National Pollutant Inventory

Emission Estimation Technique Manual

for

Electroplating and Anodising

First published in July 1999

EMISSION ESTIMATION TECHNIQUE
FOR
ELECTROPLATING AND ANODISING

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ELECTROPLATING AND ANODISING

LIST OF FIGURES, TABLES AND EXAMPLES

1.0   Introduction

The purpose of all Emission Estimation Techniques (EET) manuals in this series is to assist Australian manufacturing, industrial, and service facilities to report emissions of listed substances to the National Pollutant Inventory (NPI). This Manual describes the procedures and recommended approaches for estimating emissions from facilities engaged in electroplating and anodising activities.

The electroplating and anodising activities covered in this Manual apply to facilities primarily engaged in the plating of metals (both decorative and engineering applications) and plastics, and anodising using zinc and other metals. For calculating emissions of total and individual VOCs in parts and equipment cleaning, degreasing and other painting related activities, please refer to the Surface Coating EET Manual included in this folder.

EET MANUAL: Electroplating and Anodising

HANDBOOK: Metal Coating & Finishing

ANZSIC CODE: 2764

This Manual was drafted by the Queensland Department of Environment and Heritage on behalf of the Commonwealth Government. It has been developed through a process of national consultation involving State and Territory environmental authorities and key stakeholders (and has been considered by independent reviewers).

2.0 Process Description

2.1 Electroplating

Electroplating involves the application of a metallic coating onto various articles, such as metals and plastics, to achieve decorative or engineering requirements. Figure 1 shows this process and highlights the likely emission points for particulate matter (PM_{10}) and volatile organic compounds (VOCs).

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                    Substrate to be plated
                            │
                            │           ① ②
                            ▼              ▲        ┌──────────────────────────┐
        ┌───────────────────────────┐     │        │   ①   PM₁₀ Emissions     │
        │ Pretreatment Step -       │─────┘        │                          │
        │ Polishing, Grinding,      │              │   ②   VOC Emissions      │
        │ and Degreasing            │              └──────────────────────────┘
        └───────────────────────────┘
                            │
                            │              ①
                            ▼              ▲
        ┌───────────────────────────┐     │
        │     Alkaline cleaning     │─────┘
        └───────────────────────────┘
                            │
                            │              ①
                            ▼              ▲
        ┌───────────────────────────┐     │
        │        Acid Dip           │─────┘
        └───────────────────────────┘
                            │
                            │              ①
                            ▼              ▲
        ┌───────────────────────────┐     │
        │   Acid Anodic Treatment   │─────┘
        └───────────────────────────┘
                            │
                            │              ①
                            ▼              ▲
        ┌───────────────────────────┐     │
        │  Electroplating of Metal  │─────┘
        └───────────────────────────┘
                            │
                            ▼
                     Plated Product
```
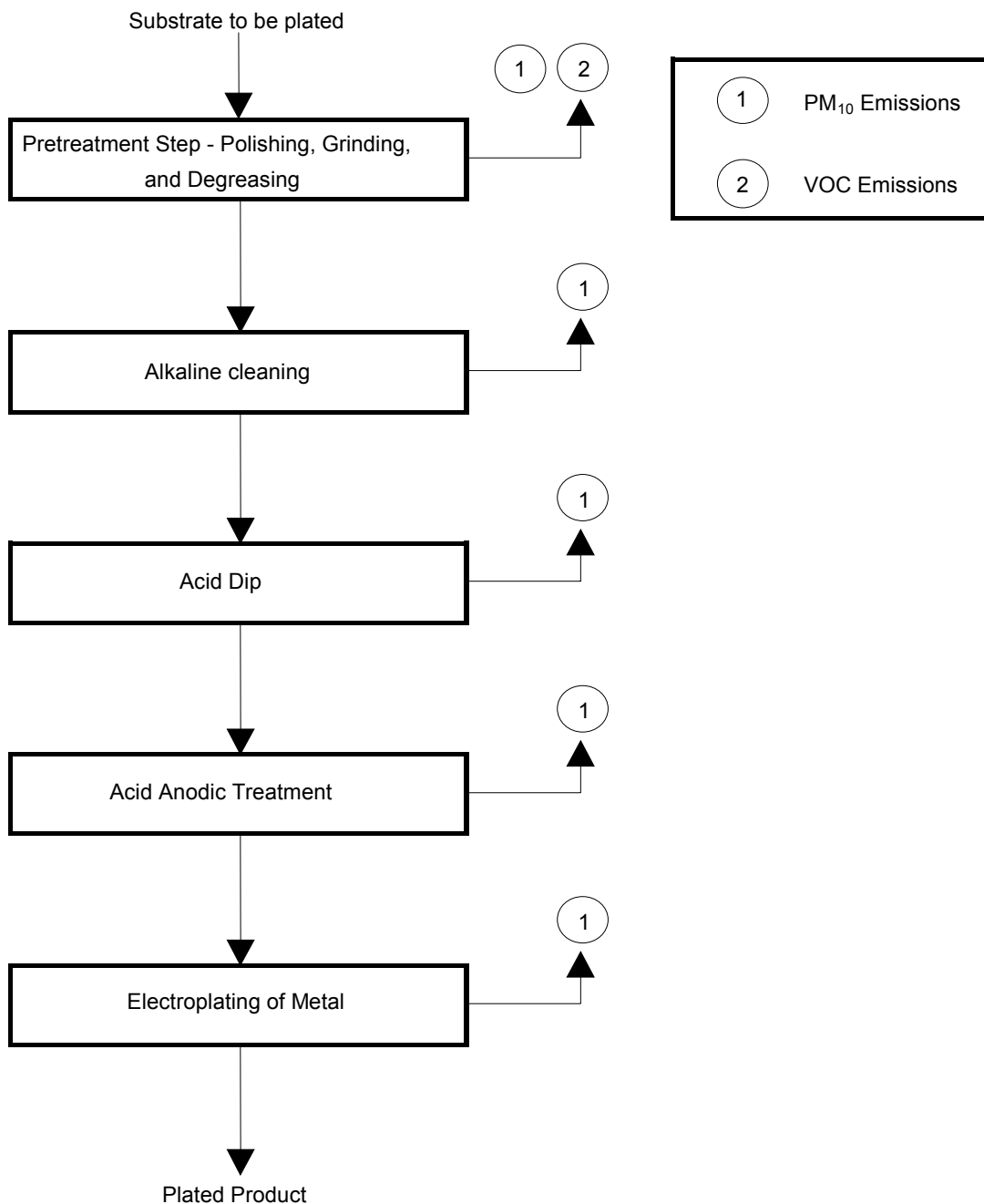
Figure 1 - Basic Process Steps in Electroplating
Source: USEPA AP-42, 1996.

The electroplating process involves passing an electric current through an electrolyte in contact with the article to be plated. This forms a surface that has different properties than material intended for plating. Special pre-coating products, (eg. metallic loaded paints), can be applied to non-electrical surfaces, such as plastic, to produce an electrically active surface for plating.

Typical metals used in electroplating are cadmium, chromium, cobalt, copper, gold, indium, iron, lead, nickel, the platinum group of metals, silver, tin, and zinc. Various alloys of these metals are also used, including brass, bronze, gold alloys, lead-tin, nickel-iron, nickel-cobalt, nickel-phosphorus, tin-nickel, tin-zinc, zinc-nickel, zinc-cobalt, and zinc-iron. Electroplated materials are generally used for a specific property or function, although there are cases where they can serve a dual purpose (eg. when a material may be electroplated for decorative use, as well as for corrosion resistance).

2.2 Anodising

Anodising is an electrolytic process that converts the metal surface to an insoluble oxide coating. Anodised coatings provide corrosion protection, decorative surfaces, a base for painting and other coating processes, and special electrical and mechanical properties. Aluminium is the most frequently anodised material. Common aluminium anodising processes include chromic acid anodising, sulfuric acid anodising, and boric-sulfuric anodising. The sulfuric acid process is the most common method.

Following anodising, parts are generally rinsed, then proceed through a sealing operation that improves the corrosion resistance of the coating. Common sealants include chromic acid, nickel acetate, nickel-cobalt acetate, and hot water. Figure 2 presents a basic anodising flowchart highlighting the likely emission points.

2.3 Chemical Conversion Coating

Chemical conversion coating includes chromating, phosphating, metal colouring, and passivating operations. Chromate conversion coatings are produced on various metals by chemical or electrochemical treatment. Solutions, usually containing hexavalent chromium and other compounds, react with the metal surface to form a layer containing a complex mixture of compounds consisting of chromium, other constituents, and the base metal. Phosphate coatings may be formed by the immersion of steel, iron, or zinc-plated steel in a dilute solution of phosphate salts, phosphoric acid, and other reagents to condition the surfaces for further processing. They are used to provide a good base for paints and other organic coatings, to condition the surfaces for cold forming operations by providing a base for drawing compounds and lubricants, and to impart corrosion resistance to the surface metal.

Metal colouring involves chemically converting the metal surface into an oxide or similar metallic compound to produce a decorative finish, such as a green or blue patina on copper or steel, respectively. Passivating is the process of forming a protective film on metals by immersion into an acid solution, usually nitric acid, or nitric acid with sodium dichromate. Stainless steel is often passivated to prevent corrosion and extend the life of the product.
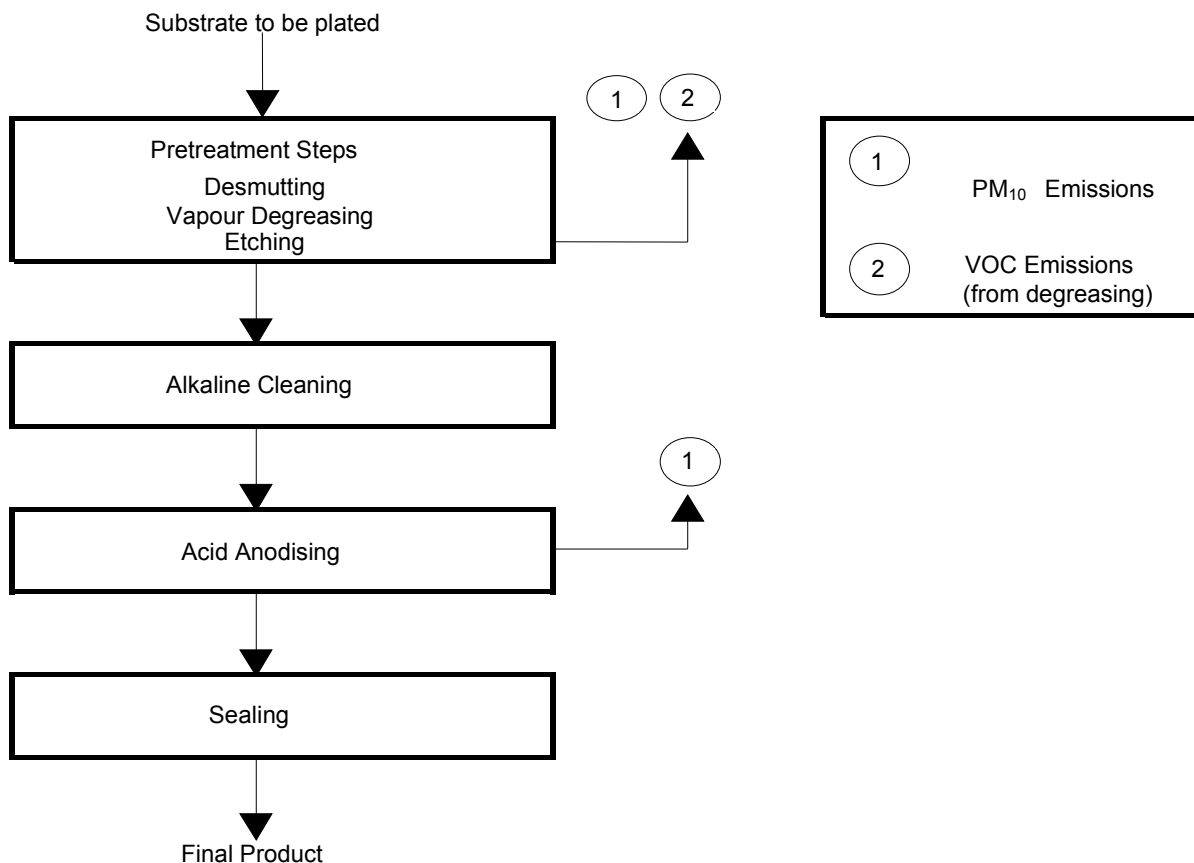
Figure 2 - Basic Process Steps in Anodising
Source: USEPA AP-42, 1996.

2.4 Electroless Plating

Electroless plating is the chemical deposition of a metal coating onto a plastic object, by immersion of the object in a plating solution. Copper and nickel electroless plating is commonly used for printed circuit boards (see EET Manual for *The Electronics & Computer Industry*). Immersion plating baths are usually formulations of metal salts, alkalis, and complexing agents (such as lactic, glycolic, malic acid salts). Electroless plating and immersion plating commonly generate more pollutant emissions than other plating techniques.

3.0 Emissions and Control Technologies

This section details the raw material inputs, the equipment used, and the processes employed that can result in emissions of NPI-listed substances. This section also provides a concise description of the potential fate (to air, land, and water) of these emissions. For the purposes of providing comprehensive information on the emissions from electroplating and anodising facilities, the fabrication of metal products prior to surface preparation, and coating and metal finishing operations are also included. Table 1 summarises the process material inputs, and the emissions of NPI-listed substances generated.

Table 1 - Material Inputs and Pollutant Emissions for Electroplating, Anodising, and Other Metal Coating Processes

Process	Material Input	Emissions to Air	Emissions to Water	Discharge to Land
Metal Shaping				
Metal cutting and forming	Cutting oils, degreasing and cleaning solvents, acids, alkalis, heavy metals	Solvent emissions (eg. acetone, toluene, xylenes, etc)	Waste oils (eg. ethylene glycol), acids (eg. hydro-chloric, nitric, sulfuric), solvents	Metal chips, metal bearing cutting fluid sludges, and solvent still-bottom wastes
Surface Preparation				
Solvent degreasing and emulsion, alkaline, and acid cleaning	Solvents, acids emulsifying agents, and alkalis	Solvents from degreasing and emulsion cleaning only	Solvent, alkaline, and acid wastes	Solvent wastes and still bottoms
Surface Finishing				
Anodising	Acids	Metal-ion-bearing mists, and acid mists	Acid wastes	Spent solutions, wastewater sludges, and base metals
Chemical Conversion Coating	Metals and acids	Metal-ion-bearing mists, and acid mists	Metal salts, acid, and base wastes	Spent solutions, sludges, and base metals
Electroplating	Acid solutions, metal and cyanide solutions	Metal-ion-bearing mists, and acid mists	Acid/alkaline, cyanide, and metal wastes	Metal and reactive wastes
Plating	Metals (eg. salts), complexing agents, alkalis	Metal-ion-bearing mists	Cyanide and metal wastes	Cyanide and metal wastes
Painting	Solvents and paints	Solvents	Solvent wastes	Still bottoms, paint solvents and metals
Other Finishing Methods	Metals and acids	Metal fumes and acid fumes	Metal and acid wastes	Polishing and etching sludges

Adapted from: *Sector Notebook Project*, USEPA, 1995.

3.1 Fabricating Metal Products

The metal fabricating process usually involves the use of cutting oils (eg. ethylene glycol), degreasing and cleaning solvents, acids, alkalis, and heavy metals. The solvents (eg. methyl ethyl ketone), alkalies, and acids (eg. hydrochloric and sulfuric), are used to clean the surface of the metals. The current trend in the Australian industry is to move towards the use of aqueous non-VOCs to clean the metals wherever possible. The use of 1,1,1-trichloroethane ceased in early 1996, and the application of methyl ethyl ketone is declining.

Metal shaping and fabricating processes result in emissions containing NPI-listed substances. For example, the application of lubricants to metal and machinery results in air emissions. Additionally, wastewater containing acidic or alkaline pollutants and solid wastes, such as metals and solvents, are usually generated during this process. Metal fabrication facilities are major users of solvents for degreasing. In cases where solvents are used solely in degreasing (ie. not used in any other plant operations), records of the amount and frequency of purchases provide enough information to estimate emissions, based on the assumption that all solvent purchased is eventually emitted.

Metalworking fluids are applied to either the tool or the metal being tooled, to facilitate the shaping operation. Fluids used in this process generally become spoiled or contaminated with extended use and reuse. Metalworking fluids are usually petroleum-based, oil-water emulsions, and synthetic emulsions. When they require disposal, these fluids can contain high levels of NPI-listed metals such as copper. Additional contaminants present in fluids resulting from these processes include acids, waste oils, and solvent wastes.

3.2 Surface Preparation

Surface preparation activities usually result in air emissions, contaminated wastewater, and solid wastes. The primary air emissions from cleaning occur because of the evaporation of chemicals from solvent degreasing and emulsion cleaning processes. These emissions can result from the volatilisation of solvents during storage, fugitive losses during use, and direct ventilation of fumes.

Wastewaters generated from cleaning are primarily in the form of rinse waters, that are usually combined with other metal finishing wastewaters (eg. electroplating) and treated on-site by conventional hydroxide precipitation. Solid wastes (eg. still bottoms, cleaning tank residues, machining fluid residues, etc) can also be generated by the cleaning operations. (eg. solid wastes are generated when cleaning)

3.3 Metal Plating

Many metal finishing operations are generally performed in baths (tanks), and are then followed by rinsing cycles. Metal plating and related emissions result in the largest volume of metal (eg. cadmium, chromium, copper, lead, and nickel) and cyanide bearing wastes. Painting operations account for the generation of solvent-bearing wastes and the direct emission of solvents (including benzene, methyl ethyl ketone, methyl isobutyl ketone, toluene, and xylenes). Paint clean-up operations can contribute to the emission of chlorinated solvents (including dichloroethylene and tetrachloroethylene).

3.3.1 Electroplating

Emissions to Air

Plating operations generate mists due to the evolution of hydrogen and oxygen gas. The gases are formed in the process tanks, on the surface of the submerged part, and on anodes or cathodes. As

these gas bubbles rise to the surface, they escape into the air, and may carry considerable amount of liquid with them in the form of a fine mist. The rate of gassing is a function of the chemical or electrochemical activity in the tank, and increases with the amount of work in the tank, the strength and temperature of the solution, and the current densities in the plating tanks. Air sparging can also result in emissions from the bursting of air bubbles at the surface of the plating tank liquid.

Emissions are also generated from surface preparation steps, that include alkaline cleaning, acid dipping, and vapour degreasing. These emissions are in the form of alkaline and acid mists, and solvent vapours. The extent of acid misting from the plating processes depends mainly on the efficiency of the plating bath, and the degree of air sparging or mechanical agitation. For many metals, plating baths have high cathode efficiencies so that the generation of mist is minimal. However, the cathode efficiency of chromium plating baths is very low (10 to 20 percent), and a substantial quantity of chromic acid mist is generated. The following paragraphs describe the methods used to control emissions from chromium electroplating although these methods can equally apply to other types of plating operations.

Emissions of chromic acid mist, because of the electro-deposition of chromium from chromic acid plating baths, occur because of the inefficiency of the hexavalent chromium plating process. Only about 10 to 20 percent of the current applied is actually used to deposit chromium on the item plated; the remaining 80 or 90 percent of the current applied is consumed by the evolution of hydrogen gas at the cathode, with the resultant liberation of gas bubbles. Additional bubbles are formed at the anode due to the evolution of oxygen. As the bubbles burst at the surface of the plating solution, a fine mist of chromic acid droplets is formed.

The principal techniques used to control emissions of chromic acid mist from chromic acid anodising operations include add-on control devices, and chemical fume suppressants. The control devices most frequently used are mist eliminators and wet scrubbers that are operated at relatively low-pressure drops. Because of the corrosive properties of chromic acid, control devices are typically made of polyvinyl chloride (PVC), or fibreglass.

Chemical fume suppressants are added to chromic acid anodising baths to reduce chromic acid mist. Although chemical agents alone are effective control techniques, many facilities use them in conjunction with an add-on control device.

Chevron blades and mesh-pad eliminators are the types of mist eliminators most frequently used to control chromic acid mist. The most important mechanism for the removal of chromic acid droplets from gas streams in mist eliminators is the inertial impaction of droplets onto a stationary set of blades, or a mesh pad. Mist eliminators are generally operated as dry units that are periodically washed down with water to clean the impaction media.

Emissions to Water and Off-Site Transfers

Wastewaters contaminated by electroplating processes occur because of workpiece rinsing and process clean-up waters. Rinse waters are usually combined with other metal finishing wastewaters, and treated on-site by conventional hydroxide precipitation. Under most State and Territory licensing conditions, wastewaters containing chromium must be pre-treated to reduce hexavalent chromium to its trivalent state. These wastewater treatment techniques can result in solid-phase wastewater treatment sludges. Other wastes and emissions generated by electroplating processes include spent solutions that become contaminated during use, and therefore, diminish performance of the process. In addition to these emissions, spent process solutions and quench bathes may be discarded periodically when the concentrations of contaminants inhibit proper function of the solution or bath.

3.3.2   Anodising

Anodising operations produce air emissions, wastewaters, and solid wastes containing NPI-listed substances. Mists and gas bubbles arising from heated fluids are a source of air emissions, and may contain metals or other substances present in the bath. When dyeing of anodised coatings occurs, wastewaters produced may contain nickel acetate, non-nickel sealers, or substitutes from the dye. Other potential pollutants include complexers, and metals from dyes and sealers.

The wet scrubbers generally used to control emissions of chromic acid mist from chromic acid anodising operations are single and double packed-bed scrubbers. Other scrubber types used less frequently include fan-separator, packed-bed, and centrifugal-flow scrubbers. Scrubbers remove chromic acid droplets from the gas stream by humidifying it to increase the mass of the droplet particles, which are then removed by impingement on a packed bed. Once-through or recirculated water is generally used as the scrubbing liquid, because chromic acid is highly soluble in water.

Chemical fume suppressants are surface-active compounds that are added directly to chromic acid anodising baths to reduce or control misting. Fume suppressants are classified as temporary, or as permanent. Temporary fume suppressants are depleted primarily by the decomposition of the fume suppressant and dragout of the solution. Permanent fume suppressants are depleted primarily by dragout of the anodising solution. Fume suppressants include wetting agents that reduce misting by lowering the surface tension of the anodising bath, foam blankets that entrap chromic acid mist at the surface of the anodising solution, or combinations of both a wetting agent and foam blanket. Polypropylene balls, which float on the surface of the plating baths, also are used as a fume suppressant in anodising baths.

Wastewaters generated by anodising are usually combined with other metal finishing wastewaters and treated on-site by conventional hydroxide precipitation. Wastewaters containing chromium are treated to reduce hexavalent chromium to its trivalent state. The conventional treatment process generates a sludge that is usually transferred off-site for metals reclamation and disposal.

Other wastes generated by anodising include spent solutions, and wastewater treatment sludges. Anodising solutions may be contaminated with the base metal being used because of the anodic nature of the process. These solutions eventually reach an intolerable concentration of dissolved metal, and require processing to remove the dissolved metal to a tolerable level for treatment and disposal.

3.3.3   Chemical Conversion Coating

Chemical conversion coating generally result in contaminated wastewaters and solid waste. Pollutants associated with these processes enter the wastestream through rinsing and batch dumping of process baths. The process baths usually contain metal salts, acids, bases, and dissolved basic materials. Wastewaters containing chromium are usually pretreated to reduce hexavalent chromium to its trivalent state. The conventional treatment process generates a sludge that is transferred off-site for metals reclamation and disposal. Characterisation of this waste is required where emission estimation is undertaken using the mass balance approach (see Section 5.0).

Other wastes generated as a result of these processes include spent solutions, and wastewater treatment sludges. Conversion coating solutions can also be contaminated with the base metal being processed. These solutions will eventually reach an intolerable concentration of dissolved metal, and require processing to reduce this concentration to a tolerable level.

3.3.4   Electroless Plating

Electroless plating can generate contaminated wastewater and solid wastes. The spent plating solution and rinse waters are usually treated chemically to precipitate out the toxic metals and destroy the cyanide. Electroless plating solutions can be difficult to treat because settling, and simple chemical precipitation, are not effective ways of removing the chelated metals used in the plating bath. The extent to which plating solution carryover adds to the wastewater and enters the sludge depends on the type of article being plated, and the specific plating method employed. However, most sludges can contain significant concentrations of NPI-listed metals, and may contain high concentrations of complex cyanides, if cyanides are not properly isolated during the treatment process.

3.3.5   Painting

Painting operations can result in emissions, contaminated wastewaters, and the generation of liquid and solid wastes. Atmospheric emissions consist primarily of the organic solvents used as carriers for the paint. Emissions can also result from paint storage, mixing, application, and drying. In addition, cleanup processes can result in the emission of organic solvents used to clean equipment and painting areas. The generation of wastewaters from painting processes is often due primarily to the discharge of water from water curtain booths. On-site processes to treat contaminated wastewater generate a sludge that is sent off-site for disposal.

Solid and liquid wastes can contain metals from paint pigments and organic solvents, (eg. paint and cleaning solvents). Still bottoms also contain solvent wastes. The cleaning solvents used on painting equipment and spray booths can also contribute organic solid waste to the wastes removed from the painting areas. The EET Manual for *Surface Coating* details emission estimation techniques for painting activities.

4.0   Emission Estimation Techniques

This section is intended to give a general overview of some of the inaccuracies associated with each of the techniques. Although the NPI does not favour the use of one emission estimation technique over other techniques, this section does attempt to evaluate the available emission estimation techniques with regards to accuracy.

Several techniques are available for calculating emissions from electroplating and anodising facilities. The technique chosen is dependent on available data, available resources, and the degree of accuracy sought by the facility in undertaking the estimate. In general, site-specific data that is representative of normal operations is more accurate than industry-averaged data, such as the emission factors presented in Section 5.0 of this Manual.

This section discusses the techniques available for estimating emissions from electroplating and anodising activities and identifies the different methods of calculation available on a pollutant basis. These emission estimation techniques are listed in no particular order and the reader should not infer a preference based on the order they are listed in this section.

Estimates of emissions of listed substances to air, water and land should be reported for each substance that triggers a threshold. The reporting list and detailed information on thresholds are contained in *The NPI Guide* at the front of this Handbook.

In general, there are four types of emission estimation techniques (EETs) that may be used to estimate emissions from your facility.

The four types described in *The NPI Guide* are:

- sampling or direct measurement;
- mass balance;
- fuel analysis or other engineering calculations; and
- emission factors.

Select the EET, (or mix of EETs), that is most appropriate for your purposes. For example, you might choose to use a mass balance to best estimate fugitive losses from pumps and vents, direct measurement for stack and pipe emissions, and emission factors when estimating losses from storage tanks and stockpiles.

If you estimate your emission by using any of these EETs, your data will be displayed on the NPI database as being of 'acceptable reliability'. Similarly, if your relevant environmental authority has approved the use of EETs that are not outlined in this handbook, your data will also be displayed as being of 'acceptable reliability'.

This Manual seeks to provide the most effective emission estimation techniques for the NPI substances relevant to this industry. However, the absence of an EET for a substance in this handbook does not necessarily imply that an emission should not be reported to the NPI. The obligation to report on all relevant emissions remains if reporting thresholds have been exceeded.

> **You are able to use emission estimation techniques that are not outlined in this document. You must, however, seek the consent of your relevant environmental authority. For example, if your company has developed site specific emission factors, you may use these if approved by your relevant environmental authority.**

You should note that the EETs presented in this manual relate principally to average process emissions. Emissions resulting from non-routine events are rarely discussed in the literature, and there is a general lack of EETs for such events. However, it is important to recognise that emissions resulting from significant operating excursions and/or accidental situations (eg: spills) will also need to be estimated. Emissions to land, air and water from spills must be estimated and added to process emissions when calculating total emissions for reporting purposes. The emission resulting from a spill is the net emission, ie., the quantity of the NPI reportable substance spilled, less the quantity recovered or consumed during clean up operations.

> The **usage*** of each of the substances listed as Category 1 and 1a under the NPI must be estimated to determine whether the 10 tonnes (or 25 tonnes for Total Volatile Organic Compounds**,** VOCs) reporting threshold is exceeded. If the threshold is exceeded, **emissions** of these Category 1 and 1a

substances must be reported for all operations/processes relating to the facility, even if the actual emissions of the substances are very low or zero.

* Usage is defined as meaning the handling, manufacture, import, processing, coincidental production or other uses of the substances.

4.1 Sampling or Direct Measurement

Sampling can be conducted to quantify point source or fugitive emissions. With point source sampling, effluent gas samples are usually collected from the stack using probes inserted through a port or stack wall. Pollutants in the gas are collected in, or on, various media that are subsequently sent to a laboratory for analysis. Pollutant concentrations are obtained by dividing the amount of pollutant collected during the test, by the volume of gas sampled. Emission rates are then determined by multiplying the pollutant concentration by the volumetric stack gas flow rate. Because there are many steps in the stack sampling procedures where errors can occur, only experienced stack testers should conduct the sampling.

Workplace health and safety data (concentrations) can be used in conjunction with exhaust system flow rates to estimate fugitive emissions from a room, floor, or building. Direct-reading instruments that may be used to obtain an instantaneous reading of vapour concentrations include photoionisation detectors, portable infrared spectrophotometers, and portable gas chromatographs. Emissions of volatile organic compounds (VOCs) from some operations, (eg. vapour degreasing, or metal cleaning and polishing), can also be measured by performing a gravimetric analysis.

The use of stack and/or workplace health and safety sampling data is likely to be a relatively accurate method of estimating air emissions from electroplating and anodising facilities. However, collection and analysis of air samples from facilities can be very expensive and especially complicated where a variety of NPI-listed VOCs are emitted and where most of these emissions are fugitive in nature. Sampling data from a specific process may not be representative of the entire manufacturing operation and may provide only one example of the facility's emissions.

To be representative, sampling data used for NPI reporting purposes needs to be collected over a period of time, and to cover all aspects of plating tank formulations.

4.1.1 Continuous Emission Monitoring System (CEMS)

A CEMS provides a continuous record of emissions over an extended and uninterrupted period of time. Various methods are used to measure the concentration of pollutants in the gas stream, and will often be based on photometric measurements. Once the pollutant concentration is known, emission rates are obtained by multiplying the pollutant concentration, by the volumetric stack gas flow rate. The accuracy of this method can be problematic when dealing with low pollutant concentrations.

Instrument calibration drift can also be problematic for CEMS, and uncaptured data can create long-term incomplete data sets. However, it is misleading to assert that a snapshot (stack sampling) can better predict long-term emission characteristics. It is the responsibility of the facility operator to properly calibrate and maintain monitoring equipment (and the corresponding emissions data).

4.2 Engineering Calculations

Theoretical and complex equations, or *models,* can be used for estimating emissions from electroplating, and other metal surface coating processes. EET equations are available for the following types of emissions commonly occurring at metal coating facilities:

- surface evaporation during bath mixing/blending operations;
- plating bath filling;
- cleaning solvent loading;
- material storage;
- spills; and
- wastewater storage.

Inputs for theoretical equations generally fall into the following categories:

1. chemical/physical properties of the material involved, (eg. vapour pressure and vapour molecular weight);
2. operating data, such as the amount of material processed and operating hours; and
3. physical characteristics and properties of the source, (eg. tank colour and diameter).

The use of emission equations to estimate emissions from electroplating and other metal coating activities is a more complex and time-consuming process than the use of emission factors. Emission equations require more detailed inputs, but they do provide an emission estimate that is based on facility-specific conditions.

See Section 5.0 for examples of theoretical equations.

4.3   Mass Balance

The mass balance approach to emissions estimation at a metal plating facility considers the facility as a *black box* where the total quantity of listed substances in the raw materials consumed, and the quantities of listed substances leaving the facility as product and waste, are compared and analysed. NPI substances can be contained in wastes, such as spent solvent or still bottoms, cutting fluid sludges, metal wastes, polishing sludges, drum residue, and wastewater.

Calculating emissions from an electroplating and anodising facility using mass balance appears to be a straightforward approach to emission estimations. However, it is likely that few Australian metal plating facilities consistently track material usage and waste generation with the overall accuracy required for the application of this method. Consequently, inaccuracies associated with individual material tracking, or other activities pertaining to each material handling stage can often result in large deviations of total facility emissions. Because emissions from specific materials are typically below 2 percent of gross consumption, an error of only ± 5 percent in any one step of the operation can significantly skew emission estimations.

When using mass balance as an EET, you should be aware of the potential difficulties and estimation errors involved with this approach. These include:

- The delivery of bulk raw materials at an electroplating facility is often tracked by volume and not by weight. Since density varies with temperature, the actual mass per unit volume of materials delivered in the summer may be less than that received in the winter months.

- Raw materials received by plating facilities can potentially be used in hundreds of coated items. In order to complete the mass balance, it is crucial that the exact quantity and characterisation of each material shipped off-site that contains NPI-listed substances is known. This involves precise analysis of the concentration of the listed pollutant of interest in each product, waste, or recycling stream.

- Plating-tank maintenance requires the manual addition of raw materials. Sometimes these additions are conducted by contractors, and are not accurately measured or recorded.

4.4   Emission Factors

Emission factors are available for many sources and processes at an electroplating facility, and are based on the results of source tests performed at an individual facility, or at one or more facilities within the electroplating industry. Basically, an emission factor is the pollutant emission rate relative to the level of source activity. The user should recognise that emission factors adopted for the NPI are often averages of available industry-wide data, (usually US or European, and seldom Australian), and vary in the degree of reliability. However, emission factors are an acceptable method for estimating emissions from all industry sectors and source categories for the National Pollutant Inventory where estimations of emissions are required to quantify medium to long-term emission trends.

Every emission factor has an associated emission factor rating (EFR) code. This rating system is common to emission factors for all industries and sectors and therefore, to all industry Manuals and Handbooks. EFRs are based on rating systems developed by the United States Environmental Protection Agency (USEPA) and by the European Environment Agency (EEA). Consequently, the ratings may not be directly relevant to Australian industry. Sources for all emission factors cited

can be found in Section 6.0 of this Manual. The emission factor ratings will not form part of the public NPI database.

When using emission factors, the reader should be aware of the associated EFR code and what that rating implies. An A or B rating indicates a greater degree of certainty than a D or E rating. The less certainty, the more likely that a given emission factor for a specific source or category is not representative of the source type. These ratings notwithstanding, the main criterion affecting the uncertainty of an emission factor remains the degree of similarity between the equipment or process selected in applying the factor, and the target equipment or process from which the factor was derived.

The EFR system is as follows:

A - Excellent
B - Above Average
C - Average
D - Below Average
E - Poor
U - Unrated

5.0   Estimating Emissions

This section provides guidance for the estimation of emissions of VOCs, metals, and inorganic compounds (eg. acids) from electroplating and other metal coating activities. Examples of the application of the various EETs are provided to illustrate some of the calculation techniques available. Table 2 lists the variables used in Equation 1 through to Equation 12.

Table 2 - List of Variables and Symbols

Variable	Symbol	Units
Electrochemical equivalent for metal m	EE_m	A-hr/mm-cm^2
Emission factor for metal m	EF_m	mg/A-hour
Cathode efficiency for metal m	e_m	%
Bath concentration for metal m	C_m	kg/Litre
Current density for metal m	D_m	A/m^2 (amperes/per sq metre)
Total VOC emissions	$E_{kpy,VOC}$	kg/yr
Vapour molecular weight	MW	kg/kg-mole
Loading emissions of VOC or PM$_{10}$ species i	$E_{kpy,i}$	kg/yr
Molecular weight of liquid mixture	MW_1	kg/kg-mole
Surface area (of spill or tank)	area	m^2
VOC emission factor	EF_{VOC}	kg/t
Amount of VOC in spent solvent processed	Q_{VOC}	tonnes/yr
Concentration of VOC or PM$_{10}$ species i in solvent or pigment i, respectively	C_i	mass %
Concentration of pollutant i in wastewater	C_{iw}	mg/L
Mass percent of species in total mixture	X_i	mass %
Volume percent of species i in total mixture	Y_i	volume %
Number of species in total mixture	n	number
Operating hours	OpHrs	hr/yr
Activity rate (area of metal coated)	A	m^2/hr
Overall control efficiency for pollutant i	CE_i	%
Amount of pigment containing species i used by the NPI reporting facility	Q_i	kg/yr, tonne/yr
Amount of pollutant i used in the reporting year	AU_i	kg/yr
Amount of pollutant i incorporated into product in the reporting year	AI_i	kg/yr
Total amount of pollutant i treated on-site, emitted to air, transferred off-site in the reporting year	AT_i	kg/yr
Amount of pollutant i in sludge	$AS_{kpy,i}$	kg/yr
Process losses of pollutant i	PL_i	kg/hr
Losses from wastewater of pollutant i	WL_i	kg/hr
Hourly volume of wastewater	V	L

Source: Queensland Department of Environment and Heritage, 1998.

5.1   Estimating Emissions from Material Loading Operations

Emissions from material loading operations can be estimated using the *Surface Coating EET Manual*.

5.2   Estimating Emissions from Plating Activities

5.2.1   Emissions to Air

Table 3 provides the emission factors for chromium electroplating. The emission factors are based on total energy input, and are presented in units of milligrams per ampere-hour (mg/A-hour). For controlled emissions from chromium electroplating operations, each of the add-on control devices used in the industry generally achieves a narrow range of outlet concentrations of chromium, regardless of the level of energy input. For this reason, total energy input may not be an appropriate basis for establishing and using emission factors in the electroplating industry. Therefore, the factors for chromium electroplating tanks in Table 3 are presented both as concentrations, and in units of total energy input.

Emission rates for controlled emissions should be estimated using the concentration factors and typical exhaust flow rates for the particular type of exhaust system in question. The factors for controlled emissions based on total energy input should only be used in the absence of site-specific information.

Table 4 provides emission factors for chromic acid anodising. The emission factors are presented in units of milligrams per hour per square metre (mg/hr/m^2) of tank surface area.

Table 5 provides emission factors for the plating of metals other than chromium although, as previously stated, emissions from plating operations (other than chromium electroplating) can be estimated using the emission factors and operating parameters for chromium electroplating.

Equation 1 below provides an estimate of uncontrolled emission factors from non-chromium plating tanks.

Equation 1

$$EF_m \quad = \quad 2.2 * 10^{-5} * EE_m * C_m * D_m / e_m$$

where:

EF_m	=	emission factor for metal m, mg/m^3
EE_m	=	electrochemical equivalent for metal m, A-hr/mm-m^2
e_m	=	cathode efficiency for metal m, %
C_m	=	bath concentration for metal m, kg/L
D_m	=	current density for metal m, A/m^2

Equation 2 provides an estimate of controlled emission factors from non-chromium plating tanks.

Equation 2

$$EF_m = 3.7 * EF_{Cr} * C_m$$

where:

EF_m = emission factor for metal m, mg/m^3
EF_{Cr} = emission factor for controlled chromium electroplating emissions (obtained from Table 4.), mg/m^3
C_m = bath concentration for metal m, kg/L

Equation 1 and Equation 2 provide an estimate of emission factors from the formation of gas as a result of the electrical energy applied to the plating tank. The equations do not account for additional emissions that result from air sparging, or mechanical agitation of the tank solution. To estimate uncontrolled emissions due to air sparging, any users who already measure surface tension and bubble diameter will need to refer to US EPA *AP42 Chapter 12.20 Electroplating*, specifically Equations 3 and 4. You will need to convert data to imperial units before insertion in the *AP42* equations. Then convert the output from AP42 into metric units for reporting to NPI.

Equations 3 and 4 in *AP42* can also be used to estimate emissions from electroless operations. It should be noted that Equation 1 through to Equation 4 (in *AP42,* not Equations 3 and 4 in this Manual) have not been validated using multiple tests. Furthermore, the emission factors that are calculated in units of concentration may not be applicable to plating lines in which there are multiple tanks that introduce varying amounts of dilution air to a common control device.

Finally, Equation 1 does not take into account the emission reduction achieved by using fume suppressants. If a fume suppressant is used, the corresponding emission factor for hard chromium plating with fume suppressant control should be used with Equation 2 to estimate emissions.

Alternatively, Equation 1 can be used and the resulting emissions can be reduced using an assumed control efficiency for hard decorative chromium electroplating, depending on which type of plating operation is most similar to the type of plating conducted. The control efficiencies for chemical fume suppressants are 78 percent for hard chromium electroplating, and 99.5 percent for decorative chromium plating.

Estimating emissions using the factors provided (units of mg/hr-m^2) in Table 4 is achieved by applying Equation 3.

Equation 3

$$E_{kpy,i} = EF_i * area * OpHrs * 10^6$$

where:

$E_{kpy,i}$	=	emissions of pollutant i, kg/yr
EF_i	=	emission factor for pollutant i, mg/hr-m^2
area	=	surface area of tank, m^2
OpHrs	=	hours per year that the plating bath of interest is in operation, hr/yr
10^6	=	conversion factor milligrams to kilograms, mg/kg

Example 1 illustrates the use of Equation 3.

Example 1 - Calculating Emissions Using Emission Factors

This example shows how total PM$_{10}$ emissions (as chromic acid) from a chromic acid anodising tank with a fume suppressant may be calculated using Equation 3 and an emission factor from Table 4. The following data is given:

EF_{PM10} =	$9.10 * 10^{-2}$ mg/hr-m^2	
area =	51.2 m^2	
OpHrs=	3 000 hr/yr	

$$
\begin{aligned}
E_{kpy,PM10} &= EF_{PM10} * area * OpHrs / 10^6 \\
&= 0.091 * 51.2 * 3\ 000 / 10^6 \\
&= 1.398 * 10^{-2} \text{ kg/yr}
\end{aligned}
$$

Table 3 - Emission Factors for Chromium Electroplating[a]

Process	Emission Factor (mg/A-hour)	(mg/m^3)	Factor Rating
Chromium Compounds [b]			
Hard chromium electroplating	7.776	NA	B
--with moisture extractor	NA	0.321	D
--with polypropylene balls	NA	0.962	D
--with fume suppressant	NA	0.366	D
--with fume suppressant and polypropylene balls	NA	$6.870 * 10^{-2}$	D
--with packed-bed scrubber	NA	$4.809 * 10^{-2}$	D
--with packed-bed scrubber, fume suppressant, polypropylene balls	NA	$5.954 * 10^{-3}$	D
--with chevron-blade mist eliminator	NA	0.202	D
--with mesh-pad mist eliminator	NA	$2.748 * 10^{-2}$	D
--with packed-bed scrubber and mesh-pad eliminator	NA	$7.328 * 10^{-5}$	E
--with composite mesh-pad mist eliminator	NA	$8.702 * 10^{-3}$	D
Decorative chromium electroplating	2.138	NA	D
--with fume suppressant	NA	$2.748 * 10^{-3}$	D
Total Particulate Matter [c]			
Hard chromium electroplating	16.2	NA	C
--with moisture extractor	NA	0.641	E
--with polypropylene balls	NA	2.015	E
--with fume suppressant	NA	0.779	E
--with fume suppressant and polypropylene balls	NA	0.144	E
--with packed-bed scrubber	NA	0.1012	E
--with packed-bed scrubber, fume suppressant, polypropylene balls	NA	$1.260 * 10^{-2}$	E
--with chevron-blade mist eliminator	NA	0.41	E
--with mesh-pad mist eliminator	NA	$5.954 * 10^{-2}$	E
--with packed-bed scrubber and mesh-pad eliminator	NA	$1.534 * 10^{-4}$	E
--with composite mesh-pad mist eliminator	NA	$1.832 * 10^{-2}$	E
Decorative chromium electroplating	4.471	NA	E
--with fume suppressant	NA	$5.725 * 10^{-3}$	E

Source: USEPA AP-42 Section 12.20, 1996.

NA = units not applicable.

[a] For chromium electroplating tanks only. Factors represent uncontrolled emissions unless otherwise noted. Emission factors based on total energy input are in units of milligrams per ampere-hour (mg/A-hour) and factors based on concentration are in units of milligrams per cubic metre of the bath capacity (mg/m^3). For controlled emissions, factors based on concentration should be used whenever possible.

[b] Comprised almost entirely of hexavalent chromium, and should be treated as such for NPI reporting purposes.

[c] All PM from chromium electroplating sources is likely to be emitted as PM_{10} (as chromic acid mist) and should be treated as such for NPI reporting.

Table 4 - Emission Factors for Chromic Acid Anodising[a]

Process	Chromium[b] Compounds (mg/hr-m^2)	Emission Factor Rating	Total PM [c] (mg/hr-m^2)	Emission Factor Rating
Chromic acid anodising	1.4	D	2.9	E
--with polypropylene balls	1.2	D	2.5	E
--with fume suppressant	$4.48 * 10^{-2}$	D	$9.10 * 10^{-2}$	E
--with fume suppressant and polypropylene balls	$1.75 * 10^{-2}$	D	$3.71 * 10^{-2}$	E
--with packed-bed scrubber	$6.72 * 10^{-3}$	D	$1.40 * 10^{-2}$	E
--with packed-bed scrubber and fume suppressant	$5.25 * 10^{-4}$	D	$1.12 * 10^{-3}$	E
--with mesh-pad mist eliminator	$3.57 * 10^{-3}$	E	$7.70 * 10^{-3}$	E
--with packed-bed scrubber and mesh-pad mist eliminator	$3.78 * 10^{-4}$	D	$7.70 * 10^{-4}$	E
--with wet scrubber, moisture extractor, and high efficiency particulate air filter	$3.36 * 10^{-4}$	D	$7.0 * 10^{-4}$	E

Source: USEPA AP-42 Section 12.20, 1996.

[a] For chromium electroplating tanks only. Factors represent uncontrolled emissions unless otherwise noted. Factors are in units of milligrams per hour per square metre of tank surface area (mg/hr-m^2).

[b] Comprised almost entirely of Cr (VI) compounds, and should be treated as such for NPI reporting purposes.

[c] Total PM includes filterable and condensable PM, however condensable PM is likely to be negligible. All PM from chromium electroplating sources is likely to be emitted as PM_{10}. Factors estimated based on the assumption that PM emissions consist entirely of chromic acid mist.

Table 5 - Emission Factors for Electroplating Metals Other than Chromium[a]

Source	Pollutant	Emission Factor (mg/A-hr)	(mg/m^3)	Factor Rating
Copper cyanide electroplating bath with mesh-pad mist eliminator	Cyanide	NA	$6.183 * 10^{-3}$	E
Copper sulfate electroplating tank with wet scrubber	Copper	NA	0.185	E
Cadmium cyanide electro-plating tank	Cadmium	2.592	NA	E
-- mesh-pad mist eliminator	Cyanide	NA	0.229	E
-- mesh-pad mist eliminator	Cadmium	NA	$3.206 * 10^{-4}$	E
-- with packed-bed scrubber	Cyanide	NA	0.135	E
-- with packed-bed scrubber	Cadmium	NA	$3.893 * 10^{-3}$	E
-- with packed-bed scrubber	Ammonia	NA	$9.618 * 10^{-2}$	E
Nickel electroplating tank	Nickel	40.82	NA	E
-- with wet scrubber	Nickel	NA	$1.534 * 10^{-2}$	E

Source: USEPA AP-42 Section 12.20, 1996.
NA = units not applicable.
[a] Factors represent uncontrolled emission unless otherwise noted. All emission factors are in energy input units of milligrams per ampere-hour (mg/A-hour), and as concentration in units of milligrams per cubic metre of the bath capacity (mg/m^3).

Speciating PM$_{10}$ Emissions

PM$_{10}$ emissions containing NPI-listed metals may require speciation into individual metal species where reporting thresholds for the metal have been triggered. Example 1 illustrated the estimation of PM$_{10}$ emissions (as chromic acid (H$_2$CrO$_4$)) using emission factors. Example 2 (below) applies Equation 4 for speciating the PM$_{10}$ emission figure calculated earlier into annual chromium (VI) emissions.

Equation 4

$$E_{kpy,PM10} = Q_i * (C_i/100) / 10^6$$

where:

$E_{kpy,PM10}$ = total emissions of PM$_{10}$ species i, kg/yr
Q_i = amount of PM$_{10}$ containing species i emitted by the facility, mg/yr
C_i = concentration of PM$_{10}$ species i in PM$_{10}$, mass %
10^6 = conversion factor, mg/kg

Example 2 - Speciating PM$_{10}$ Emissions

This example demonstrates how speciated PM$_{10}$ (chromium (VI)) emissions from chromic acid anodising with fume suppressant can be calculated using the relevant PM$_{10}$ emission factor from Table 4, the total PM$_{10}$ emissions (calculated from Example 1), and Equation 4. It is assumed that all PM$_{10}$ is emitted as chromic acid (H$_2$CrO$_4$).

$$Q_{PM10} = 13\ 978 \text{ mg chromic acid (H}_2\text{CrO}_4\text{)/yr}$$
$$C_{Cr(VI)} = 44\% \text{ Cr(VI) in H}_2\text{CrO}_4$$

$$E_{kpy,Cr(VI)} = Q_i * (C_i/100) / 10^6$$
$$= 13\ 978 * (44/100) / 10^6$$
$$= 6.15 * 10^{-3} \text{ kg/yr}$$

5.2.2 Emissions to Water

Using Sampling Data

Because of the significant environmental hazards posed by emitting toxic substances to water, most facilities emitting NPI-listed substances to waterways are required by their relevant State or Territory environment agency to closely monitor and measure these emissions. This existing sampling data can be used to calculate annual emissions using Equation 5.

Equation 5
$$E_{kpy,i} = C_{iw} * V * OpHrs / 10^6$$

where:

$E_{kpy,i}$ = emissions of pollutant i, kg/yr
C_{iw} = concentration of pollutant i in wastewater, mg/L
V = hourly volume of wastewater, L
OpHrs = operating hours per year for which data apply, hr/yr
10^6 = conversion factor, mg/kg

In applying Equation 5 to water emission calculations, monitoring data should be averaged, and only representative concentrations used in emission calculations.

Using Mass Balance

If no wastewater monitoring data exists, emissions to process water can be calculated based on a mass balance of the plating process, shown by Equation 6.

Equation 6

$$E_{kpy,i} = (AU_i - AI_i - AT_i)$$

where:

$E_{kpy,i}$	=	emissions of pollutant i, in kg/yr
AU_i	=	amount of pollutant i used in the reporting year, kg/yr
AI_i	=	amount of pollutant i incorporated into product in the reporting year, kg/yr
AT_i	=	total amount of pollutant i treated on-site, emitted to air, transferred off-site in the reporting year, kg/yr

Where an electroplating or anodising facility uses a listed mineral acid or base, but this acid or base is effectively neutralised in use or during wastewater treatment (to a pH of 6 to 8, as required by most State and Territory effluent standards), no emission quantities need be reported. However, if the acid or base is itself transformed into another listed substance the quantity of this substance coincidentally produced must be determined to assess if a threshold value has been reached. For example, sulfuric acid often yields hydrogen sulfide in effluent streams, which is itself a listed substance.

Using Emission Factors

In this Manual, emission factors for emissions to water from electroplating and other plating activities relate the quantity of pollutants emitted from a plating activity, to the area of metal coated in square metres per year (m^2/yr).

Emission factors are used to estimate a facility's emissions by the following equation.

Equation 7

$$E_{kpy,i} = [A * OpHrs] * EF_i * [1 - (CE_i/100)]$$

where :

$E_{kpy,i}$	=	emission rate of pollutant i, kg/yr
A	=	activity rate (area of metal coated), m^2/hr
OpHrs	=	operating hours, hr/yr
EF_i	=	uncontrolled emission factor of pollutant i kg/m^2
CE_i	=	overall control efficiency for pollutant i, %

Example 3 illustrates the application of Equation 7.

Example 3 - Estimating Copper Emissions to Water

Table 6 shows that 0.023 kg of copper are emitted to water for each m^2 of brass treated in a pickling bath. During the reporting year the electroplater estimates that 0.23 m^2 of brass have been produced per hour. The electroplater also estimates that 99% of copper is recovered and recycled through the bath. Emissions can be estimated using Equation 7.

EF_{Cu} = 0.023 kg/m^2
A = 0.23 m^2/hr
CE_{Cu} = 99%
OpHrs = 3000 hr/yr

$E_{kpy,i}$ = [A * OpHrs] * EF_i * [1 - (CE_i/100)]

$E_{kpy,Cu}$ = [0.23 m^2/hr * 3000 hr/yr] * 0.023 kg/m^2 * [1 - (99/100)]
= 0.16 kg/yr

Table 6 - Uncontrolled Emission Factors for Electroplating Baths[a]

Bath Description	Pollutant	Emission Factors (kg/m^2)	Emission Factor Rating
Pickling bath - steel	Hydrochloric acid	0.00012	U
Pickling bath - brass	Copper	0.023	U
Pickling bath - brass	Zinc	0.015	U
Nickel bright	Nickel	0.025	U
Nickel bright	Sulfuric acid	0.033	U
Chromium ornamental	Chromium(VI)	0.037	U
Zinc bright - cyanide bath	Zinc	0.0069	U
Zinc bright - cyanide bath	Cyanide	0.015	U
Zinc bright - non-cyanide bath	Zinc	0.003	U
Zinc bright - acid bath	Zinc	0.008	U
Copper - cyanide bath	Copper	0.01	U
Copper - cyanide bath	Cyanide	0.02	U
Copper - acid bath	Copper	0.012	U
Copper - acid bath	Sulfuric acid	0.075	U
Copper - pyrophosphate bath	Copper	0.0045	U
Cadmium - cyanide bath	Cyanide	0.01	U
Cadmium - cyanide bath	Cadmium	0.04	U
Silver	Silver	0.07	U
Silver	Cyanide	0.01	U
Lead fluoroborate bath	Lead	0.21	U
Gold - ornamental	Gold	0.0003	U
Gold - ornamental	Cyanide	0.0004	U
Gold - technical	Gold	0.0025	U
Gold - technical	Cyanide	0.0014	U
Brass cyanide bath	Zinc	0.0032	U
Brass cyanide bath	Cyanide	0.0012	U
Lead-tin fluoroborate baths	Lead	0.0035	U
Lead-tin fluoroborate baths	Fluoroborate	0.055	U
Electroless metal bath - nickel	Nickel	0.0011	U
Electroless metal bath - nickel	Phosphorus	0.004	U
Electroless metal bath - copper	Copper	0.0016	U
Anodising sulfuric baths	Sulfuric acid	0.235	U
Phosphating Baths			
Zinc phosphating	Zinc	0.0018	U
Zinc phosphating	Phosphorus	0.012	U
Iron phosphating	Phosphorus	0.004	U
Chromating Baths			
Aluminium	Chromium(VI)	0.008	U
Aluminium	Fluorine	0.004	U
zinc - yellow passivating bath	Chromium(VI)	0.0014	U
zinc - yellow passivating bath	Zinc	0.0003	U
for zinc - blue passivating bath	Chromium(VI)	0.0033	U
for zinc - blue passivating bath	Zinc	0.016	U
for zinc - blue passivating bath	Fluorine	0.0075	U

Source: Economopoulos, 1993.
[a] Units are kg/m^2 of metal coated.

5.2.3 Emissions to Land

Wastewater treatment can transport a reportable chemical to a sludge. Metal plating facilities are often required to obtain data on the concentration of metals and other substances in sludges as part of their State or Territory licensing requirement, and this data can be used to calculate the emissions as kilograms of sludge, times concentrations of the substance in the sludge. Alternatively, the loss in the sludge can be estimated by Equation 8. Although, listed substances in sludges transferred off-site do not require reporting, determining this loss can assist with determining other process losses, or may require reporting if the sludge is stored or disposed of on-site.

Equation 8

$$AS_{kpy,i} = (PL_i - WL_i) * OpHrs$$

where:

$AS_{kpy,i}$ = amount of pollutant i in sludge, kg/yr
PL_i = process losses of pollutant i, kg/hr
WL_i = losses from wastewater of pollutant i, kg/hr
OpHrs= operational hours, hr/yr

For organic chemicals in general, some degradation in treatment may occur so that not all the chemical is transferred to the sludge. Facilities can estimate the amount of organic compounds in the sludge by using measured data, or by subtracting the amount biodegraded from the total amount removed in treatment. The amount of removal can be determined from operating data, and the extent of biodegradation might be obtained from published studies. If the biodegradability of the chemical cannot be measured or is not known, reporting facilities should assume that all removal is due to absorption to sludge.

5.3 Estimating Emissions from Spills

Emissions from chemical spills can be estimated using the *Surface Coating EET Manual*.

5.4 Estimating Emissions from Surface Evaporation

Emissions from surface evaporation during organic chemical mixing operations can be estimated using the *Surface Coating EET Manual*.

5.5 Estimating Liquid Storage Tank Emissions

The most accurate (and simplest) method for estimating emissions from storage tanks is to use the *Fuel and Organic Liquid Storage EET Manual*. It is also recommended to use the US EPA software TANKS (most current version is available at http://www.epa.gov/ttn/chief/tanks.html) for calculating emissions from storage tanks. In addition, *Organic Industrial Chemical Manufacturing EET Manual* may be useful for estimating emissions from smaller tanks.

5.6   Estimating Emissions from Solvent Reclamation

VOC emissions from the loading and operation of a distillation device may be calculated using the emission factors from Table 7 and application of Equation 9.

Equation 9

$$E_{kpy,VOC} = EF_{VOC} * Q_{VOC}$$

where:

$E_{kpy,VOC}$ = VOC emissions from loading or operation of the distillation device, kg/yr

EF_{VOC} = VOC emission factor for loading of the distillation device or for the distillation column condenser vent (kg VOCs emitted/tonne VOCs processed)

Q_{VOC} = amount of VOC in spent solvent processed through the distillation device, tonnes/yr

Speciated VOC emissions are then calculated using Equation 10.

Equation 10

$$E_{kpy,i} = E_{kpy,VOC} * C_i / 100$$

where:

$E_{kpy,i}$ = emissions of VOC species i from loading or operation of the distillation device, kg/yr

$E_{kpy,VOC}$ = VOC emissions from loading or operation of the distillation device, calculated using Equation 9,kg/yr

C_i = concentration of VOC species i in the solvent processed through the distillation system, mass %

Table 7 - Emission Factors for Solvent Reclamation

Emission Source	Pollutant	Emission Factor [a] Average (kg/tonne)
Storage tank vent [b]	VOCs	0.01 (0.002 - 0.04)
Condenser vent	VOCs	1.65 (0.26 - 4.17)
Incinerator stack [c]	VOCs	0.01
Incinerator stack	Particulate matter	0.72 (0.55 - 1.0)

Fugitive emissions
    Spillage [c]
    Loading
	
	VOCs
	VOCs
		
		0.10
		0.36 (0.00012 – 0.71)

Leaks	VOCs	ND
Open sources	VOCs	ND

Source: USEPA, 1995.

[a] All emission factors are for uncontrolled process equipment, except those for the incinerator stack. Average factors are derived from the range of data points available. Factors for these sources are given in terms of kg/tonne of reclaimed solvent. Ranges in parentheses.

[b] Storage tank is of fixed roof design.

[c] Only 1 value available.

ND = no data.

Example 4 illustrates the use of Equation 9 and Equation 10.

Example 4 - Calculating Solvent Reclamation Emissions

First, total VOC emissions from operation of a distillation device may be calculated using an emission factor from Table 7 and Equation 9.

EF_{VOC} = 1.65 kg VOCs/tonne of solvent processed
Q_{VOC} = 4 tonnes of spent solvent processed/yr

$E_{kpy,VOC}$ = $EF_{VOC} * Q_{VOC}$
      = 1.65 * 4
      = 6.6 kg VOCs emitted/yr

Next, total VOC emissions are speciated using the concentration of VOC species i, mass %, and Equation 10.

$E_{kpy,VOC}$ = 6.6 kg VOCs/yr
C_i = 99% toluene in spent solvent

$E_{kpy,i}$ = $E_{kpy,VOC} * C_i/100$
     = 6.6 * 99/100
     = 6.5 kg toluene emitted/yr

If the species i concentration is provided on a volume basis from MSDS or other sources, the volume percent will need to be converted to mass percent. If molecular weight of the mixture is known, the volume percent of species i in the total mixture can be converted to mass percent, using Equation 11.

Equation 11

$$X_i \quad = \quad Y_i/100 * (MW_i / MW)$$

where:

X_i	=	mass percent of species i in total mixture, %
Y_i	=	volume percent of species i in total mixture, %
MW_i	=	molecular weight of species i, kg/kg-mole
MW	=	molecular weight of total mixture, kg/kg-mole

If the molecular weight of the total mixture is not known, the volume percent can be converted to mass percent using Equation 12.

Equation 12

$$MW = \sum_{i=1}^{n} \left(\frac{Y_i}{100} \right) * MW_i$$

where:

MW	=	molecular weight of total mixture, kg/kg-mole
n	=	number of species in total mixture
Y_i	=	volume percent of species i in total mixture, %
MW_i	=	molecular weight of species i, kg/kg-mole

5.7   Estimating Emissions from Parts Cleaning

VOC emissions factors for parts cleaning in cold cleaners, open-top vapour degreasers, or conveyor degreasers can be calculated using the *Surface Coating EET Manual*.

6.0   References

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http://www.epa.gov/ttn/chief/ap42.html

The following Emission Estimation Technique Manuals referred to in this Manual are available at the NPI Homepage (http://www.npi.gov.au) and from your local environmental protection authority (see the front of the NPI Guide for details):

- Emission Estimation Technique Manual for Combustion in Boilers;
- Emission Estimation Technique Manual for Combustion Engines;
- Emission Estimation Technique Manual for Fuel & Organic Liquid Storage;
- Emission Estimation Technique Manual for Surface Coating; and
- Emission Estimation Technique Manual for Electroplating and Anodising.