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Integrated Pollution Prevention and Control

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

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Many solutions have a narrow operating range, and cannot be operated outside of these. Other optimal operating factors may have to be considered, such as processing time.
In anodising, the heat of spent seal solutions can be used to heat the water used for a new sealing process, using a heat exchanger or piping the incoming cold water through the hot seal solution.

In automatic lines, floating spheres may be carried to the rinsing tanks by barrels or by components. The spheres may block pipes and cause malfunctions for pumps and transport tubes. This can be limited to some extent by the choice of size of spheres and installing simple coarse screens to critical pipework and equipment. The spheres can cause tidiness problems in the workplace by being carried outside of the tanks. The system can be used in manual lines, and in automatic plants.

Economics
Applicable to all heated solutions.

Floating spheres are cheap.

Capital investment for sophisticated heat-exchange systems may be high.

Driving force for implementation
Cost saving and process quality control.

Example plants
Exhall Plating Ltd, Coventry, UK; SGI, Plaisir, France, Sikel N.V., Genk, Belgium

Reference literature
[3, CETS, 2002, 18, Tempany, 2002, 165, Tempany, 2004] [85, EIPPCB,] [124, Germany, 2003] [118, ESTAL, 2003] [129, Spain, 2003].

4.4.4 Cooling of process solutions

4.4.4.1 Water cooling systems

Description
Once-through cooling systems pass cold water through the cooling system once, and then discharge the water. Water sources are described in Section 4.4.5.1. Open cooling systems recycle the water through an open cooling tower. Closed systems use a secondary system, such as refrigeration, for cooling the recirculating coolant in the primary system. These are described in Section 2.12.1.3 and more information is given in the BREF on industrial cooling systems

Water from once-through cooling systems may be re-used to utilise the heat gained, for instance in rinsing prior to drying. The water may also be used in processes, with treatment as required, see Section 4.4.5.1. Also, water used in the processes for rinsing may be used for cooling prior to discharge.

Achieved environmental benefits
Using closed cooling systems saves water.

Cross-media effects
There may be energy associated with pumping the water in any system, and increased energy consumption for refrigerated systems.

Once-through systems may deplete limited local resources, may become contaminated by chemicals and the heat content may have an impact on local ecosystems.

Open cooling systems can be the source of legionella infections. Proper design, cleaning maintenance and water treatment combined can generally minimise legionella counts but cannot be expected to eliminate them entirely in every system. Therefore, the location and design of cooling systems must also aim at minimising the distribution and transmission of legionella.

Operational data
It is not good practice to use:

- discharge cooling water through waste water treatment plant, unless treatment is necessary (such as to remove anti-corrosion additives)
- use cooling water to dilute process waste waters.

Applicability
Closed recirculatory systems are widely used. The type of cooling system may be dependent on water availability and local climatic conditions.

Where water resources locally allow, once-through systems may be used, particularly where the water can be returned to the source.

Economics
Once-through water systems are only likely to be economic where the cost of the incoming water is very low, including any charges or taxes for extraction, etc. However, they may be cost-effective where the water is re-cycled or re-used elsewhere in the installation, see Section 4.4.5.1. Water used in the processes for rinsing may be used for cooling prior to discharge, although for most situations and if other water saving techniques are in use, there is insufficient water from such sources to provide sufficient cooling.

Driving force for implementation
Closed systems can offer cost savings in water usage for once-through systems and the cost of maintenance of open cooling systems.

Example plants
Sikel N.V., Genk, Belgium, Exhall Plating, Coventry, UK, Industria Galvanica Dalla Torre Ermanno e Figli SpA, Fontane di Villorba, Italy (re-use of heated water).

Reference literature
[18, Tempany, 2002, 85, EIPPCB, , 159, TWG, 2004] [121, France, 2003] [159, TWG, 2004](personal communication, RIZA and Infomil NL).

4.4.4.2 Evaporation

Description
Evaporation is widely used to remove excessive energy from vats by evaporating water from the process solution and maintaining the process temperature at the desired level. It can be optimised by using an air agitation (see Section 4.3.4), an evaporation system or evaporator, and may be used with cascade rinsing systems to conserve materials, minimise discharges, and can assist with closing loops for materials (see Sections 2.7.4, 2.7.5, 4.7.11.2, 4.7.11.3 and 4.16.12).

Achieved environmental benefits
Evaporation combines process cooling with drag-out recovery and usually forms part of any closed loop or zero discharge systems.

Cross-media effects

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]

4.4.5.3 Rinsing stages using recycled water

Description
The technique may be regarded as an extension of the integrated treatment system (widely known as the Lancy system). Water from a rinsing stage is re-used in another rinsing stage, where the chemical or physical characteristics acquired in the first stage can be exploited in the second stage without requiring any additional treatment.

As an example, in a nickel electroplating installation water from the rinsing stage after the nickel plating process may be used again in a sequence of several rinsing stages:

1st: after cool electrolytic degreasing, then
2nd: after pickling, and eventually
3rd: after heated chemical pre-degreasing

Achieved environmental benefits
Reduction of water consumption up to 40 %.
Reduction of chemicals used to modify the pH of water after the rinsing stages.
Reduction of chemicals used to neutralise the water before to channel it into the treatment plant.

Operational data
The technique applies only to processes free of cyanides. It requires the laying of an appropriate network of pipes and pumps.

Applicability
The technique may apply to new plants. It can be applied to existing plants, depending on local circumstances.

Economics
No data available

Driving forces for implementation
Saving of water and chemicals.

Example plants
Industria Galvanica Dalla Torre Ermanno e Figli SpA, Fontane di Villorba, Italy.

Reference literature
Lancy Laboratories Inc., Zelienople, Pa (US) quoted in Bertorelle E. (1974) – Trattato di Galvanotecnica. 4th Edition, Vol. II, Hoepli Ed. Milano, pp. 693 - 697.

Driving force for implementation
Only large scale techniques for hard chromium plating, and some higher specification decorative finishes. Self-passivating in unplated areas.

Example plants
Widely applied in nearly 3000 installations worldwide.
Closed loop operation (with preceding closed loop nickel and copper) in Merrydale Industries Ltd, Wednesbury, UK.

Reference literature
[108, NEWMOA, 2003, 147, CETS, 2004] [125, Ireland, 2003, 147, CETS, 2004]

4.9.8.2 'Cold chromium' – hexavalent process

Description
A new technique using 'cold chromium' has been put into production in 2000 in an Italian plant. The temperature of the processing bath with Cr(VI) is kept at about 18 – 19 °C by a refrigeration system (instead of 25 – 30 °C). At this temperature, the concentration of Cr(VI) in the process solution may be reduced by about 50 %. The quality of plating is the same.

Achieved environmental benefits
Minimisation of hexavalent chromium released.
Minimisation of evaporation of process solution evaporation.
Less energy used in the process.
Reduction of exposure to workers.
Reduction of water consumption.
Less waste water treatment required and less sludge produced.

Cross-media effects
Additional energy required for refrigeration. It is not clear how this compares with the energy savings in the process.

Operational data
Less concentrated solutions require a longer time for processing.
Better quality because of better throwing power.
No white edges.

Applicability
The technique may only be suitable for application in a new plant.

Driving forces for implementation
As introduction to Section 4.9.

Example plants
Industria Galvanica Dalla Torre Ermanno e Figli SpA, Fontane di Villorba, Italy.

Reference literature
[112, Assogalvanica, 2003]

4.9.8.4 Trivalent chromium sulphate electroplating process

Description
For decorative nickel-chromium process. The process is carried out using sulphate electrolyte with Cr (metal) concentration between 6 and 8 g/l.

Achieved environmental benefits
Reduced Cr concentration when compared with trivalent chromium chloride (up to 20 g/l) and with hexavalent chromium (up to 450 g/l) processes.

No complexing agents (unlike chloride process) that may give rise to problems in the waste water treatment plant.

In addition to the environmental benefits achieved with chromium chloride solutions this process is more safe because there is no production of chlorine at the anode.

The solution is less aggressive and last longer. The problem of iron dissolution in the inner, hollow parts of workpieces is dramatically reduced.

Reduced drag-out thanks to the low viscosity of the solution.

Cross-media effects
No data available.

Operational data
Special insoluble anodes are used. They last much longer than graphite anodes used for trivalent chromium chloride solution (chlorine corrodes graphite anodes).

The bath is operated at 55 °C. Evaporation reduces the level of solution in the vat and therefore the addition of recovered solution is made possible. When slowly withdrawn workpieces are rather dry and drag-out is reduced.

The colour difference to hexavalent chromium coating is further reduced when compared with the colour of coatings deposited from chloride solution.

Throwing power is excellent: it increases the overall resistance to corrosion and in particular of those places usually never reached even by Cr(VI) coating and where rust will first crop out. In addition, no "burning" like patch forms when the intensity of current is high.

Applicability
The technique may apply to new and existing plants.

Economics
No data available.
The components of the solution are very expensive when compared with those of Cr(VI). These costs are only partially offset by the lower costs of waste water treatment and the smaller amount of sludge produced. However, other costs are also lower (see Cr(III) chloride case studies).

Driving forces for implementation
As for chromium (III) chloride process, see Section 4.9.8.3.

Example plants
Industria Galvanica Dalla Torre Ermanno e Figli SpA, Fontane di Villorba, Italy. About 12 more lines in Italy.

Reference literature
[161, Assogalvanica, 2004]

Description
A chromeless technique using Sn/Co alloy (Co 5 – 10 %) has been tested and run in production lines for several years in Italian installations and in the Netherlands. This technique has a high penetration capacity (it can plate more complex shapes than hexavalent chromium) and provides top quality finishing. The finishing colour may be slightly darker than that obtained with Cr(VI).

Achieved environmental benefits
Minimisation of hexavalent chromium.
Treatment of rinsing water is easy and effective.

Cross-media effects
Some tin-cobalt baths contain chelating amines which cause problems with waste water treatment. However, this does not apply to all solutions.

Operational data
The bath is rather unstable, a strict control of the operative conditions is required, in particular the pH.
A passivation stage with light Cr(VI) may be needed.
Barrels need to be made of acrylic.

Applicability
It has been approved for certain automotive interior parts since the 1990s by General Motors.
It does not have high wear resistance.

Economics
No data available

Driving forces for implementation
As introduction to Section 4.9.

Example plants
Cromotrevigiana Srl, Ponzano Veneto, Italy. Industria Galvanica Dalla Torre Ermanno e Figli SpA, Fontane di Villorba, Italy. Brandsma Metaalveredeling B.V., Hilversum The Netherlands.

Reference literature
[112, Assogalvanica, 2003] [165, Tempany, 2004] (Personal communication, Hank de Man, Brandsma Metaalveredeling BV.)

4.9.10 Chromium conversion coatings

The processes are widely used and described in Section 2.5.17. Due to the driving force of the ELV and ROHS Directives [98, EC, 2003, 99, EC, 2000], a large amount of work is being undertaken worldwide to develop alternatives to Cr(VI). Improvements and options are steadily being reported. Some reports indicate the future lies with alternative substrates, or alternative coating systems, such as replacing zinc plating with zinc alloys [149, PPT, 2004, 150, Rowan, 2003].

Phosphochromating exists with both hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)) versions and is used in the treatment of aluminium prior to painting [90, EIPPCB,] [118, ESTAL, 2003].

4.16.10.2 Flotation

Description
Solid particles (or liquid particles such as oil or grease) are combined with air bubbles producing particle/air clusters which float to the surface of a tank and are removed.

Achieved environmental benefits
Achievement of waste water emission limit values.
Recovery of sludges containing metal.
Possible reduction in anti-foaming agents, surfactants and activated carbon.

Cross-media effects
May require more coagulant than sedimentation.
Higher power consumption than sedimentation.

Operational data
Three methods are used:

- vacuum flotation, where air is dissolved at atmospheric pressure followed by a pressure drop to allow formation of bubbles
- induced air flotation, (IAF) where fine bubbles are formed and drawn into the waste water via an induction device such as a venturi or orifice plate
- dissolved air flotation (DAF) where pressurised air is dissolved into the waste water or part of the waste water and subsequently released as small bubble.

The advantages and disadvantages are:

- advantages
  - high efficiency
  - floatation speed greater than that obtained by static sedimentation, which implies smaller installations than static sedimentation.
  - pre-thickening of sludges.

- disadvantages
  - requirement for high quality flocculation to guarantee good adhesion of the air bubbles to the suspended solids
  - settings (for pressurisation) require monitoring.

Applicability
See Description above.
New and existing plants.

Economics
Site-specific
Smaller size allows more room for production capacity.

Driving force for implementation
Required to complete typical waste water treatment plant

Example plants
Industria Galvanica Dalla Torre Ermanno e Figli SpA, Fontane di Villaorba, Italy.

Reference literature
[21, Agences de l'Eau de France, et al., 2002, 87, EIPPCB,] (Personal communication, Lorenzo Dalla Torre)