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JOINT MEETING OF THE CHEMICALS COMMITTEE AND
THE WORKING PARTY ON CHEMICALS, PESTICIDES AND BIOTECHNOLOGY**

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**OECD SERIES ON EMISSION SCENARIO DOCUMENTS
Number 12**

EMISSION SCENARIO DOCUMENT ON METAL FINISHING

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English - Or. English

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OECD Environmental Health and Safety Publications

Series on Emission Scenario Documents No. 12

**EMISSION SCENARIO DOCUMENT ON
METAL FINISHING**

Environment Directorate

Organisation for Economic Co-operation and Development

November 2004

About the OECD

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This publication was produced within the framework of the Inter-Organisation Programme for the Sound Management of Chemicals (IOMC).

The Inter-Organisation Programme for the Sound Management of Chemicals (IOMC) was established in 1995 following recommendations made by the 1992 UN Conference on Environment and Development to strengthen co-operation and increase international co-ordination in the field of chemical safety. The participating organisations are FAO, ILO, OECD, UNEP, UNIDO, UNITAR and WHO. The World Bank and UNDP are observers. The purpose of the IOMC is to promote co-ordination of the policies and activities pursued by the Participating Organisations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.

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Explanatory notes

Purpose and background

This OECD Emission Scenario Document (ESD) is intended to provide information on the sources, use patterns and release pathways of chemicals used in the finishing of metals, to assist in the estimation of releases of chemicals into the environment.

This ESD should be seen as a 'living' document, which provides the most updated information available. As such, an ESD can be updated to take account of changes and new information, and extended to cover the industry area in countries other than the lead (the United Kingdom). Users of the document are encouraged to submit comments, corrections, updates and new information to the OECD Environment, Health and Safety Division (env.riskassessment@oecd.org). The comments received will be forwarded to the OECD Task Force on Environmental Exposure Assessment, which will review the comments every two years so that the lead country can update the document. The comments will also be made available to users within the OECD web-site (www.oecd.org/env/riskassessment).

How to use this document

The user of this ESD needs to consider how the information contained in the document covers the situation for which they wish to estimate releases of chemicals. The document could be used as a framework to identify the information needed, or the approaches in the document could be used together with the suggested default values to provide estimates. Where specific information is available it should be used in preference to the defaults. At all times, the values inputted and the results should be critically reviewed to assure their validity and appropriateness.

Coverage

This ESD covers the use of chemicals in applying coatings to, or producing finishes on, metal surfaces. The main processes considered in the ESD are:

- Anodising
- Conversion coating (passivation and phosphating)
- Electroless plating (autocatalytic)
- Electroplating (electrodeposition)
- Galvanising
- Mechanical plating
- Metal spraying
- Painting and lacquering
- Vacuum deposition
- Vitreous enamelling

The ESD also considers the processes used to clean and prepare the metal surfaces prior to treatment. Methods are included to estimate releases to water only.

The main industry category (IC) relevant to this ESD is IC 8, metal extraction, refining and processing industry. Some of the areas are relevant to IC 14, paints, lacquers and varnishes, although there are other ESDs which address these areas in more detail. The use categories included in the ESD are UC 9 (cleaning agents), 12 (conductive agents), 17 (electroplating agents), 50 (surfactants, wetting agents, phosphatising agents) and 0 (others).

How this document was developed

The document is based on a report produced by the Building Research Establishment for the UK Environment Agency entitled 'Use Category Document – Metal Finishing'. The original purpose of the document was to provide information to be used in risk assessments for new and existing substances in the EU. Information for the original report was largely provided by practitioners in the industry with a wide breadth of knowledge and experience. Published sources are cited where appropriate, but most of the information did not come from such sources and was based on this knowledge and experience. Unless a specific source is cited for a piece of information, it should be assumed to be derived from the experience of the original authors. The information was collected for the original report over the period 1994-1997.

The OECD Task Force on Environmental Exposure Assessment selected this original document as suitable for development as an OECD-wide emission scenario document by revising it with additional information including, where possible, information from countries outside the EU. The formal consultation took place over the period of February to May 2002.

Comments on the document were received from industry, relating to phosphating, and have been incorporated. In addition, further details on the galvanising industry have been added from the draft risk assessment report on zinc produced for the EU Existing Substances Regulation.

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1. OVERVIEW OF THE METAL FINISHING INDUSTRY

1.1 Introduction

1. Metal finishing encompasses a range of processes carried out by industry. These processes are varied and complex and involve chemical and physical processing, metallurgy and chemical engineering. Metal finishing may be defined as:

The deposition of a metallic coating onto a metallic or non-metallic substrate, or the application of an organic coating to a metallic substrate, or the treatment of a metallic substrate by the use of conversion processes, to enhance the appearance, function or performance of a product and to give added value and promote its marketability.

2. Metal finishing thus encompasses many individual technologies, of which the following are the main processes used by industry:

Anodising
 Conversion coating (passivation and phosphating)
 Electroless plating (autocatalytic)
 Electroplating (electrodeposition)
 Galvanising
 Mechanical plating
 Metal spraying
 Painting and lacquering
 Vacuum deposition
 Vitreous enamelling

3. Prior to any metal coating or finishing process, products must be cleaned, so as to be free of grease and other surface contamination. The surface must also be conditioned or activated. These pre-treatments are usually an integral part of the process plant installation. In order to produce the required surface smoothness or texture of the finished component, it is often necessary to use polishing and other abrasive techniques prior to the application of the coating.

4. The metal finishing industry can be categorised into four generic areas according to the function of the coating.

Decorative

5. Decorative coatings enhance the appearance and hence sales value of the product, for example gold plating of low cost jewellery and vacuum deposition of aluminium onto plastics for children's toys.

Decorative/protective

6. Decorative/protective coatings enhance the appearance of the product and protect it in the environmental conditions in which it is most likely to be used. Most industrial practices fall within

this group, for example painting of automobiles, electroplating of bathroom equipment, kitchen equipment, and shopping trolleys.

Processes employed include:

- Electroplating
- Anodising
- Vitreous enamelling
- Painting
- Mechanical plating
- Galvanising

Engineering

7. Engineering coatings are produced specifically to enhance the properties of the substrate. In particular these coatings are used to impart corrosion protection and wear resistance; for example use of electroless nickel and hard chromium deposits on pistons, rams and rollers; titanium nitride coatings for drills and cutting equipment; and specialist coatings containing particles to assist lubricity or non-stick properties.

Technologies employed include:

- Electroless plating of copper and nickel
- Hard chromium electroplating
- Vacuum deposition

Functional

8. A functional surface coating is one which enables a product to fulfil its function more effectively. The electronics industry uses a wide range of metal finishing techniques, for example in the production of printed and integrated circuits, in the manufacture of high grade electrical contacts and in the metallic coating of non-conductors to produce electro-magnetic interference/radio frequency interference (EMI/RFI) shielding.

Processes employed include:

- Precious metal electroplating
- Painting with metal bearing paints
- Electroless plating of nickel
- Hard anodising of aluminium
- Vacuum deposition

1.2 Industry structure

9. The industry is divided into subcontractors and manufacturing organisations. Subcontractors carry out metal finishing processes, such as electroplating and galvanising for manufacturing organisations, while manufacturing organisations may have in-house facilities for metal finishing, such as a paint finishing facility as used by the automobile companies.

10. It is estimated that, in the UK, there are some 2600 companies in the subcontractor sector each employing from 2 to 100 people (average 18). Table 1.1 gives details of the number of subcontractors employed in the different metal finishing activities, the figures indicate major activity only. It should be noted that many companies carry out several metal finishing processes. For

instance, electroplaters will generally carry out electroless plating, conversion coating and possibly anodising, whilst most painting companies use a phosphate pre-treatment before painting.

Table 1.1 Breakdown of subcontractor activity (Bennett, 1992)

Activity	Number of companies	Percentage
Anodising	103	4
Electroplating	1156	43
Painting	388	15
Galvanising and Tinning	102	4
Powder coating	404	15
Polishing	332	12
Others	180	7
Total	2665	100

11. No statistics exist for the number of manufacturing concerns that have in-house facilities though it is estimated that the number is at least equal to the number of subcontractors employed (Bennett, 1992). Suppliers of materials for electroplating suggest that 50% of sales are for in-house manufacturing concerns, whilst paint suppliers suggest a slightly higher figure.

12. In 1990 it was estimated that the metal finishing industry in the UK was worth over £3bn with an expected growth rate of about 3% pa. The industry underpins sixteen major industrial sectors. The value of these sectors with respect to selected individual metal finishing processes is shown in Table 1.2 (Hull University, 1992)

13. Notes to accompany Table 1.2:

Tin plate	Done by electroplating.
New technology	Plasma assisted vacuum processes for TiAl, TiZr, TiNb, Cr, CrAl and ion implantation.
Hard facing	Includes metal spraying.
PVD/CVD	Vacuum deposition coating

Table 1.2 Value (£m) of industrial sectors with respect to metal finishing processes in the United Kingdom

Industrial sector	Painting	Powder coating	Galvanising	Tin plate	Vitreous enamel	Electroplating	Anodising	Post treatments	PVD/CVD	Hard facing	New technology
Aerospace	46	13	0	0	0	74	9	10	7	20	6
Agriculture	48	3	52	0	1	4	1	1	0	5	1
Automotive	182	15	6	0	1	151	9	14	4	2	1
Chemical	19	8	7	0	3	10	3	7	0	8	0
Construction	274	50	123	0	6	5	12	18	2	8	0
Consumer	96	42	18	0	14	150	5	12	1	1	1
Electrical	96	30	2	0	13	80	5	8	1	1	1
Electronic	0	13	0	0	0	151	1	3	0	0	2
Food/Packaging	3	13	1	36	0	2	2	2	5	1	0
Machinery/Tool	16	25	2	0	0	9	1	2	5	15	3
Mining	16	3	4	0	0	5	1	1	0	5	1
Military	16	10	7	0	0	20	2	8	0	8	1
Offshore/Marine	16	3	2	0	0	11	1	1	0	5	1
Power generation	49	5	96	0	0	6	3	2	0	10	1
Transport	49	5	9	0	2	20	6	5	0	5	1
Water & sewage	7	3	6	0	0	6	1	2	0	2	0
General	29	13	20	4	0	5	3	4	0	4	1

1.3 Quantity of material used within the industry

14. Table 1.3 gives details of the amounts of materials used in the metal finishing industry in the United Kingdom. Whilst most materials are a coating (metallic or non-metallic) onto the product, some are treatments of the components, therefore the quantities reported are based on usage and surface area processed.

Table 1.3 Material usage

Material	Process	Tonnes per annum
Metals ^a		
Cadmium	Electro plating	80
Chromium (From chromium salts)	Electro plating	1000
Copper	Electro plating	900
Nickel	Electro plating	2000
	Electroless plating (From nickel salts)	110
Zinc	Electro plating	6000
	Galvanising	100,000
Tin	Electro plating	4100 ^b
Gold and precious metals		4
Non-metallic coatings ^c		
Organic powder	Powder coating	20,000
Organic liquid paints	Painting	200,000

Notes:

a BSTSA, 1993; ZDA, 1993; CA, 1995

b 100 tonnes is used in general electro plating and 4000 tonnes is used for tin plate.

c BCF statistics, 1993

15. Estimates are available for the amount of surface area processed. For phosphating the total surface areas processed is estimated as 334,000,000 m³ per annum respectively. The surface area processed by phosphating is based upon the United Kingdom automotive output, which accounts for some 50% of phosphate coating (SMMT, 1993/94).

16. There are no reliable statistics which can be quoted on the area of aluminium anodised per annum in the United Kingdom. There are some out dated statistics on tonnage of aluminium used in anodising, but these are largely based on figures for the double glazing industry, which has now switched to UPVC and wood. The figure given here is based on the calculated anodising capacity available in the United Kingdom.

Total number of anodisers (not including in-house anodisers) 103

Average rectifier capacity of anodisers. 4000 amps

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17. (Based upon an industry survey. There are wide variations, from 500-20,000 amps, but these are extreme figures for a very small number of operators. The figure of 4000 amps is a mean achieved by weighting in favour of the capacity used by the majority of companies.)

Total anodising capacity	412,000 amps
Normal anodising current density	150 amps/m ²
Total area anodised at any one time	2,747 m ²
Average anodising time	30 mins
Annual hours worked	2000 hours
Total area anodised per annum = $(2747 \times 60 \times 2000)/30 =$	10,988,000 m ²

18. This estimate is subject to various inaccuracies. For example, not every anodiser is listed, and none of the in-house users is listed. However, the 2000 hours assumes 100% utilisation, which will not normally be achieved 75% would be a more realistic figure. For this estimation these two factors have been assumed to be in approximate balance.

19. Table 1.4 gives an estimation of the surface area processed per usage of materials. It is not possible to express the chromium usage in terms of surface area processed due to the widely differing thicknesses that are applied. For example for decorative application the thickness is between 0.3-0.8 μm whereas for hard chromium the thickness varies between 25 μm to 2 mm.

20. The thickness of metal deposited is dependent upon the application and specification. The thicknesses used in the estimations in the table are about average for the industry.

Table 1.4 Surface area processed per usage of metals

Nickel (Electro plating)	
Density (g/cm ³)	8.9
Average thickness (mm)	0.010
Surface area covered per kg of material used (m ²)	11.2
Nickel (Electroless plating)	
Density (g/cm ³)	8.0
Average thickness (mm)	0.025
Surface area covered per kg of material used (m ²)	5.0
Zinc (Electro plating)	
Density (g/cm ³)	7.1
Average thickness (mm)	0.008
Surface area covered per kg of material used (m ²)	17.6
Zinc (Galvanised)	
Density (g/cm ³)	7.1
Average thickness (mm)	0.025
Surface area covered per kg of material used (m ²)	5.6
Copper (Electro plating)	
Density (g/cm ³)	8.9
Average thickness (mm)	0.008
Surface area covered per kg of material used (m ²)	11.2
Gold (Electro plating)	
Density (g/cm ³)	19.3
Average thickness (mm)	0.0005
Surface area covered per kg of material used (m ²)	103.6
Cadmium (Electro plating)	
Density (g/cm ³)	8.6
Average thickness (mm)	0.010
Surface area covered per kg of material used (m ²)	11.6

Table 1.4 Continued

Tin (Conventional electro plating)	
Density (g/cm ³)	7.3
Average thickness (mm)	0.008
Surface area covered per kg of material used (m ²)	17.1
Tin (Tin-plate)	
Density (g/cm ³)	7.3
Average thickness (mm)	0.001
Surface area covered per kg of material used (m ²)	137

1.4 Environmental releases

1.4.1 Releases to water

21. A number of potentially harmful chemicals are employed in the metal finishing industry. Most of the processes employed are of an aqueous nature, therefore discharges to rivers and sewers are of most concern. In the UK the industry relied historically upon dilution to meet discharge limits. The increased cost of water due to the introduction of discharge costs, time-weighted discharge volumes and legislation has resulted in a review of discharges by the industry. A survey of metal finishing companies in 1990/91 suggested that water and waste treatment costs could be as high as 10% of turnover (Ranganathan, 1991). Therefore water conservation is likely to be considered to a greater degree in the future.

22. Where the actual process solutions are aqueous based, often at elevated temperatures, water rinsing between the various process stages is an essential requirement to avoid process solution contamination. For example, strong acids need to be thoroughly rinsed off components before immersion in the subsequent cyanide process. Various methods may be used to minimise the loss of the process solution, leading to a reduction in material wastage, water usage and waste treatment costs. These include:

- Extended withdrawal times from the process solution, thereby allowing the solution to drip back into the process tank.
- Drainage trays which allow collected process solution to return to the process tank.
- Mist sprays situated at the exit from the process tank, thereby significantly reducing the concentration of the solution film on the products.
- Static drag-out tanks (static water rinses) which can be returned to the process tank continuously or periodically.

23. Other methods that may be employed are counterflow current rinses, multi-stage rinses coupled with flow restrictions (See Section 3), conductivity/resistivity controllers and pH instrumentation. Water conservation makes it easier to manage the waste because of the higher levels of contamination present.

24. For some processes, more environmentally acceptable technology has been introduced. Some examples are the use of alkaline or acid based zinc electroplating as a replacement for the

more traditionally used cyanide zinc electroplating, deposition of chromium for decorative applications from trivalent chromium solution in preference to the traditional hexavalent process, and painting using powder coatings or water based materials instead of the more traditional organic solvent based systems.

25. The majority of the industry relies on traditional waste treatment methods to comply with discharge limits. Some examples are the oxidation of cyanides, reduction of chromium and conventional hydroxide precipitation of toxic metals. After settlement or filtration and possibly de-watering, the waste is removed from site by registered disposal contractors, usually to landfill sites.

26. The exception to the above is for cadmium. Recent legislation on the use of cadmium other than in specific applications, namely in the aerospace, aircraft, defence, mining and offshore industries, and the low discharge limits for cadmium mean that the hydroxide precipitation method can no longer be applied. Electrolytic recovery in conjunction with ion exchange is used instead to ensure that the cadmium is removed before disposal. It is likely that processes using other toxic metals will also be subject to more stringent legislation and discharge limits in the future, and similar methods of recovery as used for cadmium will have to be considered.

27. Recovery and recycling techniques are available but are only used by a small percentage of the industry, the exception being in those areas using precious metals where the value of the recovered metal is in excess of the recovery costs.

28. Metal recovery can be achieved in two ways:

Recovered metal salts can be recirculated back into the process solutions.

Recovered metals can be reclaimed for sale to a metal reclaiming company or in some cases may be re-used as anode material.

29. Technologies which may be satisfactorily used are as follows:

Evaporation

Reverse osmosis

Ion exchange

Electrolytical recovery (Electrowinning)

Electrodialysis

30. These are considered in the following sections.

- Evaporation

31. Evaporation has been used successful for recovery of a variety of plating solution chemicals. Water is boiled off from the discharge and the concentrated solution is returned to the process solution. The water vapour collected by condensation may then be used for rinsing purposes. The evaporation may be carried out at atmospheric pressure or in partial vacuum. In the latter case the reduced temperatures necessary are low enough to prevent degradation of the chemical constituents. Evaporation does not remove contaminants from the solution and additional techniques may need to be used to obtain a suitable product for reuse.

- Reverse osmosis

32. Reverse osmosis is a pressure-driven membrane separating process. It uses a semipermeable membrane which permits the passage of pure water whilst retaining the dissolved salts. The salts can be recovered and returned to the process solution. The pure water passing

through is used as rinse water. The system is not suitable for all chemical materials, particularly those of a high oxidation potential such as chromic acid. In addition the membrane will not reject some non-ionised organic compounds and may necessitate the use of activated carbon filtration as an additional operation.

- Ion exchange

33. Ion exchange can be used to recover materials from diluted solutions. The diluted solution is passed through a series of resin beds that selectively remove cations and anions. The metals collected on the resin can be recovered by cleaning with an acid/alkali reagent. Collected water is of a high enough purity for reuse.

- Electrolytical recovery (Electrowinning)

34. Electrowinning is the recovery of the metallic content from solutions using the electroplating processes and can be used to recover a variety of metals such as cadmium, copper, gold, nickel, tin and zinc. In the past, the technique has been used for the recovery of gold and other precious metals where the cost of the metals recovered is in excess of the recovery costs. In a typical installation, the cathodes, made of thin sheets of either the metal to be recovered or stainless steel from which the metal can easily be removed, are arranged in an open tank using insoluble anodes.

35. The metallic slab produced can be sold to metal recovery companies or in some cases may be suitable as the anode in the actual electroplating installation.

36. The system is suitable for treatment of rinse waters which are continually recirculated through the system. Anode to cathode distances are small enough to maximise metal deposition and energy conservation.

- Electrodialysis

37. Electrodialysis uses selective membranes with an electrical potential as the driving force to separate positive and negative ions in solution into two streams. The drain water is passed through cation and anion permeable membranes. The cation membrane allows cations such as copper or nickel to pass, whilst the anion membrane allows passage of anions such as chloride, cyanide or sulphate.

38. The concentrated solutions can be recycled to the plating tank and the ion-depleted water can be recycled to the rinse tanks.

1.4.2 Releases to air

39. Air extraction systems are used to maintain a good working atmosphere for both operators and plant installations. Many of the processes used in metal finishing take place at elevated temperatures and are of an aqueous nature; in these cases the extraction system is mainly used to remove water in the form of steam.

40. In some cases contaminants from the metal finishing process may be present in the vapour released. Some examples are: fumes from chromium electroplating contain electroplating solution, electroless nickel solution fumes contain some nickel, solutions used for bright dipping of brass and aluminium release nitrogen oxides, galvanising and hot dip tinning processes produce toxic fumes and organic solvents are released from degreasers and solvent based paints. These discharges are retained by the use of integral equipment in the extraction system, such as absorption of solvents by activated carbon or after burners and water wash units. The collected material is disposed of in a conventional manner by treatment or registered contractors.

1.4.3 Releases to landfill

41. Discharges direct to soil by processing companies are rare. Waste metals are usually sold to metal reclaimers and ancillary materials, such as filter elements, anode bags (from electroplating) and lining (to collect overspray in painting) are collected by registered disposal contractors who usually dispose to landfill.

1.4.4 Environmental legislation

42. Discharge limits imposed by the local water authorities are variable across the United Kingdom. The limits imposed are dependent on the nature of the receiving waters and the treatment method employed at the sewage works. A comparison of some local water authorities' discharge limits are given in Table 1.5, while Table 1.6 details the percentage of companies required to meet different discharge limits and Table 1.7 gives details of European discharge limits. Direct discharge to rivers is rare, with most companies discharging to a waste water treatment plant. Table 1.8 gives details of discharge limits imposed on a company that does discharge direct to a river.

Table 1.5 UK discharge limits

		London	Birmingham	Liverpool	Brighton
pH		6-11	6-10	6-10	6-10
Cyanide		5 mg/l	10 mg/l	1 mg/l	1 mg/l
Total solids		1000 mg/l	400 mg/l	200 mg/l	400 mg/l
COD		500 mg/l	600 mg/l		
Metals	Copper	3 mg/l	5 mg/l		5 mg/l
	Nickel	2 mg/l	5 mg/l		5 mg/l
	Chromium	3 mg/l	5 mg/l		5 mg/l
	Zinc	3 mg/l	5 mg/l		15 mg/l ^c
	Cadmium ^a	0.02 mg/l	0.02 mg/l	1 mg/l ^b	
	Max		25 mg/l	10 mg/l	

Notes:

a Cadmium is controlled by HMIP not the water authority.

b Due to be reduced to 0.01 mg/l in 1998.

c Includes Cadmium and Mercury.

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Table 1.8 Discharge limits for direct discharge to a river (UK company, personal communication)

Parameter	Discharge limit
Maximum flow rate of river	4200 m ³ /day
pH	6-10
Suspended solids	50 mg/l
Chromium	5 µg/l
Copper	250 µg/l
Iron	500 µg/l
Zinc	70 µg/l
Nickel	100 µg/l
Chlorine (free)	50 µg/l
Cyanide	150 µg/l

Table 1.6 Comparison of discharge limits^a

Compound	Limit (mg/l)	Compliance ^b (%)	Compound	Limit (mg/l)	Compliance ^b (%)
Nickel	1	8	Copper	1	3
	2	8		2-3	21
	3-4	32		4-5	38
	5-6	28		10	28
	10	16		20	3
	25	8		25	7
Chromium	3	4	Lead	1-2	23
	4	7		4-5	42
	5-8	37		10	23
	10	33		25	12
	14	4	Cadmium	0	15
	20	4		0.1-0.5	37
	25	7		1	11
	50	4		2	11
Zinc	0.5	3	3	11	
	1	3	5	11	
	2	3	10	4	
	3	6	Cyanide	1	7
	5	15		1.5-2	13
	10	55		5	47
	15	3		10	33
	25	6			
	30	3			
	50	3			

a Christie and Gawne, 1993. Survey of 30 companies.

b Compliance means the number of companies required to meet a particular value.

Table 1.7 Discharge limits for waste water in Europe (CETS, 1993)

Compound	Discharge limits (mg/l)						
	Belgium	France	Germany	Italy	Holland	Spain	CETS proposals
Silver	0.1		0.1		0.25		0.1
Aluminium	10.0	5.0	3.0	2.0			5.0
Cadmium	0.6	0.2	1	0.02	0.2	1.0	0.2
Cyanide	1.0	0.1	0.2	0.5	1.0	5.0	0.2
Chromium VI	0.5	0.1	0.1	0.2		1.0	0.1
Total Chromium	5.0	3.0	0.5	2.0	0.5	5.0	1.0
Copper	4.0	2.0	0.5	0.1	2.0	5.0	1.0
Iron	20.0	5.0	3.0	2.0		50.0	1.0
Nickel	3.0	5.0	0.5	2.0	0.75	5.0	2.0
Lead	1.0	1.0	0.5		0.75	1.0-2.0	0.5
Tin	2.0	2.0	2.0	0.5			2.0
Zinc	7.0	5.0	2.0	0.5	1.5	5.0	2.0
COD	300.0	150.0	400.0				300.0
Hydrocarbons		5.0	0.1				3.0
Volatile organic halogens			1.0				1.0

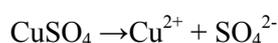
2 METAL FINISHING PROCESS DESCRIPTION AND FORMULATION

2.1 Electroplating (Electrodeposition)

2.1.1 Process description

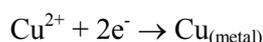
43. Virtually all metals and some metal alloys can be electroplated to produce a coating on a substrate. The substrate is usually made from a metal, though selective non-metals may also be coated. Electroplating is also referred to as electrodeposition, and both terms are in common usage.

44. In aqueous solution, metallic salts ionise to form positively charged metal ions and negatively charged acid radical ions. For example, copper sulphate in solution ionises as follows:



45. The ions exist independently of one another in solution but balance out electronically, ie the number of negative and positive charges is equal.

46. Application of a potential from a direct current source by the immersion of two electrodes into the solution causes the ions to migrate. Positively charged ions migrate to the cathode whilst negatively charged ions migrate to the anode. In the example of copper sulphate solution above, the copper ions migrate to the cathode and accept electrons from the cathode causing the copper atoms formed to adhere to the cathode.



47. If the anode is copper, the negatively charged sulphate ions give up electrons at the anode to produce copper sulphate, which then ionises to restore the equilibrium.

48. Most metal electrodeposition occurs via this route. In theory the solutions are maintained at their optimum concentrations, though it is necessary to ensure that there is an adequate supply of the anode metal source.

49. Some deposition solutions, such as those used for chromium, gold or other precious metals, use insoluble anodes. Since no metal source is present to maintain the solution in equilibrium, the solution becomes progressively depleted in metal salt and to maintain optimum solution concentration frequent additions of the salt must be made.

50. It is possible to electrodeposit metal from a single salt solution, though this is rarely used in practice. Most solutions consist of several salts which have different functions. For instance, chlorides are added to nickel plating solutions to promote anode corrosion and boric acid is added to act as a buffer to maintain pH equilibrium. Most metal cyanides are insoluble in water and must be dissolved in sodium or potassium cyanide solution. Other salts are used to promote conductivity.

51. In practice, these solutions are referred to as the basic solution. It is possible to deposit metal from basic solutions but the deposits produced are generally unacceptable to users, as they are dull, not very adhesive and crystal formation occurs. For example, in the early part of the century, nickel plated deposits were dull and required mechanical polishing prior to deposition of chromium to produce a bright reflective finish; silver deposits were similarly treated.

52. Basic solutions are generally made up by the user, usually from the necessary salts, in crystal or powder form, which are purchased from the chemical manufacturer/supplier. Some solutions, particularly those for gold and other precious metals may be purchased pre-made.

53. Modern electroplating solutions contain many complex organic or metallic organic chemicals, referred to as brighteners or addition agents. The purposes of these agents are numerous and include faster plating speeds, higher tolerance of contaminants in plating solutions, production of mirror-bright deposits, increase/decrease of hardness, changes to crystal structure of the deposit, and decrease of internal stress. These addition agents are the results of the research and development efforts of supply houses. Therefore the chemical composition of the agents is usually confidential.

54. These addition agents are co-deposited with the metal. The optimum concentration is maintained in the solution by frequent additions, often by dosing meters, based on an ampere/hour basis. Quite low concentrations may be present in the solution but fairly high maintenance additions are made frequently during production. For example the concentration in basic solution may be 3 ml/l but the rate used may be 200 ml/l per 1000 ampere hour. The solutions supplied generally contain between 3-25% of the chemical. Therefore in this example, the concentration in the actual working solution may be between 0.009-0.075%.

55. Plant installations for electroplating consist of several tanks assembled together in sequence and the articles for processing are transferred from tank to tank on racks or in barrels, by manual or mechanical means, and in the case of the latter, often by computer control. Some plants are of the return automatic type where the tanks are arranged in a double row and are typically to be found in a manufacturing organisation where high volume output of similar type articles is required.

2.1.2 Formulations

56. The formulations of the more common electroplating solutions used for industrial purposes are given in Tables 2.1 to 2.14. The operating temperature, where above ambient, and the pH are also indicated¹.

57. For reasons of commercial confidentiality, the brighteners/addition agents cannot be named and are indicated by their generic group only. They are only a small percentage of the materials which are added to the bath in aqueous solutions. The brightener solutions typically contain between 3 to 25% of the brightener compound.

¹In the formulations, sometimes liquid concentrated acids or bases are added to the bath. The amount added refers to the amount of the concentrated acid added (for solid acids and bases the amount added refers to the solid). Wherever possible, the specific gravity (sg; equivalent to relative density) of the acid or base added is given. The approximate composition of these acids and bases is shown below (if no information on the sg is given in the Tables, these compositions can be taken as being typical for the acid added). Thus, when estimating the concentration of the active ingredient of the acid or base, the percentage composition of the acid or base may need to be taken into account.

Sulphuric acid (sg 1.84) \approx 98% H ₂ SO ₄	Phosphoric acid (sg 1.685) \approx 85% H ₃ PO ₄
Ammonium hydroxide (sg 0.880) \approx 30% NH ₃	Hydrochloric acid \approx 37% HCl
Nitric acid (sg 1.42) \approx 70% HNO ₃	Hydrofluoric acid (sg 1.2) \approx 48% HF
Nitric acid (sg 1.37) \approx 60% HNO ₃	

Table 2.1 Copper electroplating solution formulations

Acid bath	
Copper sulphate (25.5 % Copper)	175-200 g/l
Sulphuric acid	45-50 g/l
Temperature	20-40°C
Addition agents (Sulphur containing compounds) and wetting agents. For example benzotriazole and thiourea.	Low concentrations
Cyanide bath	
Copper cyanide (71% copper)	15-75 g/l
Potassium cyanide	25-125 g/l
Potassium hydroxide	0-30 g/l
Temperature	50-75°C
Brighteners/addition agents are not usually required, but traces of cobalt or nickel may be employed	
Rochelle bath	
Copper cyanide (71% copper)	20-30 g/l
Potassium cyanide	25-50 g/l
Potassium carbonate	15-25 g/l
Potassium hydrogen tartrate	30-40 g/l
Temperature	50-60°C
Pyrophosphate bath	
Copper pyrophosphate (42.3% copper)	50-85 g/l
Potassium pyrophosphate	200-300 g/l
Ammonium hydroxide (sg 0.880)	3-10 g/l
pH	8.6-9.2
Temperature	50-55°C
Sulphur containing compounds may be used as addition agents. For example benzotriazole and thiourea.	

Table 2.2 Cadmium electroplating solution formulations

Cyanide bath	
Cadmium oxide (87.5% cadmium)	15-30 g/l
Sodium cyanide	40-90 g/l
Sodium hydroxide	5-15 g/l
Addition agents are available but usually prohibited	
Fluoroborate bath	
Cadmium fluoroborate	200-240 g/l
Ammonium fluoroborate	50-60 g/l
Boric acid	15-25 g/l
Liquorice (Addition agent)	1 g/l

Table 2.3 Chromium electroplating solution formulations

Decorative hexavalent	
Chromic acid (52% chromium)	350-450 g/l
Sulphuric Acid	3.5-4.5 g/l
Temperature	40°C
Note a	
Hard hexavalent	
Chromic acid (52% chromium)	200-250 g/l
Sulphuric acid	2.0-2.5 g/l
Temperature	50-60°C
Note b	
Decorative trivalent	
Chromium sulphate	20 g/l
Potassium sulphate	150 g/l
Sodium sulphate	100 g/l
Boric acid	60 g/l
Malic acid	10 g/l
Thiourea	0.1 g/l
Temperature	45-55°C
pH	3.5-3.7

Notes to accompany Table 2.3:

a Brighteners are not usually required. Some proprietary solutions called 'self regulating' have a catalyst present based on silicofluoride or a mixture of sulphate and fluoride ions. These materials are sparingly soluble and are present as a solid, with only a

very small amount in solution, up to about 4 g/l. Self regulating baths contain an excess of salt. The salt is sparingly soluble and dissolves into the solution as required. The solution may be agitated or stirred to facilitate this.

b Brighteners are not usually required. Some self regulating proprietary solutions similar to those in decorative hexavalent baths are available.

Table 2.4 Nickel electroplating solution formulations

Conventional bath	
Nickel sulphate (22.3% Nickel)	240-300 g/l
Nickel chloride (24.7% Nickel)	40-60 g/l
Boric acid	25-40 g/l
Brighteners/addition agents	See text
pH	3.5-4.5
Temperature	45-55°C
Sulphamate	
Nickel sulphamate (23.4% Nickel)	300-650 g/l
Nickel chloride (24.7% Nickel)	5-15 g/l
Boric acid	30-40 g/l
pH	3.5-4.5
Temperature	60-70°C
Where addition agents are used, saccharin is the most common for minimising stress.	

58. Brighteners and addition agents used in nickel plating solutions are more numerous than in any other deposition technology. There are two types of brightener; primary and secondary. Primary brighteners when used by themselves do not produce fully bright deposits. Secondary brighteners do produce fully bright deposits but cannot be used on their own since they can cause brittleness and induce stress in the deposit; they are therefore used at very low concentrations. Brighteners may be supplied separately or as a mixture of the two types, and are usually aqueous in nature.

59. Primary brighteners, have a sulphonic acid ($=\text{CO-SO}_2$) active group in the molecule. Table 2.5 gives some typical examples of primary brighteners. Usually the alkali salt, in particular sodium, of the acid, is used as a water soluble salt. Typical concentrations in the nickel solution vary between 0.5-4 g/l and are dependent upon the type used.

Table 2.5 Typical primary brighteners

Type of compound	Example
Aromatic sulphonic acids	1,3,6-naphthalene tri sulphonic acid
Aromatic sulphonamides	p-toluenesulphonamide
Heterocyclic sulphonic acids	Thiophen-2-sulphonic acid
Ethylenic aliphatic sulphonic acids	Allyl sulphonic acid

60. Secondary brighteners have various active groups in the molecule; Table 2.6 gives some typical examples. The concentrations used in the formulations can vary.

Table 2.6 Typical active groups in secondary brighteners

Active group	Type of compound	Example
$\begin{array}{c} \text{O} \\ \\ \text{-C-H} \end{array}$	Aldehydes	Formaldehyde
	Chlorinated and brominated aldehydes	
	Sulphonated aryl aldehydes	o-sulpho benzaldehyde
C=C	Allyl and vinyl compounds	Allyl sulphonic acid
C≡C	Acetylenic compounds	
	Alcohols	2-butyne-1,4-diol
	Amines	3-dimethylamine-1-propyne
	Aldehydes	propargyl aldehyde
$\begin{array}{c} \text{O} \\ \\ \text{-C=C-C-O-} \end{array}$	β- unsaturated esters	Coumarin Diethyl maleate
N=N	Azo dyes	p-amino azo benzene
C=N	Quinolinium and pyridinium compounds	quinoline methiodide
	Alkylene amines and polyamines	tetraethylene pentamine

61. Levelling agents may also be added to aid the formation of an even coating. These are usually acetylenic compounds and sulphur containing compounds of the sulphobetaines type. For example, pyridinium propyl sulphonate is used at a maximum concentrations of 0.2 g/l. Allyl and vinyl sulphonates may be used at concentrations of 1-4 g/l.

62. Stress relieving additives such as saccharin are used to counteract the deleterious effect of secondary brighteners. Wetting agents, also called non pitters, may be used to prevent the production of pits in the deposit and to ease the removal of gas bubbles during electrolysis. A common wetting agent is lauryl sulphonate.

Table 2.7 Zinc electroplating solution formulations

High cyanide	
Zinc cyanide (55.7% zinc)	30-45 g/l
Sodium cyanide	60-100 g/l
Sodium hydroxide	60-70 g/l
Temperature	25-45°C
Low cyanide	
Zinc cyanide (55.7% zinc)	15-30 g/l
Sodium cyanide	10-25 g/l
Sodium hydroxide	60-70 g/l
Temperature	25-45°C
Brighteners that may be used in cyanide zinc solutions include aromatic aldehydes and long chain polyethylene imines.	
Alkaline non-cyanide	
Zinc oxide (80.3% zinc)	10-20 g/l
Sodium hydroxide	70-180 g/l
Brightener/addition agent	
Temperature	20-35°C
Acid	
Zinc chloride (48% zinc)	30-60 g/l
Potassium chloride	180-200 g/l
Boric acid	25-35 g/l
Brightener/addition agents similar to low cyanide zinc	
Temperature	18-35°C

Table 2.8 Zinc/Nickel electroplating solution formulations

Acid Process	
Zinc chloride (48% zinc)	50-60 g/l
Nickel chloride (24.7% nickel)	15-100 g/l
Sodium chloride	200 g/l
Ammonium chloride	200 g/l
Addition agents eg amines	
pH	4.5-5.5
Temperature	25-40°C
Alkaline Process	
Sodium hydroxide	110-140 g/l
Zinc (as metal)	7-12 g/l
Nickel (as metal)	1-2 g/l
Amine based complexant	Sufficient to totally complex nickel
Brightener (Chemistry similar to that of Zinc brighteners)	2-10 m/l

Table 2.9 Zinc/Cobalt electroplating solution formulations

Zinc	6-10 g/l
Sodium hydroxide	75-105 g/l
Cobalt	0.5-1.0 g/l
Complexant, usually an amine.	25 g/l
Brightener	25 g/l

Table 2.10 Zinc/Tin (Tin/Zinc) electroplating solution formulations

Sodium stannate (44.5% tin)	60 g/l
Zinc cyanide (55.7% zinc)	5 g/l
Sodium cyanide	30 g/l
Sodium hydroxide	10 g/l
Temperature	60-70°C
Brighteners are not usually required	

Table 2.11 Tin electroplating solution formulations

Acid	
Stannous sulphate (55.3% tin)	36-50 g/l
Sulphuric acid	80-150 g/l
Alkaline	
Sodium stannate (44.5% tin)	60-110 g/l
Sodium hydroxide	10-30 g/l
Temperature	60-80°C

Table 2.12 Tin/Nickel electroplating solution formulations

Stannous chloride (52.6% tin)	50-70 g/l
Nickel chloride (24.7% nickel)	240-340 g/l
Ammonium bifluoride	50-60 g/l
Temperature	60-70°C

Table 2.13 Silver electroplating solution formulations

Silver potassium cyanide (54.2% silver)	20-80 g/l
Potassium cyanide	20-100 g/l
Potassium carbonate	15 g/l
Trace elements may be added to increase hardness. For example Antimony and Nickel. (Antimony not used in electronics industry)	

Table 2.14 Gold electroplating solution formulations

Cyanide	
Gold potassium cyanide (68.3% gold)	3-5 g/l
Potassium cyanide	8-10 g/l
Dipotassium phosphate	15 g/l
Temperature	60-80°C
Note a	
Neutral	
Gold potassium cyanide (68.3% Gold)	8-20 g/l
Monopotassium phosphate	75-85 g/l
Brightener. For example Silver.	
pH	6-8
Temperature	65-75°C
Acid	
Gold potassium cyanide	8-16 g/l
Potassium citrate/citric acid	60-90 g/l
pH	3.8-4.8
Temperature	30-40°C

Notes:

a Depending upon the colour required, small additions of other co-deposited metals, may be made. For white gold, nickel or silver is added; for red gold, pink gold or rose gold, copper is added; and for green gold, silver, nickel or cadmium is added. The metal is added in the form of a double cyanide for example silver potassium cyanide.

b There is also a sulphite type gold (non cyanide) though it is not generally used.

2.1.3 Releases

63. Discharge rates from electroplating operations are similar to releases from other wet metal finishing processes. Section 3.1 gives more details on the type of releases expected and discharge rates.

2.2 Painting and lacquering

64. Painting is the coating of a substrate with an organic material. Traditionally such coatings were produced using organic resins and pigments in a blend of organic aliphatic and aromatic solvents. The coatings were then applied by various techniques, including dipping, spraying, roller coating and by brush. Developments over recent years include water-borne coatings, solvent-free coatings such as powder coating, and coatings which can be deposited using electroplating technology. The following sections present some information on these areas in relation to metals. A more detailed description of spray painting of automotive bodies can be found in a draft ESD from the US EPA (US EAP 2003). Further information on the application of coatings in general (not only for metals) can be found in another draft ESD, prepared by the Environment Agency in the UK (Environment Agency, 2002).

2.2.1 Electrophoretic deposition (Electrocoating)

2.2.1.1 Process description

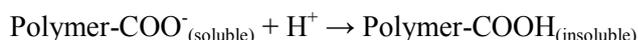
65. The development of electrophoretic coating started in the USA for the painting of automotive bodies. Whilst still often referred to as "electrophoresis", it is now known that the deposition mechanism has more to do with the electrolysis of water and de-stabilisation of polymer particles than with the simple movement of a polymer in an electrical field. Systems are available for both anodic and cathodic coating. In recent years, anodic coatings have given way to cathodic coatings.

66. The solutions used are 70-90% water and the remainder consists of resin, pigments, additives and small quantities of organic solvent. The resin systems used may be acrylic, phenolic/acrylic, epoxy, epoxy/polyester or polybutadiene. It is important that whichever resin is used, it must possess a reactive chemical group which will form a salt with an acid or a base. The choice of resin system is therefore dependent upon the use for which the coating is required.

67. The application of a potential to a solution causes the electrolytic breakdown of water at the anode and cathode. The secondary products developed begin the process of coagulation of the resin in solution. In anodic systems hydrogen ions are the secondary product whilst in cathodic systems hydroxyl ions are the secondary product. The reactions involved are:

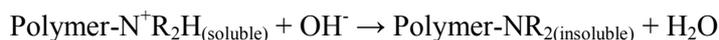
Anodic deposition:

Reaction at anode: $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$



Cathode deposition:

Reaction at cathode: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$



68. The hydrogen and oxygen released produce a foam on the wet film. This acts as an electrical resistance, hence limiting the film thickness.

69. When a direct current potential is applied, the current seeks the path of least resistance and products nearest the electrode are coated first. As the electrical resistance increases, the current seeks paths of least resistance, thus virtually all areas can be coated, even internal sections.

70. Clear lacquer coats (unpigmented) can be applied as top coat protection, for example to silverware.

71. Prior to application, the products must first be cleaned using an aqueous alkaline solution. It is then usual to apply a phosphate coating (see Section 2.3.2). After treatment in the paint bath, the product is rinsed to remove the surface material and then heated to produce a continuous coating.

72. The solution remaining on the surface of the product on removal from the bath, known as cream coat, is richer in resin than the basic solution. It is rinsed and the rinse water subject to ultra-filtration. This method of filtration uses membranes of various construction. The material passing through the membrane (permeate) is used to rinse the product, preferably during its removal from the paint bath. This is followed by rinsing in further tanks of the permeate or by spraying, followed by a final rinse in de-ionised water. The material held back during filtration, which has a higher

concentration of resin materials, is returned to the paint bath to avoid excess loss and assist in maintaining the optimum concentration.

2.2.1.2 *Solution formulation*

73. Materials for manufacture of solutions consist of a suitable resin, pigment, additive, and a small quantity of organic solvent in an aqueous solution. All formulations are proprietary and supplied in a concentrated form for dilution with de-ionised water. Typically, in use, they have a solids content between 8-14 %.

74. Anodic systems Styrene-maleic anhydride copolymers or acrylic acid-acrylic ester copolymers.

75. Cathodic systems Resin based on aminoalkylesters of acrylic acid or systems with tertiary sulphonium ions, epoxides and secondary amines.

2.2.1.3 *Releases*

76. It is claimed that discharges from electrocoating installations are very low with over 95% of solution being recycled by ultra-filtration. The filtration elements used in conventional filtration systems for the removal of foreign particles are disposed of by registered disposal contractors when no longer serviceable.

2.2.2 *Conventional painting and lacquering*

2.2.2.1 *Process description*

77. Conventional paints are synthetic (organic) chemical materials in suitable solvents (organic or water) which dry by the evaporation of the solvent, generally by the application of heat. Lacquers are similar except they are generally unpigmented or slightly tinted.

78. Methods of application are numerous and include spray, dip, flow coating and barrelling.

79. The solids content of the as-used material (that which remains on the product after drying) is usually less than 50% and as a consequence the remainder must be driven off by natural or forced evaporation methods to enable the coating to fulfil its decorative or protective requirements.

2.2.2.2 *Solution formulation*

80. Table 2.15 gives details of typical paint formulations and Table 2.16 gives details of typical lacquer formulations.

Table 2.15 Typical paint formulations

Formulations for stoving (Solvent removed by application of heat)	
Resin	Alkyd-melamine
Solvent	Aromatic hydrocarbons/butanol and Cellasolve
Non-volatile components	47-49%
Resin	Vinyl modified alkyd
Solvent	Aromatic hydrocarbons
Non-volatile components	49-51%
Resin	Acrylic
Solvent	Aromatic hydrocarbons/alcohols
Non-volatile components	40-45%
Formulations for air drying (Solvent removed by natural evaporation)	
Resin	Alkyd
Solvent	Aliphatic hydrocarbons
Non-volatile components	45-49%
Resin	Vinyl
Solvent	Xylol/alcohol/ester
Non-volatile components	28-30%

Note: Pigments are present in the formulation to produce the required colour.

Table 2.16 Formulations of lacquers

UV Cured	
Resin	Acrylic + UV absorbing agents
Solvent	Alcohols and ketones
Non-volatile components	16-18%
Stoving	
Resin	Melamine-formaldehyde alkyd
Solvent	Butanol, butyl cellosolve and hydrocarbons
Non-volatile components	40-45%
Air Drying	
Resin	Modified nitro-cellulose
Solvent	Ketones, alcohols, glycol ether and aromatic hydrocarbons
Non-volatile components	15-20%
Resin	Amino modified alkyd
Solvent	Aromatic hydrocarbons, alcohols and esters
Non-volatile	16-20%
Resin	Polyurethane
Solvent	White spirit
Non-volatile components	40-45%

2.2.2.3 Releases

81. As can be seen from the formulations of solvents and lacquers, a large percentage of the initial starting material is the solvent which has to be driven off to produce the required characteristics of the coating. In many cases the solvent is a volatile organic compound (VOC), and is therefore subject to the Environmental Protection Act (UK) limiting the discharge of carbon to 50 mg/m³.

82. Wastage of paint may be high, particularly with the technique of spraying. There is a considerable amount of overspray onto spray booth linings and into water washing booths for example. The amount of overspray can be as high as 25% which currently is not reclaimed. A recent development using ultra filtration and water based paints allows the overspray to be reclaimed. These linings and the semi-solid sludges are replaced or removed at periodic intervals for disposal. Where dipping is used, the linings from drip trays have to be replaced at periodic intervals and disposed of as solid waste.

83. Solvent and resin losses from the use of 1 litre of organic solvent/resin paint may be as follows:

Total material at start of process	1000 ml (50% solids)
Amount of material lost to overspray	(25%) 250 ml
Coating applied to article	750 ml
Solvent losses (50%):	
From overspray	125 ml
From article	375 ml
Total	500 ml
Resin loss:	
From overspray	125 ml

2.2.3 *Powder coating*

84. Powder coatings are mixtures of resins and pigments blended together and supplied in fine powder form. The materials used are usually thermoplastics or thermoset powders, for example polythene, nylon, PVC, mixed epoxy polymers, polyesters, acrylics and polyurethanes.

85. Electrostatic spray guns are generally used for the application of powders to components, although some use is made of fluidised bed principles. The component for coating is at earth potential, and is usually supported on some form of conveyor system. The powder is emitted from the gun. At the point of emission it is electrically charged and attracted to the component.

86. The essential requirements for such a system are:

- Charged powder particle
- An electrical field

87. The particles are charged by a phenomenon known as "Corona" discharge. If a voltage is applied to a needle point, the current flowing to the workpiece will be negligible at first. As soon as the high tension (HT) reaches about 20 kV, a current will commence to flow - this is the Corona discharge and is the voltage at which the air in the vicinity of the needle breaks down and becomes ionised. As the voltage is increased still further, the current flowing between the needle and the workpiece will rapidly increase. Thus, the area between the workpiece and the gun consists of an electric field, a cloud of particles and ionised air molecules.

88. Particles are attracted to areas nearest to the gun first; as the covering builds up the covered area becomes insulating and so deposition occurs on more distant areas. The process is self-limiting in terms of the thickness of the coating. The powder particles are attracted to the workpiece and remain adherent, by electrostatic forces, for sufficient time to enable the workpiece to be transferred for heating, where the particles melt to form a continuous coating.

89. Whilst some powder is lost during application, any overspray material is collected, using cyclone recovery systems for in-house re-application. Where re-use may not be economical, or colour contamination is a problem, it is often sold for less critical applications (eg automotive chassis use). If not sold it is disposed of via landfill.

90. As with all metal finishing technologies, it is essential that components are cleaned prior to powder application. Phosphating in most situations is a pre-requisite.

91. Discharges from the actual powder coating installations are minimal. The wastes produced go to landfill and no aqueous discharges occur.

92. Since the system uses no solvents, it has received widespread use, with a corresponding reduction of traditional materials. Whilst a more costly material, its near 100% utilisation, with advanced corrosion resistance has greatly increased its application. Table 2.17 gives details of powder coating usage in Western Europe.

Table 2.17 Usage of powder for coatings in the Western Europe

Country	Quantity used Tonnes per annum (1993)
Germany	45.5
Italy	39.3
France	22.0
UK	20.0
Spain	14.1
Scandinavia	10.8
Austria	6.4
Netherlands	6.1
Switzerland	5.9
Belgium	3.7
Greece, Portugal and Turkey	6.7
TOTAL	180.5

(Paintmakers Association Statistics, 1993)

2.3 Conversion coatings

93. Conversion coatings are produced by the chemical treatment of a metallic surface to produce a superficial layer of compound on the metal surface. Often these coatings are given their own terminology; passivating or chromating, phosphating, anodising and antique finishing. Passivating, phosphating and anodising are considered in Sections 2.3.1-2.3.3. Antique finish is not considered in this document, due to the very small volume of use.

2.3.1 *Passivating*

2.3.1.1 *Process description*

94. Passivating may be applied direct to a manufactured product for the following reasons:

- To extend its corrosion resistance, for example stainless steel.
- To benefit the adhesion of a subsequent coating, for example prior to painting of aluminium or zinc-based diecastings.
- To previously applied coatings of metal, in particular cadmium and zinc electrodeposits and galvanising. Passivated coatings increase the corrosion resistance of these coatings and prevent the oxidation of the coating (white rust formation).

95. Various degrees of passivation are available. These are usually designated by the colour obtained:

- Bright Colourless to pale blue
- Full Yellow, iridescent colour
Olive drab (khaki)
Black (Produced directly from a passivate solution or by dyeing of an olive drab film)

96. Generally, passivation solutions for the treatment of zinc and cadmium consist of an aqueous solution of inorganic chemicals, traditionally based on chromates or dichromates. Recently some organic based materials have been developed to comply with environmental legislation, and the use of trivalent chromium in place of hexavalent chromium salts is becoming more common. All solutions are proprietary developments of 'supply companies' from whom the product is obtained in either liquid or solid form for use in an acidic media. In addition to chromium salts, activators are also present in very low concentrations, such as acetate, formate, chloride, nitrate, phosphate and sulphamate ions.

97. The solutions are used at room temperature and fume extraction is not normally required. Discharges are due to drag-out into the water rinses. Solutions are replaced periodically and the spent solution treated for reduction of hexavalent chromium prior to discharge. The amount discharged is dependant upon the method used, such as rack or barrel. Aluminium and its alloys may be passivated prior to painting, as an alternative to the more costly process of anodising. The solutions used are similar to those used for zinc and are based on acidic hexavalent chromium. They are used at slightly elevated temperatures.

2.3.1.2 *Solution formulation***Table 2.18 Formulation of passivating solutions**

Cadmium and Zinc	
Sodium dichromate	135-180 g/l
Sulphuric acid (1.84 sg)	5-9 ml/l
For short immersion times	
Sodium dichromate	135-180 g/l
Sulphuric acid (1.84 sg)	2.5-4.5 g/l
Bright gold passivation of zinc	
Chromic acid	10 g/l
Chrome tan ^a	0.1 g/l
Nitric acid	3 ml/l
Sulphuric acid	0.7 ml/l
Copper and copper alloys	
Chromic acid	220-280 g/l
Sodium sulphate	14-26 g/l
Chromic acid	100-120 g/l
Sulphuric acid	40-50 g/l

Notes: a chrome tan contains a high proportion of trivalent chromium, essential for efficient operation of most chromates.

2.3.2 *Phosphating*2.3.2.1 *Process description*

98. Phosphating is often known under the various trade names of companies who supply the processes, for example Parkerising and Bonderising.

99. Phosphate coatings have a wide field of application, both as an aid to mechanical production operations (deep drawn presswork) and in surface finishing. The major applications are:

- As a pre-treatment operation prior to the application of paint coatings to benefit adhesion and prevent lateral corrosion if the coating is damaged.
- Prevention of atmospheric corrosion during temporary storage.
- As a lubricant carrier to provide resistance to wear.

100. Phosphate coatings consist of layers of crystalline, water insoluble metal phosphates of varying crystal size. The crystal size is dependent on the type of phosphate used and the surface condition of the product being treated. Most metal phosphates are insoluble in water but soluble in mineral acids. This forms the basis of the phosphate coating reaction. Commercial phosphating solutions are carefully balanced solutions of metal phosphates dissolved in phosphoric acid. When a reactive metal is immersed in the solution, light pickling takes place at the liquid/metal interface. When metal from the substrate is dissolved, hydrogen is evolved and the phosphate coating deposited. As the coating is formed in place at the metal surface, it incorporates metal ions dissolved from the surface of the product. The deposit formed is a conversion coating and differs from electrodeposited coatings which are added to or superimposed on the metal.

101. Phosphate coatings fall into three main types:

- Iron phosphate An amorphous coating suitable where a coating film in the order of 300-700 mg/m² is required.
- Zinc phosphate Lightweight (1.0-4.5 g/m²), medium weight (4.5-10 g/m²) and heavy weight (10-30 g/m²).
- Manganese phosphate For coatings of 10-30 g/m².

102. Solutions for phosphating are based on the tribasic acid, ortho-phosphoric acid H₃PO₄ and give rise, on neutralisation, to three series of salts:

Primary salt NaH₂PO₄.Zn(H₂PO₄)₂

Secondary salt Na₂HPO₄.ZnHPO₄

Tertiary salt Na₃PO₄.Zn₃(PO₄)₂

103. An example of a phosphating reaction is:



104. Whilst a very simple process to operate, the theoretical equations by which it occurs are complex. Phosphating from a simple phosphoric bath is time consuming, hence other chemicals may be added to reduce process times. Referred to as accelerators, they may be divided into two classes:

- Additions of heavy metals, particularly small quantities of copper and nickel in the form of a soluble salt at a concentration of 0.002-0.010%.
- Additions of oxidising agents, particularly nitrates, nitrites, chlorates and some organic nitro compounds.

105. Modification of the coating crystal structure may be made by the deposition of a mixed element layer, such as calcium or manganese.

106. The proprietary processes are usually stated, for example calcium modified zinc phosphate and nitrate accelerated zinc phosphate.

107. The product should be in a clean, rust free condition prior to treatment; therefore most installations include pre-treatment stages. Post treatment is advisable to impart the best corrosion resistance properties. Post treatments are based upon chromic acid or alkaline metal chromates or dichromates with a chromium concentration of between 0.10-0.5 g/l.

108. A typical phosphating operation may be:

Cleaning 2-5 minutes
Rinse
Rinse
Phosphating 2-30 minutes (Dependent on type and weight of coating)
Rinse
Rinse
Chromate rinse 15-60 seconds
Dry

109. The method of application may be either by immersion or spraying. There are some processes which both clean and phosphate in a single operation.

2.3.2.2 *Solution formulation*

110. All phosphate preparations are proprietary but consist of iron, zinc or manganese phosphate in phosphoric acid with low concentrations of other metals such as iron or copper and calcium. They are usually supplied as a liquid concentration and between 20-100 ml/l is used. The size of bath used varies depending upon the object to be processed, the smallest size in use is approximately 1000 litres. Table 2.19 gives the typical formulations of some phosphating solutions. Note that the concentrations in this table are those in the formulation, not those in the actual treatment bath (in contrast to most other tables in this document). Table 2.20 gives examples of concentrations of species in baths in use, from German industry.

2.3.3 *Anodising*

2.3.3.1 *Process description*

111. Anodising is an electrolytic process designed to produce an oxide film integral with the surface of the metal. In theory anodising can be applied to a number of metals such as zinc, magnesium and titanium, though its only commercial application at present is as a treatment for aluminium.

Table 2.19 Typical phosphating formulations (concentrations in formulation)

Iron	
Mono sodium phosphate	1,100 g/l
Di sodium phosphate	40 g/l
Hydroxylamine sulphate	10 g/l
Magnesium fluorosilicate	10 g/l
Phosphoric acid (1.65 sg)	5 g/l
Wetting agent	0.001%
Zinc	
Zinc oxide	150 g/l
Nitric acid (1.42 sg)	300 g/l
Phosphoric acid (1.65 sg)	400 g/l
Ammonium dihydrogen phosphate	20 g/l
Manganese	
Manganese oxide	115 g/l
Phosphoric acid (1.65 sg)	45 g/l
Nitric acid (1.42 sg)	75 g/l
Ferrous ammonium sulphate	5 g/l
Hydroxylamine sulphate	20 g/l

112. As a treatment for aluminium it has a wide range of applications. The major use is as a decorative treatment for products such as domestic hardware, door furniture, partitioning, shop fronts, display stands and a wide range of bright trim. In these applications the coating is usually 7-15 μm thick. In architecture anodising is used to coat window frames and decorative panelling for the outside of buildings. In these applications the corrosion resistance and colour fastness is of great importance and the deposit is usually around 25 μm thick. In the aerospace industry anodising is used as a basis for painting and as a protective coating.

113. The equipment and chemicals used for anodising are very similar to those used in electroplating. In the anodising process the metal, usually aluminium, is made the anode in an electrolytic cell, the cathodes are made of lead or aluminium. When current is applied the metal is oxidised to the metal oxide. With most metals the formation of this oxide produces an insulating layer, and the reaction stops. With aluminium, if sufficient voltage is applied, the attack on the base metal will continue through tiny pores in the oxide film. In this way the oxide film will increase in thickness from the bottom up, forming a layer which is not really a coating, but an integral continuation of the base metal as its oxide.

Table 2.20 Phosphating bath compositions

Iron	
Na ⁺	1.5 g/l
PO ₄ (as H ₃ PO ₄ and H ₂ PO ₄ ⁻)	6.0 g/l
Accelerator (<i>m</i> -nitrobenzene sulphonate)	0.5 g/l
Surfactant (alkylethoxylate propoxylate)	1.0 g/l
pH	4.8
Zinc (prior to painting)	
Zinc oxide	1.3 g/l
Nickel	0.8 g/l
Manganese	1.1 g/l
PO ₄ (as H ₃ PO ₄ and H ₂ PO ₄ ⁻)	18 g/l
Na	To adjust pH to about 3.0
Accelerator (NO ₂ ⁻)	0.1 g/l
Heavy zinc phosphate, prior to oiling or cold forming	
Zinc	13 g/l
Iron	5
Nickel	0.4 g/l
NO ₃	22 g/l
PO ₄ (as H ₃ PO ₄ and H ₂ PO ₄ ⁻)	30
pH	2.0
Manganese	
Manganese	5.5 g/l
Iron	2.0 g/l
Nickel;	0.15 g/l
NO ₃	4.0
PO ₄ (as H ₃ PO ₄ and H ₂ PO ₄ ⁻)	26 g/l
pH	2.0

114. Because of this unusual method of formation the anodised film has some unique properties. The aluminium oxide film is always formed with millions of pores in the surface. These pores can be sealed by immersion in boiling water, but before sealing they can be impregnated with a variety of materials. The most common use of this technology is to dye the film by impregnating the pores with a dyestuff. The pores can also be impregnated with lubricants and waxes for other applications.

115. The tank size used in anodising is variable from 500-50,000 litres, typically 2,500-5,000 litres.

2.3.3.2 Solution formulations

116. The aluminium anodising process can be divided into three broad categories, these are:

- Decorative and architectural sulphuric acid anodising.
- Hard or engineering sulphuric acid anodising.
- Chromic acid anodising.

117. Where other metals, such as titanium, are being anodised one of these processes will be used.

118. There are some minor applications of anodising with other electrolytes. Of these the only significant electrolytes are phosphoric acid, and oxalic acid. Phosphoric acid is being investigated as a replacement for chromic acid.

119. The sulphuric acid electrolyte is simply a dilute solution of sulphuric acid. The concentrations used vary with the application and the user. The chromic acid electrolyte is a solution of chromic acid in water. Table 2.21 gives some examples of electrolytes and their use and Table 2.22 gives more details on chromic acid anodising.

120. It is comparatively unusual to operate anodising solutions with additives though organic additions are made to some hard anodising baths. These are usually natural substances derived from wood pulp products. In the United Kingdom the volume of such solutions is insignificant. In the same technology area there are a few mixed acid electrolytes. These are primarily sulphuric acid electrolytes, with oxalic acid added, the volumes used being insignificant.

Table 2.21 Operating conditions for various anodising electrolytes

Electrolyte	Concentration (g/l)	Temperature (°C)	Voltage (V)	Current Density (a/dm ²)
Sulphuric acid (Bright)	180-220	22-25	15-20	0.7-1.0
Sulphuric acid (General)	180-250	18-22	15-25	1.0-1.5
Sulphuric acid (Architectural)	200-230	18-20	15-25	1.5-2.0
Sulphuric acid (Hard)	200-230	-5-+5	15-60	2.0-3.0
Chromic acid	30-100	20-55	20-50	0.3-0.8
Phosphoric acid	100-350	15-30	10-35	1.0-2.0

Table 2.21 Chromic acid anodising

Concentration	30-100 g/l Typical 80 g/l
Sulphate	Not more than 0.5 g/l as Sodium Sulphate
Chloride	Not more than 0.2 g/l as Sodium Chloride
Total chromium as CrO ₃	100 g/l (Maximum)
Cathodes	Mild steel or stainless steel
Temperature	38-42°C
Voltage	20-60 Volts (Ramped)

121. There are two colouring systems that are used by aluminium extruders in the architectural field. These are integral colour anodising and electrocolour. In integral colour anodising the electrolyte consists of organic acids. Acids commonly used are sulpho salicylic acid, succinic acid and boric acid. In electrocolour the anodising is carried out using sulphuric acid, but the colour is applied using an electrolyte that deposits metal ions into the pores. The electrolytes usually contain tin, but some contain copper, nickel, cobalt, iron and lead. A similar technique is used for sealing the pores at low temperature. In these electrolytes the metals are nickel, cobalt and copper.

122. The pre-treatment for anodising is very similar to that for electroplating. Because of the nature of aluminium it is usual not to use strong alkalis for cleaning, but hot caustic soda is often used as an etchant to produce a matt finish. These etchants dissolve considerable quantities of aluminium, which precipitates as sodium aluminate. There are two ways of dealing with the precipitate; the etchant can be discarded when the aluminium begins to precipitate, or a so called long-life etchant can be used. Long-life etchants contain complexants such as sodium gluconate to prevent precipitation of the aluminium.

123. For the anodising of bright trim there is a special pre-treatment known as aluminium chemical brightening. The basic formulation of the solution used is:

Phosphoric acid 80% v/v
 Sulphuric acid 15% v/v
 Nitric acid 5% v/v
 Operating temperature 90-100°C

124. Different manufacturers operate with small variations around this general formulation. Small additions of copper or nickel salts as metal nitrates (1-5 g/l) are made as reaction inhibitors. The process is usually operated with fume extraction and scrubbing. The effluent from the fume scrubber, a mixture of sodium nitrate and sodium nitrite at pH 10.0, is disposed of through the effluent treatment system. Most of these systems have no means of removing the nitrates and nitrites.

125. The two major solutions used in the chemical polishing of aluminium are:

Bright work:
 Phosphoric acid 75-85% v/v
 Sulphuric acid 10-20% v/v
 Nitric acid 4-6% v/v

Satin finish:
 Phosphoric acid 60% v/v
 Sulphuric acid 40% v/v

126. Both of these processes are usually used prior to sulphuric acid anodising. There is also a usage of phosphoric acid in electropolishing which is used in a variety of processes.

127. There is also a growing volume of matt chemical polishing. This is carried out in a bath containing approximately the following formulation:

Phosphoric acid 80% v/v
Sulphuric acid 20% v/v
Operating temperature 90-105°C

128. Aluminium coil coaters use an electropolishing solution of a similar formulation.

129. The final stage for almost all anodising processes is sealing, which is preceded by dyeing in many decorative applications. The dyestuffs are complex organic materials, usually at low concentrations of around 2g/l, with concentrations of 6 g/l for black dye.

130. Sealing is usually accomplished with boiling water, but sealing effectiveness can be improved by rinsing with nickel acetate. Actual concentrations of nickel acetate used vary widely, but 5-15 g/l is common.

2.3.4 Releases

2.3.4.1 Phosphating and passivation

131. At the cleaning stage, the chemicals used are alkaline in nature and sometimes pH adjustment may be sufficient before release. If an acid rinse is in the process line then virtually automatic pH control may be obtained. If the acid is used for pickling it may contain heavy metals, and so precipitation will be required followed by settlement or filtration prior to discharge. Similar treatment may also be needed if there is any significant release of metals from the substrate being cleaned during the process.

132. The requirements for effluent treatment or discharges from the phosphating rinse are dependent upon the local water authority and may require one of the following:

- Simple neutralisation
- Neutralisation and removal of suspended solids
- Neutralisation plus removal of phosphates

133. Where chromate treatment is used, no rinsing is generally undertaken, hence no waste treatment is necessary. Sludges from phosphating can be a problem during production. They can settle out at the bottom of the process tank and also coat the heating coils, immersion heaters etc. Periodically the solution must be pumped to a storage tank and the sludge removed and disposed of by registered contractors.

2.3.4.2 Anodising

134. The major discharges from the anodising industry are sodium sulphate and aluminium. There will be very minor discharges of other metals from a variety of low concentration sources. In addition there will be some discharge of oxides of nitrogen to air, and discharge of nitrates and phosphates to water from chemical brighteners.

135. The following releases are based upon information provided by a supplier to the anodising industry. The amount of phosphoric acid consumed and therefore ultimately going to effluent is 1500-2000 tonnes/annum. Nitric acid is removed from exhaust fumes by scrubbing and ultimately discharged to effluent, the total amount discharge is approximately 500 tonnes/annum. Approximately 100 tonnes/annum nitrous oxide fumes are produced, of this 25% will be scrubbed and discharged to water, the remainder being discharged to air. There is currently no significant volume of phosphoric acid recycling.

2.4 Mechanical plating

136. Mechanically deposited coatings of cadmium, tin, tin/zinc and zinc can be cold welded onto ferrous metals, individually or in combination.

137. Deposits are produced by impingement, cold welding and compaction of metal powder or granules onto cleaned and suitably activated ferrous substrates. The structure of the deposit is typified by the presence of agglomerated particles and voids in the coating. The protective and functional properties of the coatings are similar to electrodeposits of equivalent film thicknesses.

138. The main advantage of this process over electroplating is that coated parts can be produced which are free from hydrogen embrittlement; the process is especially suited to coating severely cold-worked parts, heat-treated or surface-hardened components and components manufactured from high tensile steels.

139. In common with barrel electroplating, limits exist with regard to component size, weight and shape.

140. After degreasing and cleaning, components to be coated are loaded into a barrel with the appropriate quantity of glass beads, water and promoter chemicals in order to condition the surface of the components. The metal to be deposited is then added in powder form, the quantity being dependent on the surface area of the components and the coating thickness required. Rotation of the barrel at the appropriate speed results in the generation of impact forces by the glass beads on the components, with the subsequent cold welding of metal granules on the substrate. After the prescribed time, the components are separated from the glass beads and dried.

141. A specialised version of mechanical plating operates under the proprietary name of Sherardizing. While not strictly a mechanical process, it can be compared to carburising, with which it has similarities. In carburising, heating with a carbon-bearing media causes the carbon to be absorbed into the surface. In sherardizing a similar phenomenon takes place but zinc is absorbed in the surface. In reality, the process could be called a mechanical diffusion process.

142. After the necessary cleaning and pre-treatment, the articles are loaded into a container with the pre-determined quantity of zinc dust, which is dependant upon the thickness required, and an inert filler which prevents mechanical damage and ensures even distribution of the zinc dust. The sealed container is then loaded into a furnace and the temperature raised to the required level. The temperature used is normally between 350-450°C, and is chosen so as to not affect the physical properties of the material being processed. When the operation is complete, the sealed container is removed and cooled. The parts are separated from the inert filler which after screening can be recycled. The residual zinc dust is discarded and disposed of to landfill.

143. Articles processed in this way are often given a post treatment to further increase their corrosion resistance and life-span by such treatments as passivating, phosphating or blackening/oiling. Similar to galvanising, this process gives very good uniformity of coating over contoured and recessed articles.

2.5 Galvanising

2.5.1 Process description

144. Galvanising is the most widely used of the major methods for the coating of iron and steel with zinc, particularly for corrosion resistance in the ‘as produced’ state or as a pre-coating for paint finishes. The protection afforded to iron and steel is not due solely to the barrier effect of zinc forming a continuous coating over the whole area, but largely due to its behaviour as the anode in electrochemical reactions. The result is that zinc corrodes in preference to the underlying substrate. In this context, the zinc coating acts as a sacrificial coating. Corrosion of zinc results in the development of a tenacious carbonate film which resists further attack. Zinc/aluminium alloys can also be used for coatings in a similar way.

145. Zinc coated sheet is used for many presswork applications. The zinc coating has the ability to ‘roll over’ the cut edges during the press operation, and often gives the required protection without further treatment.

146. The usage of zinc is in the order of 100,000 tonnes per annum in the United Kingdom, of which some 45% is used for continuous strip and sheet, 15% for wire and tube and the remainder for general component processing.

147. When a clean and fluxed component is dipped into molten zinc at a temperature of around 450°C, a series of zinc-iron alloys are formed by reaction of the zinc with the component surface. At the normal galvanising temperature of 450°C, the reaction between the iron and zinc is usually parabolic with time ie. the reaction is rapid at first then slows down. Hence the zinc layer reaches a certain thickness quite rapidly, after this there is no significant increase in the thickness. An exception is with high silicon steel where the reaction is linear with time and hence very high thicknesses can be produced.

148. Cleaning and acid rinsing are essential treatments prior to a specific treatment known as fluxing. Fluxing is categorised by three descriptions:

- **Old-Dry** The components are rinsed in hydrochloric acid and dried without rinsing. The acid salts on the surface act as the flux when the components are treated in the molten zinc bath.
- **Dry** After acid rinsing, the components are treated in a flux bath and dried prior to transfer to the zinc bath. Typically the flux could be based on zinc ammonium chloride of about 30% concentration.
- **Wet** The components are transferred after rinsing directly to the zinc bath, which has a blanket of molten flux floating on the surface of the zinc. The blanket is typically zinc ammonium chloride together with foaming agents to thicken the blanket and lower the surface tension.

149. There are three types of process used in the galvanising industry: general hot dip galvanising; continuous hot dip galvanising; and continuous electroplating processes. The latter process is considered in Section 2.1. Information on the other two processes has been taken from the draft risk assessment report for zinc produced under the EU Existing Chemicals Regulation².

150. In general hot dip galvanising, the components to be coated, after flux treatment as above, are dipped into a bath of molten zinc. Larger items are lowered into the bath by crane, smaller items are immersed in perforated steel baskets. The duration of the immersion varies from a few minutes to 30

² Report available from <http://www.ecb.jrc.it/existing-chemicals/>, search on ESIS for substance name “zinc”

minutes. After treatment the items are removed from the bath and excess zinc is removed – this may be returned to the bath or may be sent for reclamation. Fumes can be generated during the treatment, so the baths either have an extraction system or are located in a ventilated enclosure. The ventilation air is cleaned by bag filters.

151. The zinc used is generally of a good commercial standard (98.5%) and contains just over 1% lead, as lead is soluble to about 1% in molten zinc. Excess lead separates out at the bottom and is usefully employed to prevent the dross (a pasty zinc iron alloy of ratio 25:1) from sticking to the bottom of the bath, and hence aiding in its periodic removal. Aluminium is often present in very small quantities (0.005%) to prevent surface oxidation, improve the surface brightness and give a smoother coating.

152. Following removal from the zinc bath the components are quenched to cool and remove any residual flux, where a blanket flux has been used, to prevent staining and to facilitate easier handling.

153. In continuous hot dip galvanising, steel sheet/strip material is surface cleaned, then fed through a heat treatment furnace with a reducing atmosphere for cleaning and annealing. It is then fed directly into the galvanising bath without contact with air to prevent re-oxidation, therefore eliminating the need for fluxing. Since the substrate is already at temperature, most of the heat required for the galvanising bath is supplied from the substrate. Coils are automatically welded together before entering the system to give a fully continuous process. The speed at which the strip passes through the zinc bath means that the coating consists mainly of zinc metal rather than of zinc-iron alloys. After treatment, gas ‘knives’ are used to remove excess zinc. The strip is then cooled gradually, quenched in water and dried. Any further finishing to give the desired surface properties and appearance is then carried out, the strip is cut to the required length and then recoiled. Coils of finished galvanised steel are very valuable and are always protected against oxidation by a chromate rinse layer. An oil film, plastic wrap or interleaved paper, or a combination of these. They are stored under cover, usually with controlled temperature and humidity.

2.5.2 Releases

154. The aqueous discharges from the pre-treatment sections are similar to those experienced with other metal finishing operations (See Section 2.9).

155. The dross removed is collected and sent for reclamation, since it is rarely economical for processors to carry out reclamation themselves.

156. Zinc ash is formed by the disturbance of the surface of the liquid during the operation; as a result the zinc oxidises and particles of zinc are entrapped. The ash is therefore a mixture of zinc oxide and varying quantities of entrapped zinc which may be as high as 80%. Oxidation also occurs during idle periods and further increases the production of ash. The ash is periodically removed and subjected to various methods for zinc reclamation; these include the cylinder method, the static crucible method and the rotary crucible method. In practice it is possible to obtain a yield of about 50% by the above methods.

157. Both types of hot dip galvanising involve the use of air extraction systems, with bag filtration of the ventilation air, and recovery of zinc from the bag filters.

158. Run-off losses from continuous hot dip treated steel is considered to be negligible in view of the post-treatment handling and storage of these materials.

159. More detailed consideration of the releases of zinc from the galvanising processes can be found in the draft risk assessment report.

2.6 Vacuum deposition

2.6.1 *Physical vapour deposition*

160. In the physical vapour deposition (PVD) process material is vaporized and transmitted in the vapour phase through a vacuum or low pressure environment to a substrate where it condenses. PVD processes are used to deposit films of compound materials by the reaction of the material with the ambient gas environment or with a co-deposited material. Film thicknesses can vary (1-1000 nm) and layers can be built up to form multilayer coatings and thick deposits.

161. Vacuum evaporation is a PVD process in which material from a thermal vaporisation source reaches the substrate without collision in the gas phase. As such there is no scattering and the process is by line of sight. Typically vacuum evaporation takes place in the pressure range of 10^{-3} to 10^{-7} Pa. Vacuum evaporation is widely used to form optical interference coatings, mirror coatings, decorative coatings, barrier films and electrically conducting films as well as corrosion protection coatings. Examples of products processed include: mirrors, lamp reflectors, costume jewellery, and toys; examples of the coatings produced are anti reflective oxide coatings on spectacle lenses and sun glasses, barrier films on flexible packaging materials and abrasive and wear resistant coatings.

162. Sputter deposition is the deposition of particles vaporised from a surface. It is a non-thermal process in which the surface atoms are physically ejected by an energetic bombarding particle, usually an ion accelerated from a plasma stream. It is performed in a vacuum or low pressure gas (<0.7 Pa). The process is widely used to deposit thin films on semi-conductor materials, coating of architectural glass, reflective coatings on compact discs, magnetic films, dry film lubricants, and some decorative applications.

163. Ion plating uses concurrent or periodic energetic particle bombardment of the depositing film to modify or control the composition and properties of the depositing film. The material may be deposited by evaporation, sputtering or other vaporising sources. The particles used for bombardment may be ions of inert or reactive gas, or ions of the depositing material. Ion plating may be carried out in a plasma or vacuum environment. It is used to deposit hard coatings onto surfaces, adherent metal coatings onto surfaces and optical coatings with high densities.

164. In the United Kingdom, the number of companies using the above technologies is small. The equipment is costly to purchase and needs to be fully automated. Additionally, clean room conditions are a pre-requisite for trouble free operation, so it is not suitable for normal factory environments. It is not, at present, a main stream metal finishing technology, and has made minimal impact on the more conventional processes. There are few by-products released during the actual processing.

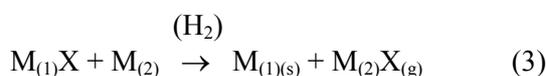
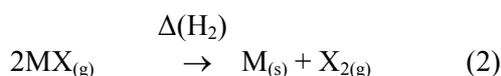
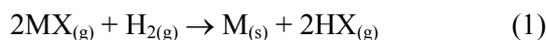
165. Similar to other metal finishing processes, it is an essential requirement that articles for processing are chemically clean. Conventional aqueous based cleaners are rarely used, solvent type cleaners are preferred leaving a dry article. Often when processing plastic substrates it is only necessary to remove particles retained by static forces by use of an anti-static air gun. In some circumstances, articles may be pre-coated using organic lacquers which not only give a gloss finish to the article, but also give some levelling to the surface (vacuum deposited coatings being very thin replicate the surface of the articles). Where the articles need to be handled after processing, a top coat of clear or tinted lacquer or a clear oxide coating may be applied. This is carried out as a second stage operation whilst still in the vacuum equipment.

166. Discharges from the process are negligible. Releases may occur during maintenance of equipment. Material on supporting equipment may be removed by dissolution of the coating in suitable chemical solutions or by the use of abrasive techniques. For example, aluminium is readily soluble in sodium hydroxide solution, the residual solution requires treatment before discharge by conventional waste treatment methods and the sludge produced is disposed of via registered contractors.

2.6.2 *Chemical vapour deposition*

167. Chemical vapour deposition (CVD) is a technique to produce coatings on a variety of substrates where specific operational protection is required. These may be components that see arduous conditions in diverse industries including power generation (nuclear, gas and steam), transport, textile and general engineering.

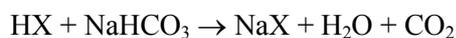
168. Chemical vapour deposition is carried out at elevated temperatures (>800°C) and generally involves the transport of volatile species to the surface of the component being coated. The volatile species then undergoes a chemical reaction and deposition can then occur. The following equations represent the common reactions that take place:



Notes: M and M₍₁₎ are the depositing material, M₍₂₎ is the substrate material and X is an halide such as chloride, iodide or fluoride.

169. The MX species is generated in a manner that is convenient with respect to its physical properties. For example where M is aluminium or titanium, then the vapour pressure of these compounds is sufficiently high to be able to generate these compounds external to the hermetically sealed retort and using only moderate heating to the line (up to 200°C) pass them into the retort along with any inert gas and/or hydrogen. MX compounds with a low vapour pressure (eg CrCl₃) are generated in the coating reactor by the reaction of the metal with HX.X₂ or a salt such as NH₄X.

170. Practical experience shows that reactions (1) and (3) commonly occur during CVD and the waste gases tend to be hydrogen, hydrogen halides and inert gases. Flow rates of the exhaust gas are not high (eg 10 litres/minute) and the high solubility of the acidic hydrogen halides in water means that a water scrubbing tower is a convenient and effective way of removing these compounds from the gas stream. Passing exhaust gases up a tower countercurrent to a mist of alkaline water (eg. water containing dissolved sodium bicarbonate) is adequate for this purpose. The resulting scrubbing solution is kept alkaline with extra additions of sodium bicarbonate as it reacts with the hydrogen halide as:



This produces an easily disposable liquor. Any heavy metals that are produced during the process (or indeed that are not consumed) will normally condense in the cooler zone of the retort and be collected for disposal at the end of the run.

2.7 Vitreous enamelling

2.7.1 Process description

171. Vitreous enamel is also known as porcelain enamel, especially in the USA. Vitreous enamel is the fusion of an inorganic coating (glass) to metal to produce a hard coating, which is permanently bonded to the metal substrate.

172. It has all of the properties of glass - hardness, temperature, chemical and abrasion resistance, durability, and colour stability. It is widely used where these properties are an advantage, for example in kitchen equipment and bathroom fittings. In these applications it is usually applied to steel or cast iron. The steel required for this application has specialist properties to make it suitable for the process. It is also used in architectural applications where its durability, fire resistance and graffiti resistance are finding increasing uses. Its chemical resistance makes it a suitable coating for agricultural and sewage storage tanks. A combination of its chemical and heat resistance properties make it suitable for use in elements for flue gas desulphurisation plants and heat exchangers for power stations. High technology applications such as printed circuit boards, heating elements and aerospace equipment are growth areas. Other applications include in jewellery and ornamental goods. Vitreous enamel materials can be produced in a range of colours and decorated by screen printing, transfers or painting.

173. The process of vitreous enamelling starts with the production of the glass, normally of the borosilicate type, which is smelted to form a 'frit'. This is formed by quenching the glass rapidly in water forming a granular or flake form. This is ground in a ball mill with high density alumina media. For wet applications (by spraying or dipping) it is ground with water into a suspension with clays and salts to produce the appropriate rheology. It can also be applied electrostatically as a dry powder.

174. In the wet process the enamel is dried to remove the majority of the water and then fired in a furnace at temperatures of about 800°C for steel substrates, and at lower temperatures for aluminium and copper substrates. The frit then fuses forming a metallurgical bond with the substrate.

175. For jewellery applications onto copper and its alloys or precious metals, the enamel is often applied as a dry powder and held in place with a gum such as Gum Tragacanth. After firing it may be polished.

176. Vitreous enamel may be applied as a single coat called the direct-on process, or by the prior application of a ground coat. Colouring pigments are complex metal-alumina-silicates formed by calcinating transition metal oxides with alumina and silica. For deep colours up to 8% pigment may be used.

177. Prior to the enamelling operation, it is important to ensure that the substrate is chemically clean and conditioned to promote the formation of the metallurgical bond and to achieve good adherence of the enamel to the substrate. The pre-treatment necessary will be dependant on whether a ground coat or direct-on process is used for enamelling.

178. If the ground coat process is used than a hot alkaline soak may be sufficient, particularly if the ground coat is highly reactive. However, it is more usual to use acid pickling followed by deposition of a thin layer of nickel applied by either electroless electrolytic plating. A typical process sequence may be:

- Hot alkaline soak
- Rinse
- Sulphuric acid

Rinse
 Nickel deposition
 Rinse
 Rinse
 Enamelling application
 Dry and fire

179. For pre-treatment of cast iron, shot blasting may be employed to provide a mechanical assistance to the adherence. In most applications on cast iron, ground coat systems are used.

180. The use of ground coat systems is also becoming more widespread due to environmental concerns about the use of sulphuric acid and nickel deposition.

2.7.2 *Solution formulation*

181. The frit may be purchased ready for use or made up on site. Table 2.23 gives some typical frit formulations.

2.7.3 *Releases*

182. Releases will be dependant upon the processing method used. Where a processor mixes their own frit there will be some discharges subject to control, for example mill washing and colouring pigments. Where enamel application is by spraying either dry or wet, then overspray will be collected by booth linings which can be disposed of by the use of registered contractors.

Table 2.23 Typical frit formulations (percentage composition)

	Ground-coat	White	Black	Green
SiO ₂	49	43	36	41
Al ₂ O ₃	9	1	4	5
B ₂ O ₃	15	13	22	14
Na ₂ O	14	8	21	12
K ₂ O	4	5	2	4
CaO	3		7	1
P ₂ O ₅	0.9	3		2.7
MnO	0.9		2.5	
CoO	0.6		0.6	
NiO	0.9		1.7	0.2
CuO				3
TiO ₂				13
ZrO ₂		22		
F ₂ (added as NaF)	2	4	4	4

Note: For deep colours, or for colour adjustments, specific additions of oxides may be required.

2.8 Electroless plating (Autocatalytic plating)

2.8.1 Process description

183. A limited number of metals can be deposited by chemical reduction rather than by electrical reduction. The basic reaction is:



184. The deposits produced by electroless plating are almost completely uniform in thickness compared to electrodeposits which vary in thickness. It is also possible to plate onto non-metallic surfaces, for example plastics and ceramics. Chemicals need to be added to the bath continually to replace materials as they are used up. This leads to a build up of breakdown products in the bath which reduces its efficiency.

185. Several metals can be deposited in this way, but in practice copper and nickel are the only two deposited on a large commercial scale. Copper is used in printed circuits and electroless plating is the major method used for depositing copper through the hole connections. Electroless copper is also used for the decorative plating of plastics, but has been largely replaced in this field by electroless nickel. The main use of electroless nickel is in engineering where it is applied as a hard, corrosion-resistant coating. Electroless gold is being developed for use in the electronics industry, though due to its high costs its use is likely to remain limited. Electroless silver is used in the electroforming industry, as a means of metallising non-metallic mandrels. Electroless cobalt has a special application in computer memory discs, and possible applications in rocket technology. The other electroless deposits have no serious commercial applications at present.

2.8.2 Formulations

186. A common factor in all electroless formulations is the presence of complexing agents. These range from very strong chelators such as EDTA to acids such as citric and tartaric acids. For electroless nickel, carboxylic acids are used extensively. For instance the following compounds are in regular use: acetic, propionic, lactic, glycollic, maleic, succinic, citric, and tartaric acid.

187. Addition agents are used sparingly in electroless formulations. Sulphur compounds such as mercaptobenztriazole are used as stabilisers, and lead and cadmium salts can be used as brighteners, though their use is declining.

2.8.2.1 Copper

188. Table 2.24 gives the typical formulation of a electroless copper bath. Copper sulphate is usually used as the source of metal ions, though copper formate and copper nitrate may also be used. Complexing agents used included the tartrates and EDTA. The stabilisers used are sulphur containing compounds such as thiourea, thiodiglycollic acid and mercaptobenzthiazole. Sodium cyanide and vanadium oxide may also be used.

Table 2.24 Electroless copper bath

Copper sulphate	15 g/l
Rochelle salt	40 g/l
Formaldehyde ^a	6 ml/l
Vanadium oxide	0.001 g/l
pH	12
Temperature	60°C
Deposition rate	1-5 micron per hour

Notes:

a Formaldehyde is historically the most popular reducing agent, though alternatives are being considered due to environmental concerns. For example sodium hypophosphite, hydrazine sulphate and dimethylamine borane may also be used.

2.8.2.2 Gold

189. There are a number of gold immersion processes which operate by a simple replacement reaction. These are limited in the thickness of deposit obtainable. There are a few electroless gold solutions and the formulations are usually confidential to the company.

190. Table 2.25 Typical electroless gold solution formulation

Gold chloride hydrochloride	0.01 mol/l
Sodium potassium tartrate (Rochelle salt)	0.014 mol/l
Dimethylamine borane	0.013 mol/l
Sodium cyanide	400.00 mg/l
pH	13
Temperature	60°C

2.8.2.3 Silver

191. The solutions used are not true electroless solutions, because the deposit cannot easily be built up in thickness. There is a special technique in operation which can overcome this difficulty. Its use has increased particularly in electroforming, in the production of slush moulds. In this case the solution is used in two parts, ammoniacal silver nitrate and hydrazine sulphate. The two solutions are sprayed onto the article using a spray gun equipped with two nozzles. The two streams meet at the surface and produce a silver mirror. The advantage of this technique is that it can metallise any surface of any size. One of the by products of the reaction is silver azide (explosive and shock sensitive when dry).

2.8.2.4 Nickel

Table 2.26 Nickel formulations

For a deposit containing 90% nickel and 10% phosphorus	
Nickel sulphate	30-35 g/l
Sodium hypophosphite	20-30 g/l
Lactic acid	20-30 g/l
Acetic acid	10 g/l
Sulphur containing compound	1-5 mg/l
Lead acetate	1-3 mg/l
pH	4.5-5.0
Temperature	85-95°C
For a deposit containing approximately 2% phosphorus	
Nickel sulphate	30 g/l
Sodium hypophosphite	15 g/l
Sodium citrate	40-70 g/l
Ammonium chloride	30-50 g/l
pH	9.5
Temperature	80-90°C
For a deposit containing approximately 2% boron	
Nickel chloride	30 g/l
Sodium hydroxide	40 g/l
Ethylene diamine	85 ml/l
Sodium borohydride	0.6 g/l
Thallium nitrate	0.007 g/l
pH	13-14
Temperature	85-90°C
Low boron content deposit suitable for coating plastics	
Nickel chloride	30 g/l
Sodium acetate	15 g/l
Dimethylamine borane	3.0 g/l
Lead acetate	2.0 mg/l
pH	5.5-6.2
Temperature	25°C

2.8.2.5 *Cobalt*

192. Electroless cobalt is used to produce magnetic thin films on computer memory discs.

Table 2.27 Typical electroless cobalt solution formulation

Cobalt sulphate	30 g/l
Ammonium chloride	50 g/l
Sodium citrate	80 g/l
Sodium hypophosphite	20 g/l
pH	8.5-9.5
Temperature	90°C

2.8.2.6 *Palladium*

193. Very little palladium is used at present but it is a possible replacement for gold in electronic applications.

Table 2.28 Typical electroless palladium solution formulation

Palladium chloride	2-4 g/l
Ammonium hydroxide	150-350 g/l
Ammonium chloride	25 g/l
Sodium hypophosphite	10 g/l
Temperature	50°C

2.8.2.7 *Alloy deposition*

194. A typical formulation for an alloy containing 7-14% copper is given in Table 2.29.

Table 2.29 Typical electroless alloy solution formulation

Nickel sulphate	30 g/l
Copper sulphate	1.5 g/l
Sodium hypophosphite	15 g/l
Sodium citrate	50 g/l
Ammonium chloride	40 g/l
pH (Ammonia)	9.0
Temperature	90°C

2.8.3 Releases

195. The losses due to dragout in normal use will be small and in many cases so small as to require little or no treatment. Waste disposal problems may occur at the end of the working life of the solution when the solution has to be discarded. The time interval between solution changes varies depending upon the size of the user. For large scale users changes may be required at 2-3 day intervals while for smaller scale users changes at intervals of 1-2 weeks may be required. The typical size of an electroless nickel tank is 200-1000 litres, though tanks up to 6000 litres are in use.

196. The solution for disposal contains a number of breakdown products. The typical content of a spent electroless nickel solution is given in Table 2.30.

Table 2.30 Typical content of spent electroless nickel solution

Nickel	Approximately 5 g/l
Sodium hypophosphite	Approximately 10 g/l
Other phosphates and phosphites	30-50 g/l
Mixed carboxylic acids	50-80 g/l
Lead	2 ppm
Sulphur compounds	1 ppm

197. Unlike electroplating solutions, electroless plating solutions have a finite life. This is usually expressed as the number of metal turnovers accomplished, and is commonly of the order of 3 to 8 metal turnovers with 6 metal turnovers being the mean.

198. At the point of disposal the solution will contain about 3-5 g/l of Nickel, together with a mixture of phosphates and phosphites, a considerably quantity of sodium sulphate, and a quantity of the complexing acids, typically acetic acid, lactic acid and glycolic acid. The actual concentrations of these acids can vary considerably, but will normally be higher at this stage than the original make up concentration, and could be as much as 50% higher.

199. Methods of disposal vary widely. Very small operators will bleed the spent solution into the main effluent treatment system, where the nickel will be partially removed, but all other materials will pass directly to the waste stream. Some operators treat the solution first to remove the nickel. There are two main methods. Precipitation of the nickel as a fine powder by the addition of a powerful reducing agent such as hydrazine or sodium borohydride is in some use. The other method is to break the complex with sodium dithionite, then precipitate the nickel as hydroxide at high pH. The resultant waste stream will still contain the various complexing acids and phosphates.

200. None of the above methods is truly satisfactory and so there is a growing tendency for spent solutions to be disposed of to landfill through licensed waste disposal contractors. There has been some investigation into nickel recovery of bulk solutions by specific ion exchange, but this has not proved financially viable. As a consequence when the material goes to landfill, it goes as a total spent solution.

201. The nickel in the solution may be removed relatively easily by oxidation, precipitation, reduction, electrowinning or ion exchange. The carboxylic acids can be removed by biological degradation, though no viable system is in use at present. There is also no viable system for the removal of phosphates at present.

202. Electroless copper solutions have a longer life. In this case the residual materials are copper and formate. The life is often extended by a system of bleed and feed, which means that small amounts are continually run to waste. As in the case of electroless nickel the final destination of these materials is landfill.

203. In electroless copper solutions the copper metal is quite strongly complexed which has led to considerable problems. The best method of removing copper is by treatment with complexing ion exchange resins. This leaves a residue containing formaldehyde, formic acid, and assorted complexing agents such as EDTA and tartrates.

2.9 Pre-treatment

204. Pre-treatment is a sequence of processes necessary to ensure that the product for subsequent coating or surface modification is in a suitable condition. For all metal finishing technologies some form of pre-treatment is an essential requirement. The three main pre-treatment methods are:

- Cleaning Aqueous, solvent and mechanical (blasting)
- Activation Acid rinsing
- Brightening Bright dipping, chemical polishing and pickling

2.9.1 Cleaning

205. Cleaning may be defined as the removal of soils from metal surfaces by employing chemical solutions or mechanical methods. Chemical cleaning can cope with a wide variety of soils including those from heavy oils and greases, light cutting oils and polishing compositions. Cleaning may be considered the most important process in metal finishing because the final appearance and acceptance depends upon the presentation of a clean and active substrate, irrespective of the final coating process.

2.9.1.1 Aqueous cleaning

206. Where products are to be treated by subsequent aqueous-based metal finishing technologies, such as electroplating, electroless plating, and electrocoating, the cleaners used are normally of an aqueous and alkaline nature. The type of cleaner used is dependent upon the nature of the soil for removal and the material of the base substrate. Where ferrous materials are to be cleaned then a highly alkaline solution may be employed, but for copper and copper alloys, zinc based alloys and aluminium, only mildly alkaline solutions are suitable.

207. Chemical cleaners act through solubilisation, emulsification and saponification of the contamination.

208. Most cleaners are supplied as proprietary product in powder form, the ingredients being selected from sodium carbonate, sodium hydroxide, sodium metasilicates, trisodium phosphate and sodium borates, with complexing agents (EDTA, gluconates, heptonates, polyphosphates) and organic surfactants to reduce the surface tension of water and to promote oil emulsification. Complex phosphates are included to chelate calcium and magnesium ions present in hard water, and to prevent their precipitation as insoluble salts. The traditional use of phosphates has been reduced in recent years due to environmental concerns.

209. The type of cleaner and strength used is dependent upon the metal being cleaned and the soil to be removed. Heavy duty cleaners may have an alkalinity of 20-30% expressed as sodium hydroxide whilst light duty cleaners may have only 5-10% alkalinity. Complexing agents in the cleaner are of the order of 1-2% by volume.

210. Many cleaners are used as soaks in which the oils and greases are softened and released from the component surface. Alternatively electrolytic means (anodic or cathodic) are used in which the gas generated assists contamination removal by its scrubbing action. The efficiency of cleaners may be increased by air or mechanical agitation. In certain applications spray cleaning is preferable. To make more efficient use of aqueous cleaning solutions the use of ultrasonic vibration is sometimes advantageous.
211. Where possible non or low foaming surfactants are used, being an essential requirement for electrolytic cleaners and spray applications.
212. Thorough water rinsing after cleaning is essential. This is true particularly where high sodium hydroxide concentrations are in use. A dip in dilute acid is required after rinsing, due to the difficulty in rinsing caustic solutions from substrate.
213. Where a sequence of cleaners is in use eg soak, cathodic and anodic, cleaners may be selected which are compatible with each other thus eliminating the need for interstage rinsing and the consequent drag-out losses.
214. Some cleaners are of the emulsion type with the use of an organic hydrocarbon solvent in an alkaline solution. Suitable emulsifiers are used to form an oil-in-water or water-in-oil emulsion. Cleaners of this type were commonplace but have been superseded by more sophisticated conventional alkaline materials. Further, these types of cleaners cannot be rinsed 100% free of solvent and produce subsequent process problems.
215. The selection of the cleaning formulation is in some cases specific to the product substrate although there are some which have a more universal application.
216. Cyanide containing formulations are still available where cold electrolytic cleaning applications are required, but their use has largely been curtailed due to the need to treat the discharge for cyanide destruction.
217. Discharges are determined by the type of articles being processed and drag out into water rinse systems (see Section 3). The outflow to effluent usually only requires pH adjustment, unless it contains cyanide.
218. Periodic replacement of the total cleaning solution is required, the frequency of which is dependent on the soil contamination removed from the articles processed, the plant throughput and the volume of cleaning media contained in the tank. As a guide solutions are disposed of after 4-8 weeks. The sludge produced is removed and disposed of to landfill. It is normal to discharge cleaning materials at the same time as the acids from the process line so that pH neutralisation is nearly automatic. Following settlement of solids the solution can then be discharged to sewer.
219. Typical cleaning formulations are given in Table 2.31.
220. Typically the concentration of a commercially available cleaner used is in the range of 25-75 g/l at 50-80°C. Periodically additions would be made to the solution after simple alkalinity analysis, to compensate for drag-out losses.

Table 2.31 Cleaning formulations

Soak	
Sodium metasilicate	38%
Sodium carbonate	38%
Sodium tetra pyrophosphate	20%
Wetting agent and dispersant	4%
Electrolytic	
Sodium carbonate	9%
Sodium hydroxide	20%
Trisodium polyphosphate	20%
Sodium metasilicate	49%
Wetting agent and dispersant	2%
Electrolytic (Cyanide type)	
Sodium carbonate	9%
Sodium hydroxide	60%
Sodium cyanide	30%
Wetting agent and dispersant	1%

2.9.1.2 *Solvent cleaning*

221. Where a product is required clean and dry, immersion in an organic solvent or solvent vapour is often employed, in some cases with the use of ultrasonic vibration. The solvents are, in general, halogenated aliphatic hydrocarbons such as trichloroethylene and trichloroethane, though the latter is being phased out due to its ozone depletion potential.

222. The world usage of chlorinated solvents in 1992 in the metal finishing industry was about 500,000 tonnes of which approximately 300,000 tonnes was trichloroethylene. (European Solvent Digest, 1994).

223. Typically, the solvent is contained in equipment referred to as a degreasing plant, often of two or more stages. The liquid phase in the systems may be subjected to ultrasonic agitation. The solvent is heated to its boiling point where it vaporises. Products for cleaning must first be immersed in the liquid phase to soften grease and oil, and then transferred into the vapour phase for final washing by vapour. The vapour condenses and runs back into the tank. To avoid vapour loss to the atmosphere the equipment contains condensing coils and freeboard so that the release of vapour is minimised. Mechanical means for lowering and raising the articles are a requirement to control the withdrawal of the product and so avoid vapour loss to the exhaust system and the environment. Covers and extraction are a health and safety requirement. Fully enclosed automatic machines are available for minimal solvent loss.

224. Due to the expensive nature of the material, on-site re-distillation facilities are normally an integral part of the installation and re-distillation is carried out at frequent intervals. The residual semi-solid sludge is removed and collected by registered contractors. Where facilities are not available, the liquid material is sold to established reclamation companies.

2.9.2 *Activation*

225. Activation is the conditioning of a cleaned product to ensure that the surface is in its best state for the subsequent coating application. As stated under the cleaning section, where highly alkaline (sodium hydroxide) type cleaners have been used which are difficult to completely rinse off, then this process ensures neutralisation. Due to the high temperature at which cleaners are used, some tarnish film may be present which this process will remove, particularly for copper and copper alloy materials.

226. This operation is normally done by rinsing in a dilute (5-10%) acid solution, or a solution of higher strength if an oxide film has to be removed. In most metal finishing processes, hydrochloric or sulphuric acids are used; other acids used are usually based on sulphamic acid. The selection of which acid to use is dependent on the substrate being processed.

227. Except where metals are dissolved, the rinse waters do not require special treatment and it is usual to discharge direct with other alkaline rinse waters.

228. Periodic disposal of the bath is usually carried out concurrently with alkaline dumping.

2.9.3 *Brightening*

229. Often articles which are to undergo subsequent processing require the removal of scale, oxide films or surface tarnish. The solutions used are usually a side installation and used as and when required, with the exception of the brightening of aluminium prior to anodising, which is part of the process plant line.

230. The solutions used are specific to the material being treated and Table 2.32 gives a selection with respect to the base substrate.

Table 2.32 Brightening solutions

Copper and copper alloys		
Sulphuric acid (sg 1.84)	10%	
Sulphuric acid (sg 1.84)	100 g/l	
Sodium dichromate	15-30 g/l	
Sulphuric acid (sg 1.84)	100 g/l	
Ferric sulphate	100 g/l	
Sulphuric acid (sg 1.84)	400 g/l	
Nitric acid	200 g/l	
Hydrochloric acid	5 g/l	
Iron and steel		
Sulphuric acid	125 g/l	For cast iron
Hydrofluoric acid	125 g/l	
Sulphuric acid	90 g/l	For cast iron
Nitric acid	40 g/l	
Zinc	5 g/l	
Hydrochloric acid	500 g/l	
Sulphuric acid	100 g/l	
Sulphuric acid	60 g/l	
Ferric sulphate	40 g/l	
Sulphuric acid	60 g/l	
Hydrochloric acid	80 g/l	
Oxalic acid	25 g/l	
Hydrogen peroxide	13 g/l	
Sulphuric acid	0.1 g/l	

Table 2.32 continued

Stainless steel	
Nitric acid (sg 1.37)	250 g/l
Hydrofluoric acid (sg 1.23)	35 g/l
Nickel and Nickel alloys:	
Nitric acid	300 g/l
Hydrofluoric acid	40 g/l
Hydrochloric acid	300 g/l
Cupric chloride	20 g/l
Zinc and zinc alloys:	
Chromic acid	200 g/l
Sodium sulphate	20 g/l
Chromic acid	350 g/l
Hydrochloric acid	100 g/l
Aluminium:	
Phosphoric acid	80-85% (v/v)
Sulphuric acid	10-20% (v/v)
Nitric acid	3-6% (v/v)
Temperature	90-105°C
Trace of copper or nickel	

231. Discharges are due to drag out losses (see Section 3). Since the solutions used remove scale and some metal, then the rinsing waters will contain salts of the metal and hence must be pH neutralised and the metals precipitated as the hydroxide. After settlement or filtration, this can be disposed of as a semi-solid sludge. Similarly, when the solutions require disposal, pH neutralisation and precipitation of the metal hydroxides is required.

2.10 Polishing

232. Polishing is the development of a lustrous surface by mechanical means and may cover the stages between initial grinding and final colouring. Prior to the development of bright coatings directly from electroplating solutions, it was necessary to use interstage or final polishing (buffing) to produce the final bright finish.

233. The operation may be carried out by differing methods:

- Manually, where the article is pressed into a felt wheel or mop rotating on a motor spindle.
- Automatically, on special purpose machines where the article is subject to contact with a felt wheel or mop.

- Mass finishing, whereby the articles are retained in a barrel or drum which is rotated. The technique is ideal for treatment of smaller articles, particularly for deburring, deflashing and descaling.

234. For manual and automatic polishing the operation is usually in two stages. In the first stage, surface imperfections and irregularities are cut away using abrasive coated felt wheels. Typical abrasives include aluminium oxide and silicon carbide. In the second stage the lustre finish is produced with mops made from calico and cotton to which mild abrasives and greases are applied. Typical buffing compositions include triploi, silica, calcined alumina, lime and rouge in a grease bond. They may be produced in solid bars or as a thick liquid.

235. All polishing applications require the use of exhaust systems to take away the particles of removed metal, abrasives and mop fibre. The systems contain catchment areas which collect the debris and prevent releases to atmosphere. Periodically the retained debris is removed for disposal.

236. For mass finished articles, the articles are barrelled with water, often with a mild detergent, and a medium of abrasive material. Common abrasive materials include granite or limestone chips, steel balls, glass balls or a variety of manufactured abrasive chips. The medium used is selective for the application and finish desired. The articles are then washed with water and dried. The detergent solution is then discharged to drain.

237. The amount of solution used varies, but is usually enough to sufficiently cover the articles. The volume of solution used is in the range of 50 to 100 litres.

2.11 General operating conditions

2.11.1 Solution make-up

238. The chemicals used for making up aqueous metal finishing process solutions are obtained from chemical manufacturers either directly or from specialised metal finishing suppliers generally in solid form. They are supplied in pure form, to specification, such that further refinement is unnecessary. Some basic salts, particularly precious metal salts may be supplied as liquid concentrates.

239. Strong acids are in liquid concentrated form in suitable containers ranging from 2.5 to 50 litres. Where large usage is required, bulk storage tanks may be used in-situ, which are serviced by tanker deliveries. Some acids are supplied in solid form.

240. The various addition agents used as brighteners are proprietary preparations of the specialised metal finishing suppliers. They are usually supplied in liquid form.

241. Occasionally some solutions, in particular those for electroless copper and nickel, are supplied by the manufacture as a liquid concentrate.

242. Pre-treatment degreasants, cleaners and activators are usually purchased as ready-mixed products, in dried or liquid form. They are simply dissolved in water or diluted prior to use. There are advantages in using liquid formulations – ease of handling, avoidance of particulate contamination in a paint shop, ease of dosing.

243. The chemicals used in the various processing stages are expensive commodities. Metal finishers are very conscious of these costs and try to avoid wastage. Containers are usually washed out and the washings added to the process solution. In the United Kingdom COSHH regulations govern the way in which chemicals are used and handled. As a consequence, losses during solution make-up for the initial set up of the process and during maintenance are of the order of 0.05% of make up volume.

2.11.1.1 *Process solutions*

244. Most metal finishing facilities have the actual process tank(s) connected to a filtration system which also has a mixing and storage facility, see Figure 1. Where no such mixing/storage facility exists, perhaps due to the small size of the operation or financial constraints, adjacent rinse tanks may be employed with the use of portable pumps. Some process solutions may be made up directly in the process tank.

245. For an initial make-up of the process solution, the required quantities of the chemicals are dissolved in water using mixing/storage tanks. Agitation by either air or mechanical means may be employed. In some cases the metal salt is insoluble in water, for example zinc oxide, zinc cyanide and copper cyanide. In these instances the metal salt will be dissolved into a sodium or potassium cyanide solution.

246. Once the required quantity of chemicals has been dissolved and transferred to the process tank, the level in the process tank will be adjusted by adding further water and the solution filtered. Electrolysis using dummy cathode sheets may be used to remove unwanted heavy metal impurities.

247. Maintenance of the process solutions to replace chemicals lost by drag-out will be carried out in a similar way to the above, except that often some of the actual process solution will be drawn back to the mixing/storage tanks to avoid use of excess water, especially where the process solutions are operated at room temperature. A small quantity of water may be used to flush out the mixing/storage facility or the small amount of residual solution may be left for the next addition. A static drag-out rinse solution may be used, thereby minimising a potential chemical loss.

248. Some process solutions, particularly chromium, may be made up directly in the process tank. The necessary salts are added to hot water contained in the process tank, with agitation or stirring. Maintenance additions to replace drag-out losses will be made similarly.

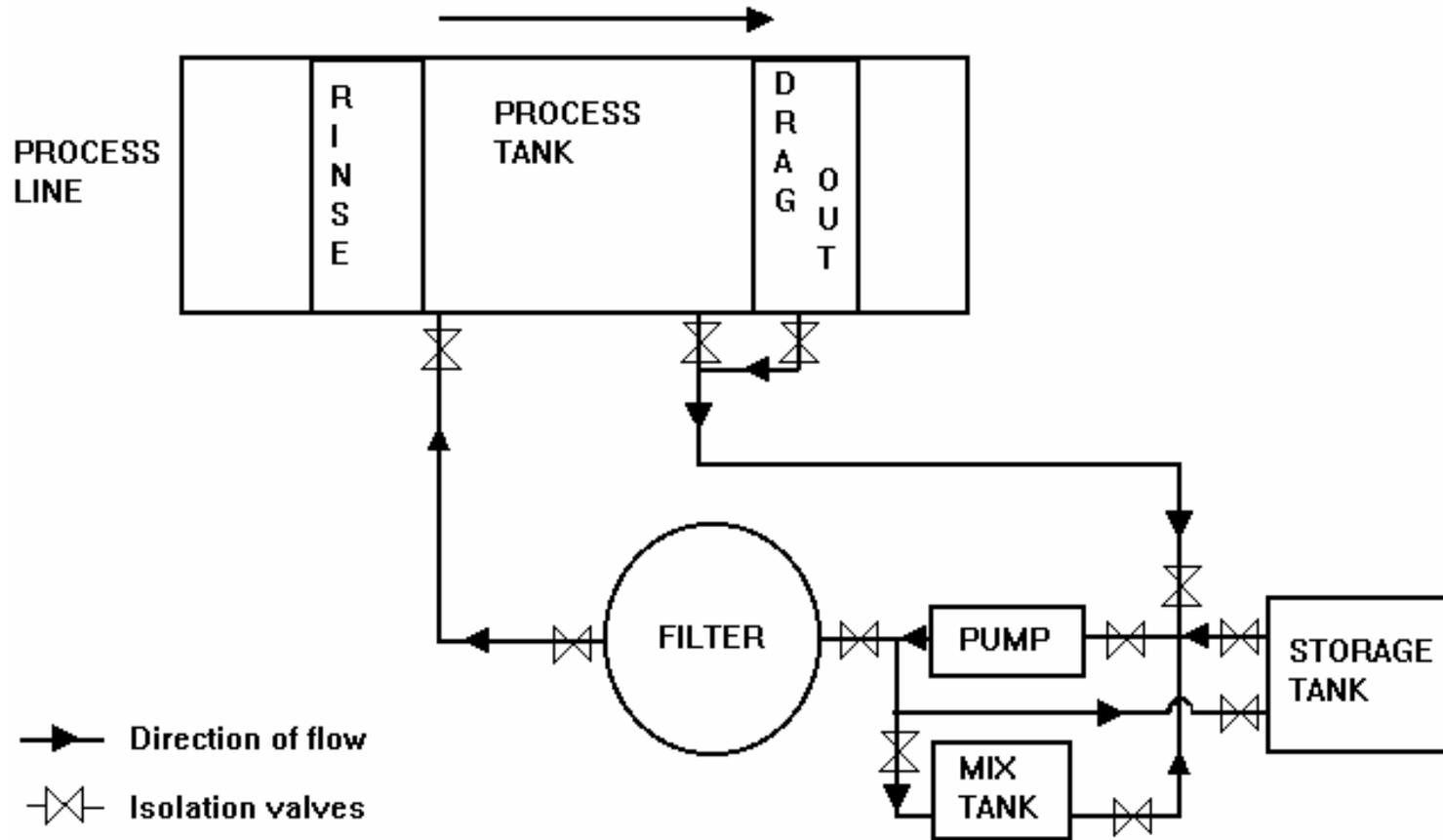


Figure 1 Schematic layout of process tank, storage, mixing and filtration system

249. It is expected that all sacks, drums etc will be disposed of in accordance with the required procedures for hazardous wastes. Suitable containers are used to store other materials, such as filter cartridges and protective clothing, and are normally sealed and disposed of by registered contractors. Containers may be returned to the supplier when spent.

250. The frequency of additions of basic chemical, is variable and dependent upon the area processed and drag-out losses. Usually these are based on chemical analysis. The following may be used as a guide to the frequency of addition;

Cyanide content of solutions (Copper, zinc)	Daily
Metal content and other constituents	Weekly

251. Where soluble anodes are used, providing the process is operated under optimum conditions, it is rarely necessary to make additions of metal salts. It can be controlled by adding or removing anodes or addition of insoluble anodes.

252. Where electroless solutions are in use, frequent additions must be made to replace the metal used and maintain the solution at optimum concentration.

2.11.1.2 Cleaners

253. Cleaners and other pre-treatment chemicals are dissolved by direct addition into the appropriate tank using agitation. Additions during the life-span of the solution will be by similar means based on simple alkalinity analysis. Frequency of analysis is variable between daily to weekly and is dependent upon the amount of contamination being removed from the articles.

2.11.1.3 Acids

254. Acid dips are made up directly in the appropriate tank, usually by a portable pump (carboy pump). Where the tanks are of a small volume, the acids may be purchased in 2.5 litre winchesters and added manually to the tank. Additions during the life of the bath are based upon simple acidity analysis. The frequency of analysis is variable between daily to weekly. Acid containers are usually returnable to the suppliers.

2.11.1.4 Brighteners and addition agents

255. The initial quantity of agents required is added directly to the process tank, either by a portable pump or manually. The material is supplied in fairly small quantities, usually 1-25 litres.

256. Since these materials are used directly according to the DC current usage, their addition rate is on an 'ampere-hour' basis as dictated by the specialised process supplier. The quantity present in solution needs to be accurately controlled for maintenance of a satisfactory, consistent finish and additions need to be small and regular. In most major installations, additions are made by use of an ampere hour meter connected to a dosing unit. As the meter records the ampere-hours used, it activates the dosing pump and the material is fed directly into the process tank. Dosing units can be set to a predetermined rate. The reservoir tank is kept topped up with material. Where more than one material needs to be added, additional dosing units are used connected to a single ampere-hour meter.

257. In smaller installations which may not warrant units as described above, additions are made manually. Some containers in which the materials are supplied are fitted with taps to enable small quantities to be dispensed without loss. Containers may be returnable to the suppliers.

2.11.2 Waste disposal

258. Legislation on waste disposal varies in different European countries and includes several EC directives. In the United Kingdom the Environmental Protection Act imparts a legal responsibility to waste producers to manage their waste arisings. Waste producers are responsible for ensuring that waste is treated and disposed of in accordance with the appropriate legislation. As a result much of the waste material from the metal finishing industry is expected to be disposed of by registered contractors.

259. Registered contractors should be technically competent and dispose of waste arisings to licensed facilities. The majority of registered contractors have their own laboratories and conduct chemical analysis of the waste. This may be done either on site or prior to disposal of the waste. The type of waste treatment employed is dependant upon the waste composition.

260. Waste solutions containing heavy metals, such as acidic, alkaline and hydrolysable liquids, are treated by physico-chemical processes to precipitate the metals as hydroxides. Following settlement the solutions are filtered, the liquid being discharged to sewer, and the solid filter cake disposed of to landfill.

261. Waste sludges may be produced by the waste producer's own in house treatment facilities or from the waste contractors treatment facilities. These sludges generally contain a large amount of water making them unsuitable for direct disposal to landfill. They are therefore filtered and dried or dewatered to produce a near dry filter cake which may be disposed of to landfill.

262. Filter cartridges and lining materials which are used in conjunction with organic processes such as painting may be disposed of either by incineration or landfill.

263. Reclamation of metals may be undertaken by some specialised contractors. In particular precious metals and products coated with precious metals such as gold, silver, palladium, platinum and rhodium are recovered.

264. Smaller quantities of materials are often collected by the smaller waste contractor operations. The quantities involved are such that they are not economic for the larger contractors to collect and the costs involved are prohibitive to the waste producer. In these cases material may be stored on site until sufficient material is available for collection.

265. In some cases waste sludge may be encapsulated and converted into a polymer or synthetic rock. It is claimed that this method greatly reduces mobility of the toxic materials. Table 2.33 gives the results of leaching tests carried out on this type of polymer made from a galvanising pickling acid waste (Chappell C L, 1979).

Table 2.33 Leaching test results

Metal	Concentration in waste (mg/l)	Concentration in leachate (mg/l)
Cadmium	5	0.1
Chromium	15	0.1
Copper	11	> 0.1
Iron	760	0.2
Lead	120	0.1
Nickel	22	0.1
Zinc	22,400	0.2

266. Some contractors carry out recovery of cleansing solvents whereby the clean solvent can either be returned to the user or re-sold. If recovery is not undertaken waste solvent may be destroyed by incineration.

267. Of the waste products produced by the metal finishing industry it is estimated that 5% are disposed of by incineration. The remainder after treatment is usually a solid which is disposed of to landfill.

268. Metal finishing plant equipment that is no longer serviceable should be disposed of correctly. If the equipment has been used with toxic materials, it should not be sold to scrap metal merchants for resale.

2.11.3 Secondary releases

269. There are two significant sources of secondary releases - product design and cleaning.

- Product design

270. The volume of process solution for disposal or treatment is a function of several factors, including product design, type of installation, process employed and the properties of the process material.

271. Flat sheet and wire products retain the least amount of process material whilst cupped or severely recessed products retain the most. Often the position of the product for optimum processing is not ideal for minimum drag-out and may warrant special mechanical means for draining prior to subsequent processing, for example tilting racks in electroplating and electrostatic detearing in painting.

272. Automatic installations with controls for removal of products at a pre-determined rate are better at minimising the amount of process solution released than manually operated plants.

273. How the product is processed will affect the amount of process solution lost due to drag-out via the film of solution retained on the product. Processing options include individually, multi racking, in bulk in barrels or as continuous strip or wire. The higher the viscosity of the processing agent the higher the degree of drag-out and slower drain off. Surface tension reducing agents aid draining and rinsing.

274. In addition to losses by drag-out, process solutions are lost by maintenance procedures which ensure that the process solutions are maintained at optimum performance.

- Losses during cleaning

275. Metal finishing coatings can only be applied to a clean product; this may be by either aqueous or solvent cleaning methods as described in Section 2.9. The removed contamination builds up in the cleaning media and if not removed or replaced at periodic intervals, renders the media unsuitable for further use.

276. Where solvent systems are used, recovery may be by distillation either by in-house equipment or by specialised companies. The contamination is removed in the form of a solid or near-solid sludge and is collected by registered disposal contractors.

277. Where the medium used for cleaning is of an aqueous nature, the solution is usually replaced at periodic intervals. In general, these are alkaline materials and it may be sufficient to adjust the pH value to the acceptable limits. However, the presence of metals and other components in solution may require further treatment. This is particularly true where older formulations

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containing phosphates are in use. Since most process installations use acids in the process line, which are discharged at similar intervals, then pH adjustments are possible. See Section 2.9 for the chemical constitution of cleaners.

278. The various coating and treatment process solutions require continuous or periodic maintenance. Filtration of these solutions is an essential requirement to prolong the life of the treatment baths. The equipment used consists of a suitable sealed container in which the filtration elements are retained. Progressive use of these elements causes a reduction in the solution flow rate so that they need replacement at intervals. The container and associated pipework holds the process solution. Where the process solution is of an aqueous nature, the units are normally washed through with water to dilute the process solution; inevitably some solution is discharged to waste water. For cleaning solutions 100% is discharged to waste water.

279. Processing solutions need periodic pumping to storage tanks to enable checking and replacement of anode material and general cleaning of plant fittings. Whilst most tanks are designed with sloping bottoms to the appropriate pipework, some solution is retained in the process tank. This is normally diluted with water and again pumped to storage. Some dilute solution will inevitably be lost to waste water.

3 RELEASE MODEL

3.1 Introduction

280. A typical metal finishing process involves a number of different stages, such as pre-treatment, electrodeposition and passivation. These processes are carried out in separate stages, though they may be on a continuous production line. After each stage the articles being processed are usually rinsed in water to avoid cross contamination, eg cyanides into acids. On removal of the articles from a bath a certain amount of the process solution is lost from the bath. This is known as drag out; the amount of drag out is dependant upon the articles being processed and the type of processed. On immersion in the rinse bath the drag in material is diluted and removed in the rinse water effluent. The rinse water effluent may then be subjected to further waste treatment before being discharged to a local waste water treatment plant.

281. Table 3.1 gives typical drag out volumes for different processing methods assuming that no recovery techniques are in use. This is only a guide; in order to know the specific discharge volume it is necessary to consider each individual processing installation.

282. For continuous strip deposition, the strip passes through wiping rollers as it emerges from the various processing solutions, such that it is virtually dry prior to immersion in the water rinse tanks, losses are therefore minimal. For barrel deposition, the discharge is both a function of the articles being treated and the size of the barrel perforations. Small articles require a fine-holed barrel whilst larger perforations can be used for larger articles. Drag-out is greater with smaller hole barrels because of the difficulty in allowing solution to escape.

Table 3.1 Typical drag out volumes (Based upon measurements in industry)

Processing method	Drag out volumes per area processed ($Q_{\text{dragout, process}}$)
Rack deposition	5 litres/100 m ²
Continuous strip/wire	0.5 litre/100 m ²
Barrel deposition	30 litres/100 m ²

283. The main releases to water occur due to loss of material via drag out and subsequent removal in rinse water. Additional losses to water may occur during the disposal of spent bath solutions. In cases where significant contamination of rinse waters is likely additional treatment may have to be undertaken to meet local discharge limits. These treatments may lead to the formation of sludges or solid material which are then disposed of to landfill.

284. In order to calculate releases from metal finishing process it is necessary to know certain characteristics about the metal finishing technologies employed. Tables 3.2 to 3.14 contain a guide to the processes employed in the different metal finishing technologies. Table 3.15 gives an example of a more detailed process description, for zinc electroplating. Section 2 gives a guide to chemicals used in the different metal finishing process solutions.

Table 3.2 Electroplating (Section 2.1)

Process	Bath Capacity	Static/Flow	Disposal frequency	Chemical replacement/addition	Releases
Cleaning (Table 3.14)					
Acid dip (Table 3.14)					
Electroplating	5000 l (500-40,000 l)	Static	not applicable	Cyanide baths (Daily) Others (Weekly) Brighteners (Hourly)	Drag out carried over to rinse waters
Rinse	1000 l	Counter flow 100 l/hour	Continuous	not applicable	Rinse water effluent
Rinse	1000 l	Counter flow 100 l/hour	Continuous	not applicable	Rinse water effluent
Passivation (Table 3.4)					
Drying					

Table 3.3 Electrophoretic deposition (Electrocoating) (Section 2.2)

Process	Bath Capacity	Static/ Flow	Disposal frequency	Chemical replacement/addition	Releases
Cleaning (Table 3.14) Aqueous alkaline solution					
Phosphate coating (Table 3.5)					
Electrocoating	no data	static	not applicable	Filtrate from ultrafiltration.	Solution remaining on product surface undergoes ultrafiltration. The permeate is used in further rinses. The filtrate is returned to the process bath. 99% recovery.
Rinse in permeate	no data	flow	Continuous	not applicable	Drag out to water rinse
Rinse in de-ionised water	no data	flow	Continuous	not applicable	Rinse water effluent
Drying					

Table 3.4 Passivation (Section 2.3.1)

Process	Bath Capacity	Static/Flow	Disposal frequency	Chemical replacement/addition	Releases
Passivation	1000 litres (500-5000 litres)	Static	Bi-weekly	Weekly (Daily, Quarterly)	Drag out carried over to rinse water.
Rinse	1000 litres	Counter flow 100 l/hour	Continuous	not applicable	Rinse water effluent.
Rinse	1000 litres	Counter flow 100 l/hour	Continuous	not applicable	Rinse water effluent.

Table 3.5 Phosphating (Section 2.3.2)

Process	Bath Capacity	Static/Flow	Disposal frequency	Chemical replacement/addition	Releases
Cleaning (Table 3.14)					
Rinse					
Phosphating ^a	5000 l (500 l)	Static	not applicable	Daily-weekly.	Drag out carried over to rinse waters. Sludge.
Rinse	no data	Flow	Continuous	not applicable	Rinse water effluent
Rinse	no data	Flow	Continuous	not applicable	Rinse water effluent
Chromate rinse ^b					
Dry					

Notes:

a In some processes the cleaning and phosphating stages are combined.

b Process will be similar to acid rinsing see Table 3.14.

Table 3.6 Anodising (Section 2.3.3)

Process	Bath Capacity	Static/Flow	Disposal frequency	Chemical replacement/addition	Releases
Cleaning (Table 3.14) ^a					
Aluminium chemical brightening ^b					
Anodising					Drag out carried over to rinse waters.
Rinse					Rinse water effluent.
Sealing					

Notes:

a Strong alkalis are not usually used for cleaning. Hot caustic soda maybe used as a etchant to provide a Matt finish.

b Special treatment used for the anodising of bright trim.

Table 3.7 Galvanising (Section 2.5)

Process	Bath Capacity	Static/Flow	Disposal frequency	Chemical replacement/addition	Releases
Cleaning (Table 3.14)					
Acid rinse (Table 3.14)					
Fluxing	Old-dry ^a				
	Dry ^b		Static		Residual flux transferred to zinc bath.
	Wet ^c				
Zinc bath		Static		Zinc ingots added to maintain Zinc concentration.	Residual flux transferred to quenching bath. Zinc ash.
Quenching		Static			Waste water containing residual flux.

Notes:

- a After acid rinsing the components are dried. The acid salts on the surface act as the flux.
b After acid rinsing the components are treated in a flux bath.
c After acid rinsing the components are transferred directly to the zinc bath.

Table 3.8 Electroless plating (Section 2.8)

Process	Bath capacity	Static/flow	Disposal frequency	Chemical replacement/addition	Releases
Cleaning (Table 3.14)					
Acid dip (Table 3.14)					
Autocatalytic plating bath	1000 l (small scale) 6000 l (large scale)	static	1-2 weeks (small scale) 2-3 days (large scale)	not applicable	Drag out carried over to rinse waters.
Rinse	1000 l	Counter flow 100 l/hour	Continuous	not applicable	Rinse water effluent.
Rinse	1000 l	Counter flow 100 l/hour	Continuous	not applicable	Rinse water effluent.
Drying					

Notes:

Significant releases may occur upon disposal of the spent bath solution.

Table 3.9 Painting (Section 2.2)

Process	Releases
Resin based system	
Cleaning (Table 3.14)	
Phosphating (Table3.5)	
Painting	Solvent losses Resin via overspray
Drying	Solvent loss
Powder coating	Negligible. Any overspray material is collected and reused.

Table 3.10 Mechanical plating (Section 2.4)

Process	Releases
Cleaning (Table 3.5)	
Plating	Negligible. Material recovered by screening
Drying	
Passivation (Table 3.4)	
Phosphating (Table 3.5)	

Table 3.11 Vacuum deposition (Section 2.6)

Process	Releases
Cleaning	
Pre-coating with lacquer ^a	
Vacuum deposition	Excess material
Coating with lacquer ^a	

Note a: a lacquer is sometimes used to give a smooth surface for coating. It can also be used to protect the finished product from marking or damage.

Table 3.12 Vitreous enamelling (Section 2.7)

Process	Releases
Cleaning (Table 3.14)	
Activation (Table 3.14)	
Enamelling process	Overspray if frit applied by spraying. Drag out if frit applied by dipping.
Drying and heating	

Table 3.13 Polishing (Section 2.10)

Process	Releases
Washing (mass produced articles)	Effluent
Buffing	Small particles removed by exhaust extraction systems

Table 3.14 Pre-treatment (Section 2.9)

Process	Bath capacity	Static/flow	Disposal frequency	Chemical replacement/addition	Releases
Cleaning					
Soak	500-5000l	Static	4-8 weeks	Daily-weekly	Drag out to rinse water effluent. Sludge on disposal
or Spray	Reservoir tank 1000l	Flow	Continuous	Daily-weekly	Drag out to rinse water effluent. Overspray.
Rinse	1000 l	Counter flow 100 l/hour	Continuous	not applicable	Rinse water effluent
Acid dip ^a	1000 l	Static	2 weeks	Daily	Drag out to rinse water effluent
Rinse	1000 l	Counter flow 100 l/hour	Continuous	not applicable	Rinse water effluent
Solvent cleaning ^b					Vapour and waste solvent recycled. Solid sludge to landfill.
Activation ^c					
Brightening		Static			Drag to rinse water effluent
Rinse	1000 l	Counter flow 100 l/hour			Rinse water effluent.

Notes:

- a Acid dipping is generally used when alkaline solutions are used in the cleaning stage. It also has other applications such as in the old-dry flux stage of galvanization.
- b Integrated liquid/vapour phase apparatus.
- c See acid dipping.

Table 3.15 Typical electroplating process for zinc

Process	Residence time (mins)	Bath composition	Bath capacity (litre)	Counter flow rate (litre/hour)
Soak Clean	5	Alkaline	1500	
Electro-clean	2	Alkali	1500	
Rinse	1		1000	100
Rinse	1		1000	100
Acid dip	2	10% HCl	1000	
Rinse	1		1000	100
Rinse	1		1000	100
Zinc Plate	15	Cyanide	5000	
Drag-out	1		1000	
Rinse	1		1000	100
Rinse	1		1000	100
Passivate	1	Chromate	1000	
Rinse	1		1000	100
Rinse	1		1000	100
Dry				

3.2 Surface area processed

285. The drag out ratios presented above are defined in terms of surface area processed; therefore the surface area processed on a site ($AREA_{process, metal}$) is required to calculate the releases from metal finishing processes. The surface area processed is chiefly dependant upon the type of plant being operated. There are three main types of plant; automatic, semi automatic and manual. These are described in more detail below. As these figures relate to the type of plant they are taken as being representative of all the processes undertaken.

Automatic plants

286. Automatic plants are typically operated by one person. The operator loads the articles onto racks and then starts the plant. After this, the time the racks spend in each tank and the movement between tanks is controlled automatically by the plant, racks been moved mechanically. The operator monitors progress, and then unloads the racks at the end of the process. A typical value for surface processed in a automatic plant is 24 m²/hr.

Semi automatic plants

287. Semi automatic plants are typically operated by 4 people. They are similar to automatic plants, but in this case the operators manually control immersion times, and initiate movement from one tank to the next. A typical value for surface processed in a semi automatic plant is 24 m²/hr.

Manual plants

288. Manual plants are typically operated by 6 people. In manual plants the racks are lifted manually from one tank and moved to the next tank by the operators. A typical value for surface processed in a manual plant is 12 m²/hr.

289. The majority of large operators generally process between 20-40 m²/hr. This may be on just one process or a variety of processes. The processing time ($T_{process}$) is almost continuous with working times of 22 hours per day typical. As a realistic worst case scenario for the following examples it is assumed that a large scale user processes 40 m²/hr for 22 hours per day. This could apply to most major metals processed such as zinc and nickel. For chromium a 12 hour day is considered more realistic. For harder chromium plating on large engineering items, the throughput in terms of area per hour would be less, as longer times are needed to build up the thickness of deposit required.

290. A smaller processor (typically working with zinc or nickel) generally processes 5 m²/hr. A working time of 10 hours per day is typical.

291. For cadmium users there are no small scale users. The area typically processed is 12 m²/hr.

3.3 Water use

292. As described above, when the articles are removed from the treatment bath they carry with them some of the process solution. In most processes the article is then rinsed to remove this excess material and avoid contamination of subsequent process baths. The chemical carried over to the rinse bath is diluted prior to discharge in rinse water effluent. The rinse bath usually has a continuous flow of water going through it. In most systems counterflow rinsing systems are used. Counterflow rinsing systems may consist of a number of rinse baths, the effluent from the second bath flowing into the first bath and so on. The

concentration of chemical is therefore greatest in the first bath. One effect of counterflow rinsing is to reduce the total amount of water needed for rinsing.

293. Some metals (and other chemicals present in the bath) may be recovered from the effluent before discharge to sewer and subsequently re-used. This can be carried out by either recycling the effluent directly, by feeding it back into the process solution to replace lost chemical, or by recovering the metal of interest from the effluent using techniques such as electrowinning and/or ion exchange.

294. Recycling of the effluent directly into the process is carried in a number of ways. If a large number of baths are in use, the concentration may be high enough for the effluent to be fed directly back into the process solution replacing lost chemical. In other cases the solution may be concentrated by evaporation before return. Typical return rates of solution to the process solution tanks are dependant upon the metal being processed. It is generally easier to return solutions when the processes are carried out at elevated temperatures. The feasibility of using this simple system is dependent on the operating temperature of the process tank. A nickel plating bath operating at 60°C will evaporate enough water to enable all the contents of the drag-out tank to be returned to the process tank. A chromium bath operating at 40°C may only evaporate enough water to allow partial return of the drag-out whilst a zinc plating bath operating at 30°C will barely lose enough water to make the system viable. Estimates for recycling rates are given in Table 3.16.

Table 3.16 Recycling rates for process solutions

Metal	Recycling rate ($F_{recycle}$)
Zinc	0-5% (1% suggested)
Nickel	50%
Chromium	25%
Other metals	0 (assumed) ^a

a This is a worst case assumption, and other values could be used if more specific information is available.

295. The recycling rates are based on the amount of metal. However, since it is effectively the whole solution that is recovered, any other chemical present in the bath will be recovered at the same rate, unless it is significantly volatile at the temperature of the bath (and so evaporates with the water).

296. Recovery of metal from the effluent stream is typically carried out for precious metals or where very low discharge is required (e.g. cadmium). The recovery rates for such metals are virtually 100%. Copper is generally recovered from the rinse water as a sludge. The metal recovered in this way can be reused. However, since the recovery method is electrochemical (electrowinning) and/or based on ion exchange, it would be expected that some of the other chemicals present will be unaffected by the recovery method and so are likely to be discharged to effluent.

297. Typical rates of rinse water flow are given in the Tables 3.2-3.14 for the various processes. Overall water volumes used are typically 1,000 l/hour (800-1,600 l/hour) for a large automatic plant and 100-150 l/hour for a small manual plant.

3.4 Calculation of chemical release to water

298. Section 3.1 summarised the stages involved in the various metal finishing processes. Tables 3.2-3.14 can be used to identify the relevant steps for a particular process.

299. The drag out rate (the rate that process solution is lost from the process bath) can be calculated for a processing step from the drag out volume and the area processed. Information on the concentration of chemicals in the process solution is provided in Chapter 2. This can be used to calculate the rate of chemical removal from the process bath. It is assumed that in the rinsing system the amount of chemical released to waste water is the same as that entering in the drag out from the processing bath. Thus the maximum release rate would be that calculated as above. However, as described in Section 3.3 most processes involve some return of the rinsing effluent to the process bath. This reduces the amount of substance removed to waste water (and the amount of new substance which needs to be added to maintain the process bath). Lastly, to calculate a release rate per day, the number of hours a process is operated in a normal day is required.

300. The equation to calculate the daily emission is:

$$E_{local, process, water} = Q_{dragout, type} \cdot AREA_{process, metal} \cdot C_{bath} \cdot 10^{-3} \cdot (1 - F_{recycle}) \cdot T_{process}$$

Explanation of symbols:

Symbol	Explanation	Unit	Default	Notes
$E_{local, process, water}$	Emission from process to water per day	kg/d		
$Q_{dragout, type}$	Amount of solution removed from treatment bath per unit area	l/m ²		Table 3.1
$AREA_{process, metal}$	Surface area of metal processed per hour	m ² /hr		Section 3.2
C_{bath}	Concentration of substance in treatment bath	g/l		Chapter 2
10^{-3}	Conversion factor for g to kg.	kg/g		
$F_{recycle}$	Fraction of dragout returned to treatment bath	-	0	Table 3.16
$T_{process}$	Number of hours worked per day	-	22	Section 3.2 (note that default is very much worst case for some metals and treatments)

301. The volume of rinse water is not used in these calculations. It could be used to estimate the concentration of chemical in the effluent, but it is felt that the quantity released per unit time is more useful. The volumes could also be used to check that the total volume released was compatible with the size of waste water treatment plant to be used in the subsequent calculations.

302. Further releases are possible from the disposal of process solutions and static dip tanks. Information on the frequency with which these tanks are changed is given in Tables 3.2-3.14. It should be assumed that the solutions disposed of will contain a chemical at its intended active concentration.

3.5 Example calculations

Electroplating of nickel

303. From Section 3.2.1 it is assumed that a large scale electroplater processes 40 m²/hour material ($AREA_{process, nickel}$) and works a 22 hour day ($T_{process}$). For this calculation it is also assumed that the rack deposition method is being used.

304. From Table 3.2 it can be seen that the electroplating process involves the following steps: cleaning, acid dip, electroplating, and drying (for some metals there would also be a passivation step). These steps will be considered separately below.

- Cleaning

305. From Table 3.14 it can be seen that cleaning involves either a soak or spray of the cleaning solution followed by a rinse. Assuming the article is cleaned by a static soak process, losses of substances in the cleaning solution will be by drag out into the rinse bath and subsequent release of the rinse water. There is no return of the rinse water here, so $F_{recycle}$ is zero. In addition, the cleaning bath is disposed of every 4-8 weeks.

306. From Table 3.1 the drag out volume for rack deposition ($Q_{dragout, clean}$) is 5 litres/100 m² processed.

307. For this calculation a wetting agent will be considered. Table 2.31 indicates that this is present at 4% in the cleaning formulation. Section 2.9.1.1 gives a typical concentration of the formulation in the cleaning bath of 25-75 g/l. Taking the maximum value gives the concentration of the wetting agent in the bath (C_{bath}) as:

$$4\% \times 75 \text{ g/l} = 3 \text{ g/l}$$

308. The chemical loss rate is then given by:

$$\begin{aligned} Elocal_{clean, water} &= 0.05 \text{ l/m}^2 * 40 \text{ m}^2/\text{hr} * 3/1000 \text{ kg/l} * (1-0) * 22 \text{ hr/d} \\ &= 0.13 \text{ kg/day.} \end{aligned}$$

309. In addition, the cleaning bath will be discharged every 4-8 weeks. Assuming a bath capacity of 1000 litres, the amount of substance released will be 3 g/l × 1000 g or 3 kg.

- Acid dip

310. From Table 3.14 it can be seen that the acid dip involves a soak followed by a rinse. Loss of the acid dip solution will again be by drag out into the rinse and subsequent release of the rinse water. In addition, the acid dip bath is disposed of every 2 weeks.

311. For this example the drag out rate will be the same as above, ie 2 l/hour. From Section 2.9.2 the acid dip is a simple dilute acid solution with few if any additives used.

- Electroplating

312. From Table 3.2, it can be seen that the electroplating process is typically carried out in 5000 l baths followed by two rinses. The electroplating baths are rarely disposed of and so the major source of release is drag out into the rinse solutions and subsequent discharge in the rinse effluent.

313. The drag out volume ($Q_{dragout, plating}$) and area processed per hour ($AREA_{plating, nickel}$) are the same as above. Considering a levelling agent, Section 2.1.2 indicates that pyridinium propyl sulphonate is used in the nickel plating solution at a maximum concentration of 0.2 g/l (C_{bath}).

314. Section 3.3 describes the return of rinsing effluent to the processing baths. From Table 3.15, the typical return rate for nickel is 50%, hence F_{cycle} is 0.5. Thus the chemical release rate is:

$$\begin{aligned} E_{local_{clean, water}} &= 0.05 \text{ l/m}^2 * 40 \text{ m}^2/\text{hr} * 0.2/1000 \text{ kg/l} * (1-0.5) * 22 \text{ hr/d} \\ &= 4.4 \times 10^{-3} \text{ hg/day.} \end{aligned}$$

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