids. The barrels are usually moved by transporter systems, although for very small components (such as contact pins being gold plated) small barrel units can be moved by hand. They are loaded from stillages of components. Usually workpieces are emptied from stillages onto the floor, and the barrels are then loaded manually using a shovel. Large-scale barrel operations may use a mechanical loader or a mechanised system. The barrel hangs from V-section cradles, which carry current at the appropriate process vats. The barrel spindle carries current to a flexible electrode which trails in the barrel from the central spindle and carries current to the loaded components in the relevant process vats. The barrel is constantly rotated usually via a drive mechanism on the side. The current is then passed through a flexible inert anode which trails in the rotating barrel and current is passed through the contacting workpieces.

**Small coils (reel to reel)**

*No information provided*

**Steel coils**

Coils can be up to 12 tonne rolls of steel up to 2008 mm wide. Coils are loaded in an entry loader section and welded onto the end of the preceding coil, Section 2.9

**Aluminium coils**

*No information provided*

**Printed circuit boards**

The transport of boards can vary during production, they are moved both as individual boards across rollers in some parts of the process lines and in other parts they are moved in sets on jigs.

### 2.3 Workpiece or substrate pre-treatment

Workpieces or substrates to be surface treated must be clean from dust, swarf and moulding flash, as well as being corrosion- and grease-free to ensure uniform application and permanent adhesion of the surface treatment. Many workpieces or substrates are oiled to prevent corrosion in transit or from a previous operation such as pressing. Usually (but not necessarily) the workpieces will need to be totally smooth to produce a high-quality treated finish. Some preparation of the workpieces may be carried out at the site producing them, but these activities are also carried out at the surface treatment installation [6, IHOBE, 1997].

Activities preparing steel coil and wires prior to surface treatment in coil coating process lines are described in [86, EIPPCB, ].
Chapter 2

While virtually all process lines include degreasing, where components are heavily oiled or surface preparation is critical it may be necessary to supplement this by an additional pre-degreasing step [104, ÜBA, 2003].

The pre-treatment steps not only remove greases and oil, but also remove oxides and provide chemically active surfaces the subsequent treatment.

**Linishing and polishing**

Individual components are linished using abrasive belts, and then polished with an abrasive paste applied on fabric mops, which removes fine marks and gives a highly polished finish. These activities are carried out less frequently as modern production techniques produce better engineered components than in the past, or use alternative materials such as plastics which can be precision moulded. Where large numbers of workpieces are handled, the linishing and polishing are usually automated.

**Environmental considerations**
Noise and dust are associated with this activity.

**Abrasive blasting**

This traditionally uses sand or grit, but may use softer, finer abrasives such as ground nut shells. These techniques may be used to de-stress the surface of the workpieces.

**Environmental considerations**
Noise and dust are associated with this activity.

**Deburring/ tumbling**

Applied to smaller, mass-produced components often followed by barrel treatment. The workpieces are mixed with abrasive stones and tumbled or vibrated for several hours.

**Environmental considerations**
Noise and dust are associated with this activity.

**Solvent degreasing**

Solvent degreasing is usually by means of chlorinated hydrocarbons (CHC), ketones, mineral spirits or hydrocarbons [90, EIPPCB, , 104, ÜBA, 2003]. In the past CHCs were used because of their good cleaning efficiency and universal applicability, as well as their quick drying and incombustibility, but their use is controlled by internationally (see environmental considerations, below).

There are two types of process:

- **cold cleaning:** The workpieces and/or substrates are immersed in the solvent or in cleaned in a stream of solvent. In some cases, the solvent is pumped round taking the liquid from near the top of a holding tank. Leaving dirt to settle at the bottom. The tank is cleaned periodically

- **vapour phase:** The solvent is vaporised in a purpose-built bath and the cold component suspended in the vapour. The vapour condenses on the component dissolving grease and draining off leaving the component clean and dry. The most common solvents are CHCs. As the vapours are heavier than air they are contained in the bath. Hydrocarbon solvent may be used.
The choice of solvents will depend on the substrate to be cleaned, the type of oil or grease to be removed, the previous manufacturing process and the requirements of the subsequent surface treatments. Chlorinated ethanes and ethylenes attack aluminium and should not be brought into contact with substrate, tanks, containers, valves, etc. made of aluminium. Dichloroethylenes in contact with copper should be avoided under all circumstances as explosive acetylidines may be formed.

Ketones and mineral spirits may be used, but are flammable. Higher hydrocarbons with a narrow distillation range give the highest flash point commensurate with solvent drying from the workpieces and/or substrate.

**Environmental considerations**
Because of the classification of certain CHCs as potentially carcinogenic materials, their water-endangering potential and problems with emissions to the atmosphere their use is strongly regulated [93, EC, 2000, 97, EC, 1999]. Other solvents may be inflammable.

**Air knives**
*No information provided*

**Centrifuges**
Centrifuges are used on a batch basis to remove excess grease, and usually applied to smaller workpieces prior to barrel treatment.

**Hot water**
Hot water is used effectively to remove oil and grease, especially from steel panels. It is widely used in the automotive industry.

**Environmental considerations**
Energy consumption.

**Dry ice**
*No information provided*

**Hand wiping**
Hand wiping with an absorbent such as ground chalk or limestone. This is carried out on large, high value workpieces such as aerospace components.

**Chemical aqueous (soak) degreasing**
The workpieces are placed in this process solution for several minutes. The solution may be acid, neutral or alkaline and normally working at increased temperatures (50 - 90 °C) because of the improved cleaning effect. The main components of the aqueous cleaning system are alkalis or acids, silicates, phosphates and complexing and wetting agents. Aqueous cleaning systems work either by forming unstable emulsions (known as demulgating systems) or stable emulsions. [3, CETS, 2002, 104, UBA, 2003]
Aqueous chemical systems avoid the use of solvents. The cleaned items can remain wet if the subsequent treatment is water-based, such as electroplating. Process solutions have a short life, dependent on throughput and the amount of oil or grease on the workpieces.

**Environmental considerations**

Process tanks operate at 50 - 90 °C and may require fume extraction to remove water vapour and alkaline or acid fumes.

Rinse waters may require simple pH treatment in effluent treatment plants.

Metals can be stripped from the substrate surface (including trace elements such as lead which may have toxic effects). They can be separated after pH adjustment.

Used acid or alkali solutions are often treated separately as they create a large pH change which may not be accommodated by continuous flow effluent treatment plants.

Cleaning solutions may need to be separated from other process effluents to avoid interference with the effluent treatment plant by excess surfactants.

**Biological aqueous degreasing**

![Diagram of biological aqueous degreasing process](image)

*Figure 2.5: Biological aqueous degreasing process*

Source: [3, CETS, 2002]

Similarly to the chemical degreasing system, workpieces are placed in the process solution consisting of mildly alkaline emulsifying cleaners. In this case, the operating temperature is lower (approximately 45 °C). The ingredients include a surfactant to lift and emulsify dirt and oil from the surfaces, naturally-occurring micro-organisms to degrade the oils to carbon dioxide and water, and nutrients for the micro-organisms. Air is bubbled into the solution at a low rate to ensure the system stays aerobic. The solution is continuously circulated through a side tank, containing the micro-organisms, where additions of nutrients and other process chemicals are made and the solution continuously regenerates itself with the occasional removal of small amounts of sludge from the side tank. [18, Tempany, 2002, 31, Biowise, 2001].
**Key issues:**

Runs at more neutral pH, lower operating temperatures.

Reduced use of process chemicals as the solution rarely needs replacement.

Reduced usage of neutralising chemicals when discharging used process solution and impact of surfactants on effluent treatment.

Reduction in use of less hazardous chemicals in the workplace.

Reduces downtime of production line to replace spent solutions.

Ensures consistent quality of degreasing versus changing quality of chemical degreasing with short service life.

Lower evaporation losses therefore less need to extract water vapour.

Not all oils and greases may be suitable for this treatment. (Verbal discussions on-site visits and with TWG members).

**Pickling and descaling**

Pickling and descaling are chemical metal-stripping procedures used to brighten the degreased metallic surface prior to other surface treatment processes. The bulk pickling of steels is described in [86, EIPPCB]. During the pickling processes disturbed or adhering layers, such as scale, oxide films and other corrosion products of the metal, are removed by chemical reaction with an acid-based pickling agent. In order to remove strong oxide layers effectively, specified acid concentrations, temperature and pickling times must be adhered to. Hydrochloric or sulphuric acids are normally used. In special cases nitric, hydrofluoric or phosphoric acid, or mixtures of acids are used. Fluoride-containing solutions are necessary for reliably pickling certain alloys. The pickling of aluminium and its alloys is usually carried out in sodium hydroxide solutions, fluorides being added where necessary. Zincate treatment of aluminium is necessary for good adhesion prior to autocatalytic or electrolytic metal plating. This solution is based on sodium hydroxide containing <20g/l zincates. [3, CETS, 2002, 104, ÜBA, 2003]

The typical pickling reaction is described by the following chemical equation:

\[ \text{Metal oxide + pickling solution} \rightarrow \text{metal ion + water} \]

Some erosion of the metallic surface is desirable, but excessive attack of the acid on the basic material is unwanted. Hydrogen is usually formed:

\[ \text{Metal + pickling solution} \rightarrow \text{metal ion + hydrogen} \]

The attack can be reduced by using so-called pickling inhibitors. These also cause an inhibition of hydrogen development, thus minimising so-called "pickling brittleness", caused by entrapment of hydrogen in the metal crystalline structure at the surface.

The concentration of the ions of the dissolved metal increase in the pickling solution while the strength of the free acid declines. The acid consumption associated with the dissolution of metal and metal oxide can be easily be supplemented by adding fresh pickling solution. However this technique is limited by the constantly increasing metal content. A maximum iron content of 8 % is recommended for sulphuric acid, 12 % for hydrochloric acid and 2.5 % for phosphoric acid. When the limiting concentrations are reached, the pickling solution must be disposed of completely or partly [104, ÜBA, 2003].
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The workpieces to be pickled must be completely grease-free, otherwise uneven pickling will occur as the acid attacks grease-free areas only. The use of wetting agents accelerates the pickling procedures as the workpieces are wetted better and more quickly. Iron materials can be derusted and descaled in so-called acid degreasing agents without prior degreasing. The commercial acid degreasing agents contain mixtures of wetting agents and emulsifying agents, which can support the emulsification of fats and oils in strong acid media.

Sulphuric acid is usually recommended for pickling. The pickling time is reduced with increasing acid concentration and temperature. In the case of a sulphuric acid concentration of 25% a maximum pickling effect is reached. Above this the pickling speeds decreases. The optimal temperature is at 60 °C.

The pickling effects can also be accelerated by movement of the workpieces in the pickling solution or movement of the pickling solution by air injection. An air extraction system may be installed.

Hydrochloric acid is also good for descaling and pickling. It works rapidly in most cases, with a concentration of 18 - 22%. However its disadvantage is aggressive vapours. Heating up to 30 - 35 °C not only increases the pickling effect but also the formation of hydrochloric acid air emissions.

Hydrofluoric acid is nearly exclusively used for the pickling of cast iron, for example engine blocks. A concentration of 20 - 25 % (as HF) and temperatures of 35 - 40 °C are generally preferred.

Environmental issues
Process tanks may need to be equipped with fume extraction to remove generated aerosols and hydrochloric acid gas and nitrous oxides if nitric acid is used.

Spent pickling solutions require either treatment and disposal through effluent treatment system or disposal as liquid wastes.

Effluents can easily be treated in normal waste water treatment plants.

Ultrasound assisted pickling

No information provided

Metal stripping

Metal stripping is necessary for the processing of defectively electroplated components or for the new treatment of nascent workpieces. It may be also used for the recovery of expensive metals (such as the precious metals), both from the base metals and the coating materials. Often scrap iron can be only be regenerated if problem metal coatings are removed. The metal stripping of jigs and/or of jig contacts used in the electroplating process extends the life of the jigs and recovers the metal deposited.

To preserve the form of the surface to be stripped, the metal stripping techniques should remove the coat material quickly and safely and not attack the base metal. In exceptional cases, an electrolytic activation of the coat can be necessary, for example with chemical chrome stripping. Chemical procedures are simple in application and they require less expenditure on plant equipment. On the other hand, electrolytic procedures usually work more quickly, more economically and with more control. They are therefore preferable for activities such as the metal stripping of rack contacts.
Environmental considerations
The use of strong acids can generate spillage capable of attacking concrete floors and subsequently polluting the soil and any groundwater beneath with acid and the dissolved metals. The disposal of used acid stripping solutions may exceed the treatment capacity of effluent systems. Acid fumes and mists are caused by reaction with the metals and substrate. These can cause local air problems, health effects in staff and deterioration of equipment in the installation.

Stripping of previous treatments is often carried out as a batch process outside of the normal process controls of an installation. They are a potentially significant source of breach of permit conditions and pollution from the industry.

There can be increased waste production (in sludges from treatment and used acids), as well as wasted energy, water and raw materials where defective components are stripped for reworking.

Electrolytic activation (also known as electrolytic degreasing)

The pickling of metals is often followed by electrolytic activation to remove the remains of unwanted residues from the surface. Oil and dirt remain trapped in the micro-roughness of the substrate surface. These are removed by the formation by electrolysis of H₂ at the surface of the cathode and O₂ gas at the surface of the anode [19, Eurofer, 2003 January]. The basic composition of the solution is similar to alkaline degreasers, although the chemical concentration is generally twice as high. Wetting agents are omitted to prevent foaming; however, cyanides or other complexing agents may be added to improve the activation of steel items. For normal applications, cyanide- and chelating-agent free electrolytes are sufficient. The solution lifetime is mainly determined by dilution through drag-in of rinse water and drag-out of process solution. [3, CETS, 2002]

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

Rinse effluents and used solutions can be treated as alkaline or cyanide solutions in waste water treatment plants.

Pre-treatment of plastics

Pickling of plastic

The pickling of plastic is a prerequisite for good metal adhesion. It is carried out in an aqueous mixture of chromic acid (380 g/l), sulphuric acid (380 g/l) and wetting agent. It is applied to ABS-type plastic surfaces to oxidise and dissolve the butadiene component, thus generating a micro-rough surface. [3, CETS, 2002]

Environmental considerations
Process tanks may 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 CrIII to CrVI.

Effluents can easily be treated in a similar manner to other hexavalent chromium containing solutions in waste water treatment plants.
Conditioning of plastics

This process step is essential in the surface treatment of plastics and printed circuit boards. It provides wetability of the surface as prerequisite for subsequent voidless covering and good adhesion of metal layers. [3, CETS, 2002, 77, BSTSA]

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).

Environmental considerations
Effluents may require pH adjustment in waste water treatment plants.

2.4 Rinsing and drag-out

Drag-out is the liquid from the previous process which adheres to the workpiece or substrate surfaces. Rinsing is necessary:

- between most process steps to prevent cross-contamination of process solutions
- to ensure there is no deterioration of the workpiece and/or substrate surface by residual chemicals, such as by over-reaction or by staining by the drying of dissolved chemicals.

A reduction of drag-out is a primary measure for minimising losses of chemicals, operating costs and environmental problems in rinse waters.

Rinsing is therefore a common activity carried out after nearly all process steps in surface treatment [3, CETS, 2002] Figure 2.6 shows a section through a typical jig plating line with six rinsing stations [65, Atotech, 2001].

Rinse water may vary in quality depending on the process requirements (see Section 2.2.2). Many rinsing techniques have been developed to reduce water consumption to a minimum, and some of these are discussed in Sections 4.5 and 4.6. There is usually a balance to be sought between achieving the requisite cleanliness of the surface, the quality and quantity of the water used, and the way rinsing is carried out.

![Figure 2.6: Section through typical jig plating process line](source)

Source: Atotech Deutschland GmbH
Environmental considerations
Rinsing is one of the largest potential sources of water-borne contamination as rinse waters carry all the process chemicals from an activity. In many cases rinse waters are treated prior to discharge (treatment options are discussed in Section 2.13.1). Key issues are:

- minimisation of the loss of materials, including possible re-use of rinse water
- metals: these are conservative, i.e. can only be treated and moved to another waste stream, but cannot be destroyed
- cyanides: these are usually treated by oxidation.
- complexing agents: (including cyanides) these may need to be treated separately to enable metals to be successfully treated subsequently
- surfactants, brighteners and other additives may interfere in waste water treatment or have their own environmental impacts
- other cations may have local water quality effects.

Rinsing is also one of the two largest water usages in installations (the other large use is cooling).

2.5 Core activities

2.5.1 Copper and copper alloy plating

[3, CETS, 2002] Copper plating is common for items in daily use, such as coins, buttons or zippers with a patina for haberdashery. These types of workpieces can be plated on jigs or in barrels. Copper plating is also essential in printed circuit board manufacture, see Section 2.11.

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 no 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.

Another high performance electrolyte is based on copper cyanide and sodium cyanide with potassium sodium tartrate providing higher current densities system, enhanced brightness of layers and reduces the tendency to anode passivation. Metal content is 40 – 60 g/l.

Potassium carbonate is generated in potassium-based systems during processing. This disrupts bright copper deposition and causes roughness at concentrations beyond 90 g/l.

Environmental considerations
Process tanks may 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 can be treated in normal waste water treatment plants, with a cyanide oxidation stage.

**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 copper plating on furniture frames, bathroom fittings, wire work, etc. The normal copper content is 50 – 60 g/l and sulphuric acid is 60 – 90 g/l.

An important technical application of acid copper electrolytes is for through-hole, panel and pattern plating of printed circuit boards and multilayers. 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 and the copper concentration is 20 g/l.

The solutions are also cyanide free, do not suffer from carbonate build-up and are more electrolytically efficient.

**Environmental considerations**

Process tanks may need to be equipped with fume extraction to remove aerosols generated by air agitation of the plating solution.

Effluents can be treated in normal waste water treatment plants for low pH and to remove copper.

**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/l) and ammonia (3 g/l).

They are used for special technical applications such as shielding on heat treated parts, as a drawing aid for wires, and for other thick bright layers that need little or no polishing, to prevent hydrogen embrittlement and as intermediate layer below nickel and silver.

Pyrophosphate electrolytes can also be used for through-hole and panel plating of printed circuit boards and multi-layers, but are currently substituted mainly by acid copper electrolytes.

Pyrophosphate is continuously decomposed by hydrolysis, shortening the lifetime of the process solution. Appropriate regeneration means are not currently available.

**Environmental considerations**

Fume extraction is normally used at process tanks.

Effluents have to be treated with lime, as sodium or potassium hydroxides do not precipitate copper from the pyrophosphate.

Due to the ammonia content, separate treatment from other metal-containing effluents is required.

**Brass**

Brass is predominantly an alloy of copper and zinc although nickel, tin, or lead may be added. A mixture of copper and zinc cyanides in solution 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 to 90 g/l and working pH around 10. The deposited alloy contains 65 to 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 different finishes can be obtained through a subsequent chemical colouring of the deposit.

**Bronze**

Bronze is copper alloyed with tin and zinc. Cyanide bronze alloy is used as a decorative plating process. It is used as a substitute for nickel in jewellery as a "nickel free" coating to avoid skin allergy effects.

The metal concentration in this stannate and cyanide-based electrolyte is 4 – 10 g/l of stannate, 4 – 20 g/l copper, and 1 – 4 g/l zinc, with 6 – 10 g/l potassium cyanide. It is used in two different colours: white or yellow bronze.

Lead is used in low concentration as a brightener in some electrolytes. Its use in the future in many products is banned by new directives. [98, EC, 2003, 99, EC, 2000]

Cyanide oxidises with the passage of current to carbonate. Solutions have to be discarded as soon as the carbonate level exceeds 40 g/l.

**Environmental considerations**

Process tanks may need to be equipped with fume extraction to remove generated aerosols.

Effluent can be treated for pH, cyanide and metals in a typical waste water treatment plant with a cyanide oxidation step.

### 2.5.2 Nickel plating

[3, CETS, 2002] Nickel deposits can be found on decoratively plated items such as screws, nuts, cutlery, trays, bathroom and furniture fittings and items inside and outside of motor vehicles. Nickel plating simultaneously provides excellent corrosion resistance for any base material. On copper layers and below final chromium layers it gives a highly reflective finish and is the usual barrier layer below silver or gold finishes.

**Overall environmental considerations**

Health effects from nickel sulphate are described in Section 1.4.4.1. Aerosols from air-agitated nickel plating solutions may be extracted from the process and a mist eliminator is often employed. Effluent from mist eliminators and scrubbers may require treatment in a typical waste water treatment plant.

**Nickel plating - watts type**

Watts-type 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 a small amount of organic semi-brightener (<1ml/l) and wetting agent (<1 ml/l) for a semi-bright finish to primary and secondary brighteners (10 - 20 ml/l) and wetting agent (<10 ml/l) for a bright finish.

The level of organic content is influenced by the quantity, quality and mixture of primary and secondary brighteners, which significantly influence the properties of ductility, levelling, brightness and hardness as well as internal stress.
Air, solution and/or workload agitation allow the use of higher current density.

The process tanks operate at 50 – 70 °C.

Regular activated carbon treatment is generally sufficient to provide unlimited lifetime of the plating solution.

A steady increase in nickel content is observed when drag-out recovery is implemented to reduce electrolyte losses. The installation of membrane anodes with individual DC supply keeps the nickel concentration at a constant level.

**Environmental considerations**
See overall environmental considerations, above.

The removal of the decomposition products of organic additives by adsorber polymers extends the lifetime of the plating solution. With other measures (see Section 4.6), closed loop operation is therefore achievable, thus reducing effluent and the need for effluent treatment to almost zero.

**Sulphamate nickel**

Sulphamate nickel-based electrolytes have a nickel content of 60 – 140 g/l 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.

A sulphamate electrolyte is more expensive than a Watts type. It is mainly used for, but not limited to, depositing thick nickel layers (>2000 µm) for technical applications, e.g. 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.

Ammonia is continuously generated and reduces the ductility of the finish and limiting the life of the plating solution. Continuous electrolytic cleaning is also necessary to keep metal contamination at the lowest possible level.

**Environmental considerations**
See overall environmental considerations, above.

Due to ammonia as a breakdown product, the effluent may require separate additional treatment to a typical waste water treatment plant.

**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. The application of a dull satin nickel layer has gained importance in many industrial areas: it is applied on decorative parts for the automotive industry as well as on bathroom and furniture fittings.

**Environmental considerations**
See overall environmental considerations, above.
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 for processes operated at ambient temperatures. Nickel strike deposits are applied for activating passive nickel surfaces and stainless steel prior to further metal plating.

Environmental considerations
See overall environmental considerations, above.

Nickel composite plating

Nickel composite coatings have a small niche market for special applications. Electrolytes contain hard particles such as silicon carbides, diamond and aluminium oxide to provide a surface with increased hardness and wear resistance, or soft particles such as PTFE, graphite and molybdenum sulphide to reduce friction.

The composition of the process solutions, process properties and environmental impact are similar to Watts-type electrolytes.

2.5.3 Chromium plating

[3, CETS, 2002] Chromium plating has found wide usage both as a decorative surface finish (bright chromium plating) and as a functional coating (hard chromium plating), because of its typical high hardness and wear resistance properties. It is also widely used in packaging applications (see Section 1.3.2).

For decoration, it is usually applied on very level 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.

Bright chromium can be plated either from the traditional hexavalent chromium electrolyte, or from the newer technology using trivalent chromium electrolyte.

Hard chromium plating (usually known as “hard chrome”) consists of heavy deposits applied on particular components (drive shafts, hydraulic cylinders, pins, valves, etc) to give high resistant to mechanical and wear damage. Hard chromium plating can only be plated from hexavalent chromium electrolytes.

Aerosols are generated from the process solution by cathodic hydrogen evolution. The health effects of hexavalent chromium are described in Section 1.4.4.1.

Overall environmental considerations for hexavalent chromium
Process tanks are normally equipped with fume extraction to extract chromium aerosols.

Fume suppressants may be used to control foaming and to reduce the amount of aerosol.

Extracted vapours may be treated through a suitable mist eliminator and the wash liquor treated with other chromium effluents.

Effluents may be treated in a typical waste water treatment plant, with reduction of CrVI to CrIII followed by flocculation and precipitation.
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Bright chromium plating (hexavalent chromium electrolytes)

Bright hexavalent chromium plating electrolytes are based on chromic acid (180 – 350 g/l) and a catalyst, containing sulphate (1.8 – 3.0 g/l) or fluoride ions (<2 % of the concentration of the chromic acid). Where high corrosion protection is required so-called "micro-cracked or micro-porous" chromium coating can be applied using readily available techniques.

Decorative chromium coating properties are determined by the characteristics of the nickel underlayer, by the CrO$_3$/ catalyst ratio and by the operating temperature (20 – 38 °C).

Environmental considerations
See overall environmental considerations for hexavalent chromium, above.

Bright chromium plating (trivalent chromium electrolytes)

Bright trivalent chromium plating electrolytes are based on chromium III compounds, such as sulphate or chloride, together with proprietary chemicals. The electrolyte contains only about 20 g/l of the trivalent chromium, compared with about 200 g/l of chromic acid in the hexavalent chromium process.

The use of trivalent chromium eliminates the carcinogenic and other hazards associated with hexavalent chromium in the workplace. Fume extraction and scrubbing, or fume suppressant are not required.

The lower electrolyte concentration has a lower viscosity than hexavalent electrolyte. This results in better draining of plated parts, and subsequently less drag-out, less loss of electrolyte, less effluent treatment required and less chromium-containing waste being produced.

Environmental considerations
There is no hexavalent chromium aerosol to control.

The significantly reduced drag-out losses result in much reduced associated effluent treatment and sludge disposal requirements: up to 90 % reduction is possible.

The waste water requires less chemical treatment as the chromium is already in the trivalent state and will precipitated at a suitable pH.

Hard chromium plating

[3, CETS, 2002, 74, BSTSA] 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 (<2 % of the content of the chromic acid)
- pre-prepared proprietary fluoride-free (<2 % of the content of the chromic acid).

The catalyst choice is fundamental to the efficiency of the electrolyte (from 16 – 17 % for the sulphate catalyst to 25 – 27 % for the pre-prepared proprietary fluoride-free type). The type of catalyst used, and the operating temperature have a great influence both on the physical properties (cracked, micro-cracked and crack-free coatings) and on the chemical and mechanical properties, e.g. the corrosion and wear resistance, the mechanical workability, etc.

Environmental considerations
See overall environmental considerations for hexavalent chromium, above.
Rinse water from the rinse section subsequent to the chromium plating tank is generally used to replenish the level of the process solution. Due to the very long plating times and to the high process temperature (50 – 60 °C) there is usually sufficient evaporation to use all this rinse water. Hard chromium plating plants therefore do not generally have a CrVI effluent.

### 2.5.4 Zinc and zinc alloy plating

[3, CETS, 2002, 78, BSTSA] Zinc and zinc alloy coatings are the most widely used electrolytic surface treatment, providing corrosion resistance and/or cheap decorative coating to a very wide variety of iron and steel items for the automotive, construction and other industries. For example, they are used for steel sheet or wire, screws, washers, nuts, bolts, shopping trolleys, construction frames (chassis) and casings for domestic appliances (such as washing machines) and many other kinds of applications (see Section 1.1).

Zinc layers require post-treatment (see Section 2.5.19): in conjunction with various coatings, zinc layers of only 6–18 µm thick will be sufficient to protect parts for their whole working lifetime.

Zinc plating has been in existence for a hundred years and because of its wide application, many different electrolyte systems are in use. The most common ones are described below.

**Overall environmental considerations**

Zinc ores contain cadmium. At the purity used for zinc electroplating, anodes contain 1 gram of cadmium per tonne of zinc. Trace quantities of cadmium may therefore appear in the effluent. These traces are largely removed in typical waste water treatment plants, and will be in the sludge produced.

**Alkaline cyanide zinc**

This is used mainly for technical (non-decorative) corrosion resistant layers. The process electrolytes are easy to operate, and have compositions of zinc oxide (10 – 30 g zinc/l), sodium hydroxide (80 – 120 g/l) and sodium cyanide (5 – 100 g/l). They operate at pH values close to 14, using both soluble and insoluble anodes.

Fineness of zinc structure deposited gives a ductile deposit for post surface treatment forming or bending.

The cyanide-based electrolyte has good throwing power into holes and blind spaces.

The plating solution has low conductivity, thus a higher voltage (6 - 8 V for jig plating, 10 -15 V for barrel plating) and a higher energy demand is needed. Power is also consumed by the electrolytic oxidation of cyanide to carbonate. Carbonate build-up can be dealt with by crystallising out (see Section 4.10.4), which also removes metallic impurities in the electrolyte...

The current efficiency is near to 50 %, but decreases with increasing current density.

Fume extraction of the process tanks to remove aerosols may be used.

**Environmental considerations**

There is an industry tendency towards decreasing the cyanide content because of environmental and safety reasons.

Cyanide in rinse waters can be readily oxidised by several methods in the effluent treatment plant.

Zinc can be readily removed in a typical waste water treatment plant.
Alkaline cyanide-free zinc

These are mainly applied for technical corrosion resistant layers (non-decorative). The process solutions contain zinc oxide (5 – 15 g zinc/l) and sodium hydroxide or potassium hydroxide (100 – 150 g/l). The weakness is lack of stabilising cyanide. The process can give better metal distribution than cyanide electrolytes.

The plating solution has a low conductivity, thus a higher voltage (6 - 8 V for jig plating, 10 - 15 V for barrel plating) and higher energy demand is needed

Current efficiency near 50 %, decreasing with increasing current density

Environmental considerations
Zinc from rinses can be readily removed in an effluent treatment plant.

Acid zinc

Acidic zinc electrolytes give bright decorative layers, and used, for example, on furniture frames, shopping trolleys and baskets. In conjunction with post-treatments, they provide corrosion resistance comparable with finishes from alkaline-type electrolytes. Metal distribution is poor to acceptable, but this improves with warm electrolytes.

Electrolytes contain zinc chloride (30 – 55 g zinc/l), potassium and sodium chloride (130 - 180 Cal g /l), boric acid (10 – 40 g/l) and wetting agent. Only soluble anodes are used. The solutions have good conductivity resulting in a current efficiency of 100 %, and in a low energy demand.

Plating tanks may be equipped with fume extraction hoods to remove chloride-containing mists, thus preventing the corrosion of equipment.

Environmental considerations
Current efficiency of the electrolyte means lower power consumption.

If the extracted air is passed through mist elimination, effluents may require treatment to adjust pH and remove zinc.

Effluents may be easily treated in typical waste water treatment plants.

Acid zinc electrolytes generate more solids in effluent treatment.

Zinc alloy plating

Zinc alloy coatings provide extended corrosion resistance and the main use is for automotive applications (see Sections 1.1 and 2.9).

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 may be equipped with fume extraction hoods to capture aerosols or ammonium chloride fumes.

The extracted air may be passed through mist elimination.
Alkaline cyanide-free effluents are treated in normal waste water treatment plants.

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

### 2.5.5 Cadmium plating

Electrolytes may be based on cyanide, sulphate or fluoroborate

*No information provided. Cadmium plating is still carried out and is currently vital to the aerospace industry and telecommunications*

### 2.5.6 Tin and alloy plating

Tin plated metal is widely used in many applications because of its unique properties. Plated tin coatings are non-toxic, ductile, resistant to corrosion, easy to coat, and have high throwing and good distribution properties. This makes it possible to plate items with complex shapes to a uniform thickness compared with hot tin dipping methods. Tin finishes are also easy to solder components onto subsequently.

Tin's main applications are the coating of steel coil for packaging of food, beverages and aerosols, etc (see Sections 1.3.2 and 2.9.9). It is also widely used in printed circuit boards (see Section 2.11), electrical connectors, appliance chassis, as well as for kitchen utensils.

Several different electrolytes are available, such as acid stannous sulphate, acid tin fluoroborate, alkaline sodium or potassium stannate and more recently the stannous organic acid base (methane sulphonate acid, MSA) system. The sulphate bath containing stannous sulphate, sulphuric acid and addition agents (antioxidants for stannous tin, plus grain refiner) is the most popular in rack and barrel applications because of its high current efficiency.

Tin lead plating is the most commonly tin plated alloy. It is used as solder coat in different alloy ratios (60/40, 90/10, 95/5) traditionally using stannous, stannic and lead fluoroborate and additives with fluoroboric acid.

Non-fluoroboric tin lead electrolytes are now available as organic acid base (MSA) methane sulphonate acid systems. They have improved stability, low sludge formation, better deposit properties and structure of the deposit. They are widely-used in reel-to-reel machines, as well as in barrel processing.

Tin-nickel has high throwing power, good distribution of metal, ductile, non-toxic, and is readily soldered to.

**Environmental considerations**

Process tanks may be equipped with fume extraction to remove aerosols generated during the electrolysis.

Effluents may be treated in normal waste water treatment plant.

Fluoroborate bath effluents should be pre-treated separately to a typical waste water treatment plant.
2.5.7 Precious metal plating

[3, CETS, 2002, 75, BSTSA] Silver and gold have been deposited electrolytically since the first half of the nineteenth century. More recently, processes for the so-called platinum metals (palladium, rhodium, ruthenium and platinum) have also been developed. Thin layers of less than 1µm are used to make a wide range of items appear valuable without commensurate cost. They also provide stain and corrosion resistance. Other specific technical properties such as conductivity, hardness and wear resistance have led to their wide-spread application in the electric and electronic industries.

Silver

The silver plating of cutlery and hollowware is one of the oldest decorative applications of electroplating (see Chapter 1). Bright silver deposits are widely used for jewellery as well as on ornaments, trophies, giftware, etc. Due to its high conductivity and mechanical and chemical properties, silver layers are to be found on many components of electrical and electronic devices. Also, silver-palladium layers as a substitute for gold on electrical connectors have recently gained importance.

The majority of silver electrolytes are based on potassium-silver cyanide (potassium dicyanoargentate). A silver content of 30 – 65 g/l with free potassium cyanide of 100 – 160 g/l and potassium carbonate (15 – 120 g/l) is necessary for good plating performance. However, a potassium carbonate concentration of over 20 g/l makes it necessary to discard the electrolytes. Attempts to replace cyanide, for example by thiosulphate, have failed due to poor stability of the complexes formed.

Environmental considerations

The cost of silver makes recovery economic. Residues of silver may recovered from rinse water through electrolysis or ion exchange. Recovery of silver from spent electrolytes may be achieved through precipitation with zinc powder.

Plating tanks may be equipped with fume extraction hoods to remove cyanide fumes.

Cyanide can be readily oxidised in typical effluent treatment in waste water treatment plants.

Gold

Alkaline cyanide gold electrolytes, based on potassium gold cyanide (potassium dicyano-aurate) with a gold content of 2 – 20 g/l and free potassium cyanide (5 – 30 g/l) were among the first electrolytes developed for electroplating.

Cyanide complexes of other metals, such as copper or silver, added to the base electrolyte allow for the deposition of gold of various colours. High molecular weight 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. Other important alloying metals are cobalt, nickel, iron, indium and tin.

Hard gold layers are plated from weak acid-based potassium gold cyanide, and from strong acid electrolytes based on potassium tetracyanoaurate (with a gold content of 7-8 g/l). Due to the wear resistance of these deposits, acid electrolytes are used for plating connectors, printed
circuit boards, bathroom fittings, giftware, tableware, buttons, jewellery, spectacle frames, bed frames and other items in regular use.

Alkaline cyanide free gold electrolytes based on the gold-sulphite complex \( \text{Au(SO}_3\text{)}_2 \) with copper (0-2%) and palladium (3-9%) as alloying metals, provide rosé and white layers of high hardness and ductility on jewellery and spectacle frames, frequently as a base layer followed by rhodium.

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

**Environmental considerations**

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

Chelating agents resistant to degradation have been largely substituted by biodegradable ones.

Effluent treatment is similar to other electroplating rinse streams in typical waste water treatment plants.

**Palladium and alloys**

Layers of palladium-nickel alloy (75 – 80 % Pd/ 25 – 20 % Ni) are hard and have a white colour with good corrosion resistance. They are suitable for coating spectacle frames and writing implements.

Pure palladium deposits are also used to substitute for nickel as a diffusion barrier below a final gold flash on spectacle frames, jewellery and buttons. Sandwich layers of nickel, palladium or palladium/nickel alloy and gold flash have proven applicability on printed circuit boards and connectors as substitutes for hard gold layers.

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

**Environmental considerations**

Besides drag-out recovery, electrolytic and ion exchange recovery of palladium are normally practical.

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

Effluents may be treated in typical waste water treatment plants.

**Rhodium**

Very thin rhodium deposits on silver have a silvery-white colour and are used to prevent staining. Their hardness and wear resistance properties are suitable for technical applications such as on reed contacts and on heavy duty connectors. Rhodium is also applied on reflectors for optical equipment and in aerospace applications.

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) or for technical purposes (thickness of layers 0.5 - >8 µm), where selenium and sulphites are added to prevent cracking.
Environmental considerations
Besides drag-out recovery, electrolytic and ion exchange recovery of rhodium are normal practice.

Tanks for sulphuric acid-containing electrolytes may be equipped with fume extraction hoods to remove acid fumes.

Effluents may be treated in typical waste water treatment plants.

Platinum
Thin platinum layers are applied for decorative purposes, with thicker layers on electrical devices and on equipment for the chemical industry. Non-soluble platinised titanium anodes and anode baskets are in common use in electroplating.

Acid electrolytes are based on chloride, sulphate, nitrate and nitrite complexes of platinum, alkaline electrolytes on phosphate, ammonia and sodium hydroxide complexes, with metal contents of 6 – 40 g/l.

Environmental considerations
Besides drag-out recovery, electrolytic and ion exchange recovery of platinum are normal practice.

Effluents may be treated in typical waste water treatment plants.

2.5.8 Autocatalytic plating (catalytic chemically reduced coatings)
This is also known as electroless plating, but the term should be avoided, according to [101, CEN, 2000]. The fundamental reaction requires the presence of a catalytic metal – the metal being deposited - that allows the reaction to proceed. The advantages of the system are:

- provided there is sufficient agitation to maintain fresh undepleted solution in contact with all surfaces at all times, the deposit is uniform over the entire surface even if the shape is highly complex
- deposits are usually less porous than the same metal deposited electrolytically
- racking or fixing is greatly simplified
- non-conductors (such as plastic) are coated
- deposits often have special chemical or physical properties since the deposit is an alloy of the metal and a compound formed from the reducing agent. For example, with hypophosphate the deposit is an alloy of the metal and the metal phosphide, and with boron reducing agents the deposit is an alloy of the metal and the metal boride.

Overall environmental considerations:
Autocatalytic coatings commonly generate more waste than other plating techniques, but efficiency can vary significantly between facilities [69, NCDPPEA, 2003].

Autocatalytic nickel on metals
Autocatalytic 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, as well as NaBH₄ and dimethylaminoborane. Solutions also contain chelating agents (organic carboxylic acids 10 – 50 g/l) and buffers as sodium hydroxide and sodium carbonate. Cadmium may be present in some formulations as a brightener at 15 mg/l in the solution, giving 0.1 % in the
plated finish (Verbal communication with TWG). An example of a nickel autocatalytic process line is shown in Figure 2.6.

Autocatalytically deposited nickel-alloy layers contain 2 – 15 % phosphorus. Their key properties are:

- uniform thickness of deposit irrespective of 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 may be required at process tanks including mist elimination to remove nickel containing aerosols.

The solution working life is short (6-8 MTO, metal turnovers) due to the formation of reaction by-products. Process performance deteriorates requiring frequent discarding of used solutions.

Separation of metal from effluents by precipitation, plate-out or ion-exchange.

The strong chelating agent may require separate waste water treatment.

There may be trace amounts of cadmium in the effluent.

**Autocatalytic copper on metals and plastics**

Autocatalytic copper plating is still a key process for the through-hole plating of multilayered printed circuit boards and as well as for the metallisation of plastics. The 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 as well as on plastic housings for electric shielding and printed circuit boards.

Copper deposition starts on metal nuclei such 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, with sodium hydroxide (15 – 20 g/l), chelating agents such as EDTA or similar (10 – 15 g/l) or tartrates (5 – 10 g/l) and reducing agents, e.g. formaldehyde (3 – 5 g/l).

The process solution lifetime is limited by the build-up of reaction products.

**Environmental considerations**

Fume extraction for the process tanks may be necessary to remove gases (formaldehyde and others).

There was an industry trend to replace EDTA as a chelating agents, although high specification work may require its use and the trend is currently being reversed [22, Fraunhofer, 2002] Effluent containing EDTA requires separate treatment as EDTA will prevent the precipitation of metals in the treatment process.
Autocatalytic nickel coating for plastics

Similarly to autocatalytic copper, electroless nickel solutions are used for generating a first conductive metal layer on plastic surfaces prior to further electrolytic metal (copper, nickel) deposition. [73, BSTSA]

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

Environmental considerations
Fume extraction may be used for alkaline or high temperature processes. Typical effluent treatment will remove metals except where effluents contain strong chelating agents, which may have to be treated separately.

Non-catalytic chemically reduced coatings
No data provided. Is this technique used with printed circuit boards?

2.5.9 Immersion or displacement coatings

Immersion deposits form whenever the substrate is more active than the ions in the solution (in terms of the electrochemical series). Although these deposits are often non-adherent and of poor physical quality, careful attention to solution composition and operating conditions can produce deposits that are acceptable for certain purposes. The zincate and stannate solutions used for plating aluminium are examples of special finishes producing acceptable deposits

No data provided. This technique is referred to be as being used, e.g. tin on aluminium, printed circuit board applications.

Overall environmental considerations
Immersion coatings commonly generate more waste than other plating techniques, but efficiency can vary significantly between facilities. [69, NCDPPEA, 2003]

2.5.10 Non-catalytic chemically reduced coatings

Non-catalytic chemically reduced coatings have been in use for many years. Their best known use in producing mirrored surfaces from silver, although other techniques can now be used (such as vapour phase deposition). Their two main drawbacks are that only relatively thin coatings can be deposited and that all surfaces, including the container, receive a coating. While these solutions are sometimes used by immersion, they are now more often applied by spraying the solutions from a dual spray gun. [38, Ullman's, 2002/3]

No data provided - is this still used for mirrored finishes?

2.5.11 Electropainting or electrocoating

Also know as: electrophoretic painting, E-coat, Elpo, electrodeposition.

Electropainting is covered in detail in [90, EIPPCB].

The activity is increasingly found alongside surface treatment activities covered in this document, both for subsequent painting and/or in conjunction with other coatings described
Lacquering

Lacquers are applied to protect and enhance decorative coatings (such as copper plating of hollowware) or to supplement corrosion protection systems such as chromating (see Section 2.5.19). They can be applied by dipping in a proprietary water-based solution or by electropainting (see Section 2.5.11 and [76, BSTSA].

Top coatings are applied immediately after chromate or trivalent chromium conversion coatings, by dipping in an appropriate proprietary medium or by electropainting (electrophoretic painting), see Section 2.5.11.

Environmental considerations
Effluents have no impact on typical waste water treatment plants. Rinsing waters may need to be treated separately to reduce BOD or TOC levels in the discharged effluent.

Oiling

See coil coating, 2.9.5 for electrostatic oiling. No description provided of other uses or environmental consideration.

Enamel

The TWG proposed that this activity should be covered by the scope of this document. No description provided.

Anodising

[3, CETS, 2002, 45, France, 2003] The anodising of metals is an electrolytic surface oxidation process which enhances the natural aptitude for the metal to oxidise; coatings can be 400 times thicker than the natural layer. Aluminium is the most important material to be anodised, with alumina (Al₂O₃) formed at the surface: magnesium, titanium, tantalum and niobium are also anodised in smaller quantities.

Aluminium may be anodised in many different types of process solutions. Sulphuric, sulphuric/oxalic acids, sulphuric/salicylic acids, and chromic acid electrolytes are usually used.
A wide variety of current forms and wave shapes may be used for the process, depending on the solution selected and the purpose of the anodic film. Direct current (DC), alternating current (AC.), and DC with superimposed AC. are all used in various processes.

The workpiece or substrate 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 metal reacts with the oxygen of the anion and a layer of oxide forms on the surface.

The alumina coating is sealed to improve corrosion resistance and retain any surface colouring (see Section 2.5.16). Sealing is described in Section 2.5.17.

**Sulphuric acid anodising of aluminium**

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 – 22 V and the temperature of the electrolyte 18 - 20 °C. The electrolyte concentration is 160 – 185 g/l H₂SO₄. A film thickness of 5 – 25 µm is used for decorative and protective sulphuric acid anodising, for example, in architectural anodising. Sulphuric acid anodised coatings are often coloured by special colouring processes. The oxide coating is sealed to obtain improved corrosion resistance (see 2.5.17).

In hard anodising, a film thickness of 25 – 250 µm is obtained. The electrolyte is operated at -3 °C to 0 °C. Processes with oxalic acid and sulphuric acid with organic additions can also be used for hard anodising. The hard anodising layer is normally not sealed. In this state it can be impregnated with lubricants.

**Environmental considerations**

Process tanks may to be equipped with fume extraction to remove generated acid aerosols and gases.

Effluent may be treated in typical waste water treatment plants.

**Chromic acid anodising of aluminium**

This forms an aluminium oxide film on most aluminium alloys ranging from a light to dark grey.

The electrolyte contains 30 – 100 g of chromic acid per litre. The temperature is kept within the range of 38 - 42 °C for most aluminium alloys. The voltage cycle used depends on the alloy treated and must be closely followed to avoid etching. The coating is thin with an average of 2 - 5 µm and is relatively soft. Its corrosion resistance is good. The coating is normally not sealed.

**Process considerations**

Process tanks may to be equipped with fume extraction to remove generated acid aerosols and gases. See Section 1.4.4.1 for health effects of chromium and Section 2.5.3 for environmental considerations for hexavalent chromium solutions.

The regeneration of anodising baths using a retardation process extends the electrolyte life by reducing its aluminium content.

**Environmental considerations**

Effluent may be treated in normal waste water treatment plants.
Anodising of magnesium, titanium, tantalum, niobium
No description provided

Anodising by mixed sulphuric/ oxalic acids, or sulphuric/ salicylic acid
No description provided

2.5.16 Colouring aluminium

Aluminium can be coloured in many shades and colours in conjunction with sulphuric acid anodising. There are four methods [3, CETS, 2002, 45, France, 2003].

Immersion colouring

This is the most widely used colouring method with a large range of dyes giving good light resistance. The anodised aluminium workpieces or substrate are immersed in a water-based organic or inorganic dye solution before sealing. The pores in the oxide layer adsorb the dye and then sealing is carried out to achieve durability. For colouring, the thickness of the oxide film should be not less than 10 µm. For good corrosion and weather resistance, 20 µm is required.

Environmental considerations
Process tanks may require fume extraction to remove generated aerosols and acid water vapour.

Some organic dyes may require additional waste water treatment.

Electrolytic colouring

The anodised aluminium is placed in an acid solution containing metal salts and an alternating (AC) current applied. This deposits oxides of the other metal in the porous structure of the alumina within 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.

Environmental considerations
Process tanks may require fume extraction to remove generated aerosols and acid water vapour.

Interference colouring

Interference colouring is a special technique based on the electrolytic colouring principle. The appearance is produced by 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 that are not 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.
2.5.17 Sealing following anodising

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 by hydrating the aluminium oxide to boehmite: the pores are close by the increased volume of the boehmite structure. The sealing process is carried out by dipping the anodised parts in hot or boiling (minimum 98 °C) deionised water for 3 minutes per µm thickness. Sealing with steam achieves the same effect.

Cold sealing

Sealing methods at lower temperatures have been developed. So-called mid-temperature sealing processes are also available operating at about 60 °C. These are not based on the hydrothermal conversion of aluminium oxide for closing the pores, but by the use of nickel salts, such as the fluoride or silicate. In the European market, there is some concern about long term-properties such as light fastness and corrosion resistance.

Environmental considerations
Some organic dyes may require additional waste water treatment.

2.5.18 Phosphating layer conversion coatings

[38, Ullman's, 2002/3, 71, BSTSA] Phosphate coatings are the most widely used conversion coatings and probably the most widely used surface treatment. They are used to treat steel, aluminium and zinc for:

- cold forming: this involves very high surface stresses and phosphating is used in all types of cold forming operations, i.e. drawing of wire, tube, or profile; deep drawing; cold heading, cold extrusion, cold forging,. These applications are described in the [86, EIPPCB]
- coil coating: steel strip electroplated with zinc is phosphated in the process line to improve formability in subsequent drawing operations, such as steel can forming, as well as for corrosion resistance and subsequent paintability, see Sections 2.9.6 and 2.9.8.9. Hot dip galvanized steel strip is discussed in [86, EIPPCB]
- rustproofing: heavy zinc and manganese phosphate coatings retain a protective oil film and provide substantial corrosion prevention, e.g. for nuts, screws, bolts, and tubes
- bearing surface lubrication: manganese phosphate improves the retention of lubricant and shortens running-in periods. It is used for pinions, camshafts, pistons, gears, and valves
- paint base: phosphating enhances the adhesion and corrosion protection of paints, see[90, EIPPCB]
- electrical insulation: phosphate layers can be used to coat the silicon steel sheets forming the cores of electric motors, generators or transformers. A phosphate coating of 1-6 µm thickness is sufficient insulation to prevent eddy currents
- vitreous enamelling: nickel phosphating can replace chemical nickel coating as a pre-treatment for vitreous enamelling. The number of process steps and the amount of nickel-containing solid waste can be reduced.
There is a wide variety of phosphating processes, but the most important are alkali (iron) and zinc phosphating. The surface weight of layers is 0.05 – 5 g/m².

Methods of application

The phosphating solutions are generally applied by spraying or by immersion depending on the number, size, and shape of the parts to be treated. The type of application may lead to differences in the composition and morphology of phosphate coatings. Coiled strip is also coated by the roll-on, dry-in-place process, in which phosphating solution is applied to the strip and, without rinsing, is dried to form the phosphate coating, see Section 2.9.6.

Phosphating requires workpieces or substrates to be degreased and pickled see Section 23. Activation prior to phosphating may be with hot water or with special proprietary titanium or manganese phosphate dispersions to induce the formation of a fine-grain phosphate coating in the subsequent step. Final rinsing may be with deionised water or passivating chemicals based such as CrVI and CrIII compounds. Rinsing with water is needed between the processing stages as described in 2.4

Overall environmental considerations for all phosphating processes

Effluents may require pH control and contain nickel, manganese, as well as zinc (according to solution make up), which can be dealt with in a typical waste water treatment plant. Anions that may be of concern include nitrite and fluoride, which may require additional treatment.

Sludges formed in the process solutions require removing as part of the solution maintenance and are removed as wastes.

Health and environmental concerns have instigated the development of:

- nitrite-free processes with hydroxylamine, nitroguanidine, or hydrogen peroxide as accelerators
- nickel-free processes
- chromium-free after-rinses based on organotitanium, inorganic zirconium, or polymeric compounds
- effluent-free phosphating lines using ultrafiltration for cleaning, hydrogen peroxide acceleration in phosphating, and precipitation plus ion exchange for chromium-free after-rinses, without compromising the performance of the subsequently painted parts.

Alkali phosphating

This is mainly used when corrosion protection does not have to satisfy stringent requirements. For steel substrates, the solutions (pH 4 - 6) consist of acid alkali phosphates, free phosphoric acid, and small amounts of additives; oxidizing agents (e.g. chlorates, chromates, or nitrites), condensed phosphates (e.g. pyrophosphate or tripolyphosphate), and special activators (e.g. fluorides or molybdates). The first reaction is the pickling reaction which produces Fe²⁺ ions from the substrate (steel). These ions react with phosphate ions from the solution to form sparingly soluble iron phosphate that precipitates and adheres strongly to the metal surface. Iron phosphating processes may not require acceleration. The coating weight varies with the bath composition. Coatings formed on ferrous surfaces contain iron oxides and phosphates. Iron phosphating solutions normally contain surfactants for cleaning and oily surfaces may thus be treated in one step (so-called ‘cleaner-coater’).

On zinc surfaces, zinc phosphate layers are formed in an analogous reaction sequence. Aluminium is usually treated with fluoride-containing solutions; thin, complex coatings are formed that contain aluminium, phosphate, and fluoride. The baths are adjusted to a concentration of 2 – 15 g/l. Treatment may be by spraying, flooding, or dipping. The bath temperature is normally 40 - 70 °C, but can be lowered to 25 - 35 °C with special bath compositions. Treatment times are 5 - 10 seconds (spraying of strip material) and 1 - 3 minutes.
(spraying or dipping of individual parts). Iron phosphating includes both thin-coating (0.2 - 0.4 g/m²) and thick-coating methods (0.6 - 1.0 g/m²). The colour of the layers is blugreen, but may be reddish iridescent. The surfaces become more matt and grey with increasing coating weight.

**Environmental considerations**
See overall environmental considerations, above.

**Zinc phosphating**

Zinc phosphating is primarily used for the surface treatment of steel and zinc (or zinc coatings on steel) as well as composites of these metals with aluminium. Application may be by spraying or immersion. Essential constituents are zinc, phosphate ions, and an oxidizing agent, often sodium nitrite. The pH value is between 2 and 3.5. Concentrations vary considerably; additives such as nitrate, fluoride, silicofluoride, nickel ions, or manganese ions are common.

The following is an example of a process suitable for the phosphating of steel sheets as a pre-treatment prior to painting:

\[ \text{Zn}^{2+} 1.2 \text{ g/l}, \text{Ni}^{2+} 0.1 \text{ g/l}, \text{H}_3\text{PO}_4 + \text{H}_2\text{PO}_4^- 15 \text{ g/l}, \text{and NO}_2^- 0.1 \text{ g/l} \]

A pH of 3.2 is achieved with sodium hydroxide. The process is usually carried out at up to 95 °C. For cold forming applications total concentrations may well be ten times higher.

Typically, the phosphating reaction may be broken down into five steps:

**Pickling reaction**
Part of the metal surface is dissolved by the acid.

\[ \text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 \text{ for Fe} \quad \text{or} \quad \text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2 \text{ for Zn} \]

The phosphating of aluminium requires fluoride ions to attack surface oxides which only slowly dissolve in phosphoric or nitric acid

\[ \text{AlOOH} + 3\text{HF} \rightarrow \text{Al}^{3+} + 3\text{F}^- + 2\text{H}_2\text{O} \quad \text{Al}^+ + 3\text{H}^+ \rightarrow \text{Al}^{3+} + 3/2\text{H}_2 \]

**Acceleration**
The pickling reaction is accelerated by oxidizing agents called accelerators, which also prevent the evolution of excessive amounts of molecular hydrogen thus minimizing hydrogen embrittlement.

\[ \text{H}_2 + 2\text{O}_x \rightarrow 2\text{HO}_x; \quad \text{Fe}^{2+} + \text{H}_x + \text{O}_x \rightarrow \text{Fe}^{3+} + \text{HO}_x \text{ for Fe} \]

**Complexation**
When coating aluminium, sufficient fluoride ions must be available for complexation of surplus Al³⁺ ions as in concentrations as low as 3 mg/l they prevent the formation of zinc phosphate coatings. If different metals including aluminium are to be treated, use of fluoride-free phosphating solutions may allow phosphating of steel or zinc without coating the aluminium:

\[ \text{Al}^{3+} + 6\text{F}^- \rightarrow \text{AlF}_6^{3-} \text{ for Al} \]
Coating formation
Metal dissolution in the pickling reaction results in a significant increase of the pH value close to the metal surface. Consequently, the equilibrium constant for the precipitation reaction is exceeded and zinc phosphate is precipitated as the metal surface offers favourable nucleation sites. Once the whole metal surface is covered the reaction ceases:

\[
3\text{Zn}^{2+} + 2\text{H}_2\text{PO}_4^- + 4\text{H}_2\text{O} \rightarrow \text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O} + 4\text{H}^+ \\
2\text{Zn}^{2+} + \text{Fe}^{2+} + 2\text{H}_2\text{PO}_4^- + 4\text{H}_2\text{O} \rightarrow \text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O} + 4\text{H}^+
\]

Sludge formation
Dissolved iron and AlF\(_6\)^{3-} ions from the pickling reaction do not accumulate in the phosphating solution but are precipitated as iron(III) phosphate or trisodium hexafluoroaluminate, respectively. When treating galvanized surfaces and in spraying processes, relatively small amounts of tertiary zinc phosphate sludge are formed as well. Nitrate-accelerated processes often do not involve sludge formation. Iron(II) nitrate accumulates until equilibrium is reached between iron dissolution and drag-out.

\[
\text{Fe}^{3+} + \text{H}_2\text{PO}_4^- \rightarrow \text{FePO}_4 + 2\text{H}^+ \text{ for Fe; } \text{AlF}_6^{3-} + 3\text{Na}^+ \rightarrow \text{Na}_3\text{AlF}_6 \text{ for Al}
\]

The sludges formed must be removed either periodically or continuously.

Pre-paint processes
Zinc phosphating processes carried out prior to painting can be classified as high-zinc or low-zinc processes. High-zinc processes operate at 3 - 4 g/l Zn\(^{2+}\) and low-zinc processes at 0.7 - 1.5 g/l Zn\(^{2+}\), the upper limit for dip applications. Low zinc concentration, i.e. high phosphate to zinc ratio, improves corrosion protection. Coatings on steel produced by low-zinc processes consist mainly of phosphophyllite and show superior paint-base performance to the high-zinc processes with their hopeite coatings, such as stone-chipping resistance and wet adhesion on galvanized substrates. Performance has further increased with the introduction of trication processes, which contain zinc, nickel, and manganese both in solution and in the coating. These processes have become commonplace in, for example, the automotive industries.

For powder coatings iron phosphate often gives optimum results [90, EIPPCB].

Low-temperature processes for cold forming
These are accelerated by nitrate, and the iron(III) concentration in the bath is limited to 5 - 8 g/l by oxidation with air, preferably continuously in a separate reaction tank. Operating temperature has thus been lowered by about 30 °C to 50 - 60 °C, and the phosphating tank remains virtually free of sludge.

Environmental considerations
See overall environmental considerations, above.

Manganese phosphating

This performed by dipping only, and iron(II) nitrate is often used for acceleration.

Environmental considerations
See overall environmental considerations, above.
2.5.19 Chromium conversion coatings


Chromium conversion coatings are used to enhance corrosion protection on various metal surfaces, including electroplated zinc and cadmium, zinc die castings, tin, aluminium, magnesium and magnesium alloys, copper, brass and bronze, nickel, silver and stainless steel. Without such protection, zinc electroplated steel surfaces have a strong tendency to white (zinc oxide) corrosion. Chromating is used in nearly all areas of the steel processing industry and is an essential post treatment step in zinc plating. The wide-spread use of the original yellow chromating was increased by the development of further layer systems of blue and black chromating, which have decorative effects in addition to corrosion protection.

The layer thickness of the chromating coats lie between 0.1 and 2 µm. They are well suited as adhesion mediators for subsequent treatment with paint layers or synthetic material coatings. Lubricants can be included in order to decrease the friction values of treated pieces. The corrosion protection of chromating can be increased by further sealing layers, described in top coatings, below.

The typical composition of chromating solutions are chromic acid, dichromate, chloride, fluorides, sulphates, borates, nitrates and acetates, which are used in different combinations and concentrations to produce different colours and layer characteristics.

Chromate (CrVI) conversion coatings

Conventional processes are all based on the use of acid oxidising solutions, the oxidant being hexavalent chromium (CrVI). The protection mechanism is based on the dissolution of the CrVI present at the surface of the film. The presence of chromate works locally to inhibit any corrosive action on the exposed metal surface.

Overall environmental and health considerations for hexavalent chromium
For health issues, see Section 1.4.4.1.

For chromium (VI) aerosols and effluents, see Section 2.5.3.

Chromate (CrVI) conversion coatings on electroplated zinc layers

Coatings are applied by chemical reaction in aqueous solutions. Numerous proprietary conversion coating processes are available, producing decorative and protective films with colours ranging from clear through iridescent-yellow to brass, brown, olive drab and black. Broadly, the deeper the colour the better the corrosion resistance.

Environmental considerations
See overall environmental considerations, above.

Chromate (CrVI) conversion coatings on copper, brass and bronze

Chromate solutions to treat copper and copper alloys are prepared with proprietary materials. The treatment not only passivates the surface but also provides effective chemical surface polishing. Consequently, chromate treatments on copper and copper alloys are used both as final finish and as a whole or partial substitute for mechanical buffing prior to nickel or chromium plating. The passivity obtained is effective in reducing corrosion and sulphide tarnishing.
Environmental considerations
See above, overall environmental considerations.

Chromate bright dipping solutions are preferred because of their non-fuming nature.

Increased effluent treatment may be required because of the dissolution of copper in the process bath.

Chromate (CrVI) 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 the immersion time, pH, solution concentration and, to some extent, on the composition of the alloy to be treated. This treatment is used on aluminium components in aerospace, electronics and other applications.

The ability of the treatment to provide corrosion resistance without a corresponding loss of conductivity is particularly useful for electronic applications.

Environmental considerations
See above, overall environmental considerations.

Chromate (VI) conversion coatings on magnesium and its alloys

Because of their corrosion characteristics chromate treatment is still the only common method to treat magnesium and magnesium alloys. This treatment is often applied at the raw material source, in order to ensure good storage characteristics. Chromate treatment is also used to prepare magnesium and magnesium alloys for subsequent plating, particularly for nickel autocatalytic plating.

There are two typical process methods in use:

- pickling is mainly used to protect parts during storage and shipment,
- dichromate treatment provides maximum corrosion protection and improved adhesion properties for paint.

Environmental considerations
See above, overall environmental considerations.

Trivalent chromium (CrIII) conversion coatings on electroplated zinc

Trivalent chromium (CrIII) conversion coating processes were first developed about 20 years ago as a more environmentally acceptable alternative to hexavalent chromium (CrVI) processes, mainly on electroplated zinc. These conversion coating systems and treatment baths do not contain hexavalent chromium and therefore avoid the environmental or health problems associated with hexavalent chromium.

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.

Trivalent chromium conversion coating processes usually 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 in comparison with iridescent hexavalent chromium passivation. However, the thickest conversion coatings (olive
drab and black) that give greater corrosion protection for zinc can only be achieved using hexavalent chromium conversion coating processes.

Compared to hexavalent chromium conversion coating processes, the trivalent chromium conversion coating:

- is normally more corrosion resistant for the same colour finish
- freshly prepared passivation solutions do not require a running in period
- the colour and performance of the processes are more uniform throughout the solution life
- the working life of the passivation solution is normally at least twice that of conventional hexavalent chromium and limited by impurities rather than consumption of the active chromium compounds, resulting in less solution disposal
- cannot produce the range of colours and corrosion resistant given by hexavalent coatings
- require more process control.

Environmental considerations
There are no specific health and safety considerations for CrIII.

Reduction of CrVI to CrIII is not required during waste water treatment.

Top coatings for chromate conversions coatings

Both hexavalent and trivalent chromate conversion films are porous and adsorbent in nature and their thickness is very limited. Their protective action can be enhanced by applying a subsequent top coating film, either organic (e.g. methacrylate, see electropainting, Section 2.5.11 and lacquering, Section 2.5.12 and) or inorganic (e.g. metasilicate) and/or mixed inorganic-organic. These 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 CrIII leaching out from the treated surface. Top coating protection is mainly due to the physical barrier of the coating itself.

Environmental considerations
No data provided

2.5.20 Metal colouring

[3, CETS, 2002] It is possible to obtain a wide range of shades and colours over different metals by heat treatment, chemical dip or electrolytic treatment. These processes are used for brass, copper and steel parts. The most commonly-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. Originally, 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 proud surface areas relieved by tumbling with an abrasive media, see Section 2.3. All sulphide treated workpieces require wet or dry scratch-brushing and must be protected by a top coat of clear lacquer.

Environmental considerations
Depending on the precise formulations used, effluents may need to be pre-treated separately prior to typical waste water treatment.
Chapter 2

2.5.21 Bright dipping

No data provided

2.5.22 Chemical blacking – oxide coatings

Immersion-type chemical oxidation coatings are used mainly for appearance, as a paint base, or for their oil-retention characteristics. [38, Ullman's, 2002/3]

Environmental considerations for all chemical blacking processes
Fumes from alkali and chromium containing processes may require extraction and possibly scrubbing. Scrubber effluents may require treatment in a waste water plant.

Rinsing waters may require treatment for pH. Other materials such as nitrogen-containing compounds, other oxidising agents and sulphides may require additional treatments to those found in a typical waste water treatment plant.

No data provided for issues relating to managing molten sodium/potassium dichromate.

Steel
Steel may be blackened in a high-temperature bath containing 480 – 840 g/l of a mixture of about 75 wt % sodium hydroxide and 25 wt % sodium nitrate. The solution is operated at the boil between 121 – 149 °C. 25 wt % sodium nitrate, 12 wt % sodium nitrate and 13 wt % sodium nitrite may also be used.

Lower boiling points are obtained by including various sulphur-containing additives. The resulting oxide coating is somewhat less corrosion resistant because of the inclusion of iron sulphide in the film. Some of the sulphide-modified materials may also be used to blacken stainless steel.

Following thorough rinsing, the oxide film is normally coated with an oil, wax, or lacquer.

Stainless steel
Stainless steel can also be blackened in molten sodium/potassium dichromate at about 370 °C provided the parts are not adversely affected by the high temperature. The resulting oxide has good corrosion resistance, and the procedure is covered by military specifications.

Copper
Copper may be blackened in a bath containing 120 g/l of a mixture of 75 wt % sodium hydroxide and 25 wt % sodium chlorite at 93 – 100 °C. The black copper (II) oxide produced has a fuzzy appearance. On bright finished parts, this fuzzy nap disappears when lacquer is applied, restoring the lustrous appearance, or it may be laid down (not removed) by gentle buffing or tumbling in sawdust or other soft abrasives (see Section 2.3).

Brass
Brass may be blackened in the same solution but may not respond, depending on zinc content and metallurgical history. Activation may be carried out by immersion in a bath containing 120 g/l of a mixture of 85 wt % sodium hydroxide and 15 wt % sodium chlorite operated at 93 - 100 °C for 5 – 10 min to dezincify the surface, after which the blackening bath will usually function normally.

Aluminium
Aluminium may be given an oxide coating by immersion by a number of different processes including the Alzac and Juratka processes. Electrolytic processes (anodising) are generally preferred.
2.5.23 Brightening

In the brightening of steel, concentrated nitric acid is used to form a very clean surface. Note that this process forms nitrous gases in the exhaust gas. [104, ÜBA, 2003]

Copper and brass are brightened by oxidising a surface layer.

Phosphoric acid pickles have specific uses such as chassis parts and bicycle frames. It is usually used at a concentration of 10 - 15 %, at temperatures of 40 - 50 °C and sometimes as high as 80 °C.

Metal surfaces must be degreased thoroughly. Poor results, such as uneven attack or stained surfaces after brightening are frequently due to insufficient pre-degreasing.

Environmental considerations
Spent brightening solutions may require treatment for low pH and possibly metal content prior to disposal as effluent. Alternatively, they may be disposed of as liquid wastes.

Acid fumes, particularly those containing NOx may require extraction, possibly with treatment.

2.5.24 Etching

Non-ultrasound assisted and ultrasound assisted etching were listed by the TWG as activities to be considered. However, no information has been provided.

2.5.25 Chemical milling

[47, France, 2003] Chemical milling is a process used to remove metal on workpieces by dissolution in a caustic or acid bath without an external source of energy (mechanical or electrical). Metal is removed off the whole surface of the part dipped in the milling bath provided this surface is in contact with the solution. Areas to remain are masked. The speed of the chemical dissolution is low, processing 0.5 to 3 mm/h compared with mechanical processes. The thickness removed is almost constant all over the surface but with a roughness created dependant on the process used.

The most important uses are on aluminium alloys for aircraft industry. It is generally used on sheets that have been previously curved and where it is necessary to save weight. Chemical milling can also be used on titanium alloys, stainless steel and some special alloys with nickel, cobalt or magnesium base.

Process chemistries used are:

- for aluminium: caustic soda with additives (sodium gluconate, sodium sulphide)
- for titanium: hydrofluoric acid (20 – 50 g/l) with nitric acid (50 – 70 g/l)
- for stainless steel: hydrochloric acid with nitric and phosphoric acid.

The main control parameters for aluminium and aluminium alloys are:

- concentration of the bath: from 100 to 150 g/l of free NaOH
- temperature: 80 °C for older processes, types up to 110 °C for high-speed processes
- concentration of dissolved metals: 70 to 90 g/l Al
- composition of the alloy chemically milled

All these parameters affect the speed of processing, the thickness regularity and roughness of the finish.
Generally, the entire surface is not milled. In order to prevent milling on some areas it is necessary to mask those areas with protecting layers such as neoprene. The usual technique is to masking the whole part and then remove the mask from the areas to be milled. The cutting of the mask is by scalpel or laser beam.

A typical process sequence is:

- Solvent degreasing
- Alkaline etching
- Rinsing
- Pickling (e.g.: sulphochromic pickling)
- Rinsing
- Drying
- Masking
- Removal of mask on surface to be treated
- Attack
- Rinsing
- Surface passivation: (e.g. sulphochromic or nitric acid)
- Rinsing
- Removal of mask
- Quality control

**Environmental issues**

The main problem for this treatment is the large quantity of sludge due to the dissolved metals. The concentration of the chemical milling bath is generally kept below 70 g/l of aluminium and so used solutions are discarded beyond this concentration. Normal waste water treatment may be used and the principle component of the sludge is Na Al O₂.

### 2.5.26 Electropolishing

*No data provided.*

### 2.6 After treatment activities

#### 2.6.1 Drying using hot water

[3, CETS, 2002] After all wet processing operations have been completed, the workpieces or substrate need to be quickly and effectively dried in order to avoid the occurrence of staining and corrosion. The simplest method of drying is by immersion in hot water. The components are immersed for a few seconds in hot water and then allowed to dry-off in the atmosphere.

The disadvantage of hot water drying is the high energy loss from the tank surface. It is however common practice in surface treatment shops moving jigs manually (and hence low throughput of workpieces).

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 of the coating 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 a preceding cascade rinsing system. The hot water stage may also be a final rinsing step.
Environmental considerations
Energy efficiency.

2.6.2 Drying using hot air

Drying in automated jig plants is most easily accomplished on automatic lines using hot air. The jigs are placed in a tank-shaped drier at the end of the process line; the tank has the same dimensions as the vats in the line to fit into the transporter system.Hot air is evenly recirculated from top to bottom of the tank at temperatures of 60 – 80 °C. Hot air escaping from the top of the drier tank makes the equipment thermally inefficient.

Environmental considerations
Poor energy efficiency.

2.6.3 Drying using air knives

There is a growing use of localised air drying by means of precision nozzles or "air knives" that is more energy efficient than hot air tank drying.

No other data provided

2.6.4 Heat treatment for hydrogen de-embrittlement

*It was agreed at the kick off meeting that this TWG should consider this technique.*

No data provided

2.7 Barrel processing

The use of barrels is described in 2 and 2.2 above. Processing is carried out as described in the generic jig sections 2.4 to 2.6. The following sections refer specifically to activities normally associated with barrel treatments.

2.7.1 Workpiece preparation

Deburring and tumbling, as well as degreasing workpieces for barrel treatment by centrifuging are described in Section 2.3. No other data provided

2.7.2 Core activities

No specific data supplied

2.7.3 Drying for barrelled components

Barrel plants use centrifugal drying or hot air drying depending upon the type of component. Centrifugal drying is effective and energy efficient. No further data provided

2.8 Continuous coil - small scale: reel to reel and wires

No data provided
2.9 Continuous coil - large scale steel

[19, Eurofer, 2003 January, 86, EIPPCB] The coating of large steel coils has traditionally associated with the production of the steel coil. Coils weigh up to 12 tonnes and can be up to 2008 metres wide.

Finished cold rolled steel (pickled, cold rolled, annealed and tempered) is a material with mechanical characteristics that make it suitable for use in many industrial applications. Unfortunately, it suffers the major disadvantage of low corrosion resistance. The use of surface treatments to improve the corrosion resistance of the coiled steel substrate is described in this document.

Electroplating is a major surface treatment for large-scale steel coil production. Other surface treatment options of printing and painting are discussed in [90, EIPPCB].

The electrolytic coating procedure is fundamentally the same as those used in jig and barrel processes, even using similar solution chemistries. It is also preceded by the same type of pre-treatments such as cleaning and pickling, and followed by post-treatments including layer conversion techniques such as chromating and phosphating. The specific activities for steel coil are described below.

There are two key differences for large-scale steel coil:

- the size and nature of the coils and the equipment used to handle and process them. These require:
  - coil handling equipment
  - loading and unloading systems (entry and exit loopers)
  - equipment to keep the coil in process at the right tension and flat (to prevent coil distortion and contact with anodes)
  - edge trimming to size.

- the continuous nature of the substrate, with only small thickness and limited width changes. This allows the use of some techniques that cannot be used for jig and barrel systems (which have constantly changing shapes of components), such as:
  - brushes to assist with activities such as degreasing and wringer rolls to reduce process solution drag-over
  - the continuous nature of the strip and the type of plant layout also lends itself to the wide-spread use of other techniques such as spay rinses and electrostatic oiling which are used less frequently in other transport systems.

A typical process outline is described below. Details for specific process lines are described in following sections.
2.9.1 Entry equipment

The reception of coils, the uncoiling and welding of the coil end with the start of the next coil allows for a continuous process. The entry equipment involves the following:

- transport between the storage of uncoated steel coils to the uncoilers by means of a transfer chain, fork lift or an air-cushion vehicle
- uncoiling of the strip (including uncoiler, magnetic strip and pressure rolls)
- the entry looper guarantees that the strip can go on moving at constant speed in the processing section even during welding when the strip end is held still at the entry section. The looper stores coil by running it through a series of vertical or horizontal loops. These are then used when the coil end is held still for welding on a new coil
- shearing of coil tails and scrap collection
- seam welding of the coil end with the start of the next coil
- continue strip thickness measurement
- tension leveller: used at the entry section or prior to any point where flatness is essential such as running between anodes or edge trimming knives. This flatness is corrected continuously by traction and flexion.

Environmental considerations

Power consumption which can be assisted by maintenance of correct settings and ensuring bearings are free running.

2.9.2 Rinsing and drag-out

These activities are described in 2.4. Specific control techniques for coil processing are described for the individual processes.
2.9.3 Pre-treatment

2.9.3.1 Degreasing and cleaning

The coiled blackplate is usually contaminated with fatty residues (oil and grease) and mill dirt (amorphous carbon or abraded iron fines) left over from the rolling process. It is essential that the surface of the steel strip is free of these impurities to ensure the entire surface is exposed to the treatment activities to ensure strong adhesion of the coatings is achieved.

Aqueous systems are now standard and solvent degreasing is no longer used.

The cleaning is usually a combination of soak and electrolytic activities, see Section 2.3. Cleaning solutions are usually based on sodium hydroxide, phosphate or polyphosphates and wetting and complexing agents.

**Electrolytic cleaning.** Impurities such as grease, oil, amorphous carbon or abraded iron fines may exist in the depressions of the surface roughness after the degreasing treatment. It is essential that these impurities are removed to ensure a strong adherence of the coating and it is achieved by electrolytic cleaning.

The uncoiled strip is polarised, either:

- directly - where the strip passes over a conductor roll, and then travels between two pairs of mild steel electrodes. Current passes from the conductor roll via the strip and electrolyte to the electrodes, or
- indirectly - grid electrodes where the steel strip travels between two pairs of mild steel plates which form two electrodes of opposite polarity. Current passes from one pair of electrodes via the electrolyte and the strip to the other pair of electrodes.

The electrolysis of the alkaline solution produces the release of H₂ gas at the cathode and of O₂ gas at the anode. The polarity of the electrodes is inverted after each coil or after a certain time to avoid polarization.

**Environmental considerations**
See Section 2.3 and the individual processes.

Where oily waste is collected from the activities it is usually treated off-site.

2.9.3.2 Pickling

Although the strip as it leaves the cleaner rinse should be free of surface oil and dirt, oxides formed during the various stages of steel processing are not removed. The purpose of acid pickle is to remove these oxides and lightly etch the strip to present as clean a steel surface as possible to the plating section. Strip pickling can be carried out by immersion, spraying or more commonly by electrolysis, with the same electrical arrangements as for cleaning, i.e. contact rollers or grids. See also Section 2.3 and [86, EIPPCB].

Lead anodes are used because of the 50 g/l (max) concentration of the sulphuric acid electrolyte.

**Environmental considerations**
See Section 2.3
2.9.4 Coating activities - electroplating

The materials commonly used for electroplating steel strip because of their special characteristics are: tin, chromium, zinc, copper, lead and some of their alloys. Electrolytic reactions are described in are described at the start of Chapter 2.

2.9.4.1 Electrolytic cells for continuous steel coil

The cleaned and pickled strip is fed through electrolytic cells. The electrolytic cells are the heart of an electrolytic line. The choice, design and sizing of the other line components and supplying sections are dependent on the choice of the electrolytic cell and its components.

The main components of a continuous coil electrolytic cell are:

- conductor roll: this gives the steel strip a negative electrical charge. The voltage is transformed into current by means of a rectifier. The negative pole of the rectifier is connected to the carbon brushes of the conductor roll
- press roll: provides good contact and high electric conductivity between conductor roll and steel strip
- anode: repels the positive ions towards the steel strip (cathode). The positive pole of the rectifier is connected to the anode
- sink roll: turns the steel strip by 180°
- wringer rolls or squeeze rolls: minimise the drag-over (drag-in) into the next cell
- edge masks: prevents zinc edge overthrow (build-up of zinc preferentially at the edge of the coil where charge density is highest)
- Conductor roll cleaning device: cleans the surface of the conductor roll to avoid surface defects on the steel strip.

The choice of an electrolytic cell depends of the industry applications the producer intends to supply, of the layer thickness they intend to deposit and of the capacity they intend to install. Electrolytic cell type is a function of four main parameters:

- cell geometry
- current density
- electrolytic solution type
- anode type

Cell geometry
The three main types of cell geometry are:

Vertical cell
The two strip sides may be coated simultaneously in one cell. On entry to the cell the strip runs from top to bottom, from the conductor roll through one pair of guiding rolls and the first anode pair down to the sink roll. From there it runs to the exit side, upwards through to the second electrode pair and wringer rolls and on to the next conductor roll.

Conventional cells are filled in with electrolyte and the sink roll and the two pairs of anodes are submerged in the electrolyte bath. In the Gravitel cell the electrolyte enters via a weir in the narrow gap between the insoluble anode and the strip, holding only a small amount of electrolyte in contact with the strip. In this case neither the anodes nor the sink roll are submerged in the electrolyte.
Radial cell

Only one side of the strip may be coated at a time in one cell. On entry to the cell, the strip runs from the top to the bottom, from the conductor roll through one pair of wringer rolls down to the sink roll. From there the strip runs to the exit side, upwards through wring rolls and on to the next conductor roll. Only the lowest part of the sink roll is plunged in the electrolyte bath.

In a variant, the carousel cell, the top rolls have the function of deflector rolls while the sink roll, equipped with a metallic winding, combines the functions of deflector roll and conductor roll.

Horizontal cell

Both strip sides may be coated simultaneously in one cell. The strip runs horizontally through the cells. At the entry to the cell, the strip leaves the conductor roll and runs through one pair of wringer rolls, then between a pair of anodes and from there to the exit side, onwards through another pair of wringer rolls to the next conductor roll. The electrolyte is continuously injected between the two anodes pairs, thereby only holding a small amount of electrolyte in contact with the strip at any one time.
Current density
Installations normally working at low current density can be differentiated from those normally working at high current density. The current density will depend on the main industrial application, the normal metal thickness required and the normal steel substrate thickness. Table 2.1 shows thicknesses for zinc and zinc alloy coil coating applications. A high current density allows a thicker metal layer to be plated onto the steel substrate with on a shorter anode length.

<table>
<thead>
<tr>
<th>Current density A/dm²</th>
<th>Main industry applications</th>
<th>Zinc layer thickness µm</th>
<th>Steel thickness minimum (mm)</th>
<th>Electrolyte relative speed m/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 to 120</td>
<td>Vehicle</td>
<td>5 to 12</td>
<td>0.5</td>
<td>1.0 to 4.0</td>
</tr>
<tr>
<td>30 to 90</td>
<td>White goods</td>
<td>2.5 to 3.5</td>
<td>0.3</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>30 to 90</td>
<td>Others</td>
<td>2.5 to 3.5</td>
<td>0.3</td>
<td>&lt;1.0</td>
</tr>
</tbody>
</table>

Table 2.1: Zinc and zinc alloy layer thickness as a function of industry application

High current density cells are equipped with systems such as electrolyte injection devices to realise a high relative electrolyte speed (electrolyte speed versus strip speed). These systems assure a sufficient supply of metal ions to the polarisation layer at the steel strip surface to carry the current.

Electrolyte bath
These are described for each processes separately, see Sections 2.9.8, 2.9.9 and 2.9.10.

Anode type and gap
Two families of anodes are available: soluble anodes and insoluble anodes, see Chapter 2, Electrolytic cells and reactions.

The gap between the anode and the steel strip differs as a function of the cell geometry and of the maximum steel strip width.

<table>
<thead>
<tr>
<th>Electrolytic cell</th>
<th>Minimum gap mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical</td>
<td>16 to 26</td>
</tr>
<tr>
<td>Vertical gravitel</td>
<td>7 to 14.5</td>
</tr>
<tr>
<td>Radial</td>
<td>7 to 15</td>
</tr>
<tr>
<td>Horizontal</td>
<td>10 to 20</td>
</tr>
</tbody>
</table>

Table 2.2: Gaps between anode and steel strip for different electrolytic cell types
2.9.5 Coating activities- oiling

A wet film of oil is applied to the surface by spray, by wringer rolls or by an electrostatic oilier. This provides a coating for improving protection against white rust (oxide layers on zinc plating) corrosion. It can also act as a lubricant film to minimise subsequent damage by abrasion, to facilitate sorting and to aid in subsequent lacquering and printing operations.

2.9.6 Layer conversion activities

In order to prevent surface damages and flaws during storage and transportation, such as white rust (zinc corrosion) caused by water condensation where there is insufficient air access, the deposited layer may be subsequently phosphated (see Section 2.5.18), passivated with a chromate treatment (see Section 2.5.19) and/or oiled prior to recoiling (see Section 2.5.13). These layers also significantly improve the processing properties, during these and subsequent processes, such as painting or deep drawing.

2.9.7 After-treatment

2.9.7.1 Drying

The strip is dried by means of hot air drying devices. The hot air temperature depends on the process stage. The drier device is usually situated at the end of the post-treatment; the same type of device is used for the phosphate and the chromate sections. See Section 2.6.

Environmental considerations
Energy efficiency according to type of drier and the installation.

2.9.7.2 Unloading - exit looper

The exit looper allows the strip end to remain at standstill in the exit section during cutting of a completed coil. It stores sufficient coil for the strip to continue moving at constant speed in the processing section. Construction and operation is the same as for an entry looper, with the coil running in the reverse direction.

Environmental considerations
Power consumption which will be minimised by maintenance of correct settings and ensuring bearings are free running.

2.9.8 Continuous electrolytic zinc or zinc-nickel plating activities

This is the electrolytic deposition of a thin layer of pure or alloyed zinc onto the surface of a steel strip substrate.

On continuous electrolytic zinc plating line the cold rolled, annealed and tempered steel strip is passed continuously through degreasing and pickling pre-treatments, then through a series of electrolytic cells containing a zinc electrolyte. It is then passed through one or more post-treatments, either layer conversion such as chromating or phosphating, or through an oiling step.

Plating lines layout may vary in design. As an example, Figure 2.11 shows a typical layout of a continuous electrolytic zinc plating line.
2.9.8.1 Entry equipment

See Section 2.9.1.

2.9.8.2 Degreasing

Degreasing of steel strip surface is by means of both chemical action (alkaline agent) and mechanical action (spray and brushes).

The cleaning process involves the following steps:

- alkaline degreasing via immersion or by spraying. This may be coupled with brushing
- rinsing with water and brushing between intermediate rinsing tanks
- drying

The degreasing and rinsing sections may be in horizontal or vertical tanks.

**Alkali degreasing:**

A typical horizontal spray degreasing section for the treatment of oiled coils consists of 3 successive stages:

- stage 1: spray nozzles and brushes
- stage 2: spray nozzles
- stage 3: spray nozzles and brushes

Cascade degreasing has the advantage of achieving a high cleaning rate using only a small amount of degreasing solution. Degreasing is performed in counter-flow direction to the steel coil movement, which means that clean degreasing solution is used in the third (final) stage where it becomes slightly contaminated. This degreasing agent is used for cleaning in the second (more contaminated) stage and subsequently in the first (most contaminated) degreasing stage. The degreasing agent overflows between any two stages are controlled by means of wring rollers.
Section 2.9.3.1 describes typical chemical degreasing systems. In steel coil coating, the degreasing agent is usually a phosphate-containing alkaline (a non-siliceous solution) containing mainly sodium hydroxides, orthophosphates and surfactant compounds with a concentration of 5 to 40 g/l, a temperature between 60 to 85 °C and a pH of about 13. The degreasing solution may be used first in the electrolytic degreasing section and be moved to the chemical degreasing stage to replace the spent chemical degreaser.

**Environmental considerations**
The use of cascade degreasing minimises the amount of raw materials and water used.

When the cleaning solution has reached the maximum oil content it is regenerated by centrifuges.

The solution may be used first in the electrolytic degreasing section.

Fumes generated in degreasing and brushing are normally collected, scrubbed and treated prior to release.

Spent degreasing agent is sent to waste water treatment before release.

The oily waste is treated off-site.

![Spraying degreasing and brushing](image)

**Rinsing**
See Section 2.4. The alkaline degreaser is completely removed by cascade rinsing in 3 stages. Cascade rinsing has the advantage of achieving a high cleaning rate using only a small amount of rinsing water. Rinsing is performed in a counter-flow direction to the movement of the steel strip: the clean water is used in the third stage where it consequently becomes contaminated. This slightly contaminated water is then used for cleaning in the second stage and subsequently in the previous rinsing stage. The water overflows between two stages are controlled by means of wring rollers. The rinsing equipment involves the following steps:

- stage 1: spray nozzles and brushes
- stage 2: spray nozzles
- stage 3: spray nozzles

The process solution in the first stage is demineralised water at a temperature of 70 to 85 °C.

Quality control techniques are used to determine the oil content in the water which gives the required standard of cleaning with minimum water usage. During processing, when the oil content in the water has reached this maximum allowed concentration, the water is sent to waste water treatment before discharge.

**Environmental considerations**
Countercurrent rinsing optimises process efficiency and minimises use of heated demineralised water.
Used water is treated to remove oil prior to discharge.

Water vapour and/or fumes generated in rinsing and brushing are collected and injected into the rinsing tanks.

2.9.8.3 Drying

The degreased strip is dried by means of a hot air drying device. The hot air temperature lies between 100 °C and 120 °C.

Environmental considerations

Energy efficiency.

2.9.8.4 Entry looper and tension leveller

See Section 2.9.1

2.9.8.5 Electrolytic degreasing

The final degreasing of steel strip surface is carried out by means of chemical (alkaline agent) and mechanical (sprays and H₂ and O₂ gases bubbles generated by electrolysis at the strip surface) actions, see Section 2.3.

The electrolytic degreasing section involves the following steps carried in cells:

- alkaline degreasing by an electrolytic system
- rinsing with water, possibly coupled with brushing.

The degreasing and rinsing sections may be in horizontal or vertical tanks.

The electrolytic degreasing is carried out by the electrolysis of the alkaline solution releasing H₂ gas at the cathode and O₂ gas at the anode. The polarity of the electrodes is inverted after each coil or after a certain period in order to avoid polarisation. The solution overflows between to the next stage is controlled by means of wringer rollers.

The degreasing solution is usually the same as that used in the degreasing section. Once the solution has reached a certain oil level it is re-used on the degreasing section (cascade use). The operating temperature of the solution lies between 60 °C and 85 °C.
Environmental considerations
Re-use of the solution in the more contaminated degreasing section is possible.

Alkali fumes generated in electrolytic degreasing cells are usually collected, scrubbed and treated prior to release to maintain a healthy working environment and to prevent corrosion of equipment and substrates.

![Figure 2.14: Electrolytic degreasing](image)

**Rinsing**
Cascade rinsing in 2 stages completely removes the alkaline solution. Cascade rinsing has the advantage of achieving a high cleaning rate using only a small amount of rinsing water. Rinsing is performed in counter flow direction, which means that clean water is used in the last stage where it consequently becomes contaminated. This slightly contaminated water is used for cleaning in the second stage and subsequently in the previous rinsing stage. The water overflows between two stages are controlled by means of wringer rolls. The rinsing equipment involves the following steps:

- stage 1: spray nozzles and brushes.
- stage 2: spray nozzles

Demineralised water having a temperature of 70 to 85 °C is used in the first stage.

Environmental considerations
Use of countercurrent rinsing to minimise use of heated demineralised water.

Water vapour and alkali fumes generated in rinsing and brushing are usually collected and injected in the rinsing tanks.

When the water has reached the maximum allowed oil content commensurate with process quality, it is sent to waste water treatment before release.

**2.9.8.6 Pickling**
Pickling removes any oxides formed during the various stages of steel processing and prepares a reactive steel surface for the plating section. [86, EIPPCB, ]
Coil pickling can be carried out by spraying, or immersion with or without electrolysis. Typical pickling sections involve the following steps:

- stage 1: pickling
- stage 2: rinsing

**Spray pickling**

Two types of pickling solution may be used:

- Sulphuric acid at a concentration within a range of 10 to 60 g/l with a temperature range of 25 °C to 60 °C.
- Hydrochloric acid at a concentration within a range of 100 to 150 g/l with a temperature range of 20 °C to 40 °C.

Both the temperature and the acid concentration are dependent on the available pickling time (which is function of the contact length and the maximum strip speed).

**Environmental considerations**

Fumes generated in pickling are usually collected and scrubbed prior to release. In some lines the contaminated water of the scrubber is treated together with the fumes from the electroplating cells in an evaporator and both the concentrate and the evaporated water are re-injected in the process.

Spent pickling solution is sent to waste water treatment before release.

**Spray rinsing**

The same system is used as for degreasing (see Section 2.9.8.5).

![Figure 2.15: Pickling section](image)

**2.9.8.7 Electroplating**

This section electrolytically deposits a light layer of pure or alloyed zinc onto the surface of a steel strip substrate. A typical plating section involves the following steps:

- stage 1: plating through several electrolytic cells
- stage 2: rinsing.

Sections 2.9.4 and 2.9.4 discuss the process and describe types of electrolytic cell. Current density for various zinc and zinc alloy thicknesses, and the industries they are used in are set out in Table 2.1.
Chapter 2

Types of electrolyte bath
Electrolyte baths in continuous electrolytic zinc plating lines are predominantly acid-based. Alkaline based-electrolytes are no longer in common use. Electrolytes can be sulphate-based or chloride-based. The sulphate-base bath is used with soluble and insoluble anode processes. The chloride-base bath is used by only with soluble anodes as chlorine gas is generated with insoluble anodes. In both baths ionic additions are made to increase the conductivity of the electrolyte bath (e.g. sodium sulphate, aluminium sulphate, sodium chloride). Buffer additions are made to stabilize the pH (e.g. CH₃COONa).

Typical sulphuric base electrolytic bath compositions are:

- **Zinc**: 70 – 120 g/l
- **Free H₂SO₄**: 3 – 25 g/l
- **Na₂SO₄**: 0 - 100 g/l
- **pH**: 1.0 to 3.0 pH units

Anodes types
These are generally described at the start of Chapter 2. For this process:

- **soluble anodes**: the zinc anodes are fixed on a supporting rail and, as they are consumed during the process, they are displaced from the entry side rail to the exit side rail.

- **insoluble anodes**: two materials are used for the anode plate: a plate substrate in titanium coated with a thin layer of tantalum oxides or iridium oxides and a plate in lead alloyed with Sn or with Ag and In.

Rinsing step
The coil is then rinsed to completely remove the electrolyte from the strip surface. Also, in some cases where the coil is coated only on one side, the rinse may be used to pickle the zinc residues on the non-coated side. Rinsing can be carried out by immersion or by cascade spraying, and in horizontal or vertical tanks depending on the available surface. The same cascade principles described in the degreasing section are applied here, see Section 2.9.3.1.

Demineralised or fresh water are used, with temperature between 20 – 50 °C and a pH 0.3 to 3 (among other control parameters).

When the water has reached the maximum allowed contaminant (electrolyte) content determined by quality control, it is sent for waste water treatment before discharge. In some lines, the contaminated water is treated in an evaporator. The evaporated water can be re-used for rinsing and the concentrate re-used in the process electrolyte.

Environmental considerations
Counter-flow cascade rinsing can maximise the rinse efficiency and minimise the use of hot demineralised water.

Re-use of the water outputs distilled from evaporators.

2.9.8.8 Strip polisher
The strip polisher is used to clean the tarnished/oxidised uncoated side of the strip and to remove any stray coating particles which may have been deposited. When producing single sided coated material, some lines dispose of the polishing technology.
A typical polishing section involves the following stages:

- stage 1: polishing
- stage 2: rinsing
- stage 3: drying

**Polishing**
Brushes are used to polish the cold reduced surface on the uncoated side. Demineralised water is used. The metal particulates are filtered from the used water.

**Environmental considerations**
The used water is sent to waste water treatment before release.

**Rinsing**
The strip is passed through a hot water rinse to remove any debris, before being dried. Rinsing can be carried out by immersion or by cascade spraying, in horizontal or vertical tanks depending of the available surface. The same principles as described for the degreasing section are applied. See Section 2.9.8.2.

**Environmental considerations**
The used water is sent to waste water treatment before release.

**Drying**
The polished strip is dried by means of a hot air drying device. The hot air temperature lies between 100 °C and 120 °C. The drier device is usually situated at the end of the post-treatment; the same type of device is used for the phosphate and the chromate sections. See Section 2.6.

**Environmental considerations**
Heat efficiency and losses.

**2.9.8.9 Phosphating**
This process forms a high-quality light phosphate coat with the hopeite chemical structure which is widely used in the automotive industry and for household appliances. Phosphating can improve the performance of the zinc-coated strip with regard to drawability, corrosion resistance and subsequent paintability. See Section 2.5.18.

The strip is treated after zinc coating using spray banks in a two-stage process:

- stage 1: activation
- stage 2: phosphating

**Activating**
The first stage consists of spray of a titanium refiner, which provides activation sites for the second stage of phosphate coating. The activation solution circulates in close loop. The pH lies in a range of 8 to 10, and the temperature is maintained below 40 °C. Spent (used, out of specification) solution is treated in the waste water treatment section.

**Phosphating**
Phosphate coatings are described in Section 2.5.18. A phosphate coat of approximately 1-1.8 g/m² is applied. The phosphate system used can either be single or tri-cationic, depending on customer requirements. The hopeite crystal $\text{Zn}_3(\text{PO}_4)_2$·4$\text{H}_2\text{O}$ incorporates approx. 1% Ni and 5% Mn. A refiner is added to ensure that the phosphate crystals deposited are small, uniform and tight, which enhances the performance of the coating.
Following phosphating, the strip is rinsed in a spray of dilute chromate solution to form a chromate seal. This seal further enhances the corrosion performance of the phosphate coating. The strip is then dried.

The phosphate solution circulates in close loop at a temperature below 40 °C.

**Environmental considerations**
See Section 2.5.18.

Spent (used, out of specification) solution is treated in the waste water treatment section.

Effluents may contain traces of nickel and manganese.

### 2.9.8.10 Full chromating and chromate rinsing

This is described in Section 2.5.19. A typical chromating section involves the following steps:

- stage 1: chromating
- stage 2: rinsing
- stage 3: drying

**Chromating**

Full chromating or chromate rinsing of the strip after zinc coating is achieved using spray banks. Chromate rinse or passivation is a spray treatment with solvents containing chromic acids. A coat of 10 – 35 mg/m² per side is applied. During passivation, CrVI is largely converted to CrIII. The strip is treated with solutions between 0.5 – 2 % of chromium and at temperatures below 40 °C. The chromate solution circulates in close loop.

**Environmental considerations**

Health and environmental issues are described in Section 2.5.19

Spent (used, out of specification) solution may be treated in a typical waste water treatment plant or disposed of as hazardous waste.

**Rinsing**

Rinsing can be carried out by cascade spraying in horizontal tanks. The same principles as described for the degreasing section are applied. See Section 2.9.8.2

**Environmental considerations**

The used water is sent to waste water treatment before release.

**Drying**

The chromate rinse strip is dried by means of a hot air drying device. The hot air temperature lies between 100 °C and 120 °C which is necessary for chemical reaction of the excess CrVI with the solution additives to become CrIII.

**Environmental considerations**

Heat efficiency and losses.

**Anti-fingermarking section**

This provides a chromate coating for improving protection against white rust corrosion. This coating has the advantage of not showing fingerprints, which is a critical for some customers.

Typical chromating section involves the following steps:

stage 1: coating. The chromate coating is applied via a roller coater system, similar to that used in paint lines.

Stage 2: drying. The wet coating is passed through an air oven to dry.
Environmental considerations
The coating is dried in place with no rinsing, so no effluent arises.

Heat efficiency and losses may need to be addressed for the oven.

2.9.8.11 Oiling

A wet film of oil is applied on the surface of the strip, see Section 2.9.5. The oiling coat is between 0.25 – 3 g/m²/side, applied in an electrostatic oiler, with the oil circulating in close loop.

2.9.8.12 Exit looper

See Section 2.9.7.2

2.9.9 Continuous electrolytic tin plating activities

Mild low carbon steel is coated can be coated with tin either equally or different thicknesses, and in a range of thicknesses.

On a continuous electrolytic tin coating line, the blackplate strip is passed through cleaning and pickling pre-treatments, then through a series of tanks containing a tin electrolyte. This process electrolytically deposits a light layer of pure tin onto the strip, which may be subsequently reflowed, then passivated and oiled prior to recoiling.

Plant layouts vary in design; some modern lines now incorporate a side trimming unit prior to pre-treatment. Figure 2.16 shows a typical layout of a continuous tin coating line.

Figure 2.16: Tin Coating Line Layout
2.9.9.1 Degreasing and cleaning

As with other surface treatments, tin plating requires appropriate preparation of the substrate as poor surface condition can lead to inadequate adhesion of the tin or even dewetting during the remelting operation. See Sections 2.3 and 2.9.3.1. Cleaning solutions are usually proprietary mixtures of polyphosphates, sodium hydroxide and wetting agents. The chemical action of the bath is enhanced by electrolytic treatment. Concentrations range from 7 to 50 g/l and the solution is operated at a typical temperature of about 90 °C maintained by circulating the solution through a heated reservoir storage tank. Additions of water and cleaning compound are made as required. Figure 2.17 shows a typical cleaner section with rinsing.

The strip is polarised using one of two methods:

- directly - where the strip passes over a conductor roll, and then travels between two pairs of mild steel electrodes. Current passes from the conductor roll via the strip and electrolyte to the electrodes
- indirectly - by grid electrodes where the steel strip travels between two pairs of mild steel plates which form two electrodes of opposite polarity. Current passes from one pair of electrodes via the electrolyte and the strip to the other pair of electrodes.

Rinsing
Rinsing is as thorough as possible to avoid contamination of the pickle liquor pre-treatment by the cleaning solution. It is carried out by spraying hot water, typically between 150 – 400 l/min.

Environmental considerations
Alkali fumes generated during cleaning are typically collected and scrubbed prior to release.

Spent cleaning agent and waste water from rinsing can be treated in a typical waste water treatment plant.

Figure 2.17: Schematic of Cleaner Section
2.9.9.2 Pickling

See Section 2.9.3.2. Lead anodes are used because of the 50 g/l (max) concentration of the sulphuric acid electrolyte. The acid is deliberately not heated, but the process current induces an equilibrium temperature of 25 to 40 °C, depending on operating conditions.

Environmental considerations
Acid fumes generated during pickling are usually collected and scrubbed prior to discharge. Spent acids and rinse waste water are sent for waste water treatment prior to discharge.

2.9.9.3 Tin plating

There are two widely used tinning processes:

- the ‘Du Pont’ process which represents 20 % of worldwide tinplate production. It has the ability to accept high current densities. However the electrolyte composition is complex, with high chloride and fluoride contents making it highly aggressive to plant materials

- the ‘Ferrostan’ process is the most widely used, with between 75 and 80 % of worldwide tin plate production. This is due to the use of less hazardous and corrosive chemicals.

The plating section of a tinning line consists of several rubber-lined steel vertical tanks arranged in tandem. Each tank contains a rubber driven sink roll at its base and two chromium plated copper conductor rolls above the electrolyte surface. Current is transferred from the roll to the strip so that the strip becomes cathodic. Soluble tin anodes are hung from bridges across the vats into the plating electrolyte. Anodes are cast from electro-refined tin which is typically greater than 99.85 % pure.
Figure 2.19: Schematic of plating tank – vertical cell

The plating electrolyte consists of stannous sulphate, phenolsulphonic acid (PSA) and an organic addition agent. The stannous sulphate provides an initial source of tin ions in solution; the PSA makes the solution highly conductive and the addition agent ethoxylated alphaphthol sulphonic acid (ENSA) aids uniform and consistent tin deposition. This is essential for making the plate bright at after the later flow-melting stage.

Typical composition of tin electrolyte to ensure good plating conditions is

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stannous tin</td>
<td>25 – 45 g/l</td>
</tr>
<tr>
<td>Phenol sulphonic acid (PSA)</td>
<td>20 – 27 g/l</td>
</tr>
<tr>
<td>ENSA</td>
<td>1.5 - 6.0 g/l</td>
</tr>
<tr>
<td>At a temperatures of</td>
<td>30 – 55 °C</td>
</tr>
</tbody>
</table>

The plating electrolyte is circulated through heat-exchangers, the rate of circulation being high enough to maintain a constant plating temperature for all coating weights.

2.9.9.4 Drag-out

After plating, the strip goes through a series of drag-out and rinsing operations.

At the drag-out tank, electrolyte is spray-rinsed with a dilute solution of PSA and a tin compound, and then returned to the electrolyte circulation tank. This tank is connected to an evaporator and the dilute electrolyte is concentrated by evaporation then recirculated back to the plating tank.

The exit squeeze rolls on the drag-out recovery tank leave the optimum amount of electrolyte on the strip required for ‘fluxing’ of the tin coating during melting. The film only needs to be dried before the strip enters the flow-melting or brightening unit which is accomplished by passing the strip through a series of hot air jets.

On high-speed lines a second drag-out recovery unit is provided to increase the dilution ratio. This means a recovery ratio of more than 90 % of the drag-out electrolyte is accomplished.

Environmental considerations
Dragged over plating solution can be concentrated and returned to the plating process.
Acid fumes generated during plating and drag-out may be collected by an extraction unit and are usually scrubbed prior to discharge.

### 2.9.9.5 Differential marking

Differential coatings are shown by marking one side of the strip usually with a solution of sodium dichromate. This is printed onto the strip in a pattern of diamonds, circles or, more commonly, lines. The solution is dried onto the strip and after melting will leave a dull, non-lustrous finish in the areas that have been contacted by the printer.

**Environmental considerations**
As for other chromium coatings, see Section 2.9.8.10.

### 2.9.9.6 Reflow – tin brightening

The tin coating deposited on the strip has a dull matt appearance. Reflowing or flow melting is the process used to give a bright lustrous finish. The strip is heated to above 232 °C (the melting point of tin) and then quickly cooled to solidify the coating. Melting is achieved by resistive heating (applying a voltage between two conducting rolls supporting the strip), supplemented by induction heating (which provides 20 % of the total energy).

![Figure 2.20: Schematic of flow-melt section](image)

The mixed resistive and inductive heating makes it easier to obtain stable melting conditions, avoiding certain cosmetic coating defects.

**Environmental considerations**
Energy efficiency and losses.

### 2.9.9.7 Passivation treatments

Passivation is carried out by a chromating treatment, see Section 2.5.19, in order to reduce the thickness of tin oxides formed during remelting. The treatment electrolytically produces a chromium-containing layer which prevents subsequent oxidation in air and also improves adhesion of the paint layer.

The operation is performed in a solution of sodium dichromate
Environmental considerations
For health and environmental issues, see Section 2.5.19.

2.9.9.8 Oiling

Prior to recoiling the treated coil a thin film of lubricant is applied to the tin plate surface. This film minimizes subsequent damage by abrasion, facilitates sorting and aids subsequent lacquering and printing operations. See Section 2.9.9.8.

A pure grade of either dioxyl sebacate (DOS) or acetyltributyl citrate (ATBC) is used. The oil can be added by two methods:

- electrostatically, where a negatively charged oil mist is driven away from similarly charged repeller plates onto the surface of the strip
- emulsion oiling, where a thin, uniform oil film is applied by flooding the surface of the tinplate with a dilute oil-in-water emulsion

The total oil levels on the strip range typically from 6.0 to 12.0 mg/m²

2.9.10 Continuous electrolytic chromium plating activities (Electrolytic Chromium Coating of Steel - ECCS)

This is also known as tin-free steel: a low carbon, mild steel, coated equally on both sides with a complex layer of metallic chromium and chromium hydroxides. The processes are described in general in Section 2.5.3, along with the health and environmental issues. Figure 2.22 shows a typical process line layout and Figure 2.23 gives a cross-section through a line. The chromium plating of the steel strip is performed electrolytically in a chromic acid bath. The coating is applied equally to both sides as a complex layer of chromium metal and chromium oxides. The overall process is similar to the electrolytic tin process – the steel strip is passed through the entry section of the line, cleaned pickled and then treated electrolytically in a solution containing chromic acid, rinsed thoroughly, dried, oiled and then recoiled.
2.9.10.1 Degreasing and cleaning

Cleaning is performed electrolytically in an alkaline bath (see Section 2.3) and sodium hydroxide is generally used at concentrations of typically 50 to 90 g/l. Wetting agents and chelating agents are also added to the cleaning agent to improve cleaning performance.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Hydroxide</td>
<td>60 – 65 %</td>
</tr>
<tr>
<td>Sodium Phosphate</td>
<td>30 – 35 %</td>
</tr>
<tr>
<td>Wetting Agent</td>
<td>0 - 2 %</td>
</tr>
<tr>
<td>Chelating Agent</td>
<td>2 - 5 %</td>
</tr>
</tbody>
</table>

**Electrodes**

Electrodes are made of mild steel plates. The polarity of the strip can be selected from anodic, cathodic or any combination of the two. The strip is polarised, either

- directly, where the strip passes over a conductor roll, and then travels between two pairs of mild steel electrodes. Current passes from the conductor roll via the strip and electrolyte to the electrodes, or

- indirectly, by grid electrodes where the steel strip travels between two pairs of mild steel plates which form two electrodes of opposite polarity. Current passes from one pair of electrodes via the electrolyte and the strip to the other pair of electrodes.

See Figure 2.14: Electrolytic degreasing

The temperature of the cleaning solution is kept constant by circulating the solution between the cleaning tank and the storage tank with a steam heater coil.
**Rinsing**
This is thorough to avoid contamination of the pickle liquor pre-treatment by the cleaning solution. It is carried out by spraying heated water typically between 150 – 400 l/min.

**Environmental considerations**
Alkali fumes generated during cleaning are typically collected and scrubbed prior to release. Spent cleaning agent and waste water from rinsing are sent for waste water treatment before discharge.

![Figure 2.23: Typical arrangement of ECCS Line](image)

2.9.10.2 **Pickling**
Sulphuric acid is used for the pickling solution at concentrations of 60 to 115 g/l at ambient temperature. See Sections 2.3 and 2.9.3.2.

**Environmental considerations**
Acid fumes generated during pickling are usually collected and scrubbed prior to release.

Spent pickling agents and waste water from rinsing are sent for typical waste water treatment before discharge.

2.9.10.3 **Chromium plating**
See Section 2.5.3 for a general description, and the health and environmental considerations.

**Pre-dip**
Before chrome plating takes place the strip is passed through a pre–dip tank. This is essential to prepare the surface of the strip for electrodeposition and prevents stains and other surface defects forming on the surface of the strip. It is carried out in a sulphuric acid solution of 0.3 – 0.5 g/l at ambient temperature.

**Electroplating**
The strip is passed through an electrolyte containing CrVI ions, which are reduced cathodically on the strip surface to form a duplex layer of hydrated chromium oxide and metallic chromium. The current applied is determined according to the strip width, line speed, current efficiency and aimed film weight and flows from the insoluble electrodes to the strip through the electrolyte, and then returns to rectifier through the conductor rolls.
Chapter 2

The plating solution is pumped from a circulation tank, passed through a heat-exchanger and then travels up into the bottom of the coating tanks, which contain inert anodes of lead-antimony. It is overflowed from the top part of the tank and then returned to the circulation tank.

A typical plating electrolyte will consists of:

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromic acid</td>
<td>110 – 130 g/l</td>
</tr>
<tr>
<td>Hydrofluoroboric acid</td>
<td>0.30 – 0.44 g/l</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>0.60 – 0.80 g/l</td>
</tr>
</tbody>
</table>

The hydrofluoroboric and sulphuric acids both act as catalysts: they improve the efficiency of the plating process but are not themselves consumed in the process. Temperature can have a marked effect on the electrolyte efficiency; the solution is far more efficient at lower temperatures. However because the electrolyte is heated by the electric current being passing through it, the temperature has to be kept constant by the heat-exchanger which cools the solution. In operation the optimum temperature of the electrolyte is 58 +/- 2 °C

Environmental considerations
The health and environmental issues are described in general in 2.5.3.

Acid fumes are generally collected and scrubbed prior to discharge. The scrubbing solutions may need treatment prior to discharge.

2.9.10.4 Drag-out and rinsing

At the drag-out tank, electrolyte is spray rinsed away and the washings are returned to the electrolyte circulation tank. This is connected to an evaporator where the diluted electrolyte is concentrated and returned the process tank. The amount of spray rinse at the drag-out recovery tank and the capacity of the evaporator are decided from the chromic acid concentration in the effluent.

Chromic acid treated strip must be fully rinsed with water before drying, oiling and recoiling. The strip is sprayed with hot water at the entry and exit ends of the rinse tank to remove any carry-over of electrolyte or water-soluble constituents in the oxide film. Spraying is carried out at 50 – 60 °C with a flowrate about 5000 – 10000 l/h. Spraying at higher temperatures and pressures could damage the freshly formed film.

Environmental considerations
The health and environmental issues are described in general in 2.5.3.

Chromium and other electrolyte components may be recovered by countercurrent rinsing and evaporation of drag-out.

Fumes generated during electrolytic plating and drag-out are collected by an extraction unit and typically scrubbed prior to discharge.

2.9.10.5 Oiling

Prior to recoiling a thin film of lubricant is applied to the chrome-plated surface. The function of this film of lubricant is to minimize subsequent damage by abrasion, to facilitate sorting and to aid in the lacquering and printing operations. A pure grade of either dioxy sebacate (DOS) or acetyltributyl citrate (ATBC) is used. The oil is usually applied by an electrostatic oiler. See Section 2.5.13.

The aim weight of oil film on the strip is 3.0 – 7.0 mg/m²
2.9.11 Continuous electrolytic lead coating of steel

The only plant operating in Europe is due to close within two years. No specific information has been exchanged. General information on analogous coil and jig processes can be used for the majority of the activities and issues.

2.9.12 Other continuous electrolytic coating of steel

No data provided

2.10 Coil and sheet processing for aluminium lithographic plates

[Ullman's, 2002/3 #38] Substrates for lithographic plates (see Section 1.3.3) must be easily and cheaply prepared, chemically resistant to acid and alkali solutions, solvent-containing inks as well as solvents. They must also be flexible for fixing to rollers, physically robust and stable in use for print runs of thousands of copies, with a well defined microroughness and hydrophilicity for retaining and spreading the dampening agent. Aluminium is the substrate of choice as it can be easily prepared by the processes described here.

2.10.1 Surface graining

Although the surface can be prepared mechanically, it is now more normal to use electrochemical graining. The raw aluminium surface is first degreased (see 2.3) and then uniformly corroded by using an AC treatment in dilute nitric acid, hydrochloric acid, or mixtures of these with other acids. This process of graining is a type of pitting corrosion which attacks the entire surface of the aluminium leaving a very uniform rough surface. The depth of roughness can be controlled within wide limits (2.5 – 9 mm) by varying the electrical parameters. Both processing speed and the uniformity of the resulting substrates depend on temperature, flowrate of the electrolyte, geometry of the tank, and other parameters. Combination processes have also been used in graining. In these processes, mechanical graining is followed by electrochemical treatment.

Graining with wire brushes produces the lowest increase in surface area of the plate, and electrochemical graining the highest. This influences not only the quality of reproduction and the optical resolution but also the printing properties (water spreading and length of run). The finer the graining of an aluminium surface, the lower is the mechanical resistance. With wire-brushed aluminium, a second hardening step is not required. However, an anodic oxidation step is essential for electrochemically grained aluminium.

2.10.2 Anodic oxidation (anodising)

Anodic oxidation (as described in Section 2.5.15) involves conversion of the uppermost layer of the aluminium workpiece to aluminium oxide, without affecting the surface topography significantly. Two processes are in general used: sulphuric acid or a phosphoric acid electrolyte. The former leads to smaller pores and thicker oxide layers than the latter.

In general, not more than 5g of oxide is produced per square metre; depending on the roughness of the surface, this corresponds to a layer thickness of about 1 µm. The oxide formed during anodising is X-ray amorphous and an extremely strong adsorbent. The properties of the substrate are greatly improved during this step, i.e. the adhesion to the light-sensitive coating; resistance of the surface to chemicals; its hydrophilicity, hardness and abrasion resistance, and
thus the potential of running length. However, the extent to which the aforementioned aspects can be effective depends on process parameters and on the process itself.

2.10.3 Post-treatment

Post-treatment of the oxide with certain hydrophilising solutions has proved advantageous in the production of presensitised (PS) plates. The main purpose of this treatment is to improve the hydrophilicity of the aluminium oxide surface. However, the adhesive properties, developability, and shelf-life of the plates are all influenced at the same time. Solutions of the following substances have been proposed for this purpose: alkali silicates, phosphonic acids, hexafluorometalates of group 4 elements (titanium, zirconium, and hafnium), heteropolyacids, oxo acids of pentavalent phosphorus, and hydrophilic colloids. All of these compounds coat the surface of the aluminium oxide to generate a very polar covering layer, which improves the hydrophilicity of the surface.

2.10.4 Coating and further processing

Preliminary treatment of the carrier is followed by in-line coating of the plate in a fully continuous process. A solution of the components of the light-sensitive coating in a more or less volatile solvent mixture is applied to the carrier in a defined wet film thickness. The coatings are generally applied with a fishtail die, with a roller coater, or by spraying. The thickness of dry coatings is 0.3 – 5 mm.

The line speed in modern plants is <1 m/s. The length of individual steps is adjusted to this process speed. After drying, the web is automatically inspected for coating defects. It is cut apart, and defective plates are removed. Cutting of the plates requires special attention. Presensitized lithographic plates are available in many sizes up to c. 3 m² (1500×2000 mm).

The finished faultless plates are stacked by using a suitable interleaving paper and packed in lightproof wrapping paper (if necessary, after shrink-film packaging).

The shelf-life required for these presensitized lithographic plates depends on the extent of their distribution. Also, the more diverse the climatic conditions under which the plates are to be stored and used, the more diverse are the requirements.

No other data provided

2.11 Printed circuit board manufacturing

[14, DG Env, 1993, 52, France, 2003, 63, CETS, 2003] Printed circuit boards are complex electronic circuits in which the wiring between components and certain fixed components themselves are printed on to a non-conducting base. The base (or board) is coated with a metal, usually copper, although other metals, such as aluminium, can be used. Single layer boards have a circuit on one side only; double layer boards have circuits on both sides; multi-layer boards consist of alternating layers of conductor and insulating material bonded together. Boards can be manufactured with up to 22 layers. Boards are usually glass resin or pressed epoxy paper. However, flexible layers are increasingly used (for example, to provide connections to screens in portable computers), as well as aluminium, and other speciality substrates. Boards are supplied ready smooth coated with copper.

Processing is complicated and will vary to produce any specific design of board. Over 40 activity stages may be used in the production of boards, although not all of them will be used for any one board design.
The following example is of the production steps involved with creating the circuit on a double sided board. Other activities are also associated with printed circuit board manufacture, such as cutting and drilling.

2.11.1 Mechanical preparation

Prior to the application of the photoresist, the blank laminate has to be cut or punched to size and shape, drilled and mechanically cleaned to remove the corroded copper surface (brushed or sandpapered), followed by rinsing.

Environmental considerations:
Copper may be mechanically recovered by centrifuging or filtration, enabling recycling of the waste-water, and possible zero discharge from this stage.

2.11.2 Metallisation

The board is then processed through a metallisation process in order to obtain a preliminary connection from one side of the board to the next.

2.11.3 Lamination of photosensitive resist to the board

In the pattern plate technique, an organic resist is applied to the copper-clad board. This process leaves a resist covering the areas to be etched away later and exposes only the circuit pattern to be plated. This method allows for the deposition of copper and tin or tin-lead resists on the required areas. During the later stage of etching, only the original copper cladding which remained under the photoresist will be removed.

2.11.3.1 Photoresist

The photosensitive resist is usually a UV sensitive photopolymer film. The photoresist is applied from rolls using automated lamination equipment in a five stage process. The boards are processed through the laminator at predetermined temperatures, pressures and speeds as it essential to achieve uniform application of the film to both sides of the board. The dry film photosensitive resist is rolled (laminated) onto the surface of the board using pressure and heat.

Stage 1

Figure 2.24: Stage 1- printed circuit board prior to lamination
Stage 2

Figure 2.25: Stage 2- printed circuit board during lamination

Stage 3

Figure 2.26: Stage 3- printed circuit board post lamination

Note: The Mylar™ is a clear protective film used by the resist manufacturer to protect and support the resist. It is laminated onto the board with the photoresist and is subsequently not removed until immediately prior to development.

Due to the UV sensitivity of the resist all lamination takes place in a yellow light area/dark room. The working environment within this area must be clean and dust free and of a constant humidity and temperature in order to ensure both film and artwork maintain dimensional stability and cleanliness.

Stage 4

Figure 2.27: Step 4- printed circuit board imaging
The imaging process usually takes place on a double sided exposure unit.

Artwork is prepared of an image of the circuit to be created. This is positioned on either side of the board prior to exposure. Areas exposed to the UV light through the clear regions of the artwork film are polymerised and are subsequently insoluble in the developer solution. Areas protected from UV exposure i.e. dark regions of the artwork film are subsequently dissolved by the developer.

**Stage 5- Developing:**

The purpose of the developer is to dissolve the unexposed and therefore non-polymerised photoresist film from the board. The chemistry used to dissolve the unexposed photoresist is usually a solution based on sodium/ potassium carbonate. Following the developing stage the boards are rinsed and dried. Process temperature is 28 – 32 °C depending upon dry film used. Dwell time: Dependant upon dry film used.

**Environmental considerations**

Process tanks are usually equipped with fume extraction to remove generated aerosols. Effluents may need treatment including neutralisation and settlement.

### 2.11.3.2 Electrolytic process

Stages required:

- degrease and cleaner, see Section 2.3
- rinse, see Section 2.4
- etch, see Section 2.5.24
- rinse, see Section 2.4
- sulphuric pre-dip, see Section 2.3
- acid copper electroplating, see Section 2.5.1
- tin or tin/lead electroplating, see Section 2.5.6.

**Environmental considerations**

Chemical coppering may be replaced by palladium, graphite or conducting copolymers, which are so-called “clean technology” techniques.

To prevent deterioration of the workplace atmosphere, process tanks may be equipped with fume extraction to remove generated aerosols.

Effluents may require treatment in waste water treatment plant. These treatments include filtering, neutralisation and settlement.

### 2.11.3.3 Resist stripping:

After electroplating, the photoresist film has served its purpose of defining the circuit image and is therefore completely removed from the board surfaces.

Resist strippers are designed to strip fully aqueous dry film and liquid photoresists. The resist strippers have been formulated in order to remove the resist rapidly without attacking the copper or the tin/ tin-lead. Controlled swell characteristics minimise lock in between fine tracks and in turn the stripper breaks down the film into large particles, which are then easily removed by filtration of the effluent.
Chapter 2

Typical operating temperature: 50 – 60 °C.
Dwell time: Approx. 60 - 120 seconds.

**Environmental considerations**
COD and copper emissions. May be concentrated using filtration and evaporation, with distillate being sent to waste water treatment (for COD) and concentrate being managed as a hazardous waste.

To prevent deterioration of the workplace atmosphere, process tanks may be equipped with fume extraction to remove generated aerosols.

Effluents may require treatment in waste water treatment plant. These treatments include filtering, neutralisation and settlement.

**2.11.3.4 Etching**

Etching is undertaken to completely remove the base copper thus leaving only the circuit pattern which is protected by the tin/ tin-lead deposit (etch resist). Typically, modern etchants will remove copper at 50 microns per minute at 50 °C.

The type of etchant used, the equipment in which it is used and the rate of etch is of great importance, as they all influence the amount of undercut that occurs. The undercut is the amount of copper dissolved from beneath the metal etch resist, which produces an overhang of the metal resist.

The etching solution is controlled as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.1 - 8.3</td>
</tr>
<tr>
<td>Temperature</td>
<td>45 °C</td>
</tr>
<tr>
<td>Copper</td>
<td>145 – 160 g/l</td>
</tr>
<tr>
<td>Halide</td>
<td>235 – 265 g/l</td>
</tr>
</tbody>
</table>

Ventilation is likely to be required to remove ammonia and achieve a comfortable work place, as well as meeting health and safety requirements. Excessive ventilation will reduce pH and ammonia levels, insufficient ventilation will allow excessive fumes and an increase in pH and ammonia. Ideally, the ventilation should be dedicated to the etch line only.

**Environmental considerations**
Processes are available to recover significant amounts of copper and minimise etchant top up as well as storage and transport of hazardous solutions.

Where ammonia etchant is used, process tanks may be equipped with fume extraction to remove generated aerosols and fumes to maintain the workplace atmosphere within health and safety levels.

Effluents may require separate treatment prior to a typical waste water treatment plant, depending on etchant chemistry.

**2.11.3.5 Tin stripping:**

This process is now typically undertaken in a horizontal mode as a two-stage tin - lead stripping technique. The first stage strips to the intermetallic layer in, then the second stage strips the intermetallic layer thus leaving a blemish-free copper surface.
Stage 1: temperature and immersion time 25 – 35 °C for 20 – 60 seconds

Stage 2: temperature and immersion time 25 – 35 °C for 10 – 30 seconds

**Environmental considerations**

To prevent deterioration of the workplace atmosphere, process tanks may be equipped with fume extraction to remove generated aerosols.

Effluents may require treatment in waste water treatment plant. These treatments include filtering, neutralisation and settlement.

### 2.11.3.6 Other activities

Other activities may include nickel and gold processing, drilling and cutting. There are water emissions associated with the metals processing and noise and dust associated with the drilling and cutting.

*No data provided*

### 2.12 Utility inputs

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

#### 2.12.1 Energy

The energy uses are described in Section 1.4.3. Electricity is used in the form of direct current for the electrochemical processes. Gas, oil, coal and/or electricity can be used for process heating, depending on availability and cost.

Electricity is also used for process cooling and fume extraction. Gas and/or electricity are used for the drying of surface treated work.

The range of the typical proportion of energy consumptions per usage for a sub-contract acid zinc plating shop are:

- Direct current for pre-treatment and zinc plating: 20 – 40%
- Process heating for pre-treatment and zinc plating: 20 – 40%
- Process cooling for zinc plating: 0 – 17%
- Fume extraction: 5 – 13%
- Drive motors, drying, space heating, lighting: 13 – 40%

#### 2.12.1.1 Electricity

Energy can be drawn from three phase supplies and/or stepping down from high voltage supplies. These AC supplies are rectified to DC power for the electrochemical reactions within the installation via a system of bus bars (usually aluminium or copper) between the rectifiers and the anodes. There can be significant energy losses associated with these activities which are highlighted in Section 1.4.3.

The electrical power consumption in the electrochemical reaction per m² of surface treated in the process can vary according to the process chemistry. Some processes, such as acid zinc are more power efficient than others (such as cyanide zinc) where energy is lost in electrochemical side reactions (in this case, the oxidation of cyanide).
2.12.1.2 Fossil fuels and process heating

Many of the process vats have to be heated above ambient temperatures to operate efficiently. Oil and gas (and possibly in some cases, coal) are used as the main heating sources for process solution. Vats are usually indirectly heated by heating coils circulating a hot liquid. High pressure hot water systems (where the water can be circulated under pressure and at temperatures above 100 °C), and thermal fluid systems (oils which can also be run at temperatures above 100 °C) can provide a greater energy input for the space used, and may be required where process operating temperatures are close to 100 °C. Unpressurised hot water can be used where process temperatures are below 85 °C.

Leakages from water-based systems do not usually damage process solutions, but may dilute solutions beyond economic recovery. Thermal fluids leaks can require the complete replacement of process solutions, but are more easily observed.

Direct heating of the tanks is not usual, although individual electric tank (immersion) heaters are widely used for process lines with small tank volumes (such as precious metals, and reel to reel), and may be used in manually operated lines with larger tank volumes but low throughputs or to assist other systems to achieve operating temperatures.

Energy use depends on the operating temperature required for the process to operate efficiently and stray heat loses from the system.

In electrochemical processes heat also comes from the passing of current through the solution, and some chemical processes may be exothermic.

2.12.1.3 Cooling of process solutions

Many processes need to be maintained within a temperature range for optimum efficiency of quality of treatment and minimising breakdown of process chemicals. They may require heat input before starting processing (such as after a shutdown period overnight), but current passed during the electrochemical reactions or some chemical reactions may heat the solution beyond the range required. More information is provided in [85, EIPPCB, ]. There are three common systems used in surface treatment:

- the simplest cooling system is once-through with water running once through cooling coils in the vats and discharging the water to foul sewer or surface water: water may come from the town supply, nearby river or a borehole extracting groundwater. Water may also be recycled from other uses in the installation (such as used rinse water or treated effluent) before discharge. The water used may require treatment before use, such as filtration of river or groundwater. These systems have the highest water usage and will be one of the biggest uses of water in an installation

- in recirculating cooling tower systems, the cooling water is recycled constantly through a cooling tower. However, running the water over the cooling tower maintains a high dissolved oxygen level which can cause corrosion within the system and evaporation of water at the tower can cause the build-up of suspended solids. The recirculating water may therefore require treatment to prevent corrosion and some of the water must be discharged periodically to prevent build-up of excess dissolved solids

- in closed systems, where the coolant is not in contact with the outside air. This minimises corrosion and there is no build-up of dissolved solids. The cooling system may be refrigerated or pass through fan-cooled radiators.

Electricity is also consumed in cooling systems for pumping and for chilling in refrigerated systems.
2.12.1.4 Other energy requirements within the installation

Electricity is also used for ancillary equipment, see Section 1.4.3 Energy use in the heating and cooling and ventilation of work and storage spaces will depend on the installation construction, the location (such as Northern or Southern Europe) and the heat and water vapour loses as well as fumes from the process lines.

2.12.2 Water

Water supply and quality is critical in this industry. It is can be used in cooling (see Section 2.12.1.3) but its other large use is in rinsing between process stages to prevent contamination of the next process, overreaction at or staining of the workpiece or substrate (see 2.4). The use of the water determines the quality required and the source(s) that can be used, and an installation may have more than one water source for different purposes. Water sources are:

- borehole
- river
- towns (mains) water
- recycling from other uses in the installation, such as rinses or treated effluents.

For basic uses such as cooling and floor and plant cleaning, only the suspended and/or total dissolved solids (TDS) content may be of importance and recycled water may be adequate; depending on the source, filtering may be required. For many process solutions and rinses, water similar in quality to drinking water is satisfactory, again possibly with filtering. For high quality work, where the staining from TDS left from drying is critical, such as decorative finishes or printed circuit boards, or interference in the process such as anodising annealing, all sources will require treatment to lower TDS to demineralised or deionised water quality.

Treatment options include:

- filtration
- deionisation/ demineralisation
- ultrafiltration
- reverse osmosis

The residues of these treatments will contain the retained solids and any saline solutions from regeneration (deionisation/ demineralisation). They may be discharged to the treatment plant of the installation or directly to foul sewers, according to local environmental requirements.

2.13 Abatement of potential releases to the environment

This section summarises abatement treatment options for potential releases. The main releases are described in Section 1.4.4. Potential environmental releases are identified as key environmental considerations for each activity described in the preceding sections of Chapter 2. The most significant environment pollution factors from the surface treatment chemical and electrolytic activities are the:

- emission of pollutants in waters
- production of hazardous waste
- emissions to air.

Emissions to air are the least significant of these [104, ÜBA, 2003].
2.13.1 Waste water

Installations for surface treatment by chemical and electrolytic activities are predominantly water-based and generate significant quantities of effluents containing both inorganic and organic pollutants. The wide range of processes and of raw materials means that effluents are complex and vary in composition by time, process and plant.

The most effective method for preventing pollutants entering the water environment is minimisation of the loss of materials. The water-based processes lose their materials by drag out into rinse waters, and minimisation of these material loses in rinsing is discussed in the sections describing methods for rinsing and drag-out control, Sections 2.4, 4.5 and 4.6.

Minimisation of water usage is also discussed in these sections.

The following issues form the basis for selecting the most appropriate means of waste water treatment address [3, CETS, 2002]:

- the fate or use of the waste water discharge (internal or external re-use, discharge to municipal waste water treatment, direct discharge to surface waters) and the associated quality standards or requirements (environmental or production)
- regulatory discharge requirements
- the processes practised which give rise to the waste water
- the size of the volume and composition of the waste water
- the composition of other streams discharging to the same water course or foul sewer (this may be for the consideration of the regulator
- wider environmental impacts of adopting any particular process (for example, high energy consumption for little environmental gain)

Waste water treatment is described extensively elsewhere, such as generally in [87, EIPPCB] and specifically for this sector [6, IHOBE, 1997, 13, UNEP, et al., 2002, 21, Agences de l'Eau de France, et al., 2002]. The following sections are therefore a brief description of the activities.

2.13.1.1 Treatment fundamentals

Waste water is contaminated by used reagents and the breakdown products from the processes. The main ingredients of concern are metal ions (cations), toxic anions such as cyanide or chromate. There are also other ions and organic substances. Note that metals are conservative, see Section 1.4.4.1. Some of the waste water treatments themselves may produce contaminants that require further treatment. All contaminants need either or both:

- treatment to destroy or change them to more readily managed chemical species
- separation from the water to predetermined levels.

The removal of the contaminants from water can be by filtering and/or settlement techniques. This typically requires pre-treatment such as chemical processing to ensure the contaminants are in the correct physico-chemical state for the separation process, followed by flocculation at the correct pH and settlement. Figure 2.28 describes the layout of a typical waste water treatment plant.
Separation is normally by removing the contaminants from the water, but can also be by removing the water from the contaminants by:

- evaporation, with or without condensation of the water vapour, with a residual sludge.
- by reverse osmosis, providing a purified, but not pure, water and with a waste water, which contains the concentrated impurities.

The residual concentrates may in turn be reduced to a solid by the addition of other materials or the evaporation of the remaining water [3, CETS, 2002].

### 2.13.1.2 Treatment options

Within the waste streams arising from surface engineering processes any or all of the following categories of constituents may be present [21, Agences de l'Eau de France, et al., 2002] and see Section 1.4.4.

- **organic materials:**
  - immiscible – non-halogenated oils, greases, solvents
  - immiscible – halogenated oils, degreasing solvents, paint solvents
  - soluble – wetting agents, brighteners, organic ions and ligands e.g. acetate, EDTA, COD
  - AOX – potentially formed in effluent treatment
● suspended solids – metal hydroxides, carbonates, powders and dusts, film residues, metallic particles etc
● ionic substances
● acids and alkalis
● metals – soluble anions from process activities
● nitrogenous materials – NH$_4^+$, NO$_3^-$, NO$_2^-$
● from greasing, scouring, coating, phosphate coating, heat treatment, chemical nickel plating etc
● cyanides – CN$^-$, SCN$^-$; from degreasing, coating, etc
● fluorides – from scouring, passivation, polishing, coating etc
● phosphated compounds – from degreasing, phosphate coating, brightening, chemical nickel plating, etc.
● other salts – Cl$^-$, SO$_4^{2-}$, K$^+$, Na$^+$, Ca$^+$

It may be preferable to segregate the waste water streams for individual treatment or to operate whole plant treatment on a mixed waste stream or streams. The waste water stream may be treated on a batch basis or continuously. In some installations the spent process waters are segregated (and may or may not be separately treated).

### 2.13.1.3 Batch or continuous treatment

Treatment may be by batches or continuously for the whole or portions of the flow. [3, CETS, 2002]

Batch treatment may be easier to control and supervise, but requires more capital plant capacity to contain the flow to be treated and may require more direct supervisory time. Continuous treatment requires more sophisticated control systems and their consequent maintenance.

### 2.13.1.4 Organic materials

**Immiscible** – non-halogenated oils, greases, solvents

**Immiscible** – halogenated oils, degreasing solvents, paint solvents

Immiscible organics may first be reduced to their solubility limit by physical separation, such as flotation (such as for oils, electropainting solids) or for volatile substances, by liquid/liquid phase separation. For volatile organics, when levels below the solubility limit are required, two options exist [3, CETS, 2002].

- air stripping, with removal from the air, e.g. by activated carbon, to circa 1 mg/l and final polishing by passing the waste water through activated carbon.
- oxidation to carbon dioxide (and halogen acid in the case of halogenated organics) using UV irradiation and hydrogen peroxide addition.

**Soluble organic materials** – wetting agents, brighteners, organic ions and ligands e.g. acetate, EDTA, etc.

Sequestering agents increase the difficulty in removing metals by flocculation and settlement by complexing them and if in surplus may solubilise metals in the outside environment [22, Fraunhofer, 2002]. The concentration of miscible organics may be reduced by oxidation (such as 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 [3, CETS, 2002].
Reduction of COD. Dissolved organics in waste water raise the Chemical Oxygen Demand. The types of compounds present have highly variable breakdown rates, both chemically and biologically. Upstream prevention is usually the easiest option in reducing COD load.

Where COD requires treatment, biological treatment by arranging discharge to the municipal waste water treatment plant is usually the easiest treatment option. However, in some circumstances, chemical treatments may be necessary and they include [21, Agences de l'Eau de France, et al., 2002]:

- physico-chemical treatment
- chemical emulsion breaking
- adsorption on activated carbon or other similar materials
- membrane techniques
- evapo-concentration
- oxidisation techniques using hypochlorite, peroxide etc.

AOX – organic chlorine compounds can be potentially be formed in effluent treatment when hypochlorite or chorine are used as the oxidising agents for cyanide oxidation.

2.13.1.5 Acids and alkalis

Acid and alkali discharges usually require pH adjustment to a range dependant on the receiving water or sewer before discharging. Continuous flow streams of opposite pH may be partially neutralised by mixing together. Batch discharges such as end-of-service life process solutions may be stored and mixed with solutions of opposite pH.

The chemistry of effluent pre-treatments, such as reduction of hexavalent chromium or oxidation of cyanide, require a pH close to that of the originating process solution and are usually carried out prior to neutralization.

Usually, pH control is on a continuous flow basis with automatic controls, although some discharges are treated on a batch basis, see Section 2.13.1.3.

2.13.1.6 Particulate material

Metal hydroxides, carbonates, powders and dusts, film residues, metallic particles etc. may be removed by settling or filtration, see Section 2.13.2.1

2.13.1.7 Metals – soluble anions

The concentration of metals re-use or for recycling, either directly or after further treatment, may be viable, depending on the chemistry of the solution and the technique used. The capture of precious metals e.g. platinum, gold, silver, rhodium and ruthenium may be achieved from waste water by electrochemical recovery or by ion exchange with the subsequent sale of the loaded resin or the concentrated regeneration liquor stream to specialist recyclers. The reclamation of other cations from waste water streams may be carried out individually or as a composite of several metals.

Where multiple processes are operated and where metal recycling is carried out, it may be preferable to concentrate or precipitate the metals arising from different metal plating lines in segregated streams. This may improve the economics and/or the practicalities of recovering the metals.
2.13.1.8 Reduction of oxidation state of metal ions

In some cases, it is necessary to reduce the oxidation state of the metal as the higher oxidation state(s) may not be readily flocculated and precipitated by pH change [3, CETS, 2002]. For instance, the reduction of CrVI by sodium dithionite:

\[ 4 \text{Na}_2\text{Cr}_2\text{O}_7 + 3 \text{Na}_2\text{S}_2\text{O}_3 + 13 \text{H}_2\text{SO}_4 \rightarrow 4 \text{Cr}_2(\text{SO}_4)_3 + 7 \text{Na}_2\text{SO}_4 + 13 \text{H}_2\text{O} \]

2.13.1.9 Precipitation of metallic floc

The multivalent metal ions are most conveniently removed by precipitation as the hydroxide and concentrations of individual metals in the post-settlement effluent 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 (Figure 2.29):

![Figure 2.29: Variation of solubility of dissolved metal with pH](image)

Simultaneous removals of several metal ions to very low levels may require selection of different pH values and settlement sequentially. The treatment of segregated streams may be preferable to sequential pH adjustments with intervening solids removal stages. The pH may require further adjustment prior to discharge.
The precipitated metals may be separated by settling. There are various types of separator or settlement tank such as:

- longitudinal
- upward flow radial
- laminar


The use of an anionic settling aid (a coagulant with high ionic charge density, such as ferric ions, aluminium chlorohydrate) or a polyelectrolyte may be beneficial in coagulating a stable floc and optimising settlement. They also assist with any subsequent sludge dewatering, see Section 2.13.2.1

For low discharge levels (for example, below about 3mg/l for zinc) the effluent will require polishing (tertiary treatment) by filtration using sand, mixed media, cartridge or pressure filters. For small discharges direct filtration of the suspension instead of settlement may be more cost effective.

The settled floc or filtrate will contain about 5% solids and is normally further concentrated by dewatering (see Section 2.13.2.1).

For residual metal ion concentrations below that achievable by hydroxide addition alone insoluble sulphide based salts may be used in conjunction with post hydroxide addition. Dithiocarbamate (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.

### 2.13.1.10 Complexing (sequestering, chelating) agents

Sequestering agents, particularly EDTA are being used in increasing quantities again in the printed circuit board industry to achieve the high specifications being demanded in modern printed circuit technology [22, Fraunhofer, 2002].

The success of precipitation processes is dependent on the reaction between the soluble metal ion and hydroxide. Complexed metals present problems as hydroxides are difficult to form and the presence of complexing agents can be a cause of failure in effluent treatment plants (i.e. breach of operating limits for metals in the effluent). Waste water streams containing the cyanide (which is a complexing agent) may be easily treated (see Section 2.13.1.15). Other sequestering agents present in a number of cleaners and proprietary electrolytes are more difficult 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 which preferentially complex with the agent. 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 which then require subsequent reduction prior to precipitation where these metals are present. Alternative organic removal treatments, e.g. activated carbon and non-ionic resins, prior to precipitation may be environmentally sound. Microbiological oxidation of organics remains a theoretical possibility.

### 2.13.1.11 Plating out

Transition metals can be removed from waste water streams by plating out on high surface area electrodes in metal recovery cells. It can also be used in combination with ion exchange as a means to concentrate metal ions, see Section 2.13.1.11.
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.

### 2.13.1.12 Ion exchange

The direct ion exchange treatment of waste water provides a means of concentrating multivalent cations for subsequent treatment on column regeneration or by plating out (Section 2.13.1.11). Ion exchange has a high energy demand and requires extensive chemical dosing; the chemical requirement for metal ion capture is generally 3 to 4 times the theoretical requirement [3, CETS, 2002].

### 2.13.1.13 Reverse osmosis

Reverse osmosis, effectively filtration of ions through a membrane at high pressure, provides an alternative means of concentrating metals impurities 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 [3, CETS, 2002].

### 2.13.1.14 Nitrogenous materials

Nitrogen-containing compounds such as $\text{NH}_4^+$, $\text{NO}_3^-$, $\text{NO}_2^-$ come from degreasing, scouring, coating, phosphate coating, heat treatment, chemical nickel plating etc [21, Agences de l'Eau de France, et al., 2002].

**Ammonia.** If recovery by steam stripping is not economic, then ammonia may be oxidised to nitrogen and water with sodium hypochlorite. Any excess hypochlorite can be reduced using sodium sulphite. Ammonia can also be oxidised biologically, usually in a municipal waste water treatment plant.

**Oxidation of nitrites.**

*No data provided*

### 2.13.1.15 Cyanides

Cyanide ($\text{CN}^-$, $\text{SCN}^-$) from degreasing and coating may be oxidised at high pH, for example, by hypochlorite, to carbon dioxide and nitrogen. Any excess hypochlorite can be reduced using sodium sulphite. Sodium hypochlorite solution can be used, or chlorine gas can be used to generate hypochlorite ions in situ at larger facilities. Other oxidising agents such as hydrogen peroxide can be used, with pH varying according to oxidising agent.

**Environmental considerations**

AOX may be formed when using hypochlorite solution or chlorine gas.

### 2.13.1.16 Sulphide

Sulphide is normally controlled by the excess of the multivalent cations present in most waste water streams, with no further treatment necessary. Where it occurs in excess, it may be precipitated out as elemental sulphur on oxidation with hydrogen peroxide or iron III salts.
2.13.1.17 Fluorides

Fluoride occurs from scouring, passivation, polishing, coating etc, and is readily precipitated out as calcium fluoride at a pH above 7. The lowest solubility of calcium fluoride is 15 mg/l at pH 11.2

2.13.1.18 Phosphated compounds

Phosphate compounds are used in degreasing processes, phosphate coating, heat treatment, brightening, chemical nickel plating, etc. Although they are not usually a problem, if necessary (because of local environmental conditions) phosphate is most conveniently precipitated out as calcium hydroxide phosphate. The solubility is less than 5 mg/l at pH greater than 10.

2.13.1.19 Other salts

Other ions such as Cl⁻, SO₄²⁻, K⁺, Na⁺, and Ca⁺ are not normally a problem, but local environmental conditions may require their removal.

Sulphate can be readily precipitated as calcium sulphate; the solubility product is 2 g/l depending on concentration of other ions.

Concentration of other ions may be desirable, and ion exchange, reverse osmosis or evaporation may be used either prior to one of the other treatments (above) or to produce a concentrate for disposal as a waste.

2.13.1.20 Final cleaning of effluent (polishing)

Whatever waste water treatment technologies are used the treated water will contain small amounts of the treated components and a significantly higher concentration of more benign materials arising from the treatment reagents used. The effluent may be treated further: examples are [3, CETS, 2002].

- fine (sand) filter (circa 5 µm) to remove residual particulate material.
- activated carbon bed to remove organic material.
- chelating, crown or thiol cation exchange resin bed to selectively remove multivalent ions

2.13.2 Wastes

2.13.2.1 Sludge dewatering

Solids removed from the main effluent by precipitation or filtering may be further concentrated using a filter press, belt press or centrifuge to produce a cake manageable as a solid. Filter press treatment of metal hydroxide sludge at pressures above 15 bars can give a final cake with 30 - 35 % solids.
2.13.2.2 Sludge drying

Filter cake may be further dried to lower water content.

Environmental considerations
Drying requires 450 kWh of thermal energy per tonne. Waste heat from other processes can be used.

Drying may create a powdery waste at a water content of less than 40%. This may cause more dust problems in handling than a solid cake.

Dried sludge containing residues of oxidising components, such as H₂O₂, NaOCl or persulphates, are reported to heat up through exothermal reactions when stored in “big-bags”, (tonne bags) and may eventually spontaneously combust [3, CETS, 2002].

In some cases, drying sludge may assist subsequent processing, such as solidification.

2.13.2.3 Liquid wastes

Some waste process solutions may be stored and disposed of as liquid waste, sent for specialist recycling or recovery or disposed of as hazardous wastes. Examples are autocatalytic plating solutions and spent etchants.

2.13.2.4 Other solid wastes

Surface treatment of metals and plastics generates other industrial wastes. These normally comprise the used packaging from raw materials (chemicals) and incoming workpieces or substrates, as well as discarded equipment such as broken jigs and barrels.

2.13.2.5 Sludge stabilisation

In some cases, such as where waste management regulations require, sludge may be stabilised [21, Agences de l'Eau de France, et al., 2002], although this is usually carried out off-site by specialist waste management contractors, [89, EIPPCB, ]. For solidification, two main types of binder are used:

- hydraulic, such as cements, fly ashes from cement kilns or coal-fired power-generation
- hydrocarbon-based, such as tars or bitumen (a process derived from the nuclear industry)

Drying of the sludge may be required prior to stabilisation.

Environmental considerations
The volume of waste solidified with hydraulic binders increases in volume 1.5- to 2- fold.

Waste treated with hydraulic binders (such as lime) may have a pozzolanic action and develop mechanical properties that increase stability with time. However, the surface active agents present may interfere with this reaction.
2.13.3 Waste gases

There are two reasons for managing waste gases in surface treatment installations:

- Where health and safety legislation applies to the workplace atmosphere for the protection of the employees from dangerous substances in the workplace
- Working atmospheres that are damp, acid, alkali or which contain other chemicals are likely to be corrosive to materials, workpieces and substrates, equipment and the fabric of buildings. This can lead to problems such as deterioration of raw materials, finished products becoming corroded and being rejected, equipment malfunctioning and buildings deteriorating at a high rate. Many installations extract water vapour, as well as acid, alkali and other gaseous or aerosol contaminants to prevent these problems.

Additional treatment of the exhaust gases may be required to meet emission values.

2.13.3.1 Emission sources and types

The main sources for emissions are layer stripping (such as pickling and stripping baths), electrolytic degreasing baths, individual treatment processes highlighted throughout Chapter 2, as well as some drag-out and rinsing processes (especially where the rinses are heated and/or sprayed).

Harmful substances can be emitted to air as gases (e.g. NOx, HF, HCl) as well as aerosols loaded with caustic, acids or other chemicals (e.g. caustic soda solution, sulphuric acid, chromium (VI) compounds, cyanide), see Table 1.5.

Emissions of solvents from solvent degreasing or drying of organic coatings (such as electropainting or lacquering) are discussed in [90, EIPPCB].

2.13.3.2 Measures for reducing emissions

Measures can be taken to minimize pollutant emissions from sources. For example:

- Air agitation of process solutions can be replaced with other methods such as:
  - Circulating the process solution by pumping
  - Mechanisms to move the jigs
- Baths not in constant use can be kept covered
- Additives can be used to suppress aerosol formation, such as for chromium plating. See Sections 1.4.4.1 and 2.5.3.

2.13.3.3 Extraction systems

Extraction systems can be installed for the capture of the emissions. Although some shops will have general extraction of the workspace, edge or lip extraction at the emitting vat is a widespread procedure. Lines may be fully enclosed with extraction systems. Transporter systems can include an integral lid which is put in place with the flight bar.
Chapter 2

The quantity of exhaust air caught by the edge exhaust and the quantity of pollutants contained depend on several parameters:

- bath size,
- continuous or intermittent operation of the bath,
- bath temperature,
- physical/chemical characteristics of the specific chemicals,
- classification and permissible concentration values in the workplace
- use of additives for the decrease and/or avoidance of the emissions to HF, NO\textsubscript{x} and Cr (VI)
- other emission control procedures
- fully enclosed treatment lines.

2.13.3.4 Waste gas treatments

The following cleaning systems are used:

- droplet separators which use a fill material to condense aerosols and droplets. Condensate is usually treated in a waste water treatment plant.
- exhaust air wet scrubbers. These may be:
  - fibrous packing scrubbers with mats of fibrous packing
  - moving bed scrubbers with a zone of mobile packing, usually low-density plastic spheres which are free to move between support grids
  - packed bed scrubbers containing a fixed bed of variously shaped packing material
  - impingement plate scrubbers
  - spray towers.

Water or specific chemical solutions are sprayed into the wet scrubbers usually (but not always) countercurrent to the gas flow.

Reduction of NO\textsubscript{x} could be achieved by selective reduction using NH\textsubscript{2}-X compounds (with X = H, CN or CONH\textsubscript{2}) injected into the gas stream. The most common reducing agent is ammonia. Both non-catalytic (SNCR) and catalytic (SCR) techniques exist.

These techniques and devices are described in more detail in [87, EIPPCB].
3 CURRENT CONSUMPTION AND EMISSION LEVELS FOR THE SURFACE TREATMENT OF METALS AND PLASTICS

3.1 Introduction - input materials and utilities

Many factors determine the consumption of raw materials as well as the emission of pollutants at surface treatment installations. There is difficulty in producing comparable statistics for both consumptions and emissions because of the large variation between installations: it is likely that no two of the 18000 installations operated in the MS15 are similar enough to be directly comparable with one another. The variations in the options for plant design are due to the large number of the operating parameters, see Sections 1.2. and the general description in Chapter 2. The most important are [104, ÜBA, 2003]:

- the input substrates (e.g. steel, non-ferrous metals, plastics etc.)
- the form of the workpieces (e.g. small components, wires, sheet metals, small and large coils, pipes, complex assemblies)
- the transport technology of the treatment (jig, barrel, continuous coil)
- the cleaning technology (aqueous, alkaline, acid, electro-chemical, etc.)
- the technology for the manufacture of a metallic bright surface (pickling with hydrochloric acid, sulphuric acid, acid mixtures, etc.)
- the coating programme (e.g. copper, nickel, chromium, zinc, tin, alloys, combinations of individual layers such as plating followed by electropainting)
- the selection of individual coatings (chemical, electrolytic and process chemistry)
- the post treatment systems (chromating type, other systems)
- the rinsing technology
- the waste water and waste gas purification technology.

The best starting point for determining emissions and consumptions for comparisons would be on a throughput measure such as ‘unit used per square metre treated’. This would enable both inter-plant comparisons and individual plants to monitor their performance when considering and managing changes within the same plant. For surface treatments the preferred basis would be surface area treated. However, the differing sizes, shapes and complexity of the workpieces and/or substrates make the accurate calculation of surface area difficult in all but the most straightforward cases.

On the emission side the situation appears simpler, as emission standards and measurements exist. However, these are largely for end-of-pipe discharges. Relating discharge quantities to throughput factors for accurate comparison would be best, but are again very difficult.

The most substantial environment pollution factors are the emission of pollutants in waters, the production of hazardous wastes as well as the energy and water consumption. The emission of pollutants into the air is has less consequence.

Some basic data is provided below. A set of studies on consumption and emission of metals for ten reference plants in Germany are included in Annex 2. (at the time of this draft three are available)

Data on the key environmental considerations such as substances of concern emitted are given with process descriptions in Chapter 2.
3.2 Overall inputs and emissions - utilities

3.2.1 Energy

Energy sources and uses are described in 2.12.1

Energy losses from the surface area of heated process solutions related to processing temperatures are shown in Figure 3.1, below. It demonstrates that the highest energy loss occurs 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 [3, CETS, 2002].

<table>
<thead>
<tr>
<th>Processing temperature (°C)</th>
<th>Without liquid agitation, without air extraction (W/m² tank surface area)</th>
<th>Without liquid agitation, with air extraction (W/m² tank surface area)</th>
<th>With liquid agitation, with air extraction (W/m² tank surface area)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>352</td>
<td>559</td>
<td>839</td>
</tr>
<tr>
<td>35</td>
<td>530</td>
<td>837</td>
<td>1209</td>
</tr>
<tr>
<td>40</td>
<td>757</td>
<td>1196</td>
<td>1677</td>
</tr>
<tr>
<td>45</td>
<td>1048</td>
<td>1635</td>
<td>2268</td>
</tr>
<tr>
<td>50</td>
<td>1426</td>
<td>2198</td>
<td>3012</td>
</tr>
<tr>
<td>55</td>
<td>1922</td>
<td>2910</td>
<td>3949</td>
</tr>
<tr>
<td>60</td>
<td>2587</td>
<td>3815</td>
<td>5129</td>
</tr>
<tr>
<td>65</td>
<td>3505</td>
<td>4973</td>
<td>6621</td>
</tr>
<tr>
<td>70</td>
<td>4824</td>
<td>6469</td>
<td>8521</td>
</tr>
<tr>
<td>75</td>
<td>6844</td>
<td>8436</td>
<td>10974</td>
</tr>
<tr>
<td>80</td>
<td>10279</td>
<td>11096</td>
<td>14212</td>
</tr>
<tr>
<td>85</td>
<td>17386</td>
<td>17386</td>
<td>21188</td>
</tr>
<tr>
<td>90</td>
<td>41412</td>
<td>41412</td>
<td>46023</td>
</tr>
</tbody>
</table>

Table 3.1: Energy losses at the surface of hot process solutions

3.2.2 Water

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 and the washing of filtration and heat-exchange equipment. It may also be used in cooling systems. Note that unless water is recycled or re-used elsewhere this consumption figure will be the discharge figure to waste water treatment.

The typical rinse water usage for an example automated barrel zinc plating plant is [3, CETS, 2002]:

- 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
Benchmarks for water usage are:

- A cleaned effluent discharge of 50 l/m² of treated surface area with effluent containing less than 0.1% of the metal used [8, Clarin and Luona, 2002]
- An industry benchmark of about 40 l/m² (Verbal information for Surface Engineering Association)
- A national regulatory maximum of 8 l/m² [58, France, 2003].

3.2.3 Cooling

No data provided

3.2.4 Overall inputs and emissions - 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 [3, CETS, 2002]:

- 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 metals 98%
- Silver 95%
- Cadmium 99%
- Electropainting coatings 98%

This data demonstrate low material efficiencies except where financial factors (such as for gold, silver) or environmental regulatory pressures (such as for cadmium) are paramount.

3.2.5 Workpiece and substrate preparation

3.2.5.1 Degreasing

[104, ÜBA, 2003]

The main emissions from aqueous degreasing processes are rinsing waters, separated oil and used degreasing solutions. Their generation, as well as consumption of degreasers, are determined by a number of factors which the operator can only partly influence. Three factors are important for the consumption of chemicals and the appropriate generation of waste water:

- degree of pollution of the workpieces
- service lifetime of the degreasing solution
- recycling of rinsing water concentrates into the degreasing tank

The following table shows the large differences which are found in practice. All the enterprises here have similar coating programmes and are considered reference plants for good practice techniques.
Chapter 3

The substantial differences show that it is difficult to set up generally valid consumption figures for this production step.

Both separated oil and oil-saturated process solutions are produced. The quantity of the separated oil is identical to the quantity of oil which is introduced with the workpieces.

Rinsing waters and used degreasing baths are usually disposed of together through a waste water treatment system. It is assumed that all materials used in the cleaning solutions end up in the waste water.

### 3.2.6 Core activities – rinsing

*No data provided*

### 3.2.7 Core activities

#### 3.2.7.1 Pickling

There are wide differences in the data for the specific consumption of acids consumed in pickling, see Table 3.3 [104, ÜBA, 2003].

<table>
<thead>
<tr>
<th>Enterprise</th>
<th>Throughput coated surface (m²/yr)</th>
<th>Acid consumption (t/yr)</th>
<th>Specific acid consumption (t/100 000 m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>158000</td>
<td>24</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>200000</td>
<td>202</td>
<td>101</td>
</tr>
<tr>
<td>3</td>
<td>63000</td>
<td>21</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>468000</td>
<td>150</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>6000</td>
<td>1.3</td>
<td>2</td>
</tr>
</tbody>
</table>

*Table 3.3: Specific consumption of pickling agent*

#### 3.2.7.2 Electrolytic coating

There are similar differences for the specific electrolyte consumption with the electro-chemical galvanizing [104, ÜBA, 2003]]:

<table>
<thead>
<tr>
<th>Enterprise</th>
<th>Throughput coated surface (m²/yr)</th>
<th>Electrolyte consumption (t/yr)</th>
<th>Specific electrolyte consumption (t/100000 m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>158000</td>
<td>38</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>200000</td>
<td>160</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>63000</td>
<td>6</td>
<td>9.5</td>
</tr>
<tr>
<td>4</td>
<td>468000</td>
<td>90</td>
<td>19.2</td>
</tr>
<tr>
<td>5</td>
<td>66000</td>
<td>15.3</td>
<td>23</td>
</tr>
</tbody>
</table>

*Table 3.4: Specific consumption of electrolyte*
3.2.7.3 Layer conversion activities including post-treatments

   No data provided

3.2.8 Post-treatment activities

3.2.8.1 Drying

   No data provided

3.2.8.2 Hydrogen de-embrittlemment

   No data provided

3.2.9 Barrel processing – consumptions and emissions

   No data provided

3.2.10 Continuous coil – small scale reel to reel consumptions and emissions

   No data provided

3.2.11 Continuous coil - large scale steel consumptions and emissions

   No data provided

3.2.12 Lithographic (offset) printing plates – coil and sheet

   No data provided

3.2.13 Printed circuit board manufacturing

   No data provided

3.3 Emissions

3.3.1 Waste water

Currently, in the Federal Republic of Germany approximately 94 % of the surface treatment industry discharges its waste water into local sewage systems [104, ÜBA, 2003]. Pre-treatment is required in the installation prior discharging. In the case of physical/chemical pre-treatment the toxic anions (such as cyanide) in the sewage are destroyed and heavy metals are removed to the required standard. Further treatment is given in the local biological municipal water treatment plant.

By using state of the art water-saving rinsing techniques and by multi-level waste water treatment plants, the waste water amount and the pollutant concentration in the cleaned waste water can be minimised. The load of pollutants from surface treatment into the waters is small, as table 3.4 shows:
In Norway, an investigation of installations using good practice derived a benchmark figure of a treated effluent discharge of 50 l/m² of treated surface area with and effluent containing less than 0.1 % of the metal used.

Some typical consent limits for some European countries are given in Table A1.1, Annex 1.

### 3.3.2 Waste

For most surface treatment shops the most significant waste is a sludge or filter cake from a batch pressure filter concentrating the solids produced in the waste water treatment plant. It contains 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 sludge contains dirt, small quantities of insoluble inorganic salts, organic compounds and metals removed (dissolved) from the surface of workpieces or substrate and chemicals, including dissolved metals, carried over from the treatment processes. The dissolved metals are usually precipitated as hydroxides, including FeII and FeIII hydroxides and oxides dissolved from steel substrates, or aluminium dissolved from the substrate in anodising precipitated as alumina. These can form large proportions of the sludge. The sludge is usually considered to be hazardous waste and requires managing according to the appropriate regulations.

Filter cake can be dried to a lower water content to reduce transport and disposal costs. It does however become dusty at a water content of less than 40 %. See Section. 2.13.2.2.

The amount of electroplating sludge generated depends on the one hand on the condition of the workpieces, and on the other hand on specific process factors during the electroplating process.

Substantial factors are:

- input of pollutions
- erosion of metal oxides of the workpieces surface
- drag out of process solution with the workpieces
- conversion from layers of metal, for example with chromating
- service lifetime of the process solutions.

From the quantity of the metals used in the electroplating shops in Germany and the drag out occurring, the amount of electroplating sludge from all the galvanic shops can be estimated. Taking an annual metal usage of 20000 t/yr as a basis, a metal loss of 4000 t can be calculated for a drag out rate of 20 % t/y. Assuming that the metals are present as sulphates and are precipitated by means of classical lime precipitation:

\[
\text{MSO}_4 + \text{Ca (OH)}_2 \rightarrow \text{M(OH)}_2 + \text{CaSO}_4 \quad (M = \text{metal})
\]

and presupposing that the electroplating sludge has a water content of 70 %, then for the ratio metal/ electroplating sludge a factor of roughly 1/10 can be calculated. This means

### Table 3.5: Heavy metal loads from galvanisation units to sewage

[104, ÜBA, 2003]

<table>
<thead>
<tr>
<th>Enterprise</th>
<th>Coated surface m²/y</th>
<th>Zinc load kg/y</th>
<th>Chromium load kg/y</th>
<th>Specific zinc load kg/100000 m²</th>
<th>Specific chromium load kg/100000 m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>63000</td>
<td>3.036</td>
<td>0.910</td>
<td>4.600</td>
<td>1.370</td>
</tr>
<tr>
<td>B</td>
<td>468000</td>
<td>0.825</td>
<td>0.187</td>
<td>0.176</td>
<td>0.040</td>
</tr>
<tr>
<td>C</td>
<td>158000</td>
<td>3.900</td>
<td>1.120</td>
<td>2.470</td>
<td>0.709</td>
</tr>
</tbody>
</table>
approximately 10 tonnes electroplating sludge result per tonne of lost metal. Consequently, in Germany 40000 t of electroplating sludge is generated by non-ferrous metal losses.

In addition to this estimation, it is necessary to take into account the metals arising from the metal pre-treatment processes, in particular pickling. Here, however, the estimation is difficult, since the condition of the delivered workpieces, which is an important factor, is unknown.

In view of these uncertainties, the amount of electroplating sludge can be only estimated. For the total number of electroplating shops in Germany 70000 to 80000 t/yr seems realistic.

At present in Germany approximately 30 % of the electroplating sludge is used as a secondary raw material in the non-ferrous metal industry. The remainder is disposed of in hazardous waste landfills.

Some service solutions reaching the end of their life are disposed of directly as liquid wastes. They may be returned to the producers for recycling (for instance, copper etchants in printed circuit board manufacture) or managed off-site as hazardous liquid wastes.

### 3.3.3 Air emissions

[104, ÜBA, 2003] Air emissions from the surface treatment of metals and plastics are not the most significant environmental impacts of the sector as the industry is not a significant contributor to wide area problems such as long-range transport of acid emission. However, local air quality may be an issue in some locations (for instance, NO\textsubscript{x} in urban areas).

Some materials used in the processes are classed as hazardous and their atmospheric concentrations in the workplace are usually controlled by health and safety legislation (see Annex 1, Table A1.2): the classifications and current emission limit values are according to TA Luft). Where workplace conditions and regulations require, these substances will need control, such as by air extraction.

The following tables show values for pickling plants in Germany [104, ÜBA, 2003]: the regulatory (TA Luft) emission limit values are compared with actual measured emission values. Further parameters are given, such as exhaust air flowrate, composition of the pickles etc. where this information is known. Simple emission control procedures were used, such as exhaust scrubbers with fill materials and countercurrent scrubbing or droplet separators.
Note: Each table differs because of variations in pickling process chemistry in different installations. The determinands measured are therefore installation-specific.

<table>
<thead>
<tr>
<th>Plant data</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Size of baths m$^3$</td>
<td>8.2</td>
</tr>
<tr>
<td>Edge exhaust</td>
<td></td>
</tr>
<tr>
<td>Emission control annex</td>
<td>Exhaust scrubbers</td>
</tr>
<tr>
<td>Exhaust air flowrate in m$^3$/h</td>
<td>6500</td>
</tr>
<tr>
<td>Wash medium</td>
<td>Water with sodium caustic solution</td>
</tr>
</tbody>
</table>

| Composition of the pickle           |          |
| Nitric acid in %                    | 20 - 40  |
| Hydrofluoric acid in %              | <7       |

| Characteristics                     |          |
| Pickling additives                  | Nitrite  |

<table>
<thead>
<tr>
<th>Values measured according to TA air in mg/m$^3$</th>
<th>TA Luft emission limit values</th>
<th>Actual measured values: minimum - max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_x$</td>
<td>500</td>
<td>4 – 45</td>
</tr>
<tr>
<td>HF</td>
<td>5</td>
<td>0.04 - 0.06</td>
</tr>
</tbody>
</table>

Table 3.6: Plant 1

<table>
<thead>
<tr>
<th>Plant data</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Size of baths m$^3$</td>
<td>&gt;10</td>
</tr>
<tr>
<td>Edge exhaust</td>
<td></td>
</tr>
<tr>
<td>Emission control annex</td>
<td>Exhaust scrubbers</td>
</tr>
<tr>
<td>Exhaust air flowrate in m$^3$/h</td>
<td>&lt;10000</td>
</tr>
<tr>
<td>Wash medium</td>
<td>Water with sodium caustic solution</td>
</tr>
</tbody>
</table>

| Composition of the pickle           |          |
| Nitric acid in %                    | <30      |
| Hydrofluoric acid in %              | <2       |

| Characteristics                     |          |
| Pickling additives                  |          |

<table>
<thead>
<tr>
<th>Values measured according to TA air in mg/m$^3$</th>
<th>TA Luft emission limit values</th>
<th>Actual measured values: minimum - max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_x$</td>
<td>500</td>
<td>&lt;15</td>
</tr>
<tr>
<td>HF</td>
<td>5</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Ni</td>
<td>1</td>
<td>&lt;0.003</td>
</tr>
</tbody>
</table>

Table 3.7: Plant 2
### Chapter 3

#### Plant data

<table>
<thead>
<tr>
<th>Plant data</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Size of baths m³</td>
<td>22</td>
</tr>
<tr>
<td>Edge exhaust</td>
<td>No</td>
</tr>
<tr>
<td>Emission control</td>
<td>No</td>
</tr>
<tr>
<td>Exhaust air flowrate in m³/h</td>
<td>12000</td>
</tr>
<tr>
<td>Wash medium</td>
<td>No</td>
</tr>
</tbody>
</table>

**Composition of the pickle**

| Nitric acid in % | 12 |
| Hydrofluoric acid in % | 4 |

**Characteristics**

Pickling additives: Nitrite, HF

**Values measured according to TA Luft emission limit values: minimum - max.**

<table>
<thead>
<tr>
<th></th>
<th>TA Luft emission limit values</th>
<th>Actual measured values: minimum - max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOₓ</td>
<td>500</td>
<td>21 - 29</td>
</tr>
<tr>
<td>HF</td>
<td>5</td>
<td>2 - 5</td>
</tr>
</tbody>
</table>

Table 3.8: Plant 3

#### Plant data

<table>
<thead>
<tr>
<th>Plant data</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Size of baths m³</td>
<td>Approx. 50</td>
</tr>
<tr>
<td>Edge exhaust</td>
<td>No</td>
</tr>
<tr>
<td>Emission control annex</td>
<td>Absorption chamber</td>
</tr>
<tr>
<td>Exhaust air flowrate in m³/h</td>
<td>3000 - 6000</td>
</tr>
<tr>
<td>Wash medium</td>
<td>Water</td>
</tr>
</tbody>
</table>

**Composition of the pickle**

| Nitric acid in % | - |
| Hydrofluoric acid in % | 5 |

**Characteristics**

Pickling additives

**Values measured according to TA Luft emission limit values: minimum - max.**

<table>
<thead>
<tr>
<th></th>
<th>TA Luft emission limit values</th>
<th>Actual measured values: minimum - max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>5</td>
<td>0.01 - 0.1</td>
</tr>
</tbody>
</table>

Table 3.9: Plant 4
### Plant data

<table>
<thead>
<tr>
<th>Size of baths m³</th>
<th>11 x 18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Edge exhaust</td>
<td>Exhaust air pipes</td>
</tr>
<tr>
<td>Emission control annex</td>
<td>Exhaust scrubbers</td>
</tr>
<tr>
<td>Exhaust air flowrate in m³/h</td>
<td>&lt;8500</td>
</tr>
<tr>
<td>Wash medium</td>
<td>Caustic soda solution</td>
</tr>
</tbody>
</table>

### Composition of the pickle

| Nitric acid in % | <40 |
| Hydrofluoric acid in % | <7 |

### Characteristics

#### Pickling additives

#### Values measured according to TA Luft emission limit values

| NOₓ | 200 | 15 - 40 |

**Table 3.10: Plant 5**

### Plant data

<table>
<thead>
<tr>
<th>Size of baths m³</th>
<th>Approx. 150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Edge exhaust</td>
<td>None</td>
</tr>
<tr>
<td>Emission control device</td>
<td>None</td>
</tr>
<tr>
<td>Exhaust air flowrate in m³/h</td>
<td>Approx. 50000</td>
</tr>
<tr>
<td>Wash medium</td>
<td>None</td>
</tr>
</tbody>
</table>

### Composition of the pickle

| Nitric acid in % | Not known |
| Hydrofluoric acid in % | Not known |

### Characteristics

#### Pickling additives

#### Values measured according to TA Luft emission limit values

| NOₓ | 500 | <12 |
| HF  | 5   | 0.05 – 0.07 |
| HCl | 30  | 0.07 – 0.27 |
| CN⁻ | 5   | 0.25 – 0.46 |
| Cr(VI)-Ions | 1  | <0.1 |
| Ni  | 1   | <0.1 |

**Table 3.11: Plant 6**
Plant data

Size of baths m³  Approx. 90
Edge exhaust
Emission control annex  Exhaust scrubbers
Exhaust air flowrate in m³/h  30000
Wash medium  Water

Composition of the Pickle

Nitric acid in %  Not known
Hydrofluoric acid in %  0

Characteristics

Pickling additives

<table>
<thead>
<tr>
<th>Values measured according to TA Luft emission limit values</th>
<th>Actual measured values: minimum - max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx  500</td>
<td>&lt;5</td>
</tr>
<tr>
<td>H₂SO₄ 5</td>
<td>&lt;0.6</td>
</tr>
<tr>
<td>HCl  30</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>Na (OH) 5</td>
<td>0</td>
</tr>
<tr>
<td>NH₃  30</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Cr(VI)-Ions 1</td>
<td>&lt;0.3</td>
</tr>
</tbody>
</table>

Table 3.12: Plant 7
Chapter 4

4 TECHNIQUES TO CONSIDER IN THE DETERMINATION OF BAT

This chapter sets out available techniques with the best environmental and economic performance or possibilities for improvement to achieve the integrated prevention and control of pollution. Management systems as well as process-integrated techniques and end-of-pipe measures are included, but a certain amount of overlap exists between these three when seeking the optimum results.

Prevention, control, minimisation and re-cycling procedures are considered as well as the re-use of materials and energy. Many options are addressed, such as using production techniques that pollute less than others, reducing material inputs, improving management practices and/or substituting less toxic chemicals. This chapter provides information on both general and specific pollution prevention and control advances that have been implemented within industry and in the surface treatment of metals and plastics in particular.

A standard structure is used to outline each technique, as shown in Table 4.1:

<table>
<thead>
<tr>
<th>Type of information considered</th>
<th>Type of information included</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description</td>
<td>Technical description of the technique</td>
</tr>
<tr>
<td>Achieved environmental benefits</td>
<td>Main environmental impact(s) to be addressed by the technique (process or abatement) including emission values achieved and efficiency performance. Environmental benefits of the technique in comparison with others</td>
</tr>
<tr>
<td>Cross-media effects</td>
<td>Any side-effects and disadvantages caused by implementation of this technique. Environmental problems of the technique in comparison with others</td>
</tr>
<tr>
<td>Operational data</td>
<td>Performance data on emissions/wastes and consumption (raw materials, water and energy). Any other useful information on how to operate, maintain and control the technique including safety aspects and operability constraints of the technique</td>
</tr>
<tr>
<td>Applicability</td>
<td>Consideration of factors involved in applying and retrofitting (e.g. space availability, process specific)</td>
</tr>
<tr>
<td>Economics</td>
<td>Information on costs (investment and operation) and any savings (e.g. reduced raw material consumption, waste charges) related to the capacity of the technique</td>
</tr>
<tr>
<td>Driving force for implementation</td>
<td>Reasons other than environmental ones for implementation (e.g. other legislation, improvement in production quality)</td>
</tr>
<tr>
<td>Example plants</td>
<td>Reference to a plant where the technique is reported</td>
</tr>
<tr>
<td>Reference literature</td>
<td>Literature for more detailed information on the technique.</td>
</tr>
</tbody>
</table>

Table 4.1: Information contained in the description of each technique included in Chapter 4

These factors are linked with each other, and achievements in one may often entail positive effects in another. However, there are often adverse effects on the environment which also have to be considered. The different environmental impacts of these techniques is assessed and compared as far as possible under the ‘cross-media effects’ heading.

If information has not been submitted for a specific technique, this is indicated by “No data” under the appropriate heading. Note: the TWG is asked to supply more data for these sections.
Key issues for the implementation of IPPC in this sector are:

- effective management systems
- efficient raw material, energy and water usage
- optimised use of chemicals in processes and directly related activities
- the substitution of less harmful substances
- minimisation, recovery and recycling of waste
- the prevention of environmental accidents and minimisation of their consequences.

Individual sections may address more than one of these issues.

Good management systems, both production and environmental are central to fully addressing integrated pollution prevention and control issues in the surface treatment of metals and plastics. Important issues for management systems to achieve optimum effect are:

- being constructively self-critical
- production and environmental systems implemented as entirely complimentary to each other
- inclusion of audits for energy and water usage, as well as raw material consumption
- the design and operation of installations to negate the impact of unplanned releases, both chronic and acute.

4.1 Management techniques

Section 4.1.1 contains the standard text on environmental management tools agreed by the IPPC Information Exchange Forum.

Sub-section 4.1.1.1 provides sector-specific information.

Additional management techniques are described in 4.1.2 and 4.1.3.

4.1.1 Environmental management tools

Description

The best environmental performance is usually achieved by the installation of the best technology and its operation in the most effective and efficient manner. This is recognised by the IPPC Directive definition of ‘techniques’ as “both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned”.

For IPPC installations an Environmental Management System (EMS) is a tool that operators can use to address these design, construction, maintenance, operation and decommissioning issues in a systematic, demonstrable way. An EMS includes the organisational structure, responsibilities, practices, procedures, processes and resources for developing, implementing, maintaining, reviewing and monitoring the environmental policy. Environmental Management Systems are most effective and efficient where they form an inherent part of the overall management and operation of an installation.

Within the European Union, many organisations have decided on a voluntary basis to implement environmental management systems based on EN ISO 14001:1996 or the EU Eco-management and audit scheme EMAS. EMAS includes the management system requirements of EN ISO 14001, but places additional emphasis on legal compliance, environmental performance and employee involvement; it also requires external verification of the management system and validation of a public environmental statement (in EN ISO 14001 self-declaration is an
alternative to external verification). There are also many organisations that have decided to put in place non-standardised EMSs.

While both standardised systems (EN ISO 14001:1996 and EMAS) and non-standardised (“customised”) systems in principle take the organisation as the entity, this document takes a more narrow approach, not including all activities of the organisation e.g. with regard to their products and services, due to the fact that the regulated entity under the IPPC Directive is the installation (as defined in Article 2).

An environmental management system (EMS) for an IPPC installation can contain the following components:

(a) definition of an environmental policy
(b) planning and establishing objectives and targets
(c) implementation and operation of procedures
(d) checking and corrective action
(e) management review
(f) preparation of a regular environmental statement
(g) validation by certification body or external EMS verifier
(h) design considerations for end-of-life plant decommissioning
(i) development of cleaner technologies
(j) benchmarking.

These features are explained in somewhat greater detail below. For detailed information on components (a) to (g), which are all included in EMAS, the reader is referred to the reference literature indicated below.

(a) Definition of an environmental policy

Top management are responsible for defining an environmental policy for an installation and ensuring that it:

- is appropriate to the nature, scale and environmental impacts of the activities
- includes a commitment to pollution prevention and control
- includes a commitment to comply with all relevant applicable environmental legislation and regulations, and with other requirements to which the organisation subscribes
- provides the framework for setting and reviewing environmental objectives and targets
- is documented and communicated to all employees
- is available to the public and all interested parties.

(b) Planning, i.e.:

- procedures to identify the environmental aspects of the installation, in order to determine those activities which have or can have significant impacts on the environment, and to keep this information up-to-date
- procedures to identify and have access to legal and other requirements to which the organisation subscribes and that are applicable to the environmental aspects of its activities
- establishing and reviewing documented environmental objectives and targets, taking into consideration the legal and other requirements and the views of interested parties
- establishing and regularly updating an environmental management programme, including designation of responsibility for achieving objectives and targets at each relevant function and level as well as the means and timeframe by which they are to be achieved.
(c) Implementation and operation of procedures

It is important to have systems in place to ensure that procedures are known, understood and complied with, therefore effective environmental management includes:

(i) Structure and responsibility
   - defining, documenting and communicating roles, responsibilities and authorities, which includes appointing one specific management representative
   - providing resources essential to the implementation and control of the environmental management system, including human resources and specialised skills, technology and financial resources.

(ii) Training, awareness and competence
   - identifying training needs to ensure that all personnel whose work may significantly affect the environmental impacts of the activity have received appropriate training.

(iii) Communication
   - establishing and maintaining procedures for internal communication between the various levels and functions of the installation, as well as procedures that foster a dialogue with external interested parties and procedures for receiving, documenting and, where reasonable, responding to relevant communication from external interested parties.

(iv) Employee involvement
   - involving employees in the process aimed at achieving a high level of environmental performance by applying appropriate forms of participation such as the suggestion-book system or project-based group works or environmental committees.

(v) Documentation
   - establishing and maintaining up-to-date information, in paper or electronic form, to describe the core elements of the management system and their interaction and to provide direction to related documentation.

(vi) Efficient process control
   - adequate control of processes under all modes of operation, i.e. preparation, start-up, routine operation, shutdown and abnormal conditions
   - identifying the key performance indicators and methods for measuring and controlling these parameters (e.g. flow, pressure, temperature, composition and quantity)
   - documenting and analysing abnormal operating conditions to identify the root causes and then addressing these to ensure that events do not recur (this can be facilitated by a ‘no-blame’ culture where the identification of causes is more important than apportioning blame to individuals).

(vii) Maintenance programme
   - establishing a structured programme for maintenance based on technical descriptions of the equipment, norms etc. as well as any equipment failures and consequences
   - supporting the maintenance programme by appropriate record keeping systems and diagnostic testing
   - clearly allocating responsibility for the planning and execution of maintenance.

(viii) Emergency preparedness and response
   - establishing and maintaining procedures to identify the potential for and response to accidents and emergency situations, and for preventing and mitigating the environmental impacts that may be associated with them.
(d) Checking and corrective action, i.e.:

(i) Monitoring and measurement
   - establishing and maintaining documented procedures to monitor and measure, on a regular basis, the key characteristics of operations and activities that can have a significant impact on the environment, including the recording of information for tracking performance, relevant operational controls and conformance with the installation's environmental objectives and targets (see also the Reference document on Monitoring of Emissions)
   - establishing and maintaining a documented procedure for periodically evaluating compliance with relevant environmental legislation and regulations.

(ii) Corrective and preventive action
   - establishing and maintaining procedures for defining responsibility and authority for handling and investigating non-conformance with permit conditions, other legal requirements as well as objectives and targets, taking action to mitigate any impacts caused and for initiating and completing corrective and preventive action that are appropriate to the magnitude of the problem and commensurate with the environmental impact encountered.

(iii) Records
   - establishing and maintaining procedures for the identification, maintenance and disposition of legible, identifiable and traceable environmental records, including training records and the results of audits and reviews.

(iv) Audit
   - establishing and maintaining (a) programme(s) and procedures for periodic environmental management system audits that include discussions with personnel, inspection of operating conditions and equipment and reviewing of records and documentation and that results in a written report, to be carried out impartially and objectively by employees (internal audits) or external parties (external audits), covering the audit scope, frequency and methodologies, as well as the responsibilities and requirements for conducting audits and reporting results, in order to determine whether or not the environmental management system conforms to planned arrangements and has been properly implemented and maintained
   - completing the audit or audit cycle, as appropriate, at intervals of no longer than three years, depending on the nature, scale and complexity of the activities, the significance of associated environmental impacts, the importance and urgency of the problems detected by previous audits and the history of environmental problems — more complex activities with a more significant environmental impact are audited more frequently
   - having appropriate mechanisms in place to ensure that the audit results are followed up.

(v) Periodic evaluation of legal compliance
   - reviewing compliance with the applicable environmental legislation and the conditions of the environmental permit(s) held by the installation
   - documentation of the evaluation.

(e) Management review, i.e.:
   - reviewing, by top management, at intervals that it determines, the environmental management system, to ensure its continuing suitability, adequacy and effectiveness
   - ensuring that the necessary information is collected to allow management to carry out this evaluation
   - documentation of the review.
(f) Preparation of a regular environmental statement:

- preparing an environmental statement that pays particular attention to the results achieved by the installation against its environmental objectives and targets. It is regularly produced – from once a year to less frequently depending on the significance of emissions, waste generation etc. It considers the information needs of relevant interested parties and it is publicly available (e.g. in electronic publications, libraries etc.).

When producing a statement, the operator may use relevant existing environmental performance indicators, making sure that the indicators chosen:
  i. give an accurate appraisal of the installation’s performance
  ii. are understandable and unambiguous
  iii. allow for year on year comparison to assess the development of the environmental performance of the installation
  iv. allow for comparison with sector, national or regional benchmarks as appropriate
  v. allow for comparison with regulatory requirements as appropriate.

(g) Validation by certification body or external EMS verifier:

- having the management system, audit procedure and environmental statement examined and validated by an accredited certification body or an external EMS verifier can, if carried out properly, enhance the credibility of the system.

(h) Design considerations for end-of-life plant decommissioning

- giving consideration to the environmental impact from the eventual decommissioning of the unit at the stage of designing a new plant, as forethought makes decommissioning easier, cleaner and cheaper
- decommissioning poses environmental risks for the contamination of land (and groundwater) and generates large quantities of solid waste. Preventive techniques are process-specific but general considerations may include:
  i. avoiding underground structures
  ii. incorporating features that facilitate dismantling
  iii. choosing surface finishes that are easily decontaminated
  iv. using an equipment configuration that minimises trapped chemicals and facilitates drain-down or washing
  v. designing flexible, self-contained units that enable phased closure
  vi. using biodegradable and recyclable materials where possible.

(i) Development of cleaner technologies:

- environmental protection should be an inherent feature of any process design activities carried out by the operator, since techniques incorporated at the earliest possible design stage are both more effective and cheaper. Giving consideration to the development of cleaner technologies can for instance occur through R&D activities or studies. As an alternative to internal activities, arrangements can be made to keep abreast with – and where appropriate – commission work by other operators or research institutes active in the relevant field.

(j) Benchmarking, i.e.:

- carrying out systematic and regular comparisons with sector, national or regional benchmarks, including for energy efficiency and energy conservation activities, choice of input materials, emissions to air and discharges to water (using for example the European Pollutant Emission Register, EPER), consumption of water and generation of waste.
Standardised and non-standardised EMSs
An EMS can take the form of a standardised or non-standardised (“customised”) system. Implementation and adherence to an internationally accepted standardised system such as EN ISO 14001:1996 can give higher credibility to the EMS, especially when subject to a properly performed external verification. EMAS provides additional credibility due to the interaction with the public through the environmental statement and the mechanism to ensure compliance with the applicable environmental legislation. However, non-standardised systems can in principle be equally effective provided that they are properly designed and implemented.

Achieved environmental benefits
Implementation of and adherence to an EMS focuses the attention of the operator on the environmental performance of the installation. In particular, the maintenance of and compliance with clear operating procedures for both normal and abnormal situations and the associated lines of responsibility should ensure that the installation’s permit conditions and other environmental targets and objectives are met at all times.

Environmental management systems typically ensure the continuous improvement of the environmental performance of the installation. The poorer the starting point is, the more significant short-term improvements can be expected. If the installation already has a good overall environmental performance, the system helps the operator to maintain the high performance level.

Cross-media effects
Environmental management techniques are designed to address the overall environmental impact, which is consistent with the integrated approach of the IPPC Directive.

Operational data
No specific information reported.

Applicability
The components described above can typically be applied to all IPPC installations. The scope (e.g. level of detail) and nature of the EMS (e.g. standardised or non-standardised) will generally be related to the nature, scale and complexity of the installation, and the range of environmental impacts it may have.

Economics
It is difficult to accurately determine the costs and economic benefits of introducing and maintaining a good EMS. A number of studies are presented below. However, these are just examples and their results are not entirely coherent. They might not be representative for all sectors across the EU and should thus be treated with caution.

A Swedish study carried out in 1999 surveyed all 360 ISO-certified and EMAS-registered companies in Sweden. With a response rate of 50 %, it concluded among other things that:

- the expenses for introducing and operating EMS are high but not unreasonably so, save in the case of very small companies. Expenses are expected to decrease in the future
- a higher degree of co-ordination and integration of EMS with other management systems is seen as a possible way to decrease costs
- half of all the environmental objectives and targets give payback within one year through cost savings and/or increased revenue
- the largest cost savings were made through decreased expenditure on energy, waste treatment and raw materials
- most of the companies think that their position on the market has been strengthened through the EMS. One-third of the companies report increasing revenue due to EMS.

In some Member States reduced supervision fees are charged if the installation has a certification.
Chapter 4

A number of studies\(^4\) show that there is an inverse relationship between company size and the cost of implementing an EMS. A similar inverse relationship exists for the payback period of invested capital. Both elements imply a less favourable cost-benefit relationship for implementing an EMS in SMEs compared to larger companies.

According to a Swiss study, the average cost for building and operating ISO 14001 can vary:

- for a company with between 1 and 49 employees: CHF 64000 (€ 44000) for building the EMS and CHF 16000 (€ 11000) per year for operating it
- for an industrial site with more than 250 employees: CHF 367000 (€ 252000) for building the EMS and CHF 155000 (€ 106000) per year for operating it.

These average figures do not necessarily represent the actual cost for a given industrial site because this cost is also highly dependent on the number of significant items (pollutants, energy consumption, ...) and on the complexity of the problems to be studied.

A recent German study (Schaltegger, Stefan and Wagner, Marcus, Umweltmanagement in deutschen Unternehmen - der aktuelle Stand der Praxis, February 2002, p. 106) shows the following costs for EMAS for different branches. It can be noted that these figures are much lower than those of the Swiss study quoted above. This is a confirmation of the difficulty to determine the costs of an EMS.

Costs for building (€):
- minimum: 18750
- maximum: 75000
- average: 50000

Costs for validation (€):
- minimum: 5000
- maximum: 12500
- average: 6000

A study by the German Institute of Entrepreneurs (Unternehmerinstitut/Arbeitsgemeinschaft Selbständiger Unternehmer UNI/ASU, 1997, Umweltmanagementbefragung - Öko-Audit in der mittelständischen Praxis - Evaluierung und Ansätze für eine Effizienzsteigerung von Umweltmanagementsystemen in der Praxis, Bonn.) gives information about the average savings achieved for EMAS per year and the average payback time. For example, for implementation costs of € 80000 they found average savings of € 50000 per year, corresponding to a payback time of about one and a half years.

External costs relating to verification of the system can be estimated from guidance issued by the International Accreditation Forum (http://www.iaf.nu).

Driving forces for implementation

Environmental management systems can provide a number of advantages, for example:

- improved insight into the environmental aspects of the company
- improved basis for decision-making
- improved motivation of personnel
- additional opportunities for operational cost reduction and product quality improvement
- improved environmental performance
- improved company image
- reduced liability, insurance and non-compliance costs
- increased attractiveness for employees, customers and investors
- increased trust of regulators, which could lead to reduced regulatory oversight
- improved relationship with environmental groups.

Example plants

The features described under (a) to (e) above are elements of EN ISO 14001:1996 and the European Community Eco-Management and Audit Scheme (EMAS), whereas the features (f) and (g) are specific to EMAS. These two standardised systems are applied in a number of IPPC installations. As an example, 357 organisations within the EU chemical and chemical products industry (NACE code 24) were EMAS registered in July 2002, most of which operate IPPC installations.

In the UK, the Environment Agency of England and Wales carried out a survey among IPC (the precursor to IPPC) regulated installations in 2001. It showed that 32% of respondents were certified to ISO 14001 (corresponding to 21% of all IPC installations) and 7% were EMAS registered. All cement works in the UK (around 20) are certified to ISO 14001 and the majority are EMAS registered. In Ireland, where the establishment of an EMS (not necessarily of a standardised nature) is required in IPC licenses, an estimated 100 out of approximately 500 licensed installations have established an EMS according to ISO 14001, with the other 400 installations opting for a non-standardised EMS.

Reference literature


4.1.1.1 Specific issues for surface treatment activities

Specific issues that may be considered:

- installing valves and numbering them for all pipes. The numbers are then used in instructions for shutdown sequences, both long and short-term shutdown

- checking all tanks and pipework regularly for leakage. This requires tank bottoms and pipes to be visible, with no accrual of dirt, rubbish, old jigs, anode ends etc. in bund areas and around tanks or pipes.

- using fixed and temporary pumps and filters over mobile tanks or drip trays with sufficient capacity to retain leakage and spills. Pipe ends are kept over the process tank or drip trays. This enables liquid residues to be collected and returned to the correct process solutions or dealt with as a waste or waste water.
• keeping all process areas clean and painted to allow chronic leakage to be readily identified.

• the identification of the use of priority pollutants in the installation (currently and in the past) such as:
  o polychlorinated biphenyls, e.g. in capacitors and other electrical equipment
  o cadmium
  o other materials that do not or are slow to degrade, such as other metals in soluble form
  o VOCs used for degreasing
  o cyanides
  o acids and alkalis

• the establishment of the use of the land and buildings of the installation prior the existing installation and/or activities and if the activities carried out could be confused with the activities of the surface treatment installation.

• monitor indicators for environmental performance as well as those affecting individual processes. Examples are:
  o raw material consumption by type
  o energy consumption
  o water consumption.
  o effluent discharged and quality
  o waste produced and type.

These figures are most meaningful when related to other relevant production parameters, such as area of workpiece or substrate throughput, number of barrels or flight bars processed, weight of workpieces or substrate processed, etc.

4.1.2 Reduction in reworking by process specification and quality control

Description
Workpieces or substrate surface treated incorrectly, to the wrong or inappropriate specification or a specification incorrectly applied can lead to significant amounts of metal stripping and rectification (in barrel and jig work) as described in Section 2.3, metal stripping. Workpieces and/or substrate may also have to be being scrapped, predominantly large scale coils and printed circuit boards, although some jig and barrel processed workpieces may be damaged irrecoverably.

Reduction in reworking and scrap can be achieved in a variety of ways, such as using formal quality management systems, QMS. As with environmental management tools, described in Section 4.1.1, to achieve success within the installation, these systems should be formally recorded and disseminated to the workforce. While many such systems are externally accredited (and this may be a customer requirement) it may not be essential. However, it is usual to have the system externally audited, to provide unbiased input to validating and updating the system, as well as giving customer confidence. These systems usually include statistical process control (SPC).

Attention to the appropriate process specification and its quality control is also an important factor. In surface treatment activities a “right first time approach” is normally anticipated and is often part of a formal system. To achieve this, it is common practice to ensure the correct process is applied in the correct manner to achieve the desired effect. This requires a proper understanding of the properties given by the surface treatment and the subsequent operations to be performed on the workpiece or substrate such as pressing, forming, bending, crimping.
drilling, welding, soldering, etc. Other techniques that form part of achieving the correct specification are discussed in SPC (Section 4.1.1.1) and in production management systems.

To match the treatment to the required objective, environmental and/or quality management systems (as appropriate) should make sufficient provision for dialogue and agreement between the operator and the customer about the correct process specification, engineering design drawings and the quality control measurement points for the workpieces and/or substrates (see Applicability, below). The following are examples of areas that can be addressed:

- surface treatments can alter the dimensions of a workpiece by the thickness of layer added (e.g. changing the size of threaded components), the characteristics of the substrate (e.g. hydrogen embrittlement with acid zinc plating) or be inappropriate for subsequent manipulation (e.g. some finishes may be brittle and may flake when a treated workpiece is subsequently bent or crimped)

- in electrolytic processes where the applied material is current-carrying, the deposits build preferentially at edges and corners of the workpiece and/or substrate, where the charge density is greatest. The method of measurement and the points to be measured for quality control of the finish may be agreed taking account of the differences of thickness at different parts of the workpiece or substrate to be finished. Some measurement methods require flat surfaces and to meet performance requirements attention may need to be given the coating thickness being significantly thinner in flat areas than at the edges (a ratio of centre thickness to edge thickness of approximately 1:3 or 1:4). Also, while specifications may be met in the flat, measured areas, edge build-up can result in flaking if the edges are subsequently manipulated, such as by crimping.

- performance specifications (such as to achieve a specified level of corrosion resistance) are preferable to total reliance on prescriptive specifications. The more usual and readily applied thickness measurements are best used in conjunction with performance specifications, when thicknesses at agreed points that meet the specified performance can be established (see also the discussion on Substitution, Section 4.9)

- alterations to the manufacturing process prior to surface treatment. For example, change in pressing oils (to a type which may become pressed into the substrate micro-structure and does not respond to normal degreasing processes), type of substrate, pressing workpieces in place of machining, hardening prior to surface treatment, etc.

- alterations to end use specification

- barrel treatment instead of jig (possibly because of cost constraints)

- major organisations or industry sectors requiring large amounts of surface treatment may write their own specifications (such as automotive or aerospace organisations). Smaller organisations often use these publicly available specifications. To meet specifications, care should be taken to ensure the latest versions are referred to, and the specifications are suitable for other products, their subsequent processing and end use

- some customers may request the highest quality specifications available, such as military and aerospace specifications involving cadmium for other products. However, military and aerospace applications are exempt from marketing and use legislation applying to cadmium.

There are many ways in which processes can be improved for stability and consistency over time and many techniques described in Chapter 4 have this advantage as well as improving environmental performance. Where this occurs it is highlighted in the subsection ‘Driving force for implementation. Examples are the use of insoluble anodes with external make up (see
Section 4.8), process solution agitation (Section 4.2.3.2) and control of concentration of process chemicals, Section 4.7.1

**Achieved environmental benefits**
Avoiding reworking minimises losses in raw material, energy and water inputs, as well minimising waste water treatment and the generation of sludge and liquid acid wastes.

Metal stripping with strong acids is often carried out as a batch process. Reduction in this activity can result in reductions in:

- spillage which can attack concrete floors and can pollute surface and groundwaters
- exceeding waste water treatment plant capacity leading to breach of permit discharge conditions
- acid fumes and mists leading to problems with local air quality, health and safety and deterioration of plant and equipment.

Reduction in surface treated scrap can reduce emission to air from other installations such as furnaces and foundries. In these, some non-ferrous metals may be vaporised and organic coatings burnt off with unknown breakdown products.

**Cross-media effects**
There are no negative cross-media effects.

**Operational data**
If specification or processing is incorrect a significant proportion of production capacity may be affected.

In some cases workpieces and/ or substrates are damaged in the reworking, or cannot be reworked and are scrapped.

**Applicability**
Applicable to all installations. However, note that the IPPC Directive applies to the installation and its management systems. It does not apply to the supply chain and products

**Economics**
There is significant economic justification for ensuring the specification is correct and is met, thus preventing reworking. Avoiding reworking is a positive action towards sustainable manufacturing and increases process throughput efficiency, as well as increasing customer confidence. There are cost savings in raw materials, hazardous waste disposal, energy and water, as well as labour. For sub-contract installations, the cost of stripping and reworking is usually born by the sub-contractor.

Conversely, there are costs associated with introducing and maintaining process management systems and SPC.

**Driving force for implementation**
Business economics and sustainability.
Customer requirements for quality management systems.

**Example plants**
All sites visited have quality management systems; some accredited, but all externally assessed. Examples are: SIKEL N.V., Genk, Belgium; Exhall Plating, Coventry, UK, SGI, Plaisir, France; Corus, Llanelli, UK; Cropu SA, Burgos, Spain.

**Reference literature**
4.1.3 Other management tools - installation and process assessment and optimisation

4.1.3.1 Benchmarking

Description
Section 4.1.1(j), Benchmarking, proposes that systematic and regular comparisons of an installation with sector, national or regional benchmarks for inputs (raw materials, energy and water) and outputs (emissions to air, water and as waste). However, appropriate benchmarking requires comparable data – a “like for like” comparison. For surface treatment activities this would be best achieved on a surface area treated basis or consumption of input basis. For instance, kg of zinc used per 10000 m² of surface, kg zinc discharged per 10000 m² of surface, kWh per 10000 m² of surface. However, such data can be difficult to acquire as workpieces have irregular shapes and estimations of surface area can vary in accuracy. Also, the shapes of workpieces affect impact on issues such as amount of process solution dragged out.

Data Envelope Analysis is a method of analysis that has been developed to compare the efficiency of organisational units when it is difficult to make the inputs or outputs comparable with unambiguous quantities. It can be applied in situations in which there are observations from many relatively homogeneous production units. In this context, homogeneity refers to the inputs and outputs that the units produce. They do not need to be organised in the same way or use the same types of production technology.

An example of DEA applied to surface treatment is given in [8, Clarin and Luona, 2002] Data variables from a survey of 15 electroplating companies was analysed in four groups:

- quantity of workpiece/substrate outputs
- labour, and capital invested in equipment
- energy and water consumption
- emissions.

The DEA results were calculated using a varying combination of input factors. The efficiency score (productive efficiency) was calculated for inputs in capital and man-hours, water and energy with various outputs to the environment. The only output quantifier was the annual revenue earned by treatment. The data was modelled using linear programming methods with weighting factors.

Achieved environmental benefits
Assists individual installations to assess their environmental performance with other installations. Assists in identifying techniques used by best performing installations.

Cross-media effects
None

Operational data
Provides benchmarks and assessment of operational environmental performance for installations and techniques.

Applicability
Data must be available for several installations with homogeneity of inputs and outputs before an individual installation can be benchmarked. The breadth of data and installations needs to be sufficient wide to be challenging; for example, [8, Clarin and Luona, 2002] benchmarks water usage at 50 litres per m². However, UK industry median is about 44 litres per m² (verbal information from TWG) and the French regulatory maximum is 8 litres per m² [58, France, 2003].
Chapter 4

Weighting factors need to be determined. Knowledge of DEA and its application with linear programming is required. This approach may be useful for a group of companies or a trade association. The technique does not readily take account of cross-media effects.

Economics
Data Envelope Analysis may need expert assistance in application.

Optimisation of plant environmental performance will usually achieve economic optimisation.

Driving force for implementation
Economic process optimisation is usually achieved commensurately with environmental optimisation

Example plants
Unnamed examples are given in [8, Clarin and Luona, 2002]

Reference literature
[8, Clarin and Luona, 2002]

4.1.3.2 Process line optimisation software

Description
Modelling tools can be used to help optimise performance of process lines by calculating the theoretical inputs and outputs required for selected options.

One software tool working on an Excel spreadsheet tool has a series of parameters for rack and barrel zinc electroplating. One data set is given for a model plant and the other set initially to a UK industry benchmark which can be adjusted to an actual plant and/or used to examine the effects of various options, such as adding rinsing stages. Other data can be entered for other processes, such as copper plating.

Achieved environmental benefits
Enables a process line to be optimised theoretically for consumption of water, energy and conservation of raw materials, as well as minimising emissions to water.

Cross-media effects
Enables optimisation of inputs (raw materials and utilities) and emissions to water at the same time.

Operational data
Can use existing data and can be used to benchmark performance as well as plan improvements.

Applicability
All multistage process lines if other data entered into the spreadsheet. Established for zinc electroplating, but readily adapted by user to other surface treatment activities. Software free, but only available in English.

Does not optimise whole installation.

Economics
Software available free of charge.
Trialing options using software can assist with process management and investment decisions before commitment.

Driving force for implementation
Environmental optimisation can optimise the plant’s process and economic performance.
Chapter 4

Example plants
No data provided

Reference literature
[26, Envirowise, 2003]

4.2 Utility inputs and their management - energy

Energy-saving measures and systems involve the design of operating tools or of equipment capable of:

- maximising use of energy consumed by installation, e.g. management of incoming electrical supply
- minimising the energy used to heat process solutions
- minimising the energy (current) loses in electrochemical processes
- minimising the energy used to cool process solution
- maximising the efficiency of other uses, such as air extraction and other electric drive motors, the operation of peripheral and recycling plants
- optimising air extraction and space heating

Individual measures may be described their specific activities, such as air extraction system optimisation is discussed in air emissions, Section 4.18.2

4.2.1 Electricity

4.2.1.1 Incoming high voltage supplies

Management of incoming supply to match phases, minimise “funny energy” losses on step down from high voltage, etc.
No data provided

4.2.1.2 Management systems to control peak use etc.

Control systems to ensure electrical energy consumed stays with installation design and contract maxima.
No data provided

4.2.1.3 DC supply

Description
Energy savings can be attained through:

- reduction of voltage drop in conductors and connectors
- regular maintenance of rectifiers and contacts (bus bars) 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 (e.g. pulse, reverse) which may improve metal deposits.
[3, CETS, 2002]
Chapter 4

Achieved environmental benefits
In total, an energy saving in DC supply of 10 – 20 % may be expected.

Cross-media effects
No data provided

Operational data
No data provided

Applicability
No data provided

Economics
No data provided

Driving force for implementation
Cost savings commensurate with saving 10 – 20 % of DC supply.

Example plants
No data provided

Reference literature
[3, CETS, 2002]

4.2.2 Heating of process solutions

Description
There are three main ways of heating process solutions, and they are by indirect heating coils using:

- high pressure hot water
- unpressurised hot water
- thermal fluids - oils

Individual electric tank (immersion) heaters may be used to heat solutions directly, and are used to supplement indirect systems, as well as being the sole source of heating in small tanks.

Information from site visits revealed the following information:

- high pressure hot water can be expensive to run and maintain
- unpressurised hot water and thermal fluids may be cheaper to run
- thermal fluid leakage may damage process solutions irrecoverably
- hot water system leakage may dilute process solutions irrecoverably, although solution may be recovered if leakage corrected before dilution is significant.

Achieved environmental benefits
No data provided

Cross-media effects
All process solutions may be damaged by leakages from heating coils, either by contamination of non-aqueous thermal fluids (oils) or by dilution from water leaks.

Operational data
Maintenance requirements are specialist for high pressure hot water systems. Other systems require monitoring of process solutions to ensure no leas are occurring into the solutions.
Applicability
No data provided

Economics
One installation claims a payback period of 11 weeks for a € 96000 investment when switching from high pressure hot water to thermal fluid boiler.

Driving force for implementation
Cost savings.

Example plants
Exhall Plating Ltd, Coventry, UK.

Reference literature
[18, Tempany, 2002]

4.2.3 Reducing heating losses from process solutions

Description, operational data and applicability – general
Energy losses from the surface area of heated process solutions related to processing temperatures are shown in Table 3.1. It demonstrates that the highest energy loss occurs 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. Other techniques to conserve energy are also described [3, CETS, 2002].

It is normal practice to minimise heating losses from process solutions but actual techniques used may depend on the options to re-use heat, the availability of renewable energy supplies and local climatic conditions.

This section briefly describes heating losses in the surface treatment industries. More information on cooling is available in [85, EIPPCB].

4.2.3.1 Reduction in the volumes of air extracted

Techniques to reduce the volume of warm air extracted and reduce energy loses by evaporation are described in Section 4.18.2.2

4.2.3.2 Agitation of process solutions

Description
It is normal for many process solutions to be agitated to keep consistent solution concentration throughout the vat, and prevent build-up of gas bubbles and contaminants at the workpiece or substrate surface.

The use of compressed air gives high evaporative heat loses, as well as its own energy consumption and especially when in conjunction with air extraction, see Table 3.1. However, the energy loses may be negligible when used in very small tanks.

Air for agitation can also be provided by a low pressure blower. Another option 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 offsets the higher energy usage of hydraulic turbulence.
Chapter 4

Achieved environmental benefits
The energy saving is substantial, see Table 3.1.

No data provided

Cross-media effects
No data provided

Operational data
Hydraulic turbulence provides greater agitation than air systems. This results in improved plating quality, reduction of rejects, and optimisation of proprietary additives consumption

Applicability
All process tanks requiring agitation.

Economics
No data provided

Driving force for implementation
Costs saved in energy consumption and improved process quality.

Example plants
No data provided

Reference literature
[3, CETS, 2002]

4.2.3.3 Reduction in the process temperature

Description

Achieved environmental benefits
Energy saving.

Cross-media effects
No adverse effects.

Operational data
Temperature changes to processes should only be made with technical support.

Applicability
This will depend on support from the proprietary process suppliers or in-house expertise in developing solutions that are viable at lower temperature ranges. It may also depend on choice of process solution chemistry (see Section 4.9).

Economics
No data provided

Driving force for implementation
Cost savings in energy consumption.

Example plants
No data provided

Reference literature
No data provided
4.2.3.4 Heat recovery

**Description**
[3, CETS, 2002] Process solutions may be heated by energy coming from process steps generating energy. Water from the cooling circuit of various process solutions may be used to heat lower temperature solutions, incoming air, etc. Alternatively, the hot cooling water is collected in a central tank 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.

**Achieved environmental benefits**
Energy saving.

**Cross-media effects**
*No data provided*

**Operational data**
*No data provided*

**Applicability**
*No data provided*

**Economics**
Capital investment for sophisticated systems may be high.
*No data provided*

**Driving force for implementation**
*No data provided*

**Example plants**
*No data provided*

**Reference literature**
*No data provided*

4.2.3.5 Insulation of process tanks
*No data provided*

4.2.3.6 Insulation of process solution surfaces
There are systems in general use using floating spheres to insulate the solution surface without restricting the access of workpieces or substrates.
*No data provided*

4.2.4 Cooling of process solutions

4.2.4.1 Water cooling systems

**Description**
These are described in Section 2.12.1.3 and more information is given in *BREF on industrial cooling systems*.

**Achieved environmental benefits**
Water saving.
Chapter 4

Cross-media effects
Increased energy consumption of refrigerated systems.

Operational data
It is unlikely to be cost-effective to use a system without recirculation, except possibly in the case of recycled water. Normally, for most situations and if other water saving techniques are in use, there is insufficient water from such sources to provide sufficient cooling.

Open cooling systems require regular maintenance to prevent algal growth and solids build-up and have been the source of legionella infections.

Applicability
Recirculatory systems are widely used. The type of cooling system may be dependant on water availability and local climatic conditions.

Economics
Running water systems for cooling are only likely to be economic where the cost of the incoming water is very low.

Driving force for implementation
Cost savings in water usage and maintenance of open cooling systems.

Example plants
SIKEL N.V., Genk, Belgium, Exhall Plating, Coventry, UK.

Reference literature
[18, Tempany, 2002]

4.2.4.2 Evaporation

Description
Evaporation is widely used to remove excessive energy by evaporating water from the process solution and maintaining the process temperature at the desired level, either as just as evaporation directly from the process solution or using an evaporator (see Section 4.6.13).

Achieved environmental benefits
Combined process cooling with drag-out recovery and usually forms part of any zero-discharge systems.

Cross-media effects
May require higher process bath temperatures with increased energy use and/or for drag out recovery.
May require energy input into the evaporator to evaporate sufficient water.
Condensed water may be re-used.

Operational data
Normally run as an integrated system with countercurrent rinsing to maximise drag-out recovery and minimise process solution losses and therefore waste treatment. With sufficient countercurrent rinsing stages and/or additional heating in the evaporator.

For electrolytic processes, evaporators are have less power input and costs are lower if the process solution temperature is as high as necessary to remove any electrolytic energy input by natural evaporation from the solution surface.

Applicability
Can be used with solutions running at ambient temperatures
Economics
Each kWh removed by evaporation is equivalent to 1.4 litres of water which can be balanced by drag-out recovery containing process chemicals and reduced rinse water.

Driving force for implementation
If direct evaporation is used, then no capital investment is required. See Section 4.6.13 for driving for solution recovery and minimum discharge processes.

Example plants
Merry Polishing and Plating, Wednesbury, West Midlands, UK, Frost Electroplating Birmingham, UK.

Reference literature
[3, CETS, 2002, 18, Tempany, 2002]

4.2.5 Utility inputs and their management - heating and cooling - other requirements of the installation

No data provided

4.2.6 Water

4.2.6.1 Control of water usage

Description
Water meters are frequently placed on all installations usage points, rinses, solution top up, washrooms etc. This identifies areas of high water usage for appropriate corrective action.

Achieved environmental benefits
Water consumption in one case has been reduced over 7 years by 83 %, from 263636 m³ to 31818 m³ by installing about 70 water meters (usually 20 – 30 mm) Other installations confirm significant savings can be made.

Cross-media effects
None reported.

Operational data
Maximum effect is gained when used in conjunction with locking flow valves set at optimum usage rate and with other monitoring data, such as water usage per flight bar or per square metre treated.

Applicability
All installations.

Economics
Installations with direct raw water abstractions from resources that are fully and continually replenished may not have a financial payback for the investment. Note that reduced water consumption also means reduced water volume discharged, and this may reflect in lower cost for discharge to municipal or third party water treatment plants.

Driving force for implementation
Rapid payback period where water costs are significant.

Example plants
Exhall Plating Ltd, Coventry, UK; Frost Electroplating Ltd., Birmingham, UK.

Reference literature
[18, Tempany, 2002]
4.3 Protection of workpieces and substrates - before and after treatment

Corrosion can take place on metal substrates prior to surface treatment and on treated surfaces of metals and plastics after surface treatment and prior to dispatch. Corrosion may cause poor adhesion of the surface treatment or damage decorative finishes and therefore require stripping and reworking or scrapping. Corroded products are likely to require additional processing to remove corrosion prior to surface treatment. Corrosion prevention can reduce the environmental impacts associated with stripping and reworking (see Sections 2.3 and 4.18.1).

Most metal surfaces oxidise or corrode when exposed to oxygen or other factors in the atmosphere; some quickly such as aluminium, others more slowly. Corrosion time is dependent on the type of material and the conditions under which the material is stored, for instance, steel components do not corrode in an atmosphere with less than 50% humidity. Humidity, temperature and acid atmospheres are factors determining how quickly corrosion takes place. All these factors are present in surface treatment installations, so controlling the exposure of stored products is important.

Protection of surfaces from mechanical damage is also important.

4.3.1.1 Shortening storage time

Description
[3, CETS, 2002] Eliminating or shortening storage between operations e.g. between manufacture and surface treatment, or between surface treatment and dispatch can avoid the need for other corrosion prevention treatment. This may be as part of a formal JIT (just in time) system or as part of good production planning.

Achieved environmental benefits
Prevention of stripping and reworking.

Cross-media effects
No data provided

Operational data
No data provided

Applicability
Most applicable for in-house installations and where transport links are short and frequent. However, may not be applicable where customers are distant and economic transport batch sizes require storage before and after processing.

Economics
The only foreseen costs are labour costs for planning and supervision of production and delivery timing. Reduced capital and running costs for storage, as well as production costs stripping and reworking reject products.

Driving force for implementation
See Economics, above.

Example plants
No data provided

Reference literature
No data provided
4.3.1.2 Storage and transport conditions

Description
[3, CETS, 2002] It is usual to store components both awaiting treatment and treated away from humid and acid air associated with many surface treatment installations. Good ventilation (see design, Section 4.18.1) of the workplace will assist, as will ensuring the vented moist and often acid exhaust air does not come into contact with products in storage or awaiting transport. Ventilation of the storage areas may also be used provided that it reduces moisture and does not draw in moist and acid air. Moisture condenses on components which become chilled during transport or storage and are subsequently delivered to a warm, humid location. Keeping products warm in transport and storage in a low humidity environment can eliminate these problems.

Achieved environmental benefits
Reduced stripping and reworking.

Cross-media effects
Increased energy usage for dehumidification or ventilation may be offset by environmental benefits from decreased reworking.

Operational data
No data provided

Applicability
All locations. However detailed application will vary with regional climatic conditions such as normal humidity levels and daily mean temperatures.

Economics
Increased costs of energy usage for dehumidification or ventilation may be offset by savings from reworking. The discounted capital cost of segregating storage may need to be balanced with add-on measures such as improved ventilation or dehumidification.

Driving force for implementation
Economic and environmental savings from reduced stripping and reworking.

Example plants
SIKEL N.V., Genk, Belgium.

Reference literature
No data provided

4.3.1.3 Packaging

Description
Workpieces or substrates may be packed with absorbent or corrosion preventing materials such as specialist papers or woodchips. Such materials can both prevent corrosion and prevent surface damage in transit and are often specified by the customer, particularly for high value components, such as printed circuit boards and aerospace components. Coils are usually protected by the outer layers, with protective strip providing immediate contact with flooring and cradles preventing unwanted movement.

Achieved environmental benefits
Reduced stripping and reworking.

Cross-media effects
Increased consumption of raw materials. This can be offset by selecting and using recyclable packaging systems.
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4.3.1.4 Corrosion prevention coating with oil or grease

Description
[3, CETS, 2002] Oil and/or grease may be used for corrosion prevention during storage. The disadvantage is that items have to be cleaned (see Section 2.3). The type of oil or grease used should be chosen according to the degree of protection required.

Achieved environmental benefits
Prevention of reworking and scrapping.

Cross-media effects
Increased chemical, energy and water usage to remove oil and grease. Increased disposal to waste water and waste routes.

Operational data
Greases are often used for military applications when components are left in storage for long periods prior to use. The duration of coating becomes significant when 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 environmentally friendly products, however these can be very difficult to remove especially if the product has been stored during a warm weather period. This may be a more important factor in warmer regions.

Applicability
Suitable in some applications and often associated with minimising tool wear in pressing etc.

Economics
The environmental and economic savings from avoidance of stripping, reworking or scrapping may offset or exceed the costs of avoiding corrosion.

Driving force for implementation
Economic, see above. Customer requirements.

Example plants
No data provided

Reference literature
No data provided
4.4 Pre-cleaning

4.4.1 Minimisation and optimisation of coatings from previous mechanical treatments: oil and grease

Description
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. Oil or grease is used to minimise tool wear, e.g. pressing sheet steel, drilling or drawing operations, or for corrosion prevention prior to surface treatment.

Any changes to remove or minimise oily coatings often take place at the mechanical production stage. This may involve discussion with the customer (see Section 4.1.2, Specifications). By changing the production method the use of oil can be minimised or eliminated. Oil usage can be minimised by regularly assessing the application methods, type and quantity of oil used. [3, CETS, 2002].

Possibilities for reduction of oil and grease applied in the mechanical production areas:

- use of volatile lubricants
- employment of minimal quantity cool lubrication
- dripping off and/or centrifuging the workpieces
- pre-cleaning the workpieces at the point of production
- shortening the storage time, see Section 4.3.1.4
- drilling with compressed air-cooling
- use of applied plastic film lubricants in pressing.

Achieved environmental benefits
Reduction in degreasing processing requirements including chemicals and energy consumption, as well as wastes produced.

Cross-media effects
Consumption of energy and/or materials of alternatives, such as dry lubricant films and air-cooled drilling.

Operational data
Can be considered for all oiled work pieces/substrates.

Applicability
Case-depdendant. The use and type of oils and grease can be critically and constructively discussed with all customers.

Economics
Case-depdendant: One installation quotes savings of € 25000 per year in oil applied by one of their customers (2000 costs), plus uncosted savings in degreasing chemicals and energy, labour and impacts on process quality.

Driving force for implementation
Subsequent process control improved; reworking reduced.

Example plants
Exhall Plating, Coventry, UK

Reference literature
[18, Tempany, 2002, 104, ÜBA, 2003]
4.4.2 Mechanical pre-cleaning

Description
Excessive oil and grease can be removed mechanically before other forms of degreasing, such as chemical or solvent. [3, CETS, 2002]

Achieved environmental benefits

Cross-media effects
Power consumption in centrifuging, etc.

Operational data
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 the components to decrease the viscosity of the oil.

Applicability
The majority of oiled small components, usually undergoing barrel treatment.

Economics
No data provided

Driving force for implementation
No data provided

Example plants
No data provided

Reference literature
No data provided

4.4.3 Other degreasing techniques

Description
Large components can be cleaned manually with cloth or paper wipers. For sheet metal and wire components the majority of oil can be removed by passing through a divider that can be mechanical (a wringer roller) or an air-knife. Clean hot water (80 - 90 °C) without chemicals can remove the majority of oil and grease. This method is used mainly in the automotive industry when cleaning pressed sheet steel. Using a high-pressure water jet further improves the effect. [3, CETS, 2002].

Achieved environmental benefits
Extends life of degreasing solutions.

Cross-media effects
No data provided

Operational data
No data provided

Applicability
Depends on size and type of components: see Description, above.
4.5 Drag-out reduction

4.5.1 Preliminary remarks

Drag-out is described in Section 2.4.

A reduction of drag-out is an effective primary measure for:

- minimising losses of chemicals in rinses
- reducing the amount of rinsing required
- reducing raw material costs
- reducing environmental problems associated with rinsing waters.

Techniques to reduce of losses of chemicals resulting from drag-out are outlined below (see also, process specific sections, such as barrel plating, coil coating, etc).

Drag-out depends on a large variety of parameters and a reduction of this key step with many impacts on the environment and process can only be achieved by close co-operation of all personnel 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, see issues such as training in environmental management systems, Section 4.1.1 [3, CETS, 2002, 104, ÜBA, 2003]

4.5.2 Reduction of drag out - jig (rack) processing

Description

[3, CETS, 2002] To allow the adhering solution to run down to the bottom edge of workpieces, the largest surfaces of the articles should be arranged in a vertical position at the jigs (racks).

The longer dimensions of the articles are normally arranged in the horizontal and/or slightly inclined to allow the adhering solution to run down, improving drainage.

The lower edge of all articles may be tilted to allow the droplets to cohere and facilitate dripping down above the process tank.

When lifted out from the process solution, the jigs may be tilted in such a way that large droplets can be formed faster and drip down from the lowest point of the suspended articles.

To allow the adhering liquid to cohere and form droplets which will drip from the articles, sufficient drainage time should be allowed above the process tank.
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By slow withdrawal of the jigs 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. Normal minimum withdrawal and dwell times are given in Table 4.2.

<table>
<thead>
<tr>
<th>Process</th>
<th>Minimum time-seconds withdrawal</th>
<th>Minimum time-seconds dwell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plating</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Cleaning/pickling</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>Passivation</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Seals/lacquers</td>
<td>10</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 4.2: Withdrawal and dwell times for jigs

Cup-shaped recesses are normally avoided where possible, and cup-shaped components jigged cup-side down on the incline so process solution is not carried into the rinse water.

In some cases, arrangements can be made with customers for components with high drag-out retention, such as cup-shaped components, to be manufactured with drainage holes by dialogue (verbal information, TWG member).

Dripping of process solution on other articles arranged lower on the jig is normally addressed by suitable positioning of the work pieces.

An automatically or manually inserted draining pan below the jigs will collect the drippings and prevent contamination of subsequent tanks and solutions.

Drag-out by jigs can be reduced by inclining supporting arms to avoid horizontal surfaces from which the adherent solution cannot run off easily.

A normal inspection and maintenance task is to check the insulation coating of the jigs to ensure smooth surfaces with no fissures or cracks in damaged insulation to trap and retain solution.

Jig insulation coatings are normally hydrophobic to assist draining of drag out.

Achieved environmental benefits
Key step in reducing loss of soluble chemicals from process vats to the environment via rinsing.

Cross-media effects
None reported.

Operational data
The dragged-out volume is (according to K. G. Soderberg):

\[ W = 0.02 A \cdot \sqrt{\frac{a \cdot p}{t \cdot d}} \]

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 Pascal second)
t is the withdrawal time in seconds
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 e.g. by chemical or volumetric analysis, the following typical data can be used for rack plating:

<table>
<thead>
<tr>
<th>Type</th>
<th>Drag-out Rate (l/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat surfaces</td>
<td>0.1</td>
</tr>
<tr>
<td>Contoured surfaces</td>
<td>0.2</td>
</tr>
<tr>
<td>Cup shapes</td>
<td>1</td>
</tr>
</tbody>
</table>

In some processes, such as chromium passivation, excessive drainage time may affect the quality of treated surface, see Section 2.5. Where a rapid stopping of the surface reaction is required this is often achieved by rapid dilution of the remaining process solution on the surface [104, ÜBA, 2003].

**Applicability**

All jig (rack) plants.

**Economics**

All these measures can be incorporated into the operation of any jig (rack) plant. Jigs have a relatively short operating life, are not capital intensive, and design can be improved and implemented over time. Correct positioning of workpieces on jigs is usually achieved by staff training.

Other measures, such as draining and dwell time will depend on transporter control equipment used.

**Driving force for implementation**

Cost savings in chemical usage and reduction in waste water treatment costs.

**Example plants**

*No data provided*

**Reference literature**


### 4.5.3 Reduction of drag out - barrel processing

**Description**

[3, CETS, 2002] The plastic material of the barrel normally has a smooth surface and is inspected for worn areas, and the formation of recesses or bulges around the holes.

The bores of holes in the panels usually have a sufficient cross-section to minimise capillary effects, and the thickness of the panels of the cylinder just thick enough to meet the mechanical strength requirements.

The total proportion of the body of the barrel that is perforated is usually as high as possible to allow the drag-out to drop back easily into the process tank. This also improves the efficiency of the whole plating process by allowing easier solution access and decreasing voltage drop.

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

A further reduction of drag-out can been achieved by the application of draining ledges within the barrels to allow the draining liquid to flow together and to drain out of the rotating the barrel.
In a barrel, the workpieces mainly lie with the main surfaces horizontal. To achieve better draining, inclined lifting of the barrels from the tanks should be considered. The suspension and hoisting systems may be adapted to this requirement. However, in conventional systems this is difficult to realise.

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

**Achieved environmental benefits**
Key step in reducing loss of soluble chemicals from process vats to the environment via rinsing.

**Cross-media effects**
None reported.

**Operational data**
To minimise the volume of liquid dragged out, the barrel should be withdrawn from the liquid slowly to decrease the drag-out effectively, with a sufficient draining time afterwards as described in Table 4.3.

<table>
<thead>
<tr>
<th>Process</th>
<th>Withdrawal</th>
<th>Dwell</th>
<th>Stationary periods (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plating</td>
<td>5</td>
<td>24</td>
<td>3 x 8</td>
</tr>
<tr>
<td>Cleaning/pickling</td>
<td>5</td>
<td>24</td>
<td>3 x 8</td>
</tr>
<tr>
<td>Passivation</td>
<td>5</td>
<td>16</td>
<td>2 x 8</td>
</tr>
<tr>
<td>Seals</td>
<td>5</td>
<td>24</td>
<td>3 x 8</td>
</tr>
</tbody>
</table>

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

**Table 4.3: Withdrawal and dwell times for barrels**

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 may be 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

Data for zinc barrel plating:

<table>
<thead>
<tr>
<th>760 mm barrel width</th>
<th>1200 mm barrel width</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat and contoured surfaces</td>
<td>1 – 2 l/barrel</td>
</tr>
<tr>
<td>Cup shapes</td>
<td>2 – 4 l/barrel</td>
</tr>
</tbody>
</table>

**Table 4.4: Drag-out retention, barrel diameter 380 mm with 8 mm holes**

<table>
<thead>
<tr>
<th>760 mm barrel width</th>
<th>1200 mm barrel width</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat and contoured surfaces</td>
<td>2 – 4 l/barrel</td>
</tr>
<tr>
<td>Cup shapes</td>
<td>3 – 6 l/barrel</td>
</tr>
</tbody>
</table>

**Table 4.5: Drag-out retention, barrel diameter 380 mm with 2 mm holes**

In some processes, such as chromium passivation, excessive drainage time may affect the quality of treated surface, see Section 2.5. Where a rapid stopping of the surface reaction is required this is often achieved by rapid dilution of the remaining process solution on the surface.

**Applicability**
All barrel process activities.
Economics
Many of these measures can be incorporated into the operation of any barrel plant. Barrels have a limited operating life, require maintenance, are not capital intensive, and design can be improved and implemented gradually.

Other measures, such as draining and dwell time will depend on transporter control equipment used.

Driving force for implementation
Savings in chemicals and other inputs for degreasing. Reduction in wastes produced.

Example plants
No data provided

Reference literature
[3, CETS, 2002]

4.5.4 Properties of process solutions – effect on drag-out

Description
The drag-out also depends on the properties of the process solutions.

Drag-out can be reduced by raising the temperature of the process solution which normally lowers the viscosity of the solution.

Lowering the concentrations of the process solutions will effectively reduce the drag-out, by lowering the amount of material contained in the dragged-out solution, as well as reducing surface tension and viscosity of normal ionic solutions.

The addition of wetting agents to the process solution reduces the drag-out by reducing surface tension.

To avoid excessively increased concentrations, the process solution should be controlled to a constant composition during regeneration and maintenance. This, and the selection of appropriate process solutions is an important step in the reduction of drag-out.

Achieved environmental benefits
Key step in reducing loss of soluble chemicals from process vats to the environment via rinsing.

Cross-media effects
Increasing the temperature of process solutions uses extra energy. The addition of wetting agents is an increase in the amount of chemicals used.

Operational data
Reducing the concentrations of chemicals in solutions below prescribed levels will need technical expertise in-house or from suppliers.

Ensuring constant compositions of process solutions is a part of SPC, see Section 4.1.1.1

Applicability
All process solutions.

Economics
No data provided

Driving force for implementation
Improved process control and costs.
4.5.5 Transition from drag-out draining to rinsing

Description
There is a close connection between minimising drag-out and the rinsing steps that follow. In outline:

In barrel plating, sucking off or blowing off a considerable part of the drag-out above the process tank is a proven measure to reduce losses of process solutions. This treatment can be combined with a pre-rinse, returning water from the first static rinse to the process solution.

When jigs (racks) or barrels 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 achieves 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.

Achieved environmental benefits
Key step in reducing loss of soluble chemicals from process vats to the environment via rinsing.

Cross-media effects
Energy usage in compressed air for blowing drag-out off workpieces.

Operational data
No data provided

Applicability
All jig and barrel installations.

Economics
Costs in energy consumption and pumping may be offset by savings in chemicals and waste water treatment

Driving force for implementation
No data provided

Example plants
No data provided

Reference literature
[3, CETS, 2002]
4.6 Rinsing techniques and drag-out recovery

4.6.1 Introduction

[3, CETS, 2002] This section discusses techniques for two connected purposes:

- how drag-out by different means can be reduced
- how rinsing water consumption can be reduced.

However, elimination of drag-out is impossible.

Drag-out of process solution and drag-in of rinse water leads to continuous dilution and drop of chemical concentration in process solutions.

Note: All formulas mentioned in this section provide exact theoretical results which do not 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. The theoretical formulas have been used, as little operational data has been provided.

Figure 4.1: Drop of chemical concentration in process solution due to drag-in of rinse water and drag-out of process solution without replenishing

\[ C_{0n} = \left\{ \frac{V}{V+D} \right\}^n \cdot C_0 \]

- \( C_0 \): 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.

Reference data for Figure 4.1:

**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

General cross-media and operational effects
Drag-out can be used as a means for regeneration of process solution, as it continuously removes process-disturbing residues of degradation products from brighteners and other organic additives. This ignores the simultaneous loss of valuable undegraded components. However, the use of drag-out minimisation and recovery techniques are likely to increase the need for properly designed techniques to reduce or remove contaminants in situ, see Section 4.10.

4.6.2 Exceptions to minimised rinse water

In certain applications, such as in pickling and chromating, the workpiece surface must be cleaned rapidly of the adhering process solution to stop the surface reaction.

The stopping of the surface reaction succeeds only when there is quick dilution in the first rinsing stage, which requires the use of high quantities of water. In such cases, the concentration of the reacting chemicals in the first rinsing stage must kept low. [3, CETS, 2002, 104, ÜBA, 2003]

4.6.3 Evaporation as prerequisite for drag-out recovery

Recovery of drag-out is made feasible by using the used rinse water to equalise the evaporation losses from process solutions. These are caused by evaporation due to:

- elevated processing temperature, such as >80 °C for electroless nickel and >55 °C, for electrolytic nickel and phosphating at >90 °C (see Figure 4.)
- cooling of the process solution by evaporation to maintain a constant processing temperature, such as in cyanide zinc barrel plating at <25 °C, bright chromium at 40 °C and hard chromium at 60 °C.

The evaporation of 1 litre of water requires approximately 1.4 kWh.

Figure 4.2: 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:

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

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

Equivalent quantities of rinse water with diluted process solution can be added back 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 a technique for drag-out recovery shown in Section 4.6.4.

#### 4.6.4 “Eco” rinse or pre-dipping

**Description**
Some drag-out from process solutions working at (but not limited to) ambient temperature can be recovered through a single rinse station in which the workload is dipped before and after being processed. Figure 4.3 shows the sequence of workload transport schematically.

![Figure 4.3: Drag-out recovery through ‘Eco’ rinse](image)

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 0.5C₀ will be reached. The solution has to be changed only when the tank itself and/or the tank walls have to be cleaned.

An “Eco” rinse tank can also be used in conjunction with other options to reduce water usage, see Sections 4.2.6.1 and 4.6.

**Achieved environmental benefits**
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) is approximately 50 %.

**Cross-media effects**
None reported.
**Chapter 4**

**Operational data**

*No data provided*

**Applicability**
May be considered where other alternatives are not achievable or as part of several rinses steps.

**Economics**

*No data provided*

**Driving force for implementation**
Where the process solution is running at ambient temperatures and/or there is little evaporation taking place.

**Example plants**

*No data provided*

**Reference literature**

[3, CETS, 2002]

### 4.6.5 Spray rinsing

**Description**
Spray rinsing may be carried out in two ways: over the process solution or in a separate empty tank.

Spraying prior to rinsing, (or pre-rinse) above the process bath is an effective method of rinsing. The rinsing water is sprayed on the workpieces while they still are above the bath surface. This may be manually for small process lines or automatically. For the pre-rinse the amount of water to be used should equal that dragged out from the process tank (as compensation to maintain the water balance). The pre-rinse causes a direct feedback of process solution into the process tank.

Rinsing in a separate tank acts as a first rinse. The solution can then be recycled back to the process solution in amounts equal to evaporative and drag-out loses.

**Achieved environmental benefits**
Key step in reducing loss of soluble chemicals from process vats to the environment via rinsing.

**Cross-media effects**

*No data provided*

**Operational data**
Spraying above the bath recovers process solution directly back into the tank. No additional tank is required.

Spraying in a tank reduces over-spray.

**Applicability**
Can be considered for all installations, but may be limited where there is a risk of drying and residues being left on workpieces or substrate.

**Economics**

*No data provided*

**Driving force for implementation**

*No data provided*

**Example plants**

SGI, Plaisir, France.
4.6.6 Chemical rinses

Description
[3, CETS, 2002, 6, IHOBE, 1997] An accelerated technique to achieve the required cleaning efficiency is obtained by means of chemical rinses called the Lancy process. Here the dragged-out process solution is reacted chemically with the rinsing liquid at the same time.

Achieved environmental benefits
Reduces the effluent treatment capacity required by reducing or eliminating the primary waste water treatment stages.

Cross-media effects
The main use of the Lancy process, the oxidation of dragged-out cyanides by rinsing in chlorine bleaching caustic solution, is now reduced because of concerns about the associated AOX-generation.

Does not recover dragged-out process solution.

Operational data
Technically simple to operate.

Incorporation of chemical rinsing can reduce the number of rinse stations with consequent increase in contaminated rinsing.

Applicability
Requires a suitable chemical reaction that can readily take place in the conditions of the first drag-out tank. Main uses are:

- oxidation of cyanide
- reduction of hexavalent chromium.

Limited contact time may not eliminate the target chemical, especially cyanide. This limits the usefulness to reduction of CrVI, particularly where workpieces have complex geometry and retain CrVI solution. The usual system is a vat after the chromium bath with sulphuric acid and sodium busulphite.

Economics
No data provided

Driving force for implementation
Can be used where waste water treatment capacity is limited.

Example plants
No data provided

Reference literature
[6, IHOBE, 1997, 104, ÜBA, 2003]
4.6.7 Regeneration of rinsing water

Description
By feeding the rinsing water through cation and/or anion exchangers the cations become exchanged for H\(^+\), and the anions for OH\(^-\), and water of a quality approaching demineralised water is achieved. This is fed back to the rinsing system.

Achieved environmental benefits
Minimised water usage.

Cross-media effects
Construction and operation of ion exchanger with consumption of energy and regeneration chemicals.

Operational data
For protection against mechanical blocking, a filter is used before the ion exchanger.

Applicability
No data provided

Economics
No data provided

Driving force for implementation
No data provided

Example plants
No data provided

Reference literature
[104, ÜBA, 2003]

4.6.8 Multiple rinse techniques for drag-out recovery

General description
Multiple stage rinsing is particularly suitable to achieve a high rinsing rate with a small amount of rinsing water.

For example, in cascade rinsing, the water flows in the opposite direction to the workpieces, as shown in Figure 4.4. This results in a rinsing water requirement of constant rinsing quality (the rinsing criterion), and is mathematically expressed in the term:

\[
\frac{Q}{t} = \sqrt[4]{Sk \cdot \frac{V}{t}}
\]

Q/t = necessary rinsing water amount (in l/h) to reach the rinsing criterion
Sk = rinsing criterion
n = rinsing stage number
V/t = drag out (in l/h)

The main effect of saving is reached with the transition from the first into the second stage. As Table 4.6 shows a smaller rinsing quantity of water can be achieved by the selection of the correct rinsing system. The effect of water saving decreases with an increasing number of rinsing stages. However, the volume of water required decreases to the point where direct make up for water loses from process solutions at ambient temperatures can be considered. The achievable recovery rate is, at a given volume of evaporation, directly related to the concentration of process chemicals in the first rinse station [CETS, 2002 #3]
Table 4.6: Specific rinsing quantity of water (litres rinsing water per litre out-drag electrolyte) as a function of given rinsing criterion and the number of cascades

<table>
<thead>
<tr>
<th>Number of stages</th>
<th>Necessary rinsing quantity of water in l/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single stage</td>
<td>10000 5000 1000 200</td>
</tr>
<tr>
<td>Two stages</td>
<td>100 71 32 14</td>
</tr>
<tr>
<td>Three stages</td>
<td>22 17 10 6</td>
</tr>
<tr>
<td>Four stages</td>
<td>10 8 6 4</td>
</tr>
<tr>
<td>Five stages</td>
<td>6 5 4 3</td>
</tr>
</tbody>
</table>

Some options and variations are outlined in Sections 4.6.9, 4.6.10, 4.6.11 and 4.6.12. They may be used in conjunction with other techniques, such as those described in Sections 4.6.1, 4.6.4, 4.6.5, 4.6.6, and 4.6.7.

Only a description of each option is given, other factors are described in this general section.

Achieved environmental benefits for all options described

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

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

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. (See 4.12.1, above).
Chapter 4

<table>
<thead>
<tr>
<th>Rinse technique</th>
<th>Medium cyanide zinc barrel</th>
<th>Bright nickel, jig</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triple counter flow rinse</td>
<td>&lt;24 %</td>
<td>&lt;57 %</td>
</tr>
<tr>
<td>This technique does not provide satisfactory recovery rates in barrel plant, since WD&gt;3*WR. Taking into consideration that no major additional investment is necessary, a rate of 57 % in jig plant seems attractive.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triple static rinse</td>
<td>&gt;40 %</td>
<td>&gt;95 %</td>
</tr>
<tr>
<td>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 &gt;95 % can be attained again without major additional investment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dual static rinse plus flow rinse</td>
<td>&gt;90 %</td>
<td>&gt;98 %</td>
</tr>
<tr>
<td>For a high drag-out recovery is required, this technique should be used in barrel plating. Changing of rinse water is required after 24 hours operation. The installation of an appropriate ion exchanger plant or a counter-flow rinse system will minimise the use of water.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.7: Achievable recovery rates

The closer to a zero discharge the more complete the recovery of process chemicals and the less the requirement for waste water treatment.

Cross-media effects for all options described
There may be increased energy used for evaporation (see Section 4.6.13)

Operational data for all options described
A build-up of breakdown materials which may reduce process quality is likely unless other solution maintenance measures are taken, see Section 4.10.

A combination of spray rinsing, particularly if carried out over the process solution, as part of a multiple rinsing system may combine the advantages of multiple stage water usage reduction with minimum extra space requirement.

Applicability of all options described
There are options and combinations suitable for all installations.

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

One example plant avoided the need to construct a waste water treatment plant by using multi-stage cascade rinsing combined with process solution evaporation, see Section 4.6.13.2.

Driving force for implementation for all options described
See Economics, above.

Example plants

Reference literature
4.6.9 Multiple stage counter-flow rinse

Description

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

\[
R = \frac{C_0}{C_n} = \left(\frac{q^{n+1}}{q-1}\right)
\]

where \( q = \frac{W}{D} \)

- \( C_0 \) = 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 4.5, below.

![Diagram of multiple stage counter-flow rinse](image)

**Figure 4.5: Recovery of drag-out with triple counter flow rinse**

In cases where \( E \geq W \), drag-out recovery rate

\[
R_{cR} = 1 - \frac{C_3}{C_0}
\]

In cases where \( E = W R < W \), drag-out recovery rate is reduced to

\[
R_{cR} = \frac{(1 - C_3)WR}{W}
\]

- \( C_0 \) = Concentration of chemicals in process solution,
- \( C_3 \) = Concentration of process chemicals in rinse station 3,
- \( E \) = Evaporation losses,
- \( R_{cR} \) = 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 4.6 shows the specific water consumption of triple and quadruple counter flow rinses in litres per litre drag-out.

![Graph showing specific water consumption of triple and quadruple counter flow rinses](image)

Figure 4.6: Specific water consumption “w” of triple and quadruple counter flow rinses

### 4.6.10 Multiple static rinse

**Description**


Figure 4.7 shows the arrangement of tanks and the process sequence of a triple static rinse.

![Diagram of triple static rinse](image)

Figure 4.7: Recovery of drag-out with triple static rinse
Instead of continuous inflow and overflow, rinse 1 is discharged into holding tank only when C3 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.

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:

\[
\begin{align*}
C_{1n} &= (1-q^n)\times C_0 \\
C_{2n} &= \{1-(n+1)\times q^n + n\times q^n (n+1)\} \times C_0 \\
C_{3n} &= \{1-(1/2)\times(n+1)(n+2)\times q^n + n\times(n+2)\times q^n (n+1) - (n/2)(n+1)\times q^n (n+2)\} \times C_0
\end{align*}
\]

\[q = V/(V+D)\]

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

### 4.6.11 Dual static rinse followed by final flow rinse with recirculated water

[3, CETS, 2002] 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 4.9.
Description
Rinse 1 should be discharged into a 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 4.9).

This technique allows for concentrations $C_2 \leq 0.2C_0$, 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 quantity of chemicals loaded on the ion exchangers. The design flowrate of recirculated water has to be 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 flowrate).
4.6.12 Multi-cascade rinsing with limited process line space

Description
[104, ÜBA, 2003] In the case of existing plants the use of a larger number of tanks is often not possible within the plant because of reasons of space. In such cases the employment of so-called external cascades (where the cascades are external to the process line) may be possible. In the treatment line there is only one rinsing tank per process step. Each rinse tank is connected to several external several tanks which work as rinsing stages according to the cascade principle. The workpieces or substrate are brought into the rinsing tank and rinsed successively with the water from the individual rinsing stage tanks, becoming progressively cleaner. Rinsing can be by sprays or filling the tank to immerse the workpieces or substrate. Figure 4.11 shows a spray rinsing system with the first rinse holding tank being concentrated. The concentrate is returned to the process solution and the cleaned water returned to the final rinse holding tank. Concentration techniques are described in 4.6.13.

![Diagram](diagram.png)

Figure 4.11: External cascade system: Single spray compartment with external cascade and concentrate recycling

4.6.13 Increasing drag-out recovery rate

[3, CETS, 2002] Where the quantity of water needed for appropriate rinsing (to achieve process control and product quality) exceeds evaporation losses, and recovery rates >90 % are expected, the amount of water in the drag-out recovery system has to be decreased.

Techniques for this purpose in use are, for example:

- addition of an “Eco” rinse tank
- atmospheric evaporation, AE
- vacuum evaporation, VE
- electro dialysis, ED
- reverse osmosis, RO
The principle of rinse water removal and chemical concentration is shown in Figure 4.12. The concentrate is used to replenish the process solution whilst the condensate can be reutilised as rinse water.

![Diagram of rinse water and chemical recovery through concentration](image)

**Figure 4.12:** Rinse water and chemical recovery through concentration

**Overall achieved environmental benefits**
Can achieve recovery rates above 90% and are used in zero-discharge systems.

**Cross-media effects**
See Overall applicability.

**Operational data**
See individual techniques

**Overall applicability**
Adding an “Eco” rinse tank requires additional space on the process line: the other four techniques require additional energy, which means cost, which may be offset by savings in cooling energy and drag-out recovery. The chemical content of rinse water to be processed also affects the appropriate choice.

**Overall economics**
See Overall applicability. Capital and running cost of the techniques may be offset by increased recovery of process chemicals, which can be >95%. Also, these techniques can reduce running costs and/or investment in waste water treatment plant

**Overall driving forces for implementation**
See Overall economics.

**Example plants**
See individual techniques

**Reference literature**
4.6.13.1 Addition of an “Eco” rinse tank

Description
The operation of an “Eco” tank is described in Section 4.6.4. Adding an “Eco” tank can increase recovery rates above 50 % is to add an “Eco” rinse tank. This alone can recover 50 % of drag-out; the total rate can be calculated when 50 % of the values in Table 4.7 are taken, for instance, triple static rinse in barrel plating:

\[ R_{cR \text{ total}} = 50 \% + 0.5(40) \% = 70 \%, \]

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

Achieved environmental benefits
See above.

Cross-media effects
No data provided

Operational data
Requires additional process line space as well as an additional process station programming into automatic lines.

Applicability
See Overall applicability.

Economics
See Overall economics.

Driving force for implementation
See Overall economics.

Example plants
No data provided

Reference literature
[3, CETS, 2002]

4.6.13.2 Evaporation

Description
This is the evaporation from a process tank to air that occurs in normal process operation. The amount of energy necessary for evaporating corresponds roughly to the energy which is released in the process tank as heat energy due to poor electrical efficiency of the solution; thus the system is energetically self-sufficient

Achieved environmental benefits
High recovery of drag-out.
Can be part of achieving zero discharge for specific process steps.

Cross-media effects
Energy used in process heating.
Possible aggressive fume formation at higher operating temperatures in some processes.

Operational data
Evaporation is most readily used with process solutions working at elevated temperatures, in particular chromium electrolytes. In connection with multi-stage rinsing technology (in practice
up to 5 rinsing stages) the procedure can be operated almost waste water free. Sufficient evaporation can occur at ambient temperature. Chromic acid dragged out from the process bath into the rinses is virtually completely recovered. Minimum chromium acid losses are to be expected through the exhaust air and with the regeneration of the electrolytes.

**Applicability**
All process solutions, particularly heated ones, or those with poor electrical efficiency where the process solution heats and is often cooled by evaporation (see Section 4.2.4.2)

Regional weather patterns may also affect applicability.

**Economics**
Requires no capital installation.

**Driving force for implementation**
See Overall economics.

**Example plants**
*No data provided*

**Reference literature**
[18, Tempany, 2002, 104, ÜBA, 2003]

### 4.6.13.3 Evaporator

**Description**
[104, ÜBA, 2003] In electrochemical installations evaporators are used for the concentration of rinsing water, which are fed back into the process tank. Industrially used evaporators usually work at temperatures between 40 °C and 100 °C and at operating pressures between 0.1 and 1 bar. Usually the evaporators used in electroplating shops are equipped with energy recovery (vacuum evaporators with vapour consolidating or heat pump) and need approx. 150 – 200 kWh per cubic meter of evaporated water.

The working principles of evaporators and evaporators are approximately the same, yet the evaporator is more universally applicable in practice, since its performance is adjustable independently of the process conditions.

![Figure 4.13: Schematic diagram of the evaporator](image-url)
Achieved environmental benefits
See Overall environmental benefits.

Cross-media effects
Additional energy may be used in evaporators, either as heat input and/or reducing pressure.

Operational data
With the evaporation of diluted electrolytes at normal boiling temperature of the water, organic additives of the electrolytes can be destroyed. Therefore vacuum evaporator systems have been developed which work at much lower pressure and low temperatures. Due to high demands on the materials in such systems, they are more expensive than simpler systems.

To prevent gas and water droplets being emitted to air, the evaporation tank can be equipped with a mist eliminator at the outlet side. The performance of the evaporation tank depends on the air temperature and humidity, and there are likely to be significant regional variations.

Applicability
All process solutions, particularly heated ones, or those with poor electrical efficiency where the process solution heats and is often cooled by evaporation (see Section 4.2.4.2)

Regional weather patterns may also affect applicability.

To ensure appropriate investment all process chemicals contained in the process solution must be tested for their application in an evaporation system before introduction of the technique.

Beside the evaporation of chromium electrolytes, evaporators are also used for concentration of rinsing waters from the acid or cyanide zinc, nickel and cadmium electroplating. With zinc solutions, there is a tendency for the electrolytes to form foam which requires additional treatment.

Evaporators are increasingly used for electrolyte feedback from rinsing waters. The complete closing of material cycles with an evaporator enabling the complete feed back of rinse water for certain process stages is achievable.

Economics
See Overall Economics.

Driving force for implementation
See Overall Economics.

Example plants
Frost Electroplating Ltd, Birmingham, UK; Merrydale, Wednesbury, UK, SEKEL N.V. Genk, Belgium.

Reference literature
[18, Tempany, 2002, 104, ÜBA, 2003]

4.6.13.4 Electrical dialysis

Description
The electrical dialysis is a diaphragm procedure, in which an electrical field forces material transport. It is used both for the concentration of diluted solutions and for the demineralisation of water.
Achieved environmental benefits
Reduced water consumption.
Increased drag-out recovery.

Cross-media effects
Requires energy inputs.

Operational data
To achieve long service life of the diaphragms the following points must to be considered:

- the diaphragms must be protected by a pre-filtration stage against mechanical pollution
- the blocking of the diaphragms by organic materials (such as oils) must be prevented
- blocking at the diaphragm surface can be avoided by regular rinsing and pole reversal (pole changes).

Applicability
Criteria for an economic application of electrical dialysis are the service lifetimes of the diaphragms, the separative efficiency of the plant and the yield per electric power input.

Economics
No data provided

Driving force for implementation
No data provided

Example plants
No data provided

Reference literature
[104, ÜBA, 2003]
4.7 Optimisation of raw material usage

4.7.1 Control of concentration of process chemicals

Description
Process solutions become increasingly ineffective when the working concentration of certain process chemicals drops below specification. By topping up of the consumed process chemicals the service lifetime of a solution can be extended, see Section 4.1.2, [ÜBA, 2003 #104]. SPC controls some production operators tendency to add more material than is necessary.

Existing processes can be optimised by suppliers and/or in-house expertise to reduce the concentration of chemicals, particularly those with significant environmental or health effects.

There are two cases to differentiate between:

Metals
The balance of the metal ions in electroplating is theoretically constant between the amount dissolved from the anode and the amount deposited at the cathode, but this is not true in practice, see Section 4.8.

In the electroless metal deposition or with the use of inert anodes the metal ions must replaced according to their deposition rate and their drag out.

Process chemicals
The concentration of other remaining chemicals in the process solution, such as acids, alkalis, salts, gloss additives/brighteners or buffer substances is reduced automatically by drag out of electrolyte or by degradation in the process.

Achieved environmental benefits
Extension of service life of solutions.
Reduction in over-use of chemicals through uncontrolled additions.

Cross-media effects
No data provided

Operational data
Measurement of key process solution components at pre-set intervals is necessary to monitor consumption, breakdown rates and additions made.

The consumption of the individual ingredients of the process solutions does not happen uniformly. Selected ingredients which are subject to a higher consumption, should therefore selectively be topped up. The selected dosage of components can be problematic where the individual material components are not known to the operator and not always available on the market. Chemical suppliers can assist with advising on control parameters and provide concentrates for topping up. The top up may have to be based on empirical investigations (operational experience) and can often only be automated with difficulty.

Applicability
All process solutions. The top up of process chemicals to the original composition is general process technology and in practice found everywhere

Economics
Extends working life of most process solutions.
Improved process quality and consistency.

Driving force for implementation
See Economics. Is frequently required by customers.
Chapter 4

Example plants
All sites visited; for example, SGI, Plaisir, France. Sikel N.V. Genk, Belgium, Corus, Llanelli, UK.

Reference literature
[18, Tempany, 2002, 104, ÜBA, 2003]

4.8 Electrode techniques

4.8.1 Different electrode yields

Description
During the electrolytic metal deposition the concentration of the metal ions theoretically remains constant by dissolving of the anode material at the same rate as deposition. However, in practice, different electricity yields to anode and cathode must be adjusted. For example, a higher anodic yield leads to an increase of the metal ion concentration. This is observed frequently with nickel and zinc electrolytes (verbal discussions with TWG) [60, Hemsley, 2003].

There are four options to dealing with this problem, which may be used alone or together:

- where solution electrochemistry allows, use insoluble (inert) anodes with external dissolution of the metal and controlled solution strength (see Chapter 2, Electrolytic cells and reactions)
- run workpieces or substrate requiring higher thickness coatings
- ‘plating out’ on steel sheet
- removing anodes.

Achieved environmental benefits
Minimisation of energy usage and waste of process metal in drag-over.
Reduction of plating over the required specification thickness.
Reduction in environmental effects from reworking due to problems with over-plating.

Cross-media effects
Additional equipment required where external dissolution tanks are used.

Operational data
All techniques improve process control, but see Applicability. Use of external make-up tanks or process additions requires increased process quality control and maintenance.

Applicability
Many zinc and electrolytic nickel processes can utilise insoluble electrodes and use external make up tanks, or separate solution additions. An inert anode system with external make up requires additional investment but addresses the problem consistently over time. Plating out does not recover anode metal. Removal of anodes also reduces current density and therefore throughput, taking time more time to reduce the process solution metal concentration. The right balance of specifications for work pieces (i.e. combination of thicker and thinner coating thickness requirements) may not coincide with the need to remove excess dissolved metal, especially for jobbing shops.

Economics
Investment in an inert anode system with external makeup is usually self-financing through materials saving and improved process quality. Other options are cheaper in the short term, but lack long-term consistency and savings.
Driving force for implementation
Process economics.
Process uniformity over time and reduction in reworking.

Example plants
Metal Colours, Slough, UK., SIKEL N.V. Genk, Belgium.

Reference literature
[18, Tempany, 2002]

4.8.2 Other electrode options
Separately supplied and controlled electrodes, controlling over-voltage, etc.

No data provided

4.9 Substitution - choice of raw materials and processes

General description
Surface treatment uses a wide range of chemicals in a wide range of processes. Section 1.4.4. Annex IV of the Directive requires the use of less hazardous substances to be considered [1, EC, 1996] and it is also a PARCOM recommendation [12, PARCOM, 1992]. However, there may be other environment tal benefits to be gained, either in conjunction with using less harmful substances, or for the other gains in their own right. Examples of more than one environmental benefit are biological degreasing using less harmful chemicals can produce less waste and use less energy, and acid zinc plating replacing cyanide zinc has better energy efficiency (verbal discussions with TWG members industry at site meetings and [60, Hemsley, 2003] ).

Substitution can be achieved by:

- substitution directly of one substance by a less harmful one. An example is the replacement of EDTA or NTA with derivatives of gluconic acid. There are limited opportunities for this in surface treatment
- substitution by different process chemistries or methods. This is used where there is no direct replacement, for example, replacement of zinc cyanide by cyanide-free alkali or zinc acid solutions. Different coating process chemistries give treatments with different properties, even for the same materials (see Table 4.8)
- substitution by different surface treatments, such as substituting autocatalytic nickel or vapour deposition of chromium for hard chromium plating. If the substitution is for the core treatment, the final properties may be different.

A list of surface treatment activities is given in Table 4.8 with the reference to their description in Chapter 2. References to environmental benefit achieved are given in the Chapter 4 reference.

Key issues, such as options for a single chemical e.g. hexavalent chromium, are discussed in subsections to this section. Others are dealt with by process type, such as degreasing.

Overall achieved environmental benefits
Reduction in the use of harmful substances and the amounts subsequently entering the environment.
Other improvements in environmental performance, such as energy saving, production of less waste, emission of less noise or dust, etc.
Overall cross-media effects
Each alternative technique should be considered. May have effects such as increased energy usage (vapour deposition techniques), increased waste production (acid zinc) or increased water or raw material consumption.

Failure to meet requirements (see Overall applicability) will lead to increased rejects and reworking, with consequent environmental impacts (see Section 4.1.2).

Overall operational data
See individual examples.

Overall applicability
In all cases it is advisable to discuss the changes with the customer in advance of making the substitution, and both parties to facilitate monitoring of quality and performance to required specification (see Section 4.1.2). Changes should not be made without full knowledge of the final performance characteristics required. Failure to meet these characteristics, particularly without warning can lead to loss of customer confidence and increased rejects.

Economics
This will be on a case by case basis. In some cases, there will be economic incentives from energy saving etc.

Driving force for implementation
Health and safety of employees is a major driver for substituting less harmful substances, e.g. substituting for hexavalent chromium.

Example plants
SGI, Plaisir, France, Sikel N.V., Genk, Belgium.

Reference literature
## Chapter 4

### 2.3 Workpiece or substrate preparation

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### 2.5 Core activities

#### 2.5.1 Copper and copper alloy plating

- Copper cyanide
- Acid copper
- Pyrophosphate copper
- Brass
- Bronze

#### 2.5.2 Nickel plating

- Nickel plating - Watts type
- Sulphamate nickel
- Satin nickel (decorative matt nickel)
- Nickel strike
- Nickel composite plating

#### 2.5.3 Chromium plating

- Bright chromium plating (hexavalent chromium electrolytes)
- Bright chromium plating (trivalent chromium electrolytes)
- Hard chromium plating

#### 2.5.4 Zinc and zinc alloy plating

- Alkali cyanide zinc
- Alkali cyanide free zinc
- Acid zinc
- Zinc alloys

#### 2.5.5 Cadmium plating

#### 2.5.6 Tin and alloy plating

#### 2.5.7 Precious metal plating

- Silver
- Gold
- Palladium and alloys
- Rhodium
- Platinum

#### 2.5.8 Autocatalytic plating (catalytic chemically reduced coatings)

- Autocatalytic nickel on metals
- Autocatalytic copper on metals and plastics
- Autocatalytic nickel coating for plastics
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Table 4.8: Options for surface treatment
4.9.1 Substitution for EDTA and other strong complexing agents (chelating agents)

Description
The problems of strong chelating agents particularly EDTA are described in Section 1.4.4.5. They are widely used in process solutions such as degreasing and etchants used for printed circuit board manufacture.

They may be replaced by weaker and biodegradable ones, such as those based on gluconic acid.

Achieved environmental benefits
Reduced solubilisation of metals in waste water treatment systems and in environment systems.

Cross-media effects
No data provided

Operational data
No data provided

Applicability
Printed circuit board manufacture: specifications for latest technology may require the return to using EDTA.

Economics
No data provided

Driving force for implementation
No data provided

Example plants
No data provided

Reference literature

4.9.2 Substitution for cyanide – overview

Overall description
Cyanide has been widely used in many electrolytic processes such as zinc, copper, cadmium and gold plating. It is also extensively used in other surface treatment processes, such as degreasing processes and nickel stripping.

For details of alternatives to cyanide-containing process solutions, refer to the appropriate heading in Table 4.8

Overall achieved environmental benefits
Reduction of use and emission of cyanide.
AOX may be generated through chemical oxidation of cyanide in waste water treatment with sodium hypochlorite and chlorine.
Cyanide electrochemical baths have low current efficiency compared with alternative products, due to the continuous oxidation of cyanide.

Overall cross-media effects
See specific applications for data on each application.
Chapter 4

Overall operational data
Free cyanide is easy to manage and treat.

See specific applications for data on each application.

Applicability
There is no single chemical substitution for cyanide.

Other factors affecting cyanide substitutions are:

- poorer degreasing ability of cyanide-free electrolytic degreasing electrolyte
- increased maintenance and skill level required for alternative processes (bath control, bath analysis etc)
- possible new environment risks from by cyanide substitutes No data provided
- modification of the coating characteristics

Economics
There may be increased costs with running non-cyanide systems. However, these may be offset by reduced effluent treatment.

Driving force for implementation
Decreased health and safety risk.
Public perception of the use of cyanide.
Improved compliance with environmental quality standards.
Decrease in risk of environmental accidents.

Example plants
Metal Colours Ltd, Slough, UK, SIKEL N.V. Genk, Belgium

Reference literature
[3, CETS, 2002, 18, Tempany, 2002]

4.9.3 Substitution and minimisation for hexavalent chromium

Introduction
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

Hexavalent chromium has been classified as carcinogenic by inhalation, and regulations apply to its use in processes.

The health and environmental issues associated with hexavalent chromium are described in 1.4.4.1. In addition, chromate films containing hexavalent chromium may release CrVI during the handling and the usage of the finished product.

Any zinc-plated part is usually post-treated with a suitable chromate conversion process as well as many substrates (such as die-castings). The colour of the finishes of existing hexavalent chromium conversion processes and the level of their corrosion protection is directly in relation to their thickness and to their hexavalent chromium content.
The following table shows the releases of CrVI from different coloured passivations, based on several statistical industrial determinations [3, CETS, 2002].

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<th>Chromate conversion coating</th>
<th>CrVI release</th>
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<td>Zinc</td>
<td>Clear-blue CrVI</td>
<td>0.05 – 0.1 µg/cm²</td>
</tr>
<tr>
<td></td>
<td>Clear-blue CrIII</td>
<td>0.0 µg/cm²</td>
</tr>
<tr>
<td>Yellow-Tropical</td>
<td>CrVI</td>
<td>0.3 – 0.6 µg/cm²</td>
</tr>
<tr>
<td>Green</td>
<td>CrVI</td>
<td>0.7 – 0.9 µg/cm²</td>
</tr>
<tr>
<td>Black</td>
<td>CrVI</td>
<td>0.7 – 1.0 µg/cm²</td>
</tr>
<tr>
<td>Yellow-Tropical</td>
<td>CrVI</td>
<td>0.1 – 0.2 µg/cm²</td>
</tr>
<tr>
<td></td>
<td>Followed by a top coat layer</td>
<td></td>
</tr>
<tr>
<td>Black</td>
<td>CrVI</td>
<td>0.02 – 0.1 µg/cm²</td>
</tr>
<tr>
<td></td>
<td>Followed by a top coat layer</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.9: Release of chromium (VI) from treated substrate

Because of these environmental and health and safety concerns, European directives limit the use of hexavalent chromium in the automotive, electrical and electronic industries. [96, EC, 2003, 98, EC, 2003, 99, EC, 2000] This is the driving force for innovative hexavalent chromium-free technologies. Various EU R&D projects are nearing conclusions on CrVI management, [28, DG-RTD, 2002].

4.9.3.1 Minimisation of release of hexavalent chromium

Description
[3, CETS, 2002] Top coatings for chromium passivation systems are described in Section 2.5.19. From Table 4.9, it can be seen that an application of a suitable top coating layer on the chromate conversion coating is sufficient to dramatically reduce release of chromium VI.

The chromium VI release is also 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.

Achieved environmental benefits
Reduced hexavalent chromium releases in subsequent handling and use.

Cross-media effects
*No data provided*

Operational data
*No data provided*

Applicability
*No data provided*

Economics
*No data provided*

Driving force for implementation
Reduction of hexavalent chromium released from product.

Example plants
*No data provided*

Reference literature
*No data provided*
4.9.3.2 Trivalent chromium electroplating processes

**Description**

See Section 2.5.3

The plating bath runs at a concentration of 20g/l instead of 200g/l for hexavalent chromium (in the case study).

**Achieved environmental benefits**

Reduction of hexavalent chromium released. Reduced solution viscosity means less chromium dragged-out.

In the case study the following were found:

- in conjunction with electrolytic removal of chromium (as hydroxide), waste water treatment sludge reduced from 20 tonnes per year to 2 tonnes per year
- about 30% reduced power consumption.

**Cross-media effects**

No negative effects reported.

**Operational data**

Historic problems with colour difference and variation during processing compared with hexavalent chromium have been overcome by new solutions and using carbon filtration and ion exchange, or proprietry solution treatment processes. Control by these methods and minimising carry-over from previous processes crucial.

Requires training staff and increased process control. Process control similar to that required for bright nickel.

Thicknesses can be measured by same equipment (e.g. Couloscope, X-ray diffraction)

**Applicability**

Cannot replace hard chromium plating.

Has successfully been used with no loss of customer confidence (see Section 4.1.2). Reject rate from 5-10% to 0.5% due to CrIII’s better throwing power and higher current capacity, reducing rough deposits (i.e. burning in high current density areas) and reduced ‘whitewashing’ from plating interruption.

**Economics**

One-off costs include disposal of old hexavalent chromium solution, replacing lead vat lining with PVD, replacing lead/antimony anodes with carbon. An ion exchange system is required for controlling metal contamination, and the resin requires changing at approximately 3 year intervals. The base chemicals are more expensive.

These are more than offset by:

- 30% saving in energy
- reduction in solid waste produced and disposed of
- reduced effluent treatment costs (no CrVI to reduce)
- reduced air monitoring
- reduced staff medical monitoring
- reduced reject rate
- significantly reduced risk of employee ill health.
Driving force for implementation
Reduced risk to employee health. Reduces health and safety requirements, as well as expenditure on aerosol suppression, air extraction, monitoring for hexavalent chromium in the workplace atmosphere, as well as medical monitoring of staff.

Example plants
Townroe (Hi-Tech Plating) Ltd, Sheffield, UK (case study)

Reference literature
[43, SEA, 2001]

4.9.3.3 Chromium free processes – other coating processes

Description
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. [3, CETS, 2002].

Achieved environmental benefits
Minimisation of hexavalent chromium released.

Cross-media effects
No data provided

Operational data
No data provided

Applicability
Chromium-free solutions on the market are not yet fully able to provide zinc and aluminium corrosion protection equivalent to chromate conversion coatings. 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

Economics
No data provided

Driving force for implementation
As introduction to Section 4.9

Example plants
No data provided

Reference literature
No data provided

4.9.3.4 Trivalent chromium conversion processes

Description
[3, CETS, 2002] Trivalent chromium passivation is described in 2.5.19. The protection mechanism of the trivalent chromium conversion coatings is not yet fully understood. 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. As can be seen from Table 4.9, there is no release of trivalent chromium from workpieces where it is used.
Achieved environmental benefits
Reduction in hexavalent chromium releases.

Cross-media effects
None.

Operational data
*No data provided*

Applicability
The corrosion protection achievable with these processes is currently limited to the protection level provided by the equivalent clear blue and yellow iridescent finishes achieved with hexavalent chromium. Although trivalent chromium can now exceed the equivalent hexavalent chromium performance for these colours, they are not capable of replacing brown, olive drab and black finishes. Their corrosion resistance can however, be extended by using additional coatings, see Section 2.5.12 and Section 2.5.19.

Economics
*No data provided on process costs.*
Savings in reduced effluent treatment costs, and health and safety management, including scrubbing any extracted air.

Driving force for implementation
Also reduces health and safety requirements, as well as expenditure on aerosol suppression, air extraction and monitoring for hexavalent chromium in the workplace atmosphere.

Example plants
*No data provided*

Reference literature
*No data provided*

### 4.9.3.5 Chromium free conversion processes

**Description**
Chromium-free processes are based on treatment with a composite organic-zirconium fluoride solution, treatment with titanium fluoride, or treatment with organic silicon derivatives (silanes). They may require a subsequent polymer layer, such as electrophoretic laquer, to achieve required corrosion resistance, see Section 2.5.12. [3, CETS, 2002].

There are black dyeing methods, which must be supplemented by sealing or top-coats for appearance and anticorrosion [76, BSTSA, , 104, ÜBA, 2003].

Achieved environmental benefits
Minimisation of hexavalent chromium released.

Cross-media effects
*No data provided*

Operational data
*No data provided*

Applicability
Chromium-free solutions on the market are not yet fully able to provide zinc and aluminium corrosion protection equivalent to chromate conversion coatings. 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

Economics

No data provided

Driving force for implementation

As Section 4.9.3

Example plants

No data provided

Reference literature

No data provided

4.9.4 Substitution for polishing and buffing

Description

Acid copper plating has excellent levelling capability. Can be used to replace polishing and buffing processes. [3, CETS, 2002]

Achieved environmental benefits

Replaces polishing and buffing which produce dust and noise.

Cross-media effects

Increased waste water treatment requirements.

Operational data

No data provided

Applicability

Suitable for workpieces prior to decorative nickel and copper plating.

Economics

Investment in polishing and buffing is replaced by investment in acid copper processing.

Driving force for implementation

Simplified health and safety requirements.

Example plants

No data provided

Reference literature

No data provided

4.9.5 Substitution and choices for degreasing

Insufficient or no data provided on:

- Air knives,
- Dry ice
- Cyanide degreasing
- Centrifuges
- Hot water
- Hand wiping
4.9.5.1 Solvent degreasing

Description
See 2.3.

Achieved environmental benefits
No data provided

Cross-media effects
Because of the classification of certain CHCs as potentially carcinogenic materials, their water-endangering potential and problems with emissions to the atmosphere their use is strongly regulated. [12, PARCOM, 1992, 93, EC, 2000, 96, EC, 2003, 97, EC, 1999]

Alternative solvents are inflammable.

Operational data
Good cleaning efficiency, quick drying.

Applicability
Universally applicable.

Economics
No data provided

Driving force for implementation
No data provided

Example plants
Widely used.

Reference literature
No data provided

4.9.5.2 Chemical aqueous (soak) degreasing

Description
This subsection refers to cyanide-free aqueous degreasing, see Section 2.3.

Achieved environmental benefits
Acids and alkalis simple and easy to treat, unless strong chelating agents present (see EDTA, Section 4.9.1).

Cross-media effects
Process tanks operate at 50 - 90 °C and may require fume extraction to remove water vapour and alkaline or acid fumes.

Metals can be stripped from the substrate surface (including trace elements such as lead which may have toxic effects). They can be separated after pH adjustment.

Used acid or alkali solutions are often treated separately as they create a large pH change which may not be accommodated by continuous flow effluent treatment plants.

Cleaning solutions may need to be separated from other process effluents to avoid interference with the effluent treatment plant by excess surfactants.
Operational data
Short process solution life, depending on the throughput and the amount of oil and grease removed.

Applicability
All installations except where substrate is incompatible, such as zinc and aluminium

Economics
No data provided

Driving force for implementation
No data provided

Example plants
Wide-spread usage.

Reference literature

4.9.5.3 Unstable emulsion (demulgating) degreasing

Description
[104, ÜBA, 2003] Surface-active agents used in demulgating degreasing solutions are developed chemically so they do not form a stable emulsion with the removed oils and greases. The degreasing tanks are drained to a holding tank (usually for a group of degreasing tanks) for the removal of floating oils and sediments. Demulgating cleaning solution separates by itself, so that simple mechanical systems (skimmers) can be used for the removal of the oil. By the continuous removal of contamination via the holding tank and feedback of the cleaned degreasing solutions in the bath a high service lifetime is achieved. Demulgating degreasing systems offers thereby a compromise between the two requirements for degreasing systems: They show a smaller oil-absorbing capacity than strongly-emulsifying degreasing baths; however they can be substantially more easily regenerated and re-used. The type of systems to be used can be derived from these characteristics.
Figure 4.15: Unstable emulsion degreasing system with holding tank for cleaning
Source: UBA

**Achieved environmental benefits**
Minimisation of chemical and power consumption in cleaning.

**Cross-media effects**
Small additional power consumption in pumping and oil recovery.

**Operational data**
The advantage of a demulgating system is that the clean solution is constantly being refreshed by having the oil removed.

**Applicability**
Numerous cases are known in practice, were the conversion to demulgating degreasing systems has given satisfactory cleaning.

Workpieces with strongly adhering pollution or with very viscous oils or grease on the surface cannot be cleaned by demulgating systems. Applicability should be determined on a case by case basis.

**Economics**
*No data provided*

**Driving force for implementation**
Improved down-stream process control.

**Example plants**
*No data provided*

**Reference literature**
[104, ÜBA, 2003]
4.9.5.4 Biological degreasing

**Description**
See Section 2.3.

**Achieved environmental benefits**
Runs at more neutral pH, with lower operating temperatures of 45 °C.
Reduced use of process chemicals as the solution rarely needs replacement.
Reduced usage of neutralising chemicals when discharging used process solution and lower impact of surfactants on effluent treatment.
Ensures consistent quality of degreasing versus changing quality of chemical degreasing over short service life.
Lower evaporation losses therefore less need to extract water vapour.

**Cross-media effects**
None identified.

**Operational data**
Some operators report the process may not be suitable for all oils and greases (possible problems with sulphur containing oils).

**Applicability**
Test in all applications before applying. Sufficient installations are using this technique commercially for it to be considered.

**Economics**
One operator reports chemical savings of 6 – 7 k€ per year (2002) on two 50 kg barrel lines.
Another operator reported chemical savings of 3.4 k€ per electroplating line first year savings and 3.8 k€ per year per line thereafter (1999).
None of these figures include savings in water, energy, labour in reduced solution make up time, increased efficiency (line downtime) and improved process performance (with less rejects).

**Driving force for implementation**
Reduces process line downtime for degreasing solutions to be changed.
Reduces amounts of hazardous chemicals in use in work place (replaces strong caustic and surface active solutions).

**Example plants**
Dundee Electroplating Ltd, Dundee, UK; Exhall Plating Ltd, Coventry, UK; Merrydale Industries Ltd, Wednesbury, UK; Metal Colours Ltd, Slough, UK.

**Reference literature**
[18, Tempany, 2002, 31, Biowise, 2001]

4.9.5.5 High performance degreasing systems

**Description**
For high-quality cleaning aqueous systems are used which can be supplemented by electrolytic action. High-quality cleaning is essential with modern process solutions such as acid zinc, etc.

In the case of strongly oiled parts multi-stage degreasing can be advantageous. For the first stage a hot water pre degreasing or an unstable emulsion cleaning solution is used (see Section 4.9.5.3). For a second stage a more strongly emulsifying cleaning solution is used. Also the combination of any two degreasing baths in sequence with the second, cleaner bath being used...
to replenish or replace the first, dirtier bath extends the service life of the degreasing solutions considerably.

**Achieved environmental benefits**

**Cross-media effects**
Energy consumption in higher temperature systems.

**Operational data**
*No data provided*

**Applicability**
*No data provided*

**Economics**
Case specific.

**Driving force for implementation**
Improved quality of work pieces or substrate for subsequent processing.

**Example plants**
*No data provided*

**Reference literature**

### 4.9.6 Zinc electroplating

#### 4.9.6.1 Alkaline cyanide zinc

**Description**
See Section 2.5.4

**Achieved environmental benefits**
Cyanide can be readily oxidised in waste water treatment plants

**Cross-media effects**
Requires waste water treatment.
May require fume extraction.
Poor process efficiency of 50 % of power input, decreasing with current density.

**Operational data**
Does not require high standard degreasing.
Easy to operate and maintain.

**Applicability**
Ductile deposit with good throwing power.

**Economics**
*No data provided*

**Driving force for implementation**

**Example plants**
*No data provided*
Reference literature

No data provided

4.9.6.2 Alkaline cyanide-free

Description
See Section 2.5.4.

Achieved environmental benefits
No cyanide used.
Reduced waste water treatment requirements.
No special requirement for fume extraction.

Cross-media effects
Poor current efficiency of about 50 % of power input.

Operational data
Needs to be preceded by high quality degreasing systems.
Needs skilled process control and management.

Applicability
Better metal distribution than cyanide processes.

Economics
No data provided

Driving force for implementation
See Section 4.9.2, Overall driving forces.

Example plants
No data provided

Reference literature
No data provided

4.9.6.3 Acid zinc

Description
See Section 2.5.4.

Achieved environmental benefits
High current efficiency, approaching 100 %.
No cyanide used.
Reduced waste water treatment requirements.
No special requirement for fume extraction.

Cross-media effects
Increased sludge production (from dissolution of some of steel substrates).
May require fume extraction for acid chloride mists.

Operational data
Needs to be preceded by high quality degreasing systems.
Needs skilled process control and management.
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Applicability
Metal distribution poor to acceptable, increasing with warm electrolytes. Only soluble anodes can be used.

Economics
Large savings in power consumption.

Driving force for implementation
See Section 4.9.2, Overall driving forces.

Example plants
Metal Colours Ltd, Slough, UK; Sikel N.V. Genk, Belgium.

Reference literature
[18, Tempany, 2002]

4.9.6.4 Zinc alloys
*No data provided*

4.9.7 Chromium plating
See Section 4.9.3 on hexavalent chromium.

4.9.8 Chromium conversion layers
See Section 4.9.3 on hexavalent chromium

Other activities with no techniques to consider in the determination of BAT

- Copper and copper alloy plating
  - Copper cyanide
  - Acid copper
  - Pyrophosphate copper
  - Brass
  - Bronze
  - Autocatalytic copper on metal

- Nickel plating
  - Nickel plating - Watts type
  - Sulphamate nickel
  - Satin nickel (decorative matt nickel)
  - Nickel strike
  - Nickel composite plating
  - Autocatalytic nickel on metals

- Cadmium plating
  - Zinc alloys

- Tin and alloy plating

- Precious metal plating
  - Silver
  - Gold
  - Palladium and alloys
  - Rhodium
  - Platinum
- **Autocatalytic plating (catalytic chemically reduced coatings)**
  - Autocatalytic nickel on metals
  - Autocatalytic copper on metals and plastics
  - Autocatalytic nickel coating for plastics
  - Non-catalytic chemically reduced coatings
  - Immersion or displacement coatings
  - Non-catalytic chemically reduced coatings

- **Electropainting or Electrocoating**
  See [90, EIPPCB]

- **Lacquering**

- **Oiling**

- **Enamel**

- **Anodising**
  - Sulphuric acid anodising of aluminium
  - Chromic acid anodising of aluminium
  - Anodising of magnesium, titanium, tantalum, niobium
  - Anodising by mixed sulphuric/ oxalic acids, or sulphuric/ salicylic acid

- **Colouring aluminium**
  - Immersion colouring
  - Electrolytic colouring
  - Interference colouring
  - Integral colouring

- **Sealing following anodising**
  - Hot sealing
  - Cold sealing

- **Phosphating layer conversion coatings**
  - Alkali phosphating
  - Zinc phosphating
  - Manganese phosphating

- **Metal colouring**

- **Bright dipping**

- **Chemical blacking – oxide coatings**

- **Brightening**

- **Etching**

- **Chemical milling**

- **Electropolishing**

- **Metal stripping**

- **Drying**
  - Drying using hot water
  - Drying using hot air
  - Drying using air knives

- **Heat treatment for hydrogen de-embrittlement**

- **AOX in raw materials**

- **NPE and surfactants**

### 4.9.9 Substitution by alternative processes

**Description**

Manufacturing industry is moving towards performance standards, such as corrosion resistance achieved. This is being catalysed where the use of traditional coatings (such as zinc and hexavalent chromium passivation) are being challenged by recent directives being implemented limiting the amount of hexavalent chromium in end of life products [94, EC, 1999, 96, EC, 2003, 98, EC, 2003, 99, EC, 2000]. This change is challenging traditional specifications.
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To achieve modern high standards for corrosion prevention, multi-layer systems are increasingly used. This enables the operator to offer alternative systems to customers which achieve the same performance criteria, and the potential to move away from more polluting processes. For example:

- electroless nickel for some hard chromium applications
- zinc alloys in place of zinc and chromium passivation, in conjunction with organic laquers applied by dipping or electropainting
- electropainting in conjunction with phosphating.

Note: Substitution has already been widely achieved for cadmium electroplating as marketing and use regulations required many specifications to be changed to utilise alternative surface treatments. [30, EC, 2003]

Other alternative processes
Metals can be applied by physical methods, such as vapour phase deposition. They are not within the scope of this document. However, an operator may wish to consider them as a clean technology option, as set out in IPPC Directive, Annex IV. It should be born in mind, that while such techniques are ‘clean technology’ at the point of use, they may cross-media effects, such as higher energy usage.

Examples of such techniques are:

- Vapour phase deposition of aluminium on plastic for automobile lighting reflectors
- Vapour phase deposition of chromium as a decorative finish, such as bathroom fittings

The US Defense Department are funding a study on alternatives for chromium conversion coatings [106, NCMS, 2003], and USEPA have also researched the replacement of chromate conversion coatings on aluminium and zinc [66, PPRC, 2003, 68, USEPA, 2003].

Achieved environmental benefits
Reduction of toxic emissions.

Cross-media effects
To be investigated for each application.

Operational data
To be determined for each application.

Applicability
To be determined for each application.  
May be limited by existing specifications.

Economics
To be determined for each application.  
Overall, regulation of mass customer sectors will drive a shift away from traditional standards for surface treatment.

Driving force for implementation
Health and safety and product regulations, such as automotive and electronics directives.

Example plants
No data provided

Reference literature
4.10 Process solution regeneration

Proper control of bath operating parameters will result in more consistent workpiece quality as well as longer bath life. This requires determining critical operating parameters and maintaining them within the established acceptable limits [67, IAMS, 2003].

Contaminants which affect the quality of treatment accumulate in process solutions as conversion or decomposition products during processing or drag-in from preceding solutions with the workpieces/substrates. Batch or continuous maintenance and regeneration are therefore necessary especially when the renewing function of drag-out is eliminated through drag-out recovery.

In principle, there is a difference between electro-chemical and chemical process solutions.

Electro-chemical procedures with dissolving anodes are based on metal ions migrating to the cathode in the applied electrical field and are reduced to the metal. In electroplating, the workpiece or substrate is connected as a cathode, while the anode usually consists of the metal to be deposited. Within the electrical field ideally the same quantity of metal dissolves from the anode, as is cathodically deposited, so that the composition of the process solution remains essentially constant. That means that the service life of the process solution of electro-chemical processes is theoretically infinite. However in practice the process solutions suffer quality losses by the entry of impurities and formation of interfering substances by different causes, such as:

- introduction of interfering substances from preceding process solutions due to insufficient rinsing
- dissolving of base metal (in particular with acid working process solutions)
- chemical change of the process solutions (reduction of CrVI to CrIII with the chromium plating, carbonate formation by reaction of CO₂ from air in alkaline/cyanide process solutions)
- higher dissolution of anode metal than separation at the cathode
- decomposition of organic compounds in the process solutions

In other processes, chemicals are also consumed, such as the reduction of metal ions to metal by chemical reducing agents at activated sites on the basic material in autocatalytic plating, or other chemical reactions take place (such as layer conversion). Metal ions, reducing agents and other chemicals must be added in salt form constantly, so in principle the service life of these solutions are limited.

Because of these degradation processes, the quality of a process solution can worsen to the extent that it must be discarded, unless it is possible to keep the quality of the process solutions constant by application of one of the described regeneration techniques.

The procedures described this section are not limited exclusively to electrolytes. They include the care of pickling and etching solutions, degreasing solutions, etc. The remarks are limited to the technical description of the individual procedures for avoidance and decrease of environmental nuisance.

The following table shows the most significant disturbing solution pollutants for many processes. Some are dealt with elsewhere and are cross-referenced:
<table>
<thead>
<tr>
<th>Process Solution</th>
<th>Disturbing Pollutants</th>
<th>Remarks</th>
<th>Regeneration means</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soak Cleaner</td>
<td>Sludge</td>
<td>Dragged in with the work</td>
<td>- Sludge: decanting of process solution, discarding of sludge to waste water treatment</td>
<td>4.18.3</td>
</tr>
<tr>
<td></td>
<td>Oil, liquid grease, metal slivers</td>
<td></td>
<td>- Skimmer - Gravity separation - Bio-degradation - Ultrafiltration of static rinse water prior to balance drag-out and evaporation losses of treatment solution</td>
<td>4.10.9.1  4.10.9.3  4.10.9.2  4.10.1  4.6</td>
</tr>
<tr>
<td>Pickling of metals</td>
<td>Dissolved metal</td>
<td>Large volumes only</td>
<td>- Retardation</td>
<td>4.10.3</td>
</tr>
<tr>
<td>Pickling of plastics</td>
<td>Dissolved resin</td>
<td>Balance situation</td>
<td>- Reoxydation through electrodialysis</td>
<td>4.10.2</td>
</tr>
<tr>
<td>Desmear of multilayers</td>
<td>Dissolved resin CrVI and O^-</td>
<td></td>
<td>- Electrolytic re-oxidation</td>
<td>4.10.9</td>
</tr>
<tr>
<td>Electrolytic cleaner Cyanide copper</td>
<td>Dissolved metal, oil, grease</td>
<td>Use overflow compartment</td>
<td>- Skimmer</td>
<td>4.10.9.4</td>
</tr>
<tr>
<td></td>
<td>Redundant copper</td>
<td></td>
<td>- Insoluble anodes with individual DC supply</td>
<td>4.2.1.3   4.8</td>
</tr>
<tr>
<td></td>
<td>decomposition products of organic additives carbonates</td>
<td></td>
<td>- Active carbon treatment - Dilution of solution</td>
<td>4.10.5</td>
</tr>
<tr>
<td></td>
<td>Acid copper</td>
<td>Redundant copper</td>
<td>- Dilution of solution</td>
<td>4.10.5</td>
</tr>
<tr>
<td></td>
<td>Electroless copper</td>
<td>Decomposition products of organic additives</td>
<td>- Feed and bleed</td>
<td></td>
</tr>
<tr>
<td>Dull nickel, Watt's type</td>
<td>Redundant nickel,</td>
<td></td>
<td>- Membrane anodes with individual DC supply</td>
<td>4.2.1.3   4.8</td>
</tr>
<tr>
<td></td>
<td>By-metals</td>
<td></td>
<td>- Selective plating cathode at low current densities</td>
<td>4.10.8</td>
</tr>
<tr>
<td>Bright nickel, Watt's Type</td>
<td>Redundant nickel</td>
<td></td>
<td>- Membrane anodes with individual DC supply</td>
<td>4.2.1.3   4.8</td>
</tr>
<tr>
<td></td>
<td>Decomposition products of organic additives</td>
<td></td>
<td>- Active carbon treatment - Electrodialysis - Adsorber resin treatment</td>
<td>4.10.5   4.10.2  4.10.6</td>
</tr>
<tr>
<td></td>
<td>By-metals as Zn, Cu, Fe</td>
<td></td>
<td>- Elective plating cathode at low current densities</td>
<td>4.10.8</td>
</tr>
<tr>
<td>Sulphamate nickel</td>
<td>Decomposition products of surfactants</td>
<td></td>
<td>- Active carbon treatment</td>
<td>4.10.5</td>
</tr>
<tr>
<td>Electroless nickel for plastics</td>
<td>Orthophosphite, sulphate, sodium Palladium</td>
<td></td>
<td>- Replace after lifetime</td>
<td></td>
</tr>
<tr>
<td>Electroless nickel for metals</td>
<td>Orthophosphite, sulphate, sodium</td>
<td></td>
<td>- Replace after lifetime</td>
<td></td>
</tr>
<tr>
<td>Bright chromium and hard chromium</td>
<td>CrIII, by-metals, dissolved from plated items</td>
<td></td>
<td>- Static rinse water recirculated over cation exchanger prior to balance evaporation losses of treatment solution</td>
<td>4.10.6   4.6</td>
</tr>
<tr>
<td>Alkaline zinc</td>
<td>Carbonates</td>
<td></td>
<td>- Crystallisation of carbonate by low temperature treatment, batch and/or continuously</td>
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#### Disturbing Pollutants

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<td></td>
<td>Free ferri-ammonium oxalate</td>
<td>- Reduction? with H₂O₂</td>
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<td>Organic Colouring</td>
<td>Numerous pollutants</td>
<td>- Regeneration difficult</td>
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<td>Decomposition products, potassium carbonate</td>
<td>Based on potassium&lt;br&gt;- Feed and bleed</td>
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<td>Static Rinses</td>
<td>Metal hydroxides, depending on pH, surfactants and algae</td>
<td>Filtration</td>
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Table 4.10: Regeneration of process solutions

### 4.10.1 Filtration of process solutions

**Description**

Particles suspended in electrolytes can generate negative effects on the layer quality (in particular by inclusion of the particles into the layer). The filtration of process solutions is used to remove particles (e.g. splinters or dirt), which were introduced by the workpieces, anode mud, dust from the air or the insoluble compounds developed during the process (usually metal hydrolysates). In order to guarantee a continuous removal of the solids, the filter is operated in a bypass to the process tank. [104, ÚBA, 2003]
Achieved environmental benefits
Extension of the process solution life.

Cross-media effects
Energy consumption for pumping.

Renewable materials are preferred as a filtration medium, since increased waste results from disposable filters.

Filters which cannot be used any more despite back flushing are usually contaminated with hazardous solution remainders and need to be disposed of as hazardous waste.

Operational data
No data provided

Applicability
Many solutions can benefit. The filtration of process solutions in surface treatment is part of the normal practice to extend process solution life.

Economics
The investment required for filtration is small with costs of few hundred to thousand euros. They are usually economic viable, as insufficient filtration causes surface quality problems and the process solution must be rejected earlier than it otherwise need be, as well as the cost of reworking reject workpieces.

Driving force for implementation
Reduction in frequency of replacing solution.
See Economics.

Example plants
No data provided

Reference literature
No data provided
4.10.2  Electrodialysis

Description
See pickling, see Section 4.10.10.2. Electrodialysis is a suitable means for recovering, for example, 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. [3, CETS, 2002]

Achieved environmental benefits
No data provided

Cross-media effects
No data provided

Operational data
No data provided

Applicability
No data provided

Economics
No data provided

Driving force for implementation
No data provided

Example plants
No data provided

Reference literature
No data provided

4.10.3  Retardation

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

When pumping a metal containing solution upstream 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 re-used. A depletion rate of between 40 and 60 % can be achieved, depending on the type of acid and metal. [3, CETS, 2002]

Achieved environmental benefits
Extension of process solution life.

Cross-media effects
No data provided

Operational data
No data provided

Applicability
The efficiency of retardation decreases in the following sequence:
HCl > HNO₃ > HClO₄ > H₂SO₄ > (HF)ₙ > H₃PO₄ > tartaric acid
4.10.4 Crystallisation of carbonates and metal sulphates

Description
Cold crystallisation is a technology by which interfering salts can be separated selectively from a process solution. These salts are formed by the dissolving of metals or metal oxides (pickling) or by unwanted reactions (oxidation of cyanide to carbonate). By cooling down a solution to <5 °C the solubility of most of the salts is reduced. Only certain salts in the selected salt mixture crystallise with the cooling down of a solution, while the remaining salts stay in the solution. [104, ÜBA, 2003]

Figure 4.17: Operating principle of cold crystallisation

Achieved environmental benefits
Extension of the process solution life.

Cross-media effects
Additional energy will be required for cooling, where this is applied. This may be necessary in warmer countries.
Chapter 4

Operational data
The service lifetime extension attainable by cold crystallisation depends on:

- the type of salts to be frozen out from the electrolyte,
- the process of salt formation
- the time necessary for the process.

In many cases, this is carried out in winter, especially during shut down periods, such as Christmas, when the solution can be cooled naturally.

Applicability
Due to the diversity of each application an individual examination of each case is recommended.

Economics
No data provided

Driving force for implementation
No data provided

Example plants
No data provided

Reference literature
No data provided

4.10.5 Activated carbon treatment

Description
Activated carbon filtration is a special form of filtration. Organic decomposition products in electrolytic solutions 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 the products to be removed. Up to 10 g/l maybe necessary.

Activated carbon is mixed into the electrolyte and removed by filtration after a suitable reaction time. A combination of normal filtration and active carbon cartridges in by-pass is used to continuously remove both solid contaminants and soluble organic decomposition products from the electrolytes. [3, CETS, 2002, 104, ÜBA, 2003]

Achieved environmental benefits
Extension of process solution life.
Theoretically, contaminated activated carbon can be regenerated, but this is usually not economical or has associated limiting cross-media effects.

Cross-media effects
Additional energy in pumping. Used carbon filters may need to be disposed of as hazardous waste.

Operational data
The process is non-specific and removes active process substances as well. Compensating additions need to be made to the process solution.

Applicability
The process is widely used, and frequently for bright nickel electrolytes.
4.10.6 Purification of metallic contamination by ion exchange

Description
Ion exchange serves to selectively remove unwanted metal ions (cations) from aqueous solutions. Cation exchange resins with special properties, such as resistance to strong oxidants, are used. [3, CETS, 2002]

Achieved environmental benefits
Extension of the process solution life.

Cross-media effects
Eluates arising from ion exchange column regeneration have to be treated in waste water plants.

Operational data
No data provided
Chapter 4

Applicability
This technique is applied in by-pass for the regeneration of process solutions, such as phosphoric acid pickling and chromium plating electrolytes.

The cleaning of passivating solutions is also possible as long as chemicals such as trivalent chromium or silver are not present (TWG to provide further data: one source says trivalent chromium must not be present, the other says it can be removed.)

Economics
No data provided

Driving force for implementation
No data provided

Example plants
No data provided

Reference literature
No data provided

4.10.7 Electrolysis - purification of process solutions

Description
Some metallic contaminants can be removed selectively from electrolytes at low current densities from 0.05 to 0.3 A/dm². The efficiency of this selective cleaning can be enhanced with increased electrolyte throughput. [3, CETS, 2002]

Achieved environmental benefits
Extension of process solution life.

Cross-media effects
No data provided

Operational data
Not only unwanted metals, but also unused organic additives can be removed. Therefore electrolytic purification should be reduced to a minimum or compensatory additions of organic process materials will be necessary.

Applicability
No data provided

Economics
No data provided

Driving force for implementation
No data provided

Example plants
No data provided

Reference literature
No data provided
4.10.8 Electrolysis – removal of surplus metal in process solution

**Description**
Metal process solutions where there is higher anode yield than required in solution (such as zinc and nickel) suffer from increasing metal concentration leading to overplating. The concentration can be lowered by electrolysis – usually called plating out, see Section 4.8.1. [104, ÜBA, 2003]

![Diagram of electrolytic removal of surplus and contaminating metals](image)

**Achieved environmental benefits**
- Reduction of reworking.
- Minimising dissolved metal drag-over into rinses.

**Cross-media effects**
Unwanted metal in solution increases dragged out quantities.

**Operational data**
High anode yield can be better controlled by using insoluble anodes and external metal dissolution, see Section 4.8.1.

**Applicability**
Zinc and nickel electroplating with soluble anodes.

**Economics**
*No data provided*

**Driving force for implementation**
Process control and minimisation of reworking.

**Example plants**
*No data provided*

**Reference literature**
*No data provided*
4.10.9 Electrolysis - re-oxidation of by-products

Description
[3, CETS, 2002] Chromium/sulphuric acid pickling of ABS plastic items oxidises and dissolves the butadiene component of the substrate, simultaneously generating trivalent chromium. Both the organic decomposition product and the trivalent chromium will disturb the process if a tolerable concentration level is exceeded.

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

Achieved environmental benefits
Extension of the process solution life.

Cross-media effects
No data provided

Operational data
No data provided

Applicability
Chromium/sulphuric acid pickling of ABS plastic items.

Economics
No data provided

Driving force for implementation
Product and process quality.

Example plants
No data provided

Reference literature
No data provided

4.10.9.1 Maintenance of degreasing solutions – simple methods

Descriptions of simple methods
Mechanical separation by skimmers.

Gravity oil separators working in by-pass separate oil/grease by allowing agglomeration of small droplets of oil to larger globules which float to the surface and are then removed. This may be enhanced by dissolved air flotation.

Separating emulsified oil by breaking the emulsion. The easiest route is by chemical addition which breaks down the wetting agent system and releases the oil, at the same time destroying the de-greasing effect.

Achieved environmental benefits
All remove oil and extend working life of degreasing solutions.

Cross-media effects
Energy consumption for skimmers and for dissolved air flotation. Chemicals used for demulsifying.
Operational data
Gravity separation is the lowest maintenance system.

Applicability
All degreasing solutions, depending on solution life, and investment costs.

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

Driving force for implementation
Improved cleaning results in improved performance and reliability of subsequent surface treatments. This in turn decreases rejects and reworking.

Example plants
No data provided

Reference literature
No data provided

4.10.9.2 Diaphragm filtration of emulsifying degreasers

Description
Where for technical reasons the use of strong degreasing systems are necessary, regeneration of the cleaning solution may become expensive or even impossible.

Diaphragm filtration technology, particularly micro-filtration, can be used for the regeneration of oil-loaded aqueous degreasing solutions. The dimensions of the pore size of the diaphragms must be such that the emulsified oil is held back, while surface-active components pass through the diaphragm, and remain in the degreasing solutions. [3, CETS, 2002, 104, ÜBA, 2003]
Achieved environmental benefits
Reduced chemical and energy consumption in degreasing heavily-contaminated workpieces or substrate.

Cross-media effects
Power consumption of pumping to micro-filtration.

Operational data
For the successful use of micro-filtration it is crucial that the composition of the surface-active agent of the cleaning solution does not change by substantial partial permeation of the components. However, since a shift of the surface-active agent composition is always to be expected with micro filtration, the composition of the chemicals in the cleaner must be maintained.

Applicability
Only a few operators have successfully retained the cleaning quality in practice over longer periods. For this reason the successful employment of the diaphragm cleaning system for degreasing solutions requires the close co-operation of operators, equipment manufacturers and chemical supplier.

The success of cost effectiveness of this technique is based on the likelihood of finding the membrane for the wide range of pollutants encountered in a degreasing bath. Most of the equipment is installed in in-house shops where the composition of oils to be removed is more constant.

Economics
No data provided

Driving force for implementation
Heavily-oiled/ greased components requiring an emulsifying system.

Example plants
No data provided

Reference literature
No data provided

4.10.9.3 Multi-stage maintenance of degreasing solutions

Description
[104, ÜBA, 2003] Multi-stage systems using a simple method removing the majority of oil/grease followed by diaphragm filtration. For example, gravity filtration followed by ultrafiltration.

Achieved environmental benefits
All remove oil and extend working life of degreasing solutions.

Cross-media effects
Energy consumption for skimmers and for dissolved air flotation, as well as in pumping for subsequent diaphragm filtration. Chemicals used for demulsifying.

Operational data
improved process reliability both of cleaning and subsequent treatments.
Gravity separation is the lowest maintenance simple system.
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Applicability
Where large amounts of oil and grease are present on incoming workpieces or substrate, where process line throughput is high, and/or where the quality of degreasing is highly critical to the following treatments.

Economics
Reduced size of ultra-filtration and Mechanical separation by skimmers is the simplest and cheapest simple method.

Driving force for implementation
Improved cleaning results in improved performance and reliability of subsequent surface treatments. This in turn decreases rejects and reworking.

Example plants
No data provided

Reference literature
No data provided

4.10.9.4 Maintenance of electrolytic degreasing processes

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

4.10.10 Pickling

4.10.10.1 Measures for decreasing acid consumption

Description
Pickling solutions lose activity by the constant entry of rinsing water from the previous process stage, so much that they must be renewed at relatively short intervals. At present no techniques exist in practice to extend the service life of pickling solutions, although two-stage or drag-in through a used picking solution may be considered see Section 2.3. A three-stage countercurrent hydrochloric acid system running at 0.5 l/min is being used successfully to remove hardening scale [18, Tempany, 2002].

The prevention of the overpickling is important. Overpickling is the attack of the pickling solution on the basis metal, and in surface technology is an unwanted side effect, as it:

- leads to increased acid consumption with increased metal erosion and thus also increasing waste generation (from the dissolved metal being precipitated in waste water treatment and the increased amount of waste acid generated).
- causes substantial quality losses in the base material (hydrogen brittleness)
- can degrade the quality of the workpiece surface and/or change the geometrical measurements of the workpiece adversely.

Overpickling can be prevented by the addition of so-called pickling inhibitors which are widely used. [104, ÜBA, 2003]

Achieved environmental benefits
Extending chemical process life. A three-stage cascade system has reduced chemical usage from 2 tonnes per day to 1 tonne of 32 % hydrochloric acid.

In a countercurrent system, a small, stable flow of hydrochloric acid is readily treated in a normal waste water treatment plant, replacing the problems caused by batch discharges of acid to treatment.
Cross-media effects

No data provided

Operational data

No data provided

Applicability

Widely used.

Economics

Cost of materials offset the increased amount of plant required for multi-stage pickling.

Driving force for implementation

For multi-stage pickling, increased process stability

Example plants

Metal Colours Ltd, Slough, UK

Reference literature

[18, Tempany, 2002, 104, ÜBA, 2003]

4.10.10.2 Extension of the service life of pickling solutions by dialysis

Description

If the concentration of the metal salts in the pickling solution, formed by dissolution, becomes too high, no more pickling effect can be achieved even with further addition of acid. At this point, the pickling bath is useless and is usually discarded. Further use of the pickling solution is possible only by selective separation of the dissolved metal salts. The removal of the metal salts is achieved by the application of dialysis techniques.

Figure 4.21: Regeneration of pickling solutions by dialysis
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In the dialysis cells the raw acid to be cleaned and distilled water are separated from each other by anion exchanger diaphragms. Mineral acid contained in the raw acid diffuses relatively slowly through the diaphragm, while the metal salts are held back.

<table>
<thead>
<tr>
<th>Separating integral parts</th>
<th>Parameters</th>
<th>Feed</th>
<th>Emissions</th>
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<tr>
<td></td>
<td></td>
<td>Etching solution</td>
<td>Water</td>
</tr>
<tr>
<td>HCl, AlCl₃</td>
<td>HCl (g/l)</td>
<td>100</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>AlCl₃ (g/l)</td>
<td>30</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>Flowrate (l/h)</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>H₂SO₄, NiSO₄</td>
<td>H₂SO₄ (g/l)</td>
<td>32</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>Ni (g/l)</td>
<td>1.7</td>
<td>&lt;0.04</td>
</tr>
</tbody>
</table>

Table 4.11: Shows the results of the dialysis treatment of etching solutions

Achieved environmental benefits
Extension of service life of chemical process solution.

Cross-media effects
Power consumption in dialysis.

Operational data
To prevent mechanical blocking pickling acids must be pre-filtered before using dialysis.

Applicability
No data provided

Economics
No data provided

Driving force for implementation
No data provided

Example plants
No data provided

Reference literature
[104, ÜBA, 2003]

4.11 Process metals recovery
This refers to recovery systems within installations, not to external processes.

4.11.1 Electrolytic recovery
Description
Metals may be recovered by electrolysis. The system is widely used for precious metal recovery, but can also be used to recover other metals such as nickel and chromium from drag-outs. Suitable electrolysis cells are marketed in different sizes and can operate down to metal contents of less than 100 mg/l.

Achieved environmental benefits
Recovery of metals for re-use.
Reduction of metals in drag-out and their consequent decrease in effluent concentrations.
In the electrolytic separation of cyanide-containing metal solutions, the anodically oxidative destruction of the cyanide takes place parallel to the metal winning.

**Cross-media effects**
Power consumption at low current efficiencies.

**Operational data**
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 all cases, a simple flat plate cathode would be sufficient in theory, but when high current efficiencies are required (for both precious and transition metals) sophisticated cathode design is needed (rotating tube cell, graphite fibre cathode). In all cases (including anodic oxidation) the anode must be of the “insoluble” type.

Cathodes are usually sheets, foil or particles, generally made 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 metallised beads and metallised fabrics are all examples of common materials used. Cathode material selection is largely determined by 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 the 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 of 10, cell voltage 8V, current density 20 Amp/dm², temperature >60 °C, and an anode-cathode gap from 8 to 16 cm.

Further advantages of the electrolytic recovery over the ion exchange method are:

- it does not produce any increase in the dissolved salt concentration
- 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.

For electrolytic metal recovery the following streams are particularly suitable:

- rinsing (dragout) concentrates from electroplating metal (except chromium baths and chloride-containing solutions)
- rinsing (dragout) concentrates and used process solutions from chemical metal plating excluded phosphate containing electrolytes
- sulphuric-acid regenerates of cation exchangers from the treatment of nonferrous metal-containing rinsing waters.

The purity of the generated metals may permit a direct in-house use as an anode material, otherwise re-use is via the scrap metal trade.
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Applicability
Gold and silver have been recovered electrolytically for well over 50 years. Can also be used for transition metals. May have wider applicability than precious metals, see reference plants in Annexe 2 and [18, Tempany, 2002]

Economics
Cost-effective for precious metals. Can be cost-effective for transition metals, for example, where it reduces the waste water treatment costs (capital and running costs). [3, CETS, 2002]

In-house electrolysis has costs in investments and personnel (both time and skills) as well as a substantial energy expenditure because of the low electricity yield (kg/amphour). This may be offset for cyanide solutions where the cyanide is destroyed in parallel.

Driving force for implementation
See economics.

Example plants
For nickel and chromium, Townrow (Hi-Tech Plating) Ltd, Sheffield.

Reference literature
[3, CETS, 2002, 18, Tempany, 2002]

4.11.2 Ion exchange - recovery of precious metals from rinses

Description
Precious metals in concentrated solution are usually recovered electrolytically (see Section 4.11.1), while more dilute solutions, sometimes of no more than a few mg/litre, are treated by adsorption of the metal content on ion exchange resins.

Ion exchange provides only a concentration of the metal in the resin, the subsequent recovery being possible by incineration of the resin or by releasing the metal in dissolved form, but at higher concentration. The final metal recovery by incineration is in an oxygen-rich atmosphere at 500 – 600 °C; metals are found with the residual ash. Recovery is about 95 % efficient.
[3, CETS, 2002]

Achieved environmental benefits
Recovery of precious metals.

Cross-media effects
Emissions from incineration of the resin. Increased salt concentrations in resin regeneration.

Operational data
For gold and precious metals, the principle of the method is based on treating the rinse water with a strong basic type of anionic ion exchange resins, in the OH⁻ or in the Cl⁻ form. This does not work well for alkaline cyanide or chloride-based rinses. Ion exchange resins are quoted as having a useful capacity of 100 g of gold per litre of resin.

Typically the equipment consists of two ion exchange resin columns in series, with the first unit taking the main load, while the downstream column takes any excess. Each resin column needs to contain around 4 litres or more of ion exchange resin to be effective.

With very large volumes of rinse water is used, an option is the treatment of the static rinse which workpieces pass through after precious metal plating tank. The treatment is through a
closed loop resin column. 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 requires using weak basic anionic ion exchange resins, followed by regeneration and subsequent electrolytic recovery of the regenerate. Typically the resin capacity is in the range of 50 – 75 g of Ag/litre (gold per litre) of resin. A further option is the use of ion exchange units built into a recirculation rinse loop with periodical regeneration. Precious metal is then recovered by electrolysis from the concentrate. This has been successfully used for silver.

Palladium used in the PCB industry is recovered from chloride-containing acid solutions (pH about 2), where it is present as a 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.

Applicability
No data provided

Economics
No data provided

Driving force for implementation
Cost recovery.

Example plants
No data provided

Reference literature
No data provided

4.11.3 Coating processes – autocatalytic plating of plastics
No data provided

4.11.4 Chromating

Description
Unlike electroplating chromating, the hexavalent chromium in chromating solutions is exhausted after a certain time. The solutions also dissolve and accumulate zinc and other metals and eventually lose their workability, and must then be rejected and renewed.

Numerous attempts have been made to recycle chromating solutions, predominantly via ion exchangers or via diaphragm technology.

Achieved environmental benefits
Extended bath life and recovery of metal.

Cross-media effects
Energy and chemicals used in regeneration techniques.

Operational data
No data provided

Applicability
No data provided
Chapter 4

Economics
Regeneration is usually only cost-effective with relatively concentrated and expensive solutions, for example, black chromating solutions containing silver.
New yellow chromating process solution for zinc only costs €3 to 4/100 litre (2002). This makes it difficult to recover the costs of capital, the energy expenditure and maintenance for the recovery measures.

Driving force for implementation
No data provided

Example plants
No data provided

Reference literature
[104, ÜBA, 2003]

4.12 Post treatment activities – techniques relevant to the determination of BAT

4.12.1 Drying
Options exist such as hot water drying, hot air, air knives.
No data provided

4.12.2 De-embrittlement
No data provided

4.13 Barrel processing
Specific data for techniques relevant for BAT are dealt with in the appropriate sections. There is a special section on the reduction of drag-over by barrels: Section 4.5.3

4.14 Continuous coil – small scale
No data provided

4.15 Continuous coil – large scale steel
No data provided

4.16 Lithographic (offset) printing plates coil and sheet
No data provided

4.17 Printed circuit board processing

4.17.1 Recycling of alkali etchants

Description
Ammonia and copper pollution from the alkaline etching solution can be removed by a commercially available process. The patented unit is installed in a closed loop within an alkaline etching system and achieves the following functions:
regeneration of the alkaline etchant bath
uninterrupted recovery of the etchant copper in the form of metal of electrolytic quality
purification of the rinsing water after etching

The spent etchant with 150 g/l of Cu is passed through the first solvent extractor and comes out as regenerated etchant with 110 g/l of copper. After passing through the first extractor, the solvent is loaded with 50 g/l of copper.

Spent rinse water with 5 g/l (5000 mg/l) of Cu goes through the second solvent extractor and comes out as regenerated rinse water with 56 mg/l of copper. After passing through the second extractor, the solvent is loaded with an additional 5 g/l of copper.

The solvent is passed through the third extractor containing water-based electrolyte and comes out without copper. After passing through the third extractor the electrolyte is loaded with approximately 55 g/l of copper.

The copper is plated onto the cathode in the electro-winning cell.

**Chemistry:**

For etching copper from printed circuit boards:

\[
\text{Cu}^0 + \text{Cu(NH}_3\text{)}_4\text{Cl}_2 \rightarrow 2 \text{Cu(NH}_3\text{)}_2\text{Cl (dissolution)}
\]

\[
2 \text{Cu(NH}_3\text{)}_2\text{Cl} + 0.5 \text{O}_2 + 2 \text{NH}_3 + 2 \text{NH}_4\text{Cl} \rightarrow 2 \text{Cu(NH}_3\text{)}_4\text{Cl}_2 + \text{H}_2\text{O (oxidation)}
\]

In summary:

\[
\text{Cu}^0 + 2 \text{NH}_3 + 2 \text{NH}_4\text{Cl} + 0.5 \text{O}_2 \rightarrow \text{Cu(NH}_3\text{)}_4\text{Cl}_2 + \text{H}_2\text{O}
\]

For extracting copper from spent etchant and used rinse water:

\[
\text{Cu(NH}_3\text{)}_4\text{Cl}_2 + 2 \text{RH (org)} \rightarrow \text{CuR}_2\text{(org)} + 2 \text{NH}_3 + 2 \text{NH}_4\text{Cl}
\]

For extracting copper from the organic to the electrolyte:

\[
\text{CuR}_2\text{(org)} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + 2 \text{RH (org)}
\]

For electrowinning copper metal from the electrolyte:

\[
\text{CuSO}_4 + \text{H}_2\text{O} \rightarrow \text{Cu}^0 + \text{H}_2\text{SO}_4 + 0.5 \text{O}_2
\]
Achieved environmental benefits
Reduction of ammonia and copper in the effluent.
Recovery of about 600 kg high quality copper per month (in example plant).
Decreased noise to local residential property from delivery and disposal vehicles.

Cross-media effects
Some additional power consumption for the unit.
The copper recovered is too high a purity to re-use in-plant and is sold to a supplier.

Operational data
The equipment must be maintained by a skilled operator

Applicability
Alkali copper etchants.
Patented process.

Economics
Investment of €100 k to 150 k (2003).
Payback: more than 3 years cost-recovery from high quality copper resale, reduced effluent treatment and cost of replenishing etchant solution.

Driving force for implementation
Improved production quality of the printed circuit boards due to:
- constant etchant strength which allows constant speed through the etching process
- less handling problems of hazardous chemicals in delivery and disposal
- reduction of replenisher addition.
Other advantages:
- no storage of spent etchant
- no transport and delivery of etchant solutions, reducing handing risks etc.
- improved public perception of operation at neighbouring residential property.

Example plants
SOFRA-PCB, Mennecy, France

Reference literature
[49, France, 2003]

4.18 Emissions

4.18.1 Pollution prevention from unplanned releases - planning, design, construction and other systems

Description
Section 1.4.2 identifies the sector as still having the potential to cause environmental accidents, or unplanned releases. A planned, integrated approach can decrease this, starting with the identification of those aspects of an installation that may have significant impacts on the environment. The identified risks are then tackled by careful design and construction, as well as by management systems that address the prevention, mitigation and management of accident and emergencies, and the breaches of permit conditions.

Regulatory and/or good practice systems for pollution prevention are in use in some countries, for example, see Reference literature, below. Many installations in the sector have benefited from the introduction of such techniques. The effects of unplanned discharges, both chronic and acute, are minimised in terms of materials and quantities released and their impacts. The techniques can also make the management of acute pollution easier, and facilitate the following activities, making them environmentally safer and more cost effective:

- routine and non-routine maintenance including maintenance of solutions, see Section 4.10
- delivery and storage of raw materials, workpieces and substrates, see Section 4.3
- process control, process and environmental monitoring, see Section 4.1.

Key issues for delivery and storage of consumable raw materials are identified in Section 2.1.2 and chemicals of environmental or health effects are identified in Section 1.4.4. The storage of chemicals is discussed in [23, EIPPCB, 2002]. In surface treatment activities, the process solutions are usually kept in open tanks with connecting pipework in situations analogous to storage of chemicals and many of the same techniques can be applied, such bunding.

Some key aspects of preventing pollution given in the references are:

- the identification of hazard and pathways
- a simple ranking of hazard potential
- a three step implementation of actions for pollution prevention:
  - primary (structural)
    - sufficient plant dimensions
    - selection of sealing materials, e.g. for flooring, bunded areas
    - stability of the process line and components (including temporary and infrequently used equipment).
Chapter 4

- **secondary**
  - double skinned tanks for risk materials or bunding of risk areas of a process line or the whole installation
  - correct specification of size and strength of tanks to receive pumped-out liquors (see also stability, in primary above)
  - sealing risk surfaces (floors) within the installation
  - leak identification systems.

- **tertiary**
  - inspections, external experts and internal (see maintenance)
  - emergency plans
  - test programmes.

The identification of pathways and targets for the environmental effects can inform the choice of site, plant and equipment as well as design and construction of the infrastructure and plant.

**Achieved environmental benefits**
Minimisation of unplanned chronic and acute discharges to surface waters as well as municipal waste water treatment systems) from installation activities.
Minimisation of groundwater and soil contamination.

**Cross-media effects**
No adverse implications: helps protect surface water systems and sewage sludge management as well as groundwater and soil.

**Operational data**
Careful planning and design utilising operational experience can make routine operation, maintenance and monitoring easier, cheaper and environmentally safer.

**Applicability**
These measures can be considered by all installations; however they are best implemented at the proposal and initial design and build stages. Many changes can be incorporated in major upgrades, while some improvements can be made to existing installations during normal maintenance periods, although retrospective improvement may be more difficult, and may not be as effective. Various standards and guidance can also form part of longer term planning for plant improvements.

**Economics**
These are part of the investment costs with initial investments or upgrades. Some techniques may be no-cost options at a new-build or upgrade stage. Often costs can be recovered by more efficient working, maintenance, and the avoidance of the cost of dealing with accidents and breaches of permit.

*No data provided*

**Driving force for implementation**
Business duty of care and possible liability for any environmental damage arising.

**Example plants**
Widely used in many countries.

**Reference literature**
4.18.2 Air

Description
For workers’ health and safety it is often necessary to limit certain emissions inside surface treatment installations. Chapter 2 identifies processes which lead to emissions of concern, for example: pickling, certain etching processes, brightening, certain plating tanks, etc. Typical substances emitted described in 3.3.3.

It is widespread practice to minimise the amount of humid and/or corrosive fumes. This not only protects employee health, but also:

- protects workpieces or substrates in storage or in the various stages of processing, see Section 4.3
- protects the installation infrastructure
- protects control systems in process control and other sensitive equipment (computers, etc).

[80, INRS, 104, ÜBA, 2003]

4.18.2.1 Options for controlling emissions - descriptions

Some or all of these measures may be used together.

4.18.2.1.1 Additives

According to manufacturer’s data, the formation of nitrite ions and CrVI ions in the pickles are prevented by pickling additives. Thus the emissions of HF and NO_x can also be reduced so that it is not necessary to install an exhaust air scrubber.

Due to the changes in the physical chemical characteristics of the solution brought about by the additives, it is possible to increase the quantity of metal ions in electrolytes, for example 2.5-fold, consequently also lowering the chemical consumption.

It is also possible to reduce or prevent CrVI aerosol emissions from chromium plating tanks by the use of additives.

4.18.2.1.2 Lids

Covering the tanks when either the immersion time for a jig or barrel needs extended time or the baths are not used. A description of some options for lids is given in Section 4.18.2.2

4.18.2.1.3 Air extraction

Edge exhausts are normally employed to meet industrial health and safety requirements and various configurations are described in Section 4.18.2.2.

The quantity of exhaust air sucked off by the edge exhaust, and the quantity of pollutants it contains are influenced by the following parameters:

- tank size
- continuous or intermittent operation of the bath
- bath temperature
- physical/chemical characteristics of the assigned chemicals
- classification and permissible concentration at the workplace
- use in conjunction with pickling additives to decrease and/or avoid of the emissions of HF and NO_x gases and CrVI aerosols
- emission control procedures etc.
The pollutants emitted with the drawn off exhaust air are separated where necessary to achieve emission standards by the following exhaust air cleaning devices:

- exhaust air scrubbers with fill materials and droplet separator
- exhaust air scrubbers with the following combination:
  - cyanide and cyanide acid separation in an alkaline scrubber
  - nitrogen oxides and hydrofluoric in an acid scrubber
  - CrVI-containing exhaust air by droplet separators.

In the case of some combinations of different systems there are slight deviations to the exhaust air purification measures described above.

**Achieved environmental benefits**

Additives can decrease the formation of gases and CrVI aerosols and may extend the life of pickling acids.

Lids reduce the amount of gases and aerosols emitted to the atmosphere.

The tables Table 3.6 to Table 3.12 in Section 3.3.3 show that the use of simple extraction systems using droplet separators and/or counter-flow scrubbing readily achieved normal target values.

No data is available for the effectiveness on emissions of the other process measures (additives and lids).

**Cross-media effects**

Air extraction can have a significant effect on power consumption in three ways:

- additional electricity to power fans and pumps
- unwanted loss of heated workspace air during working periods when outside temperatures are below about 12 °C (this may be more significant in Northern and Central Europe)
- unwanted cooling of process solutions by increasing evaporation requiring additional process energy input.

**Operational data**

Options to reduce the volume of extracted air and decrease the energy loses are discussed in Section 4.18.2.2, below.

**Applicability**

One or more of these options is suitable for all installations.

**Economics**

*No data provided*

**Driving force for implementation**

Workplace health and safety.

**Example plants**

*No data provided*

**Reference literature**

[66, PPRC, 2003, 80, INRS, , 104, ÜBA, 2003]
4.18.2.2 Reduction of the volume of extracted air

Operational data

Figure 4.23: Fume extraction on top of treatment tank

[3, CETS, 2002] 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 the 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 \((W<0.5\ m)\)  
\[
V = 2\ v_x\ L\ W\ (W/L)^{0.2}
\]

Double-sided extraction \((W>0.5\ m)\)  
\[
V = 2\ v_x\ L\ W\ (W/2L)^{0.2}
\]

\(V\) = volume of extracted air, m³  
\(v_x\) = minimal air velocity at point \(x\), m³/s  
\(L\) = length of extraction area, m  
\(W\) = width of extraction area, m

Single-side extraction is normally used for tanks of width \(W<0.5\ m\), see Figure 4.24, and double-sided extraction for wider tanks \((W>0.5\ m)\), see Figure 4.25.
Reduction of free surface area above tanks

Figure 4.26 and Figure 4.27 show different means of minimising the air volume extracted and thus energy consumption.

Figure 4.26: Lid protecting free surface area, fixed to and moved with the flight bar

Figure 4.27: Lid protecting free surface area above extraction hood, movable by transporter

Figure 4.26: 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 a reduction in the surface area.

Figure 4.27: 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 % (subject to a German patent). 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 the lids are opened. A reduction in extraction rate of up to 90 % may be achieved.

Push - Pull System

This method is designed to create an airflow over the surface of the processing bath. It works with an extraction hood opposite a blowing duct. The surface of the processing solution must not have any frame or obstacle to the airflow. Therefore its application remains quite limited.
Enclosure of the Plating line
Recently, the complete segregation of the process plant has been achieved in some installations. 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 figures other techniques cannot be expected.

Process control techniques
Air extraction should only be operational during operating periods for the solutions of concern, and when conditions require, such as when process solutions are fully heated and working. Care should be taken that the air extraction system does not operate when it is not required, especially when outside temperatures are low and/or workplace cooling or heating are functioning. Timers can be installed.

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. Savings from energy recovery are only a fraction of these costs, a feasibility study prior to installation including economic considerations is essential to ensure sound investment.

Applicability of techniques
No data provided
Attention needs to be paid to energy efficiency in all installations using air extraction. Process control is feasible for all installations. Other options will depend be site-specific.

Economics of all techniques
No data provided

Driving force for implementation of techniques
Health and safety in the workplace.

Example plants
No data provided

Reference literature
[3, CETS, 2002]

4.18.3 Waste water
The bulk of emissions to the environment from an installation for the surface treatment of metals and plastics occur to water, see Section 1.4.2. Minimisation (including minimisation spills), recycling and re-use are important issues for the management of waste waters [13, UNEP, et al., 2002] and are dealt with elsewhere, in Sections 4.18.1, 4.2.6, 4.5 and 4.6.

Waste water treatment is described extensively elsewhere, such as generally in [87, EIPPCB, ], and specifically for this sector [6, IHOBE, 1997, 21, Agences de l'Eau de France, et al., 2002]. The following sections are therefore a brief description of relevant techniques.

Process waters are usually treated in a waste water treatment plant with a sequence of process steps see Section 2.13.1, which also illustrates a typical waste water treatment plant (Figure 2.28).
Chapter 4

4.18.3.1 Elimination and/or separation of the individual pollutants at the point of generation

Description
Some chemicals are most effectively managed by treating them separately before mixing with other effluents [12, PARCOM, 1992, 13, UNEP, et al., 2002].

Other chemicals such as pickling acids and chemical degreasers, are discharged irregularly and in large quantities that can exceed the capacity of a continuous-flow treatment plant, and can breach of permit conditions. They can be managed by:

- avoiding bulk discharges (see counter-flow pickling, Section 4.10.10.1)
- containing in bulk and bleeding to waste water treatment over a period of time, within the treatment plant’s capacity
- containing in bulk and using alkali degreasing solutions to neutralise acid pickling solutions.

Achieved environmental benefits
For some substance, contaminant treatment and removal only possible after separate treatment. Avoidance of bulk discharges exceeding treatment plant capacity and breach of permit conditions.
Use of waste alkali solutions (such as degreasers) to neutralise waste acid solutions saving chemicals.

Cross-media effects
Will be case-dependant.

Operational data
Cyanide-, nitrite- and chromate-containing flows must be pre-treated separately before being mixed together or with other waste waters.

The nitrites can be oxidised or reduced; both reaction types need a slightly acid solution (pH 3 - 4).

The cyanide oxidation must be accomplished in alkaline solution (pH >10).

The chromate reduction takes place at pH values <2.5.

In order to limit the use of additional chemicals, acid waste water can be neutralised with alkaline waste water, which must be however be free of complexing agents.

Other substances can be managed separately to reduce the amount of contaminant discharged, and reducing or eliminating the need for further treatment. Examples are the use of countercurrent rinsing and evaporation to achieve zero-discharge from copper, nickel and chromium plating, and the use of electrolytic cells with chromium and nickel plating.

Applicability
Consideration should be given at every process discharge point to whether treatment (or recycling or re-use) be better carried out on the separated stream, before mixing flows for subsequent treatment.

When using waste alkali flows to neutralise waste acids, additional chemicals may be required to achieve a suitable pH for discharge through a flocculation system.

Economics
Capital and treatment costs may be significantly reduced by treating individual waste water streams separately.
Driving force for implementation
The specific process chemistry will dictate which chemicals may require separation. Separate treatment streams may be more efficient and cost-effective.

Example plants
Townrow (Hi-Tech) Plating Ltd, Sheffield, UK for countercurrent rinsing and electrolytic treatment of chromium and nickel drag-out streams.
Merrydale Industries Ltd, Wednesbury, UK for countercurrent rinsing and evaporation for copper, nickel and chromium plating.
Frost Electroplating Co. Ltd, Birmingham, UK, for zero discharge from nickel plating by 4-stage countercurrent rinsing with evaporation.
Metal Colours Ltd, Slough, UK, for countercurrent pickling.
SGI, Plaisir, CIRE Bellegarde, and SOFRA-PCB, Champoreaux, France for treatment of separate streams, then bulking for final treatments and settlement.

Reference literature
[18, Tempany, 2002]

4.18.3.2 Separation from oils and greases (hydrocarbons) from waste water
Generally the separation of oils and greases is done while managing the degreasing solutions. In special cases a de-oiling of raw waste water before the inorganic treatment is necessary, and the procedures for this application are described in Section 4.10.9.1.

4.18.3.3 Cyanide oxidation
Description
Cyanides can be removed from waste water using different procedures:

- oxidation with different oxidising agents:
  - sodium hypochlorite
  - hydrogen peroxide
  - oxygen (O₂)
  - ozone (O₃)
- transfer into insoluble metal complexes (e.g. iron cyanide connections)
- removal by ion exchangers
- destruction of the cyanide by thermal procedures
- radiation-assisted oxidation (oxidising agents and UV radiation)
- anodic oxidation.

In practice the chemical oxidation of cyanide is the most commonly-used technique. [ÜBA, 2003 #104]

Achieved environmental benefits
Destruction of cyanide.

Cross-media effects
Use of chemicals and energy (for thermal, radiation and anodic techniques) and the possible production of AOX if using hypochlorite.

Operational data
The use of sodium hypochlorite is associated with the formation of organic chlorine compounds, measured as AOX. For this reason the replacement of sodium hypochlorite as an oxidising agent in the cyanide oxidation has been much discussed. However, since none of the
alternatives mentioned show a universal solution for efficient cyanide destruction, the employment of sodium hypochlorite is still the most used procedure. Anodic oxidation is a suitable technology for the destruction of cyanide complexes in cyanide-containing process solutions and rinsing waters from zinc- and copper plating. The residual cyanide content attainable with the anodic oxidation is below 0.1 g/l. A limit value of <0.2 mg/l is achieved by an additional chemical treatment with sodium hypochlorite. Additionally to the cyanide destruction the dissolved metals are recovered and can be re-used.

**Applicability**
Chemical oxidation is widely used. Hydrogen peroxide can readily replace hypochlorite, but the cost is higher.

**Economics**
*No data provided*

**Driving force for implementation**
Water pollution protection legislation.

**Example plants**
*No data provided*

**Reference literature**
[21, Agences de l'Eau de France, et al., 2002]

### Nitrite treatment

**Description**
Nitrite can be oxidised either to nitrate or reduced to nitrogen. Both reactions take place in weak acid conditions around pH 4. [104, ÜBA, 2003]

**Achieved environmental benefits**
Destruction of nitrite.

**Cross-media effects**
Possible AOX formation if Hypochlorite is used.

Low pH with high nitrite concentrations can lead to NOx formation.

**Operational data**
For oxidation H2O2 is normally used.

Sodium hypochlorite used to be used most frequently as a nitrite oxidising agent, but use is decreasing because of the possibility of associated AOX-formation.

Air extraction may be necessary as pH-lowering with high nitrite concentrations leads to the formation of nitrous gases. Since nitrous gases by themselves dissolve badly in water, an exhaust air scrubber with alkali solution may be necessary.

**Applicability**
*No data provided*

**Economics**
*No data provided*

**Driving force for implementation**
Water pollution protection legislation.
4.18.3.5 Chromate treatment

Description
Hexavalent chromium compounds (chromates or dichromate) are difficult to precipitate and are normally reduced to trivalent (chromium III ions), which are subsequently precipitated as chromium III hydroxide on neutralisation. The reduction is made at pH values under 2.5. The most common reducing agent is sodium hydrogen sulphite (bisulphite).

Achieved environmental benefits
Reduction and removal of chromium VI

Cross-media effects
Care should be taken with sodium hydrogen sulphite (bisulphite), as SO₂ fumes are formed. Workplace ventilation may be required.

Operational data
If only a small amount of chromium VI is present at high pH values, the reaction can also be carried out in the alkaline area with sodium dithionite or iron II compounds, whereby the formation of salt by acidifying is not necessary if using iron II compounds.

Applicability
Widely used.

Economics
No data provided

Driving force for implementation
Water pollution protection legislation.

Example plants
No data provided

Reference literature
[21, Agences de l'Eau de France, et al., 2002]
Operational data
Caustic solution usually precipitates the heavy metals as hydroxides or phosphates. If several metals exist in the effluent at the same time, the precipitation of any metal that is more difficult to precipitated is facilitated. (TWG: the reverse is stated in Chapter 2. More information on which is correct, please)

The solubility of the metals increases with increased neutral salt concentrations. The metals partly precipitate in very fine particles (especially lead and tin), therefore the addition of flocculating agents (iron(III)chloride, lime) and/or flocculants (polyelectrolyte) are necessary for better separation and filtration. However, this leads to an increase in the quantity of sludge (waste) produced as iron compounds and lime need to be added in significant quantities. Polyelectrolytes have much higher charge density and need a far lower dose rate.

To meet stringent emission limit values fine filtration may also be necessary. Sometimes a post-treatment is also necessary, for example with sulphide and/or selective ion exchangers.

Applicability
Widely used. Settlement tanks need space and may be costly to install.

Economics
No data provided

Driving force for implementation
Water pollution protection legislation.

Example plants
No data provided

Reference literature
[21, Agences de l'Eau de France, et al., 2002]

4.18.3.6.2 Sulphide precipitation

Description
If the hydroxide precipitation followed by a post-cleaning stage with selective ion exchangers is not sufficient to meet limit values for discharge, a precipitation with sodium sulphide or organo-sulphide can achieve lower levels, see Table 4.12. Since the solubility of the metal sulphides is generally substantially lower, than that of the metal hydroxides, smaller residual concentrations can be achieved with sulphide precipitation.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Solubility product (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hydroxide</td>
</tr>
<tr>
<td>Aluminium</td>
<td>$2 \times 10^{-32}$</td>
</tr>
<tr>
<td>Lead</td>
<td>$1 \times 10^{-7}$ to $10^{-13}$</td>
</tr>
<tr>
<td>Cadmium</td>
<td>$1.3 \times 10^{-14}$</td>
</tr>
<tr>
<td>Chromium (III)</td>
<td>$3 \times 10^{-28}$</td>
</tr>
<tr>
<td>Iron (II)</td>
<td>$2 \times 10^{-15}$</td>
</tr>
<tr>
<td>Iron (III)</td>
<td>$8.7 \times 10^{-18}$</td>
</tr>
<tr>
<td>Copper</td>
<td>$2 \times 10^{-19}$</td>
</tr>
<tr>
<td>Nickel</td>
<td>$5.8 \times 10^{-15}$</td>
</tr>
<tr>
<td>Silver</td>
<td>$1.24 \times 10^{-8}$</td>
</tr>
<tr>
<td>Zinc</td>
<td>$4 \times 10^{-17}$</td>
</tr>
<tr>
<td>Zinc(II)</td>
<td>$6 \times 10^{-25}$</td>
</tr>
</tbody>
</table>

Table 4.12: Solubility products of metal hydroxides and sulphides
Source: UBA
Achieved environmental benefits
Low emission values for transition metals.

Cross-media effects
Care in using sulphides; avoid acid conditions to prevent emission of hydrogen sulphide.

Operational data
The addition of a flocculant is necessary with metal sulphides precipitation as the precipitate formed as well as colloidal sulphur do not neither settle or are filtered easily.

Applicability
No data provided

Economics
[21, Agences de l'Eau de France, et al., 2002]

Driving force for implementation
Water pollution protection legislation; low emission values where environmental quality standards require.

Example plants
No data provided

Reference literature
[82, Agences de l'Eau, 1996, 104, ÜBA, 2003]

4.18.3.7 Complexing agent

Description
Complexing agents used in certain processes make the precipitation of transition metals more difficult, if they are mixed before treatment with other waste waters.

Copper can be precipitated from complexes by reduction with sodium dithionite. By using of stronger reducing agents, like sodium hypophosphite, other metals such as nickel and tin can be reduced. The metals are frequently precipitated as sulphides from hard complexes. Cationic metal complexes with ammonia or amines such as triethanolamine and Quadrol can be removed with weakly acid cation exchangers (for example, selective ion exchange resins with iminodiacetate groups). However treatment with ion exchangers is not possible in connection with citrate, EDTA and NTA.

The most common complexing agents are cyanides, polyphosphates, amines, citric acid, tartaric acid, gluconic acid, ammonia, NTA, EDTA, and Quadrol.
[104, ÜBA, 2003]

Achieved environmental benefits
Ensures that metals are not solubilised and carried into municipal waste water treatment or resolubilised in the wider aquatic environment.

Cross-media effects
Additional chemicals and energy consumption, depending on the technique used.

Operational data
Where using complexing agents, particularly strong ones, separation of metals and complexing agents as far as possible prior to other treatments (such as flocculation and precipitation of the metal) is advisable.
4.18.3.8 Precipitation of anions

4.18.3.8.1 Fluoride Precipitation

Description
Free fluoride ions can be precipitated with calcium, for example when neutralising with lime. [3, CETS, 2002]

Achieved environmental benefits
Meeting fluoride emission standards.

Cross-media effects
No data provided

Operational data
Fluoride precipitation can only be carried out quantitatively if at least one calcium equivalent is present for every fluoride equivalent. Otherwise, additional calcium ions must be added, for example as calcium chloride.

Applicability
No data provided

Economics
No data provided

Driving force for implementation
Water pollution protection legislation.

Example plants
No data provided

Reference literature
No data provided

4.18.3.8.2 Phosphate precipitation

Description
It is not usually necessary to eliminate phosphate. However, when it is required, it is rarely a problem, since sufficient metal ions are nearly always present in surface treatment waste waters to form insoluble phosphate compounds. If this is not the case, iron or aluminium
compounds must be added. Precipitation can also be achieved with lime at pH values over 10. [3, CETS, 2002]

**Achieved environmental benefits**
Meeting phosphate emission limit values where applicable.

**Cross-media effects**
Additional chemicals may be required.

**Operational data**
*No data provided*

**Applicability**
*No data provided*

**Economics**
*No data provided*

**Driving force for implementation**
Where water legislation and local environmental quality standards require.

**Example plants**
*No data provided*

**Reference literature**
*No data provided*

---

### 4.18.3.8.3 Sulphate precipitation

**Description**
Sulphate control is important for the protection of the materials in the sewerage system, although discharge limit values are normally high, about 1000 mg/l. It is readily precipitated as calcium sulphate [3, CETS, 2002]
*No other data provided*

**Achieved environmental benefits**
Meeting sulphate emission limit values where applicable, usually for discharge to foul sewer.

**Cross-media effects**
The use of additional chemicals

**Operational data**
According to its solubility product, calcium sulphate has a solubility of 1404 mg/l as sulphate. This rises strongly with increasing neutral salt concentration, so that in the presence of 1 val/l neutral salt (this corresponds to a concentration of approximately 58.5 g/l common salt) the sulphate only precipitate at concentrations of 5000 mg/l, which corresponds to the solubility of the calcium sulphate. Different neutral salts have thereby a different influence on the attainable precipitation.

**Applicability**
*No data provided*

**Economics**
*No data provided*

**Driving force for implementation**
Where water legislation and local environmental quality standards require.
4.18.3.9 Thermal procedures

Beside the classical waste water treatment by chemical/physical procedures it is possible to avoid the discharge of waste water completely by the use of evaporation techniques. Instead of the metal hydroxides a mixture of water-soluble salts results from evaporation, whose disposal requires a deposit in a suitable landfill, possibly with solidification.

At present two basic techniques are available for evaporation of the effluent:

- vacuum evaporators with vapour compression and
- infrared evaporators at atmospheric pressure

4.18.3.9.1 Vacuum evaporators with vapour compression

Description
By the use of vacuum evaporators with vapour compression it is possible to lower the energy demand to an economic level. [104, ÜBA, 2003]

Achieved environmental benefits
Zero water discharge from all or part of an installation.

Cross-media effects
Increased energy usage in evaporation and concentrate drying. Waste produced may be more difficult to manage than conventional sludges.

Operational data
The evaporator produces a concentrate which requires an additional drying procedure. Thus the investment and operating cost rises to an extent where this technology is usually only economic in exceptional cases.

Applicability
This is only technically possible by the use of a large energy input and high capital plant investment. There may little or no environmental benefit or requirement to clean a waste water discharge containing ‘neutral’ salts (i.e. alkali metal salts, Na, K, Ca) left from traditional treatments. There are three possible cases:

- small effluent quantity
  Effluent quantity may drastically reduced by in-plant measures described in this section.; at the same time the concentration of the soluble contents rises accordingly. It may then be difficult to treat the effluent with by classical methods. It may then be difficult to meet strict concentration values for effluent and sewage regulation. In such a case evaporation can be more economic than conventional treatment, despite the energy consumption.

- ingredients difficult to remove by normal operation
  Complexing agents such as EDTA are difficult to destroy in the effluent. Howvere, their use is essential for some processes and specifications. For an installation which relies on using such chemicals, the complete evaporation of the relevant flows may be the only solution.
• **regulation**
  An enterprise whose production has no waste water discharge may be free from or less subject to supervision by the environmental regulatory authorities.

**Economics**
See Operational data.

**Driving force for implementation**
See Applicability.

**Example plants**
*No data provided*

**Reference literature**
[104, ÜBA, 2003]

### 4.18.3.9.2 Infrared evaporators

**Description**
The liquid to be evaporated is placed in a conical container. The liquid surface is then warmed with infrared radiation produced by gas infrared emitter. Controlled and bubble-free evaporation is achieved by radiation absorption as the liquid presents an extremely thin layer at the ‘shallow end’. The crystallised solids sink in the residual water because of their higher specific gravity in the "cold" layers of the evaporator. The crystal mash formed is discharged via a valve to a filter bag. The filtered mother liquor is fed back to the evaporator vessel. The water vapour mixture leaves the evaporator by an extraction system. [104, ÜBA, 2003]

**Achieved environmental benefits**
Zero discharge from all or part of an installation.

**Cross-media effects**
Increased energy usage in evaporation: the energy consumption of 100 m³ natural gas per m³ of water evaporated is high.

Waste produced may be more difficult to manage than conventional sludges.

**Operational data**
Advantages of the technique:

- durable, resistant technology
- direct, contactless heating
- clean exhaust gas because of aerosol evaporation
- consistent performance with salt solutions, acids and alkalines
- fully automatic salt discharge possible
- reducing or oxidising atmosphere in the evaporator area as required
- no pollution and/or encrustation problems
- no additional chemicals needed, for example for cleaning purposes
- very high plant throughput availability due to safe continuous operation
- CrVI reduction is possible without additional chemicals
- evaporating of ammonia solutions without effluent problems
- noiseless operation.

**Applicability**
See Section 4.18.3.9.1
4.18.4 Waste

4.18.4.1 Generation and management of waste

Annex IV (point 3) of the Directive requires the operator to further the recovery and recycling of substances generated and used the process and of waste, where appropriate.

The rinsing processes in surface treatment installations produce rinse waters containing concentrates. In addition to rinsing waters, the following metal-containing waste waters streams result:

- used process solutions from the electrochemical processes (electrolytes)
- used process solutions from chemical coating processes
- used process solutions from the pre- and post-treatment (cleaning, pickling, phosphating and chemical conversion)
- solutions from separation and regeneration processes, such as ion exchange, retardation, dialysis, electrolysis
- solutions from associated activities, such as exhaust scrubbers and filters, as well as from plant cleaning.

Generally the solutions and effluents are discharged into the effluent system. The treatment of the metal-containing streams in the system essentially precipitates the dissolved metal ions as insoluble compounds. Normal precipitation with caustic soda solution and/or lime precipitates the metals as hydroxides and/or oxide hydrates. Precipitation may also be as carbonates and sulphides. The sludge produced has a water content of usually over 95 % and is drained by means of filter presses to about 60 % water content and is disposed of in this form as sludge.

The amount of sludge depends on various processing factors:

- contamination of the input material
- amount of metal oxides of the workpiece surface (corrosion)
- discharge of process solution with the workpiece (drag out)
- service lifetime of the process solutions.

That means that the generation of sludge without internal recycling measures is directly proportional to the drag out and the service lives of the process solutions. Generally, the metal losses by drag out related to the metal input material lies between 5 and 30 %.

Surface treatment sludge is usually a mixture of metal hydroxides. It contains all non-ferrous metals used during the process, the workpiece substrate metals iron and aluminium, as well as calcium, potassium and sodium from the precipitation chemicals.
Depending on the plating process the non-ferrous metal contents (Cu, Ni) can amount to up to 30 %, for example, with monosludges (i.e. sludges from one process type only). The major part of the electroplating sludge is a mixture and has nonferrous metal contents of about 10 %, as Table 4.13 shows.

<table>
<thead>
<tr>
<th></th>
<th>Cu %</th>
<th>Ni %</th>
<th>Zn %</th>
<th>Pb %</th>
<th>Cr %</th>
<th>Fe %</th>
<th>Ca %</th>
<th>Cl %</th>
<th>SO₄</th>
<th>Water %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu sludge</td>
<td>5 – 10</td>
<td>1 - 5</td>
<td>1 - 5</td>
<td>0 – 1</td>
<td>0 - 2</td>
<td>5 – 15</td>
<td>2 - 10</td>
<td>0 - 3</td>
<td>0 - 20</td>
<td>50 – 70</td>
</tr>
<tr>
<td>Ni sludge</td>
<td>0 – 2</td>
<td>10 - 15</td>
<td>1</td>
<td>0 – 1</td>
<td>0 - 2</td>
<td>0 – 5</td>
<td>0 - 5</td>
<td>0 - 3</td>
<td>0 – 5</td>
<td>50 – 70</td>
</tr>
<tr>
<td>Mixed sludge</td>
<td>0 – 2</td>
<td>0 - 2</td>
<td>2 - 3</td>
<td>0 - 1</td>
<td>0 - 2</td>
<td>5 – 15</td>
<td>5 - 15</td>
<td>0 - 3</td>
<td>5 - 20</td>
<td>50 – 70</td>
</tr>
</tbody>
</table>

Table 4.13: Typical composition of electroplating sludge of different origin

Some liquid wastes, such as end-of-life electrolytes or layer conversion solution may be also be concentrated and treated in the in-house waste water treatment plant.

4.18.4.2 Avoidance and minimisation of waste

There are three key factors for the avoidance and minimisation of waste in surface treatment:

- extension of the service lifetime of the process solutions
- decrease of the drag-out of process solutions
- feedback of the dragged-out process solutions into the process tanks.

These measures have been described in detail in Sections 2.4, 4.5 and 4.6.

4.18.4.3 Re-use and recycling of waste

Description

Part of the electroplating sludge may have a high value material content and recycling can be arranged in many cases. Recycling includes refining of the metals copper, nickel, chromium and zinc from suitable electroplating sludge as metals or metal compounds.

The following subsequent uses are possible:

- hydro and pyrometallurgical companies engaged in non-ferrous metal refining
- inorganic chemical companies and the glass and ceramics industry which use metals or metal compounds intentionally in the manufacture of products
- manufacture of usable metal concentrates.

Techniques where the metals are merged non-specifically into mineral matrices (glass, ceramics, cement) are not considered recycling, but may be an option.

In the surface treatment installation used electrolytes, coating and conversion solutions which are no longer suitable for regeneration become liquid waste. These solutions can be transferred under certain conditions to the chemical suppliers for re-use in the direct manufacture of new electrolytes.

The preferred aim is the recovery for use of the raw material, i.e. winning the metals copper, nickel and zinc from the redundant electrolytes. This technique also exists in principle for semi-concentrates such as the contents of the static rinses. It may be favourable to further concentrate these strong solutions by evaporation, which lowers the transport costs and at the same time increases the valuable material content.

[104, ÜBA, 2003]

Achieved environmental benefits

Recovery of commodity metals which are conservative (i.e. non-degradable).
Cross-media effects
Emissions from and energy used in recovery processes. Chemicals used to achieve a suitable waste for reprocessing.

Operational data
Consideration should be given to the balance of recovery and recycling. For instance, some in-process re-use in the process solution may recover a small amount of metal, but reduce the metal content of the installation’s sludge below the environmental and economic recovery breakeven point. The sludge then disposed of may still contain more metal than could have been recovered. TWG: has this happened in practice?

Recycling opportunities are favoured if the streams within the effluent system are kept separate according to their metal contents. The amount of separation applied depends on the requirements of the recycling companies.

Copper, nickel, chromium and zinc are regularly recovered. Some small quantities of precious metals, tin, lead and cadmium also arise. Sodium and calcium occur as precipitating chemicals. Re-use is technically possible if sludges are produced by appropriate pre- or post-treatment measures which satisfy the requirements of recycling plants in their consistency and material composition. These requirements include:

- physical parameters such as consistency and water content
- meeting or exceeding the minimum content of usable metals
- producing a mixture of metals which is usable
- minimum content of substances which disturb the recycling process.

The requirements of the recycling plants for consistency and composition of the electroplating sludge differ substantially from each other, depending on the particular recycling process and require assessing on a case by case basis.

Applicability
Dependant on the availability of suitable re-use options and the suitability of the sludge. For instance, recovered chromium oxides with high chloride content may not be suitable for recovery of the chromium in some processes.

Transport (distance to the recycler) may also be a factor.

Economics
Case dependant.

Cost of disposal of surface treatment wastes, which are usually classed as hazardous.

Driving force for implementation
Increasing disposal costs for hazardous wastes.

Example plants

Reference literature
[104, ÜBA, 2003]

4.18.4.3.1 In-house electrolytic recovery

See Section 4.10.8.
5 BEST AVAILABLE TECHNIQUES
6 EMERGING TECHNIQUES
7 CONCLUDING REMARKS
REFERENCES


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71 BSTSA "Metal Pre-treatment".

73 BSTSA "Electroless Nickel".

74 BSTSA "Hard Chromium".

75 BSTSA "Precious Metals".

76 BSTSA "Laquers for Metal Finishing".

77 BSTSA "Electroplated Plastic Components".

78 BSTSA "Zinc Plating".

80 INRS "Guide pratique de ventilation: Cuves de traitement de surface", 2.


82 Agences de l'Eau (1996). "Prevention des pollutions accidentelles dans les industries de la chimie, du traitement de surface, etc.

85 EIPPCB "Reference Document on Best Available Techniques for Industrial Cooling Systems", EC.

86 EIPPCB "Reference Document on Best Available Techniques in the Ferrous Metals Processing Industry", EC.

87 EIPPCB "Reference Document on Best Available Techniques in the Waste Water and Waste Gas Treatment/ Management Systems in the Chemical Sector", EC.


89 EIPPCB "Reference Document on Best Available Techniques for the Waste Treatment Industries", EC.

90 EIPPCB "Reference Document on Best Available Techniques for Surface Treatment using Solvents", EC.

References


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### General Glossary

#### 1. General terms, abbreviations, acronyms and substances

<table>
<thead>
<tr>
<th>ENGLISH TERM</th>
<th>MEANING</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>alternating current</td>
</tr>
<tr>
<td>acid</td>
<td>proton donor. A substance that, more or less readily, gives off hydrogen ions in a water solution.</td>
</tr>
<tr>
<td>acute effect</td>
<td>an adverse effect on any living organism in which severe symptoms develop rapidly and often subside after the exposure stops.</td>
</tr>
<tr>
<td>acute toxicity</td>
<td>adverse effects that result from a single dose or single exposure of a chemical; any poisonous effect produced within a short period, usually less than 96 hours. This term is normally used to describe effects in experimental animals.</td>
</tr>
<tr>
<td>acute pollution</td>
<td>pollution arising from infrequent events, unplanned events or accidents (see also: chronic pollution)</td>
</tr>
<tr>
<td>aeration</td>
<td>the act of mixing a liquid with air (oxygen).</td>
</tr>
<tr>
<td>aerobic</td>
<td>a biological process that occurs in the presence of oxygen</td>
</tr>
<tr>
<td>alkali</td>
<td>proton acceptor. A substance that, more or less readily, takes up hydrogen ions in a water solution.</td>
</tr>
<tr>
<td>anaerobic</td>
<td>a biological process that occurs in the absence of oxygen.</td>
</tr>
<tr>
<td>anion</td>
<td>a negatively charged ion; an ion that is attracted to towards the anode in electrochemical reactions</td>
</tr>
<tr>
<td>anode</td>
<td>positive electrode</td>
</tr>
<tr>
<td>anodising (GB)</td>
<td>anodic oxidation. Electrolytic process in which the surface layer of a metal, such as aluminium, magnesium or zinc is converted to a coating, usually an oxide, having protective, decorative or functional properties [101, CEN, 2000]</td>
</tr>
<tr>
<td>anodizing (US)</td>
<td>anodic oxidation. Electrolytic process in which the surface layer of a metal, such as aluminium, magnesium or zinc is converted to a coating, usually an oxide, having protective, decorative or functional properties [101, CEN, 2000]</td>
</tr>
<tr>
<td>AOCl</td>
<td>adsorbable organic chlorine compounds</td>
</tr>
<tr>
<td>AOX</td>
<td>adsorbable organic halogen compounds. The total concentration in milligrams per litre, expressed as chlorine, of all halogen compounds (except fluorine) present in a sample of water that are capable of being adsorbed on activated carbon.</td>
</tr>
<tr>
<td>APE</td>
<td>alkyl phenol ethoxylates</td>
</tr>
<tr>
<td>aquifer</td>
<td>a water-bearing layer of rock (including gravel and sand) that will yield water in usable quantity to a well or spring.</td>
</tr>
<tr>
<td>assimilative capacity</td>
<td>the ability of a natural body of water to receive waste waters or toxic materials without harmful effects and without damage to aquatic life.</td>
</tr>
<tr>
<td>ATBC</td>
<td>acetyl tributyl citrate</td>
</tr>
<tr>
<td>autocatalytic plating</td>
<td>deposition of a metallic coating by a controlled chemical reduction that is catalysed by the metal or alloy being deposited [101, CEN, 2000]</td>
</tr>
<tr>
<td>bactericide</td>
<td>a pesticide used to control or destroy bacteria</td>
</tr>
<tr>
<td>barrel</td>
<td>a rotating container used to contain workpieces when they are treated in bulk. Barrel processing: surface treatment activities carried out using barrels. For example, barrel cleaning, barrel electroplating</td>
</tr>
<tr>
<td>BAT</td>
<td>best available techniques</td>
</tr>
<tr>
<td>ENGLISH TERM</td>
<td>MEANING</td>
</tr>
<tr>
<td>--------------</td>
<td>---------</td>
</tr>
<tr>
<td>bath</td>
<td>a solution of chemicals for a specific surface treatment activity, e.g. pickling bath. Also refers to the relevant vat or workstation in a process sequence</td>
</tr>
<tr>
<td>BF</td>
<td>Batch-wise flocculation</td>
</tr>
<tr>
<td>biodegradable</td>
<td>that can be broken down physically and/or chemically by microorganisms. For example, many chemicals, food scraps, cotton, wool and paper are biodegradable.</td>
</tr>
<tr>
<td>BOD</td>
<td>biochemical oxygen demand: the quantity of dissolved oxygen required by micro-organisms in order to decompose organic matter. The unit of measurement is mg O₂/l. In Europe, BOD is usually measured after 3 (BOD₃), 5 (BOD₅) or 7 (BOD₇) days.</td>
</tr>
<tr>
<td>BREF</td>
<td>BAT reference document</td>
</tr>
<tr>
<td>BTEX</td>
<td>benzene, toluene, ethylbenzene, xylene</td>
</tr>
<tr>
<td>BTX</td>
<td>benzene, toluene, xylene</td>
</tr>
<tr>
<td>cathode</td>
<td>negative electrode</td>
</tr>
<tr>
<td>cation</td>
<td>a positively-charged ion: an ion that is attracted towards the cathode in electrochemical reactions</td>
</tr>
<tr>
<td>CF</td>
<td>chemical oxygen demand: the amount of potassium dichromate, expressed as oxygen, required to oxidize chemically, at about 150 °C, substances contained in waste water.</td>
</tr>
<tr>
<td>COD</td>
<td>chemical oxygen demand: the amount of potassium dichromate, expressed as oxygen, required to oxidize chemically, at about 150 °C, substances contained in waste water.</td>
</tr>
<tr>
<td>CPI</td>
<td>corrugated plate interceptor - oil separation device utilizing inclined corrugated plates to separate free non-emulsified oil and water based on their density difference</td>
</tr>
<tr>
<td>chelating agent</td>
<td>a compound capable of chelation with metal ions.</td>
</tr>
<tr>
<td>chelation</td>
<td>the formation of a closed ring of atoms by the attachment of compounds or radicals to a central polyvalent metal ion (occasionally non-metallic). See sequestration, complexing agent</td>
</tr>
<tr>
<td>chronic pollution</td>
<td>pollution occurring from regular or continuous events, such as effluent discharge (see acute pollution)</td>
</tr>
<tr>
<td>complexing agent</td>
<td>see chelating agent</td>
</tr>
<tr>
<td>corrosion</td>
<td>surface chemical reaction especially on metals, by the action of moisture, air or chemicals.</td>
</tr>
<tr>
<td>DAF</td>
<td>dissolved air flotation</td>
</tr>
<tr>
<td>DC</td>
<td>direct current (electrical supply)</td>
</tr>
<tr>
<td>DDC</td>
<td>dithiocarbamate</td>
</tr>
<tr>
<td>deburring</td>
<td>removal of burrs or sharp edges by electropolishing, grinding, finishing or pickling</td>
</tr>
<tr>
<td>de-embrittlement</td>
<td>a specific type of embrittlement of a metal or alloy caused by absorption of atomic hydrogen, for example, during electroplating, cathodic cleaning, or pickling processes and manifested by delayed fracture, brittle fracture or a reduction of ductility [101, CEN, 2000]</td>
</tr>
<tr>
<td>demulgating solution</td>
<td>(from the German demulgen) a weakly emulsifying solution used for degreasing. The oils in the solution can be easily removed enabling the cleaned solution to be re-used</td>
</tr>
<tr>
<td>dialysis</td>
<td>a separation technique: the separation of colloids in solution from other dissolved substances by selective diffusion through a membrane</td>
</tr>
<tr>
<td>diffuse emission</td>
<td>emissions arising from direct contact of volatile or light dusty substances with the environment (atmosphere, under normal operating circumstances). These can result from:</td>
</tr>
<tr>
<td>ENGLISH TERM</td>
<td>MEANING</td>
</tr>
<tr>
<td>--------------</td>
<td>---------</td>
</tr>
<tr>
<td>inherent design of the equipment (e.g. filters, dyers…)</td>
<td>-</td>
</tr>
<tr>
<td>operating conditions (e.g. during transfer of material between containers)</td>
<td>-</td>
</tr>
<tr>
<td>type of operation (e.g. maintenance activities)</td>
<td>-</td>
</tr>
<tr>
<td>or from a gradual release to other media (e.g. to cooling water or waste water).</td>
<td>-</td>
</tr>
</tbody>
</table>

Fugitive emissions are a subset of diffuse emissions.

diffuse sources | sources of similar diffuse or direct emissions which are multiple and distributed inside a defined area

displacement coating | see immersion coating

DOS | dioxyl sebacate

drag-in | liquid (from a previous bath) carried into a bath by the workpieces or substrate introduced during treatment

drag-out | liquid carried out of a bath by the workpieces or substrate during treatment

DS | dry solids (content). The mass of a material remaining after drying by the standard method of test

DSA | dimensionally stable anodes. Metal anodes that are not consumed during use as graphite anodes are, hence dimensionally stable.

EC50 | effect concentration 50. The concentration at which effects are observed in 50% of the test population after administering a single dose. Effects include the immobilisation of daphnia, inhibition of growth, cell division or biomass production, or the production of chlorophyll by algae.

ECCS | electro-chemical chromium plating

EDTA | ethylenediaminetetraacetic acid. An important chelating agent

EDDS | ethylene diamine disuccinate

‘Eco’ rinse | a static rinse tank where workpieces are passed through before and after plating, allowing the collected drag-out to be re-used as drag-in

effluent | physical fluid (air or water together with contaminants) forming an emission

EIPPCB | European IPPC Bureau

electrode | a conductor by which an electric current enters or leaves an electrolyte in an electro-chemical reaction (or an electric arc or a vacuum tube) [101, CEN, 2000], See anode and cathode

electrogalvanising | a term often used to translate the German galvanische Metallabscheidung, or from other languages. Should not be used, as it is easily confused with hot dip galvanising.

electroplating | electrodeposition of an adherent metallic coating upon an electrode for the purpose of securing a surface with properties or dimensions different from those of the base metal (see electrogalvanising, galvanising. German = galvanische Metallabscheidung). Note: plating alone cannot be used in this sense. [101, CEN, 2000]

electroless plating | see autocatalytic plating. Use of this term discouraged [CEN, 2000 #101]

electrolyte | a substance that is capable of conducting an electric current in solution or fused state

electropolishing | smoothing and brightening of a metal surface by making it anodic in an appropriate solution. [101, CEN, 2000]

emerging techniques | (name of a standard chapter in BREFs)

emission | the direct or indirect release of substances, vibrations, heat or noise from individual or diffuse sources in the installation into the air, water or land
<table>
<thead>
<tr>
<th>ENGLISH TERM</th>
<th>MEANING</th>
</tr>
</thead>
<tbody>
<tr>
<td>emission and consumption levels associated with the use of BAT</td>
<td>the mass, expressed in terms of certain specific parameters, concentration and/or level of an emission, which may not be exceeded during one or more periods of time</td>
</tr>
<tr>
<td>emission limit values</td>
<td>environmental management system</td>
</tr>
<tr>
<td>“end-of-pipe” technique</td>
<td>a technique that reduces final emissions or consumptions by some additional process but does not change the fundamental operation of the core process. Synonyms: &quot;secondary technique&quot;, &quot;abatement technique&quot;. Antonyms: &quot;process-integrated technique&quot;, &quot;primary technique&quot; (a technique that in some way changes the way in which the core process operates thereby reducing raw emissions or consumptions)</td>
</tr>
<tr>
<td>ENSA</td>
<td>ethoxylated alpha-naphthol sulphonic acid</td>
</tr>
<tr>
<td>EOP</td>
<td>end-of-pipe</td>
</tr>
<tr>
<td>EP</td>
<td>electrostatic precipitator</td>
</tr>
<tr>
<td>etching</td>
<td>The act, art, or practice of engraving by means of acid which eats away lines or surfaces left unprotected in metal, glass, or the like</td>
</tr>
<tr>
<td>EU-15</td>
<td>the current 15 Member States at 26 June 2002</td>
</tr>
<tr>
<td>eutrophication</td>
<td>the pollution of a body of water by sewage, fertilisers washed from the land, and industrial wastes (inorganic nitrates and phosphates). These compounds stimulate the growth of algae, reducing the oxygen content in the water, and so killing animals with a high oxygen requirement.</td>
</tr>
<tr>
<td>existing installation</td>
<td>an installation in operation or, in accordance with legislation existing before the date on which this Directive is brought into effect, an installation authorized or in the view of the competent authority the subject of a full request for authorization, provided that that installation is put into operation no later than one year after the date on which this Directive is brought into effect</td>
</tr>
<tr>
<td>flocculation</td>
<td>the coagulation of finely divided particles into particles of greater mass [39, 1993]</td>
</tr>
<tr>
<td>fugitive emission</td>
<td>emission caused by non-tight equipment/leak: emission into the environment resulting from a gradual loss of tightness from a piece of equipment designed to contain an enclosed fluid (gaseous or liquid). Fundamentally caused by a difference of pressure and a resulting leak. Examples of fugitive emissions: leak from a flange, a pump, a sealed or tightened equipment…</td>
</tr>
<tr>
<td>funny energy</td>
<td>the energy losses on transforming down from high voltage supplies (&gt;220v)</td>
</tr>
<tr>
<td>galvanising</td>
<td>In UK English, hot dip metal coating (German: Schelztauchüberzug; French: galvanisation à chaud).</td>
</tr>
<tr>
<td></td>
<td>(a term often used to wrongly translate the German galvanische Metallabscheidung, or from other languages. This term should be translated by electroplating).</td>
</tr>
<tr>
<td>global warming</td>
<td>greenhouse effect: The short-wave solar radiation passes through the Earth’s atmosphere but after being reradiated by its surface as</td>
</tr>
<tr>
<td>ENGLISH TERM</td>
<td>MEANING</td>
</tr>
<tr>
<td>--------------</td>
<td>---------</td>
</tr>
<tr>
<td>infrared radiation, some of it is absorbed by gases in the atmosphere causing a rise in temperature (known as global warming. It is calculated that 55% of global warming is caused by absorption of energy by CO₂. The remaining 45% is caused mainly by energy absorption by methane and damage to the ozone layer as a result of the use of various VOX.</td>
<td></td>
</tr>
</tbody>
</table>

| IEF | Information Exchange Forum (informal consultation body in the framework of the IPPC Directive) |

| immersion coating | metal produced by a replacement reaction in which one metal is replaced by another from the solution [101, CEN, 2000]. For example: |

\[
\text{Fe} + \text{Cu}^{2+} \rightarrow \text{Cu} + \text{Fe}^{2+}
\]

(also known as displacement coating) |

| installation | in the Directive, a stationary technical unit where one or more activities listed in Annex I are carried out, and any other directly associated activities which have a technical connection with the activities carried out on that site and which could have an effect on emissions and pollution |

| IPPC | integrated pollution prevention and control |

| jig | see rack |

| JIT | just-in-time; a manufacturing management technique, when components are delivered for the next stage of assembly just as they are needed, and not held in stock |

| LAS | linear alkylbenzene sulphonate |

| LC50 | lethal concentration 50. The lowest concentration of a substance in water or ambient air in milligrams per litre sufficient to cause death in 50% of the test population within a defined period (e.g. 96 hours for fish, 48 hours for daphnia). |

| LD50 | lethal dose 50. The lowest dose of a substance administered to species such as mice and rats sufficient to cause death in 50% of the test population within a defined period (no more than 14 days), expressed in milligrams of test substance per kilogram of bodyweight. |

| finishing | directional grinding of flat surfaces by means of an abrasive bonded to an endless flexible belt (US: graining) [101, CEN, 2000] |

| looper unit | unit in coil coating that contains loops of the continuous substrate. In entry loopers the length of the loops is decreased, allowing the end of the substrate to remain motionless when attaching a new coil; in exit loopers the loops are increased in length while holding the receiving coil motionless while cutting the end of a completed roll |

| MAC | maximum allowable concentration |

<p>| metallizing, metallising | application of a metallic coating to the surface of non-metallic material |</p>
<table>
<thead>
<tr>
<th>ENGLISH TERM</th>
<th>MEANING</th>
</tr>
</thead>
<tbody>
<tr>
<td>Note: It is recommended to restrict the term metallizing to this meaning and in particular not to use it as a synonym for metal spraying or in the sense of depositing a metallic layer on a metallic substrate [101, CEN, 2000]</td>
<td></td>
</tr>
<tr>
<td>microelectronics</td>
<td>the brand of electronics that deals with miniature components</td>
</tr>
<tr>
<td>microrough</td>
<td>microscopic irregularities in the surface of a material</td>
</tr>
<tr>
<td>macrothrowing power</td>
<td>ability of an electroplating solution to produce a coating with a surface smoother than that of the substrate. Cf. throwing power [101, CEN, 2000]</td>
</tr>
<tr>
<td>microthrowing power</td>
<td>ability of an electroplating solution under a specific set of conditions to deposit metal in pores or scratches. Note: Good microthrowing power does not necessarily imply good macrothrowing power [101, CEN, 2000]</td>
</tr>
<tr>
<td>ml</td>
<td>millilitre</td>
</tr>
<tr>
<td>monitoring</td>
<td>process intended to assess or to determine the actual value and the variations of an emission or another parameter, based on procedures of systematic, periodic or spot surveillance, inspection, sampling and measurement or another assessment methods intended to provide information about emitted quantities and/or trends for emitted pollutants</td>
</tr>
<tr>
<td>MSA</td>
<td>methane sulphonic acid</td>
</tr>
<tr>
<td>MTO</td>
<td>metal turnover. The number of times the original quantity of metal in a bath is replenished (or turned over) by additions</td>
</tr>
<tr>
<td>multi-media effects</td>
<td>see cross-media effects</td>
</tr>
<tr>
<td>n/a</td>
<td>not applicable OR not available (depending on the context)</td>
</tr>
<tr>
<td>n/d</td>
<td>no data</td>
</tr>
<tr>
<td>NPE</td>
<td>nonyl phenyl ethoxylate</td>
</tr>
<tr>
<td>NTA</td>
<td>nitriloacetic acid</td>
</tr>
<tr>
<td>operator</td>
<td>any natural or legal person who operates or controls the installation or, where this is provided for in national legislation, to whom decisive economic power over the technical functioning of the installation has been delegated</td>
</tr>
<tr>
<td>pcb</td>
<td>(i) printed circuit board. An electronic circuit in which the wiring between components and certain fixed components themselves are printed on an insulating board. (Notes: 1. This is the main use in this document. 2. Flexible films and other substrates can be instead of insulating board) [39, 1993] (ii) polychlorinated biphenyl. Chlorinated derivatives of biphenyl. Bioaccumulateable toxic compounds used in synthetic resins and as electrical insulators. The only use in this document is discussing chemicals potentially used in installations of this sector (see Section 4.1.1.1) [39, 1993]</td>
</tr>
<tr>
<td>pickling</td>
<td>for metal: Removal of oxides or other compounds from a metal surface by chemical or electrochemical action [101, CEN, 2000] for plastic: A mixture of chromic and sulphuric acid applied to ABS-type plastic surfaces to oxidise and dissolve the butadiene component, thus generating a microrough surface as part of the preparation for...</td>
</tr>
<tr>
<td>ENGLISH TERM</td>
<td>MEANING</td>
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<td>-------------------</td>
<td>----------------------------------------------------------------------------------------------------------------------------------------</td>
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<tr>
<td>autocatalytic plating</td>
<td>(German: Beizen, although Dekapieren seems to fit the same description)</td>
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<tr>
<td>PSA</td>
<td>phenyl sulphonic acid</td>
</tr>
<tr>
<td>PI</td>
<td>process-integrated</td>
</tr>
<tr>
<td>polishing, mechanical</td>
<td>smoothing of a metal surface by action of abrasive particles</td>
</tr>
<tr>
<td>pollutant</td>
<td>individual substance or group of substances which can harm or affect the environment</td>
</tr>
<tr>
<td>primary measure / technique</td>
<td>a technique that in some way changes the way in which the core process operates thereby reducing raw emissions or consumptions (see end-of-pipe technique)</td>
</tr>
<tr>
<td>profiles, architectural</td>
<td>substrate and workpieces manufactured to specific cross-sectional dimensions and cut to size for assembly and use in the building construction industry. For example, door and window frames.</td>
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<tr>
<td>PS</td>
<td>presensitised; used in this document with lithographic plates which are surface treated with a photosensitive coating as part of the manufacturing process, and prior to distribution.</td>
</tr>
<tr>
<td>PTFE</td>
<td>polytetrafluoroethylene</td>
</tr>
<tr>
<td>QAC</td>
<td>quaternary ammonium compound</td>
</tr>
<tr>
<td>rack, or jig</td>
<td>frame for suspending workpieces during surface treatment activities. In electrochemical activities, the rack also carries current to the workpieces</td>
</tr>
<tr>
<td>reference conditions</td>
<td>the melting of an electroplated tin coating to give a bright finish</td>
</tr>
<tr>
<td>rectification</td>
<td>Rectification is the reworking of products with reject quality surface treatment to the required specification. In practice, the terms reworking and stripping are sometimes confused and may be used to indicate both activities.</td>
</tr>
<tr>
<td>secondary measure / technique</td>
<td>see end-of-pipe technique</td>
</tr>
<tr>
<td>SME</td>
<td>small and medium enterprise(s), see [61, EC, 2002]</td>
</tr>
<tr>
<td>solubility product</td>
<td>the product of the concentrations of the ions of a dissolved electrolyte when in equilibrium with undissolved substance</td>
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<tr>
<td>specific emission</td>
<td>emission related to a reference basis, such as production capacity, or actual production (e.g. mass per tonne or per unit produced)</td>
</tr>
<tr>
<td>SPC</td>
<td>statistical process control; a process management technique. Regular measurements of process parameters (such as bath temperature, pH, concentration of key process components) are analysed on a continuous basis to ensure compliance within statistical parameters (such as 3 x the standard deviation) to control the quality of the process</td>
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<tr>
<td>SS</td>
<td>suspended solids (content) (in water) (See also TSS)</td>
</tr>
<tr>
<td>strip, stripping</td>
<td>process or solution used for the removal of a coating from a base metal or undercoat. See rectification</td>
</tr>
<tr>
<td>STM</td>
<td>surface treatment of metals and plastics. Refers to topics within the scope of this document</td>
</tr>
<tr>
<td>ENGLISH TERM</td>
<td>MEANING</td>
</tr>
<tr>
<td>-------------</td>
<td>---------</td>
</tr>
<tr>
<td>throwing power</td>
<td>improvement of coating (usually metal) distribution over that given by the primary current distribution on an electrode (usually a cathode) in a given solution, under specified conditions cf macrothrowing power. Note: the term may also be used for anodic processes for which the term is analogous cf: macrothrowing power [101, CEN, 2000]</td>
</tr>
<tr>
<td>TS</td>
<td>total solids (content). Solid content before drying of the material</td>
</tr>
<tr>
<td>TSS</td>
<td>total suspended solids (content) (in water) (See also SS)</td>
</tr>
<tr>
<td>tumbling</td>
<td>bulk processing in barrels in either the presence of abrasives or burnishing shot for the purpose of improving the surface finish</td>
</tr>
<tr>
<td>TWG</td>
<td>technical working group</td>
</tr>
<tr>
<td>US</td>
<td>(i) American English (ii) United States of America</td>
</tr>
<tr>
<td>uv</td>
<td>ultraviolet light</td>
</tr>
<tr>
<td>V.I.</td>
<td>viscosity index</td>
</tr>
<tr>
<td>VOC</td>
<td>volatile organic compounds (includes VOX and non-VOX compounds)</td>
</tr>
<tr>
<td>VOX</td>
<td>volatile organic halogenated compounds</td>
</tr>
<tr>
<td>WHB</td>
<td>waste heat boiler</td>
</tr>
<tr>
<td>WWTP</td>
<td>waste water treatment plant</td>
</tr>
<tr>
<td>wetting agent</td>
<td>substance that reduces the surface tension of a liquid. This allows the liquid to spread more easily and more uniformly on a solid surface</td>
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</table>
2. Common units, measurements and symbols

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<thead>
<tr>
<th>TERM</th>
<th>MEANING</th>
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<tbody>
<tr>
<td>ACkWh</td>
<td>kilowatt-hours (alternating current)</td>
</tr>
<tr>
<td>atm</td>
<td>normal atmosphere (1 atm = 101325 N/m²)</td>
</tr>
<tr>
<td>bar</td>
<td>bar (1.013 bar = 1 atm)</td>
</tr>
<tr>
<td>barg</td>
<td>bar gauge (bar + 1 atm)</td>
</tr>
<tr>
<td>billion</td>
<td>thousand million (10⁹)</td>
</tr>
<tr>
<td>°C</td>
<td>degree Celsius</td>
</tr>
<tr>
<td>cgs</td>
<td>centimetre gram second. A system of measurements now largely replaced by SI.</td>
</tr>
<tr>
<td>cm</td>
<td>centimetre</td>
</tr>
<tr>
<td>cSt</td>
<td>centistokes = 10⁻² stokes</td>
</tr>
<tr>
<td>d</td>
<td>day</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
</tr>
<tr>
<td>GJ</td>
<td>gigajoule</td>
</tr>
<tr>
<td>Hz</td>
<td>hertz</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>ha</td>
<td>hectare (10⁴ m²) (=2.47105 acres)</td>
</tr>
<tr>
<td>J</td>
<td>Joule</td>
</tr>
<tr>
<td>K</td>
<td>kelvin (0 °C = 273.15 K)</td>
</tr>
<tr>
<td>kA</td>
<td>kiloampere</td>
</tr>
<tr>
<td>kcal</td>
<td>kilocalorie (1 kcal = 4.19 kJ)</td>
</tr>
<tr>
<td>kg</td>
<td>kilogram (1 kg = 1000 g)</td>
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<tr>
<td>kJ</td>
<td>kilojoule (1 kJ = 0.24 kcal)</td>
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<tr>
<td>kPa</td>
<td>kilopascal</td>
</tr>
<tr>
<td>kt</td>
<td>kilotonne</td>
</tr>
<tr>
<td>kWh</td>
<td>kilowatt-hour (1 kWh = 3.6 MJ)</td>
</tr>
<tr>
<td>l</td>
<td>Litre</td>
</tr>
<tr>
<td>m</td>
<td>metre</td>
</tr>
<tr>
<td>m²</td>
<td>square metre</td>
</tr>
<tr>
<td>m³</td>
<td>cubic metre</td>
</tr>
<tr>
<td>mg</td>
<td>milligram (1 mg = 10⁻⁹ gram)</td>
</tr>
<tr>
<td>MJ</td>
<td>megajoule (1 MJ = 10⁹ joule)</td>
</tr>
<tr>
<td>mm</td>
<td>millimetre (1 mm = 10⁻³ m)</td>
</tr>
<tr>
<td>m/min</td>
<td>metres per minute</td>
</tr>
<tr>
<td>mmWG</td>
<td>millimetre water gauge</td>
</tr>
<tr>
<td>Mt</td>
<td>megatonne (1 Mt = 10⁶ tonne)</td>
</tr>
<tr>
<td>Mt/yr</td>
<td>megatonnes per year</td>
</tr>
<tr>
<td>mV</td>
<td>millivolts</td>
</tr>
<tr>
<td>MWₑ</td>
<td>megawatts electric (energy)</td>
</tr>
<tr>
<td>MW₉₇</td>
<td>megawatts thermal (energy)</td>
</tr>
<tr>
<td>ng</td>
<td>nanogram (1 ng = 10⁻⁹ gram)</td>
</tr>
<tr>
<td>Nm³</td>
<td>normal cubic metre (101.325 kPa, 273 K)</td>
</tr>
<tr>
<td>Pa</td>
<td>pascal</td>
</tr>
<tr>
<td>ppb</td>
<td>parts per billion</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million (by weight)</td>
</tr>
<tr>
<td>ppmv</td>
<td>parts per million (by volume)</td>
</tr>
<tr>
<td>s</td>
<td>second</td>
</tr>
<tr>
<td>sq ft</td>
<td>square foot (= 0.092 m²)</td>
</tr>
<tr>
<td>St</td>
<td>stokes. An old, cgs unit of kinematic viscosity. 1 St = 10⁻⁶ m²/s</td>
</tr>
<tr>
<td>t</td>
<td>metric tonne (1000 kg or 10⁶ gram)</td>
</tr>
<tr>
<td>t/d</td>
<td>tonnes per day</td>
</tr>
<tr>
<td>trillion</td>
<td>million million (10¹²)</td>
</tr>
<tr>
<td>TERM</td>
<td>MEANING</td>
</tr>
<tr>
<td>------</td>
<td>---------</td>
</tr>
<tr>
<td>t/yr</td>
<td>tonne(s) per year</td>
</tr>
<tr>
<td>V</td>
<td>volt</td>
</tr>
<tr>
<td>vol-%</td>
<td>percentage by volume. (Also % v/v)</td>
</tr>
<tr>
<td>W</td>
<td>watt (1 W = 1 J/s)</td>
</tr>
<tr>
<td>wt-%</td>
<td>percentage by weight. (Also % w/w)</td>
</tr>
<tr>
<td>yr</td>
<td>year</td>
</tr>
<tr>
<td>~</td>
<td>around; more or less</td>
</tr>
<tr>
<td>ΔT</td>
<td>increase of temperature</td>
</tr>
<tr>
<td>μm</td>
<td>micrometre (1 μm = 10^-6 m)</td>
</tr>
<tr>
<td>Ω</td>
<td>ohm, unit of electrical resistance</td>
</tr>
<tr>
<td>Ω cm</td>
<td>ohm centimetre, unit of specific resistance</td>
</tr>
<tr>
<td>% v/v</td>
<td>percentage by volume. (Also vol-%)</td>
</tr>
<tr>
<td>% w/w</td>
<td>percentage by weight. (Also wt-%)</td>
</tr>
</tbody>
</table>
### List of chemical elements

<table>
<thead>
<tr>
<th>NAME</th>
<th>SYMBOL</th>
<th>NAME</th>
<th>SYMBOL</th>
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<tr>
<td>actinium</td>
<td>Ac</td>
<td>mercury</td>
<td>Hg</td>
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<td>molybdenum</td>
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<td>Sb</td>
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<td>As</td>
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<td>At</td>
<td>niobium</td>
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<td>Ba</td>
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<td>Ho</td>
<td>tellurium</td>
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<td>hydrogen</td>
<td>H</td>
<td>terbium</td>
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<tr>
<td>indium</td>
<td>In</td>
<td>thallium</td>
<td>Tl</td>
</tr>
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<td>iodine</td>
<td>I</td>
<td>thorium</td>
<td>Th</td>
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<td>iridium</td>
<td>Ir</td>
<td>thulium</td>
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<td>Lr</td>
<td>uranium</td>
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<td>Pb</td>
<td>vanadium</td>
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<td>ytterbium</td>
<td>Yb</td>
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<td>Y</td>
</tr>
<tr>
<td>manganese</td>
<td>Mn</td>
<td>zinc</td>
<td>Zn</td>
</tr>
<tr>
<td>mendlevium</td>
<td>Md</td>
<td>zirconium</td>
<td>Zr</td>
</tr>
</tbody>
</table>
## ANNEX 1

<table>
<thead>
<tr>
<th>Substance</th>
<th>Classification</th>
<th>Dangerous material reference number (Germany)</th>
<th>Maximum job concentration</th>
<th>TA Luft</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen oxides (NOx)</td>
<td>• fire supporting</td>
<td>TRGS 900</td>
<td>5 mg/m³</td>
<td>350 mg/m³</td>
</tr>
<tr>
<td></td>
<td>• corroding</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen fluorine (HF)</td>
<td>• very toxic</td>
<td>TRGS 900</td>
<td>2.5 mg/m³</td>
<td>3 mg/m³</td>
</tr>
<tr>
<td></td>
<td>• corroding</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen chloride (HCl)</td>
<td>• corroding</td>
<td>TRGS 900</td>
<td>8 mg/m³</td>
<td>30 mg/m³</td>
</tr>
<tr>
<td>Sulphuric acid (SOx)</td>
<td>• corroding</td>
<td>TRGS 900</td>
<td>1 mg/m³</td>
<td>350 mg/m³</td>
</tr>
<tr>
<td>Aerosols with NaOH</td>
<td>• corroding</td>
<td>TRGS 900</td>
<td>2 mg/m³</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Chromium(VI) compounds</td>
<td>• toxic</td>
<td>TRGS 900</td>
<td>0.1 mg/m³</td>
<td>0.05 mg/m³</td>
</tr>
<tr>
<td></td>
<td>• environmentally dangerous</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table A1.1: Emission limits values for surface treatment waste water in Europe (values in mg/l)
(Source: CETS)

### Table A1.2: Air pollutants in surface technology
(Source: UBA)
ANNEX 2

Reference Plants in Germany

Reference plant A

Age of the plant:
20 years

Number of employees in surface treatment:
22 coworkers (18 in production, 4 in the administration)

Type of installation:
In-house shop

Production units of the complete business
- foundry for plastics and zinc (pressure pouring)
- mechanical treatments (pressing and machining)
- paint shop
- plating
- assembly.

Production program for this plating unit:
Barrel plant for small articles with the following process steps:
- hot-degrease
- electrolytically degrease
- cyanide copper plating
- black nickel plating
- half gloss-nickel plating
- chemical nickel plating.

The base materials of the treated workpieces are approximately:
- 60 % die-cast zinc
- 30 % steel
- 10 % brass and copper.

Throughput
- 54000 m²/yr of small articles, involving
  - 5000 operation hours per year
  - 5000 to 10000 barrels/yr
  - workpieces 100000 kg/yr.
Figure A2.A1: Plant A; Process flow diagram

- Loading
- Intermediate holding prior to loading/unloading
- Drier
- Drier
- Hot rinse
- Hot degrease
- Electrolytic degrease
- Electrolytic degrease
- Static rinses
- Flow rinses
- Pickling
- Static rinses
- Flow rinses
- Chemical nickel plating
- Rinses
- Static rinses
- Nickel electroplating
- Static rinse
- Black nickel
- Static rinses
- Flow rinses
- Flow rinses
- Hot degrease
- Hot degrease
- Cyanide copper plating
- Flow rinse
- Static
<table>
<thead>
<tr>
<th>Chemicals used, including trade names</th>
<th>Process step (E)</th>
<th>Quantity or volume of bath</th>
<th>Concentration</th>
<th>Annual consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rivolta BRX</td>
<td>Hot degrease</td>
<td>300 l</td>
<td>50 g/l</td>
<td>220 kg</td>
</tr>
<tr>
<td>Bonder V358</td>
<td>Hot degrease</td>
<td>320 l</td>
<td>100 g/l</td>
<td>325 kg</td>
</tr>
<tr>
<td>Entfetter 2032</td>
<td>Electrical degrease</td>
<td>320 l</td>
<td>150 g/l</td>
<td>450 kg</td>
</tr>
<tr>
<td>Sodium cyanide</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper cyanide</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additive part 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additive part of 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additive part of 5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper anodes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Start solution</td>
<td>Black nickel</td>
<td>250 l</td>
<td>140 ml/l</td>
<td>600 kg</td>
</tr>
<tr>
<td>Lead salt</td>
<td></td>
<td></td>
<td>60 g/l</td>
<td>100 kg</td>
</tr>
<tr>
<td>Additive BP</td>
<td></td>
<td></td>
<td>10 ml/l</td>
<td>400 kg</td>
</tr>
<tr>
<td>Additive 67</td>
<td></td>
<td></td>
<td>5 ml/l</td>
<td>40 kg</td>
</tr>
<tr>
<td>Wetting agents</td>
<td></td>
<td></td>
<td>n/d</td>
<td>n/a</td>
</tr>
<tr>
<td>Nickel sulphate</td>
<td>Semi-bright nickel</td>
<td>320 l</td>
<td>65 g/l (Ni^{2+})</td>
<td>900 kg</td>
</tr>
<tr>
<td>Nickel chloride</td>
<td></td>
<td></td>
<td>25 g/l (Cl^-)</td>
<td>400 kg</td>
</tr>
<tr>
<td>Boric acid</td>
<td></td>
<td></td>
<td>40 g/l</td>
<td>300 kg</td>
</tr>
<tr>
<td>Wetting agent</td>
<td></td>
<td></td>
<td>5 ml/l</td>
<td>90 kg</td>
</tr>
<tr>
<td>Brightener additive</td>
<td></td>
<td></td>
<td>20 ml/l</td>
<td>150 kg</td>
</tr>
<tr>
<td>Nickel anodes</td>
<td></td>
<td></td>
<td>n/a</td>
<td>500 kg</td>
</tr>
<tr>
<td>Solution C-A1</td>
<td>Chemical nickel station 27</td>
<td>320 l</td>
<td>67.2 ml/l</td>
<td>300 kg</td>
</tr>
<tr>
<td>Solution C-A2</td>
<td></td>
<td></td>
<td>67.2 ml/l</td>
<td>150 kg</td>
</tr>
<tr>
<td>Solution C-A3</td>
<td></td>
<td></td>
<td>0.75 ml/l</td>
<td>15 kg</td>
</tr>
<tr>
<td>Regenerate C-A5</td>
<td></td>
<td></td>
<td>18.56 l/MTO</td>
<td>300 kg</td>
</tr>
<tr>
<td>Solution C-A6</td>
<td></td>
<td></td>
<td>n/d</td>
<td>180 kg</td>
</tr>
<tr>
<td>Regenerate C-A8</td>
<td></td>
<td></td>
<td>pH maintenance</td>
<td>230 kg</td>
</tr>
<tr>
<td>Nitric acid</td>
<td></td>
<td></td>
<td></td>
<td>1260 kg</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemicals</td>
<td>Process step</td>
<td>Quantity/volume</td>
<td>Operational</td>
<td>Annual</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>concentration</td>
<td>consumption</td>
</tr>
<tr>
<td>NaOH</td>
<td></td>
<td></td>
<td></td>
<td>20980 kg</td>
</tr>
<tr>
<td>NaOCl</td>
<td></td>
<td></td>
<td></td>
<td>38000 kg*</td>
</tr>
<tr>
<td>HCl</td>
<td></td>
<td></td>
<td></td>
<td>2082 kg</td>
</tr>
<tr>
<td>Amidosulphonic acid</td>
<td></td>
<td></td>
<td></td>
<td>700 kg</td>
</tr>
<tr>
<td>Flocculating agents</td>
<td></td>
<td></td>
<td></td>
<td>540 kg</td>
</tr>
<tr>
<td>Lime, solid</td>
<td></td>
<td></td>
<td></td>
<td>175 kg</td>
</tr>
</tbody>
</table>

* NaOCl consumption 1 June 99 was only 9770 kg, since nitrite treatment was changed over to amidosulphonic acid

Table A.2.A1: Input materials for Plant A
<table>
<thead>
<tr>
<th>Process step</th>
<th>Material</th>
<th>Refill amounts</th>
<th>Refill cycle</th>
<th>Analytic control cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot degrease</td>
<td>Rivolta BRX</td>
<td>4.4 kg/w</td>
<td>Weekly</td>
<td>Weekly</td>
</tr>
<tr>
<td>Hot degrease</td>
<td>Bonder V358</td>
<td>6.3 kg/w</td>
<td>Weekly</td>
<td>Weekly</td>
</tr>
<tr>
<td>Electrical</td>
<td>Entfetter 2032</td>
<td>9 kg/w</td>
<td>Weekly</td>
<td>Weekly</td>
</tr>
<tr>
<td>Cyanide copper</td>
<td>Sodium cyanide copper</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cyanide</td>
<td>1.2 kg/d</td>
<td>Daily</td>
<td>Daily</td>
</tr>
<tr>
<td></td>
<td>Additive part 3</td>
<td>360 g/d</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Additive part 4</td>
<td>120 g/d</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Additive part 5</td>
<td>120 g/d</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Copper anodes</td>
<td>3.6 kg/d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Black nickel</td>
<td>Start solution</td>
<td>2.4 kg/d</td>
<td>Daily</td>
<td>Daily</td>
</tr>
<tr>
<td></td>
<td>Lead salt</td>
<td>400 g/d</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Additive BP</td>
<td>1.2 kg/d</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Additive 67</td>
<td>160 g n.b.*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Semi-bright nickel</td>
<td>Nickel sulphate nickel</td>
<td>18 kg/w</td>
<td>Weekly</td>
<td>Weekly</td>
</tr>
<tr>
<td></td>
<td>Chloride</td>
<td>8 kg/w</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Boric acid</td>
<td>6 kg/w</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wetting agent</td>
<td>1.8 kg/w</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gloss additive</td>
<td>3 kg/w</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nickel anodes</td>
<td>10 kg/w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical nickel</td>
<td>Solution C-A1</td>
<td>1.2 kg/d</td>
<td>Daily</td>
<td>Daily</td>
</tr>
<tr>
<td></td>
<td>Solution C-A2</td>
<td>600 g/d</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solution. C-A3</td>
<td>60 g/d</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Regenerate C-A5</td>
<td>1.2 kg/d</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solution. C-A6</td>
<td>720 g/d</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Regenerate C-A8</td>
<td>920 g/d</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nitric acid</td>
<td>5 kg/d</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table A2.A2: Plant A; Service life time of the feeds, cycles of monitoring and refill of chemicals

Substitution for problematic materials used

Cyanide-free systems for the copper plating of die-cast zinc materials are not available.

Attempts for the substitution of sodium hypochlorite (AOX problem) with the cyanide oxidation by employment of a UV-radiation supported oxidation failed. In order to keep the quantity of NaOCl used low, the nitrite treatment was changed over to reduction with amidosulphonic acid, which results in a saving of approximately 50 % of the sodium hypochlorite solution quantity previously used.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Input materials</th>
<th>Concentration (g/l)</th>
<th>Temperature (°C)</th>
<th>Service life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot degrease</td>
<td>Rivolta BRX</td>
<td>50</td>
<td>60</td>
<td>1 month</td>
</tr>
<tr>
<td>Hot degrease</td>
<td>Bonder V358 M</td>
<td>100</td>
<td>60</td>
<td>1 month</td>
</tr>
<tr>
<td>Electrolytic degrease</td>
<td>Entfetter 2032</td>
<td>150</td>
<td>60</td>
<td>3 months</td>
</tr>
<tr>
<td>Cyanide</td>
<td>NaCN</td>
<td>25</td>
<td>50</td>
<td>No change</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>55</td>
<td></td>
<td>No change</td>
</tr>
<tr>
<td>Black nickel</td>
<td>Beginning solution lead salt</td>
<td>7 60</td>
<td>60</td>
<td>No change</td>
</tr>
<tr>
<td>Semi-bright nickel</td>
<td>Ni²⁺</td>
<td>65</td>
<td>60</td>
<td>No change</td>
</tr>
<tr>
<td></td>
<td>Cl⁻</td>
<td>25</td>
<td></td>
<td>No change</td>
</tr>
<tr>
<td></td>
<td>H₃BO₃</td>
<td>40</td>
<td></td>
<td>No change</td>
</tr>
<tr>
<td>Chemical nickel</td>
<td>Ni²⁺</td>
<td>4.7</td>
<td>90</td>
<td>2 months</td>
</tr>
<tr>
<td></td>
<td>reducing agent</td>
<td>24.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table A2.A3: Plant A; Service life of the process baths
Annexes

Measures taken for the extension of bath service life time

The service life of nickel and copper electrolytes - with the exception of chemical nickel solutions - are practically infinite, because the drag out is sufficiently high that the impurities do not achieve a harmful concentration. Special bath care measures are not necessary. Impurities are removed from the black nickel and electrolytic solution electrolytic solutions by filtering in a bypass system. For the remaining feeds, no special care measures are used; the service life times obtained are regarded as sufficient.

Measures for the reduction of the drag out

The barrels for this line are specifically equipped with *(equipment type to be clarified)*, in order to achieve better draining of the liquid in the drum. After lifting out from the bath the barrel is turned, in order to make better draining off possible. The general dripping off times are fixed to 5 seconds, with the exception of the copper and nickel plating tanks, where the time is 15 seconds.

The plant runs a wide variety of programmes. As a consequence, the dripping-off time for pre-treatments and rinses is limited to 5 seconds.

Feedback of dragged-out electrolytes

The feedback of drag-out electrolytes takes place in different ways:

- evaporation losses of the electrolytes are made-up by topping-up from the static rinses
- pre-dipping (‘Eco’ rinse) in the static rinse after the copper, black and semi-bright nickel returns drag-out to the bath. Chemical nickel electrolyte cannot fed back meaningfully, since the simultaneous build-up of impurities would reduce the service life time of the solution drastically

Evaporation systems for the rinse water for the feedback of out-dragged electrolytes are not used in this company.

Rinsing technology

Generally, the rinsing system used is "static rinse / flow rinse”, but with only a two-stage rinsing technology, where the flow rinse is led across ion exchangers in cycle. Since the workpiece throughput is to only 1 - 2 drums per hour and drag-out is only small, a very small amount of waste water results. The static rinses are renewed only weekly, and their accumulated waste water amounts to approximately 1.1 m³/week; a small amount of waste water from the eluate of the ion exchangers is added to this.

The ion exchanger plant for rinse water of the flow rinses is operated as a central plant for all the surface treatment units of the enterprise. At present, 17 rinses are discharged in a cycle; five of them from the described copper/nickel unit. The ion exchanger plant has an output of 20 m³/h and consists of exchanger columns each with 500 l resin contents. Every 7 working days the cation and of an anion exchanger are regenerated. This gives an effluent of 8 m³/week.

The static rinse after copper plating is led in a bypass across an electrolysis cell at 150 l/h, in order to recover the copper present. The service life of the rinse is increased to approximately 6 months, at the same time 120 kg/yr of copper are recovered electrolytically. The energy consumption for the electrolysis cell amounts to about 950 kwh annually.
Waste water treatment

There is a central waste water treatment plant for all the production areas, so the copper/nickel plant represents only a small part of the total spectrum of waste water treated.

The nickel/ferrous-cyanide containing acid or alkaline waste waters are caught and treated separately.

The waste water treatment plant consists of two static treatment tanks of 10 m$^3$ each. The usual treatment exists in the separate treatment of the Cyanide and nitrite-containing streams are mixed afterwards with the remaining concentrates for neutralization and heavy metal precipitation. For post – treatment, the treated water is led over gravel filters and selective ion exchangers before discharge to the municipal waste water system.

The waste water streams are:

- 10 m$^3$/week cyanide containing streams
- 1.5 m$^3$/week nickel/ferrous containing streams
- 20 m$^3$/week acid/alkaline streams as well as
- 5.7 m$^3$/week eluate (ion exchange eluate?) on the average.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Limit values</th>
<th>Internal control measurements</th>
<th>External analysis 8.7.98</th>
<th>External analysis 2.3.99</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>0.5 mg/l</td>
<td>0.13 mg/l</td>
<td>0.63 mg/l</td>
<td>0.18 mg/l</td>
</tr>
<tr>
<td>Nickel</td>
<td>1.0 mg/l</td>
<td>0.13 mg/l</td>
<td>0.20 mg/l</td>
<td>0.34 mg/l</td>
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<tr>
<td>Zinc</td>
<td>2.0 mg/l</td>
<td>0.24 mg/l</td>
<td>0.15 mg/l</td>
<td>0.05 mg/l</td>
</tr>
</tbody>
</table>

Table A2.A4: Plant A; Emission values for heavy metals

Heavy metals loads in the waste water

With an average of 35 – 40 m$^3$ waste water per week, and average values of 0.25 mg/l Cu, 0.25 mg/l Ni and 0.15 mg/l Zn, there is an annual heavy metal load of 440 g to 500 g copper, 440 to 500 g nickel and 260 to 300 g zinc.

Waste amount

Waste is mainly with 7 tonnes of electroplating sludge produced annually from the waste water treatment. Some alkaline concentrates which are also externally treated. There are also small quantities of absorption and filter materials.

<table>
<thead>
<tr>
<th>Type of waste</th>
<th>European Waste Catalogue</th>
<th>Yearly quantity</th>
<th>Disposal or recycling</th>
<th>Costs including transport</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludges containing dangerous substances</td>
<td>11 0109</td>
<td>7.02 t</td>
<td>Pyrometallurgical nickel recycling</td>
<td>€ 225 per tonne</td>
</tr>
<tr>
<td>Caustic solutions</td>
<td>11 01 07</td>
<td>2.0 t</td>
<td>Chemico-physical treatment</td>
<td>€ 450 per tonne</td>
</tr>
<tr>
<td>Absorption and filter materials with dangerous impurities</td>
<td>15 02 02</td>
<td>0.15 t</td>
<td>Chemico-physical treatment</td>
<td>€ 420 per tonne</td>
</tr>
</tbody>
</table>

Table A2.A5: Plant A; Waste quantities
Annexes

The electroplating sludge from the waste water treatment is used completely as a secondary raw material in a pyrometallurgical recycling plant.

### Electroplating sludge

<table>
<thead>
<tr>
<th>Cations</th>
<th>Content</th>
<th>Anions</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>55.1 g/kg</td>
<td>Sulphur</td>
<td>10.7 g/kg</td>
</tr>
<tr>
<td>Iron</td>
<td>37.3 g/kg</td>
<td>Chloride</td>
<td>9.1 g/kg</td>
</tr>
<tr>
<td>Nickel</td>
<td>49.5 g/kg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>26.9 g/kg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>38.1 g/kg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Titanium</td>
<td>1.0 g/kg</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Trace components**

<table>
<thead>
<tr>
<th>Trace components</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>109.9 mg/kg</td>
</tr>
<tr>
<td>Manganese</td>
<td>33.3 mg/kg</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>458.1 mg/kg</td>
</tr>
<tr>
<td>Barium</td>
<td>79.7 mg/kg</td>
</tr>
<tr>
<td>Tungsten</td>
<td>253.9 mg/kg</td>
</tr>
<tr>
<td>Lead</td>
<td>319.3 mg/kg</td>
</tr>
</tbody>
</table>

Table A2.A6: Plant A; Metal constituents of electroplating sludge

### Cost considerations

**The capital outlays amounted to**

- € 150000 for the barrel plant
- € 125000 for the waste water treatment plant
- € 15000 for the electrolytic copper recovery from the static rinse
- € 4000 for a filter unit for the cleaning of the feedwaters

**Maintenance and maintenance cost amount to**

- € 5000 annually for the barrel plant,
- € 2500 annually for the effluent treatment

The staff expenditure for the shift operation amounts annually to € 45000.

**View of the economics of the electrolytic copper recovery plant**

The total costs of the plant are calculated roughly from the following factors, where the energy costs are set at € 0.08/kWh.

- Capital costs = 8 % € 600/yr
- Maintenance/maintenance (portion measured) € 300/yr
- Energy expenditure = 950 KW x DM 0.16/kWh = € 76/yr

**Sum of the annual costs:** € 976/yr

These costs savings arise from the saved quantity of water (smaller discharge of the static rinse), the saved waste production, proceeds of the recycled copper and the reduced use of neutralisation chemicals. Unit savings are:

- Fresh water € 3/m³
- Proceeds for the copper € 0.9/kg,
- 50 % NaOH € 0.23/kg
Savings per year are:

- saved fresh water = 10 m³/a x € 3/m³ = € 30/yr
- proceeds copper = 90 kg/yr x € 0.9/kg = € 78.8/yr
- saved precipitation chemicals (NaOH) = 133.3 kg: 0.76 kg/l x € 23/l = € 33.5/yr
- saved disposal costs of the sludge = 0.345 t x € 275/t = € 95/yr

Sum of annual savings $E$ = € 237/yr

Since the yearly costs exceed annual savings, there is no economic driver for this technique. This is already known by the operator.

**Estimation of inputs and outputs**

For enterprise A the following figures can be estimated from the available data:

Input nickel quantity = about 1023 kg/yr, consisting of

- nickel sulphate 900 kg/yr, according to 341.5 kg of Ni/yr
- nickel chloride 400 kg/yr, according to 181.2 kg of Ni/yr
- nickel anodes 500 kg/yr

![Figure A2.A2: Plant A; Nickle inputs](image1)

Emitted nickel quantities = 347 kg/yr, 34 % of the input material used, consisting of

- 0.5 kg/yr in waste water
- 346.5 kg/yr as waste

![Figure A2.A3: Plant A; Nickle outputs](image2)
Input copper quantity = 1065 kg/yr, consisting of:

- copper cyanide 300 kg/yr, equates to 165 kg of Cu/yr
- copper anodes 900 kg/yr

Emitted copper quantities = approx. 189 kg/yr, equates to 18% of the material used, consisting of:

- 0.5 kg/yr in waste water
- 188.3 kg/yr in wastes

As all the metal containing waste is recycled in metallurgical plants, the overall losses of metals are minimized. The only complete losses from the system are those emissions in the waste water.
Reference plant C

Age of the plant:
No data

Type of the plans:
In-house shop

Number of employees:
180

Production units of the business
- foundry for plastics (injection moulding) and zinc (pressure pouring)
- mechanical treatment
- galvanizing
- assembly

Production processes in the plating unit
- copper plating
- nickel plating
- chromium plating

with all necessary pre- and post- treatment processes

Basic material:
Zinc die casting and brass

Throughput:
No data available

Volume of the treatment vats
- metal stripping 2.2 m$^3$
- pre- degreasing 3.2 m$^3$
- degreasing 4.8 m$^3$
- electrolytic degreasing 7.2 m$^3$
- acid copper plating vat I 5.9 m$^3$
- acid copper plating vat II 14.1 m$^3$
- nickel plating 13 m$^3$
- chromium-plating 3.8 m$^3$

The sum of the process baths is more largely than 30 m$^3$; the plant is therefore subject to approval under the IPPC directive

Input of material
See plant data
Figure A2.C1: Plant C; Process flow diagram

Substitution of problematic material used

Methanol was used as a brightener with the acid copper plating bath, but was replaced due to its toxicity (with?). Cyanides cannot be replaced when copper plating die-cast zinc parts (because acid zinc plating attacks the substrate?). The main part of the cyanide in the waste water is electrolytically oxidised, which minimises the use of the sodium hypochlorite. However, sodium hypochlorite cannot be replaced totally, and is still used with the cyanide-containing rinse water.

Measures for the reduction of the drag out

Low concentrations of the process solutions are generally used. The draining times are up to 10 seconds, which achieves relatively good draining off and thus smaller losses result.

Measures for extension the service life time

Pickling, copper and nickel electrolytes are filtered, as are the two pre rinses, whose service life could be increased thereby to the six-fold.

The copper electrolytes are treated with activated charcoal, which achieves an almost unlimited service.
Rinsing technology

The rinsing technology is generally three step cascade. In addition the rinse waters are recycled via ion exchangers.

Feedback of out dragged electrolytes

There is automated feedback of rinse water into the process solutions to a pre-determined working level. This is with all degreasing solutions and the cyanide copper, satin nickel and chromium electrolytes

A pre-dip (‘Eco’ rinse type) is used with the bright nickel electrolyte, achieving about 50 % recovery.

Plant Data

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant throughput:</td>
<td>25000 racks/yr</td>
</tr>
<tr>
<td></td>
<td>40000 to 50000 m² treated surface/yr</td>
</tr>
<tr>
<td>Anode material:</td>
<td>nickel (no data)</td>
</tr>
<tr>
<td></td>
<td>copper 750 kg/yr</td>
</tr>
<tr>
<td>Chromic acid:</td>
<td>2400 kg/a, which is 1248 kg Cr/yr</td>
</tr>
</tbody>
</table>
The electroplating sludge has the following composition:

- **Dry residue**: approximately 50%
- **Copper**: 4.3 g/kg
- **Nickel**: 14.8 g/kg
- **Iron**: 17.5 g/kg
- **Zinc**: 2.2 g/kg
- **Calcium**: 112.5 g/kg
- **Chromium**: 44.5 g/kg
The concentrations of the heavy metals in the waste water effluent are

<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>0.25</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.2</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.10</td>
</tr>
<tr>
<td>Iron</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Metal balances:

a) Copper
- Input copper quantity (anode material): 750 kg/yr
- Copper discharge with the waste water treatment sludge: 114 kg/yr
- Copper discharge with the waste water: 1.04 kg/yr

About 15.3 % of the copper is lost from the process (84.7 % usage); 0.14 % of the total is lost on the waste water.

b) Nickel
- Input nickel quantity (anode material): 10815 kg/yr
- Nickel discharge with the waste water treatment sludge: 394 kg/yr
- Nickel discharge in the waste water: 0.83 kg/yr

Of the input nickel quantities (10815 kg), 703.1 kg are emitted annually mainly as waste. This corresponds to 96.3 % use. The nickel portion emitted with the waste water amounts to <0.01 % of the input quantity.

c) Chromium
- Input chromium quantity (as H2CrO4): 1248 kg/yr
- Chrome discharge with the waste water treatment sludge: 336 kg/yr
- Chrome discharge with the waste water: 0.4 kg/yr

About 27% of the input chromium quantity is emitted (again, mainly as waste), with 73 % used. The waste water route contributes 0.32 %.

Overall
The plating sludge is entirely used as secondary raw material in metallurgical processes. The loss of input metals from the overall system is <1 % (actually 0.018 %), and this is as emissions in the waste water.
Reference plant E

Age of the plant
20 years; last modernisation more than 7 years ago.

Type of the plant
In-house shop.

Production program of the entire enterprise
- zinc plating and chromate finishing of steel parts
- copper plating, nickel plating and tinning of steel parts
- copper plating, nickel plating and tinning of non-ferrous metal parts
- silver plating of non-ferrous metal parts

Production program of the described plating unit
The plating unit considered is an electroplating unit, which consists of the following process steps: Hot degrease, pickling, electrolytically degreasing, cyanide electroplating, lightening (?), blue chromating.

Throughput
63000 m²/yr at 2400 working hours per year.
### Annexes

#### Table A2.E.1: Plant E; Input materials

<table>
<thead>
<tr>
<th>Chemicals used including brand names</th>
<th>Process step</th>
<th>Quantity</th>
<th>Concentration used</th>
<th>Annual consumption</th>
<th>Annual consumption in €</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 3 cleaner</td>
<td>Hot degreasing</td>
<td>2500 l</td>
<td>50 g/l</td>
<td>192 kg</td>
<td>480</td>
</tr>
<tr>
<td>Hydrochloric acid, tensides</td>
<td>Pickle:</td>
<td>2500 l</td>
<td>250 g/l</td>
<td>21354 kg</td>
<td>3203</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25 g/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-acid</td>
<td>Electrical degreasing</td>
<td>1250 l</td>
<td>130 g/l</td>
<td>1796 kg</td>
<td>4040</td>
</tr>
<tr>
<td>Zinc anodes zinc cyanide</td>
<td>Zinc electrolyte</td>
<td>8000 l</td>
<td>Zn: 20 g/l 40 g/l</td>
<td>4036 kg</td>
<td>5400</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>85 g/l</td>
<td>150 kg</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>525 kg</td>
<td>920</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1415 kg</td>
<td>481</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>Clarification</td>
<td>1000 l</td>
<td>29 g/l</td>
<td>1000 kg</td>
<td>250</td>
</tr>
<tr>
<td>Tridur Zn blue</td>
<td>Blue chromate finishing</td>
<td>1100 l</td>
<td>70 ml/l</td>
<td>2370 kg</td>
<td>7110</td>
</tr>
<tr>
<td>Sum:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caustic soda 50 %</td>
<td>Effluent treatment system</td>
<td>--</td>
<td>--</td>
<td>120300 kg</td>
<td>36090</td>
</tr>
<tr>
<td>lime hydrochloric acid 30 %</td>
<td></td>
<td></td>
<td></td>
<td>19000 kg</td>
<td>2850</td>
</tr>
<tr>
<td>sodium hypochlorite</td>
<td></td>
<td></td>
<td></td>
<td>40000 kg</td>
<td>7000</td>
</tr>
<tr>
<td>ferrous sulphate</td>
<td></td>
<td></td>
<td></td>
<td>19000 kg</td>
<td>5130</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3000 kg</td>
<td>450</td>
</tr>
<tr>
<td>Sum total:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>51700</td>
</tr>
<tr>
<td>Proportional</td>
<td>23.5 % of the total system</td>
<td></td>
<td></td>
<td>12150</td>
<td></td>
</tr>
</tbody>
</table>

#### Substitution of problem materials used

Due to the current safe design and operation of the plant, no substitution of input materials, e.g. cyanides, is planned at present.

#### Table A2.E.2: Plant E; Service life of the solutions - cycle of the monitoring and refill of chemicals

<table>
<thead>
<tr>
<th>Material (E)</th>
<th>Refill cycle</th>
<th>Analytic control cycle</th>
<th>Service life time</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 3 - cleaners</td>
<td>12/year</td>
<td>2/month</td>
<td>52 weeks</td>
</tr>
<tr>
<td>Hydrochloric acid 30 %</td>
<td>20/year</td>
<td>1/week</td>
<td>17 weeks</td>
</tr>
<tr>
<td>Non-acid</td>
<td>3/day</td>
<td>1/week</td>
<td>17 weeks</td>
</tr>
<tr>
<td>Zn NaCN NaOH</td>
<td>1/week</td>
<td>1/week</td>
<td>infinitely</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>1/day</td>
<td>1/day</td>
<td>1 week</td>
</tr>
<tr>
<td>Tridur Zn-blue</td>
<td>continuously</td>
<td>1/week</td>
<td>2 weeks</td>
</tr>
</tbody>
</table>

#### Measures for extension the service life time

The service life of the zinc electrolyte is practically infinite, as the drag out is sufficiently high that the impurities do not achieve a concentration that deteriorates plating quality. Special bath care measures are not necessary.

The hot degreasing solutions are released by oil separator (skimmer) from fats, oils and other pollutants.

The chromating solution is not regenerated.
Measures for the reduction of the drag out

Spray rinse over hot and electrolytic degrease tanks.

Feedback of out-dragged electrolytes

- partial direct feedback of contents of the static rinse into the process tanks
- pre-dip in the static rinse of the zinc plating stage; resulting to a 50 % feedback of dragged out electrolytes.

Rinsing technology

See flow sheet.

Waste water treatment

See flow sheet.

The central waste water treatment plant for Enterprise E
The portion attributable to the described zinc plating unit is 23.5 %

Figure A2.E2: Plant E; Waste water treatment plant flow diagram
The waste water of this plating unit is treated together with the waste water from other surface treating unit of the enterprise. The fraction amounts to 23.5% of the total waste water of the whole plant.

**Special isues in waste water treatment**

**Electrolysis cell for the oxidation of cyanide and the recycling of zinc and copper from rinse waters**

An electrolytic cell is used for the treatment of the cyanide-containing rinse waters coming from the copper- and zinc plating units, in order to oxidise the cyanide-ion (at the anode) and to separated the metals (at the cathode). This greatly reduces the use of sodium hypochlorite and therefore the formation of AOX. Anodic oxidation of the cyanide-containing solutions achieves a cyanide concentration of less than 100 mg/l.

At the cathode 331 kg copper and 183 kg of zinc are separated; at the anode 571 kg of cyanide is oxidised.

For cyanide oxidation and metal reduction 6753 kWh/yr at are used. For this reaction current costs of 0.9 €/kg cyanide oxidised assuming a price of 0.075 €/kWh (the metal utilisation is not considered here). The average concentrations of the cyanide input stream is 3.7 g/l and 0.018 g/l in the output stream.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Emission concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Limit values</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.5 mg/l</td>
</tr>
<tr>
<td>Cyanide</td>
<td>0.2 mg/l</td>
</tr>
<tr>
<td>Zinc</td>
<td>2.0 mg/l</td>
</tr>
</tbody>
</table>

Table A2. E.3: Plant E; Waste water emission values for heavy metals

**Loads of heavy metals**

With a water usage of 3036 m³ per year and metal concentrations of 1 mg/l Zn and 0.3 mg/l Cr respectively, there is an annual heavy metal load of 3036 g zinc and 910 g chromium released to the sewer.

**Waste-amount**

The quantity of waste from the described plating unit is 10 t/yr (water content 65%).

<table>
<thead>
<tr>
<th>Type of refuse</th>
<th>European waste catalogue number</th>
<th>Yearly proportional quantity</th>
<th>Utilisation/disposal type</th>
<th>Costs (including transport)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanide-free waste, containing chromium</td>
<td>110109</td>
<td>10 t</td>
<td>Landfill</td>
<td>175 € per tonne</td>
</tr>
</tbody>
</table>

Table A2.E.4: Plant E: Waste-produced

**Refuse disposal**

The waste is disposed of at a special landfill. It has a zinc content of 40 g/kg dry body.
Costs considerations

The annual costs of the entire galvanic shop amounts to 2.3M€ as:

- 55% fixed costs of plant writing-off, building, personnel reallocation
- 35% variable costs (materials for processes, waste water, maintenance, energy)
- 10% direct labour costs: four persons for serving the plating units; related to the zinc portion of the zinc drum plant 0.67 man-years are calculated with costs per worker of 56500 €/a

Personnel expenditure for maintenance of the entire plants and the electrolytes (1.2 persons) as well as operation and maintenance of the effluent treatment (1 person) is contained in the fixed costs.

The capital outlays for the "anodic oxidation" amounted to 30000 € (at 1993 costs); in the case of 10 a year old writing-off at 3000 €/yr, the portion of the zinc-containing rinses amounts to 18%, so that there is 501 € annual amortisation costs for this plan (is this correct?).

The cost of electricity is set at 0.075 €/kWh. The costs of fresh water (drinking water) from public supply amount to 1 €/m³ and for the discharge of waste water into the local municipal sewerage system 1.50 €/m³.

Estimated metal loss/ efficiency

For enterprise E the following typical figures can be derived from the available data:

- zinc used on workpieces = 80.6%
- total zinc input = 4036 kg/yr, consisting of zinc metal 99.95 % Zn
- emitted zinc quantity = 786 kg/yr, which is 19.4 % of the material used, consisting of:
  - 3 kg/yr to waste water (<0.1 %)
  - 600 kg/yr over the waste to removal (14.9 %)
  - 183 kg/yr metal recuperated by electrolysis (4.5 %).

\[
\begin{array}{|c|}
\hline
\text{Waste water emission (<0.1)} \\
\text{Waste emission (19.4)} \\
\text{Used on workpieces (80.6)} \\
\hline
\end{array}
\]

Figure A2.C3: Plant C zinc emissions

<table>
<thead>
<tr>
<th></th>
<th>Specific costs €/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plating process chemicals</td>
<td>0.28 (with anodes 0.35)</td>
</tr>
<tr>
<td>Chemicals for waste water treatment</td>
<td>0.19</td>
</tr>
<tr>
<td>Electricity for anodic oxidation</td>
<td>0.0015</td>
</tr>
<tr>
<td>Water purchase</td>
<td>0.005</td>
</tr>
<tr>
<td>Waste water</td>
<td>0.0125</td>
</tr>
<tr>
<td>Waste for removal</td>
<td>0.03</td>
</tr>
<tr>
<td>Manpower for plant operation</td>
<td>0.61</td>
</tr>
<tr>
<td>Manpower for maintenance</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Table A2.E5: Plant E; Unit costs per m²