



National Pollutant Inventory

Emission Estimation Technique Manual

for

Surface Coating

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**EMISSION ESTIMATION TECHNIQUE
FOR
SURFACE COATING**

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SURFACE COATING

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1.0 Introduction

The purpose of all Emission Estimation Technique (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 surface coating operations.

Surface coating industries covered by this Manual include facilities primarily engaged in the application of paint (both waterborne and solvent based), powders, abrasive blasting, and other industrial surface treatments. Electroplating, anodising, and galvanising activities are covered by separate Manuals.

EET MANUAL: Surface Coating

HANDBOOK: Surface Coating

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This Manual was drafted by the NPI Unit of 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 industry stakeholders.

2.0 Process Description and Emissions

There are three basic steps in most surface coating operations: surface preparation, painting, and equipment cleaning. Table 1 presents a list of some of the typical emissions generated and the steps are described separately below.

Table 1 - Raw Material Inputs and Emissions Generated from Surface Coating Operations

| Typical Process | Typical Raw Material Used | Emissions of NPI-Listed Substances |
|---|---|---|
| Surface preparation and abrasive blasting | Clean blasting grit, solvents, detergents, acids and caustic soda | Particulates as PM ₁₀ (including lead and other listed metals), spent solvents in paint sludge, solids, and wastewater |
| Painting | Paint, lacquer, varnish, primers | Individual and total volatile organic compounds in coatings and thinners. |
| Equipment cleaning | Solvents, thinners | Individual and total volatile organic compounds in coatings and thinners, spent solvents, and wastewater |

Source: Queensland Department of Environment and Heritage, 1998.

2.1 Surface Preparation

Very few surfaces can be painted without some form of preparation. Proper surface preparation is essential to ensure adequate adhesion, durability, and dependability of the coating. Without a properly cleaned surface, even the most expensive coatings will fail to adhere or prevent corrosion.

Surface preparation involves two steps:

- (1) removing the old finish; and
- (2) cleaning the surface for the new finish.

Processes used to accomplish these results include cleaning the surface with a detergent or solvent, and solid-medium or bead blasting. Detergents remove most surface dirt and residue. Solvents can remove oils and greases and can be used to strip paint as well. Vapour degreasing and acid or caustic baths can be used to clean surfaces. Solid-medium or bead blasting (abrasive blasting) involves removing the surface with hard pellets or beads. The impact of the pellets or beads causes the paint on the surface to flake off.

Abrasive blast cleaning produces high volumes of waste, often containing lead and other metals (see Table 4). Generally, where expendable abrasives are used, the spent abrasive is contaminated with the old paint residue. Cleaning of recyclable abrasives produces a smaller waste stream, but often has the contaminants present at higher concentrations. Where air extraction with filtration of the exhaust air is used with a containment (or blast room), the dust collected may also contain NPI-listed substances such as lead and other heavy metals.

2.2 Painting

Painting involves the application of decorative or protective materials onto the surface of a substrate. Substrates vary in form, from whitegoods to motor vehicles and construction materials. These decorative or protective materials can be in the form of a primer, sealant, finish coat, or another type of material such as an anti-corrosion coating. The coating material will have different components and properties depending on its intended use. Paint will usually consist of a binder, a pigment, a solvent or thinner, and a drier. Paint may also be solvent- or water-based.

Most paint spray-gun operations take place in a paint booth. A pressurised spray gun applies the paint as a fine mist or aerosol. The spray gun is passed over the surface of the part to be painted until the coating is of the proper thickness. A pressurised spray gun will usually transfer approximately 50 percent of the paint to the surface. The rest of the paint that misses or bounces off the surface, is termed overspray. The booth usually has a system that is used to remove paint aerosols and volatiles from the air. In many operations, the exhaust will also have a dry filter to collect solids.

Essentially, all of the VOCs emitted from the surface coating facilities are from the solvents that are used in the paint formulations, to thin paints at the coating facility, or for clean-up purposes. All unrecovered solvent can be considered potential emissions. Monomers and low molecular weight organics can be emitted from those coatings that do not include solvents, but such emissions are negligible.

2.3 Equipment Cleaning

Paint spray guns, brushes, booths, and other equipment must be cleaned after each use in order to be used again. Water and detergents are used for cleaning equipment that applies water-based coatings, while solvents are used to clean equipment used for applications of solvent-based paint. Paint thinner is used to clean the spray gun and nozzles and to prevent clogging.

The first step in undertaking emission estimation for a surface coating operation is to identify the emission points. An effective means of evaluating points of emission for NPI-listed substances is to draw a process flow diagram identifying the operations performed, input of materials and NPI-listed substances, and the waste sources and emissions resulting from the operation of each process. Figure 1 below illustrates possible sources of emissions from a typical surface coating operation.

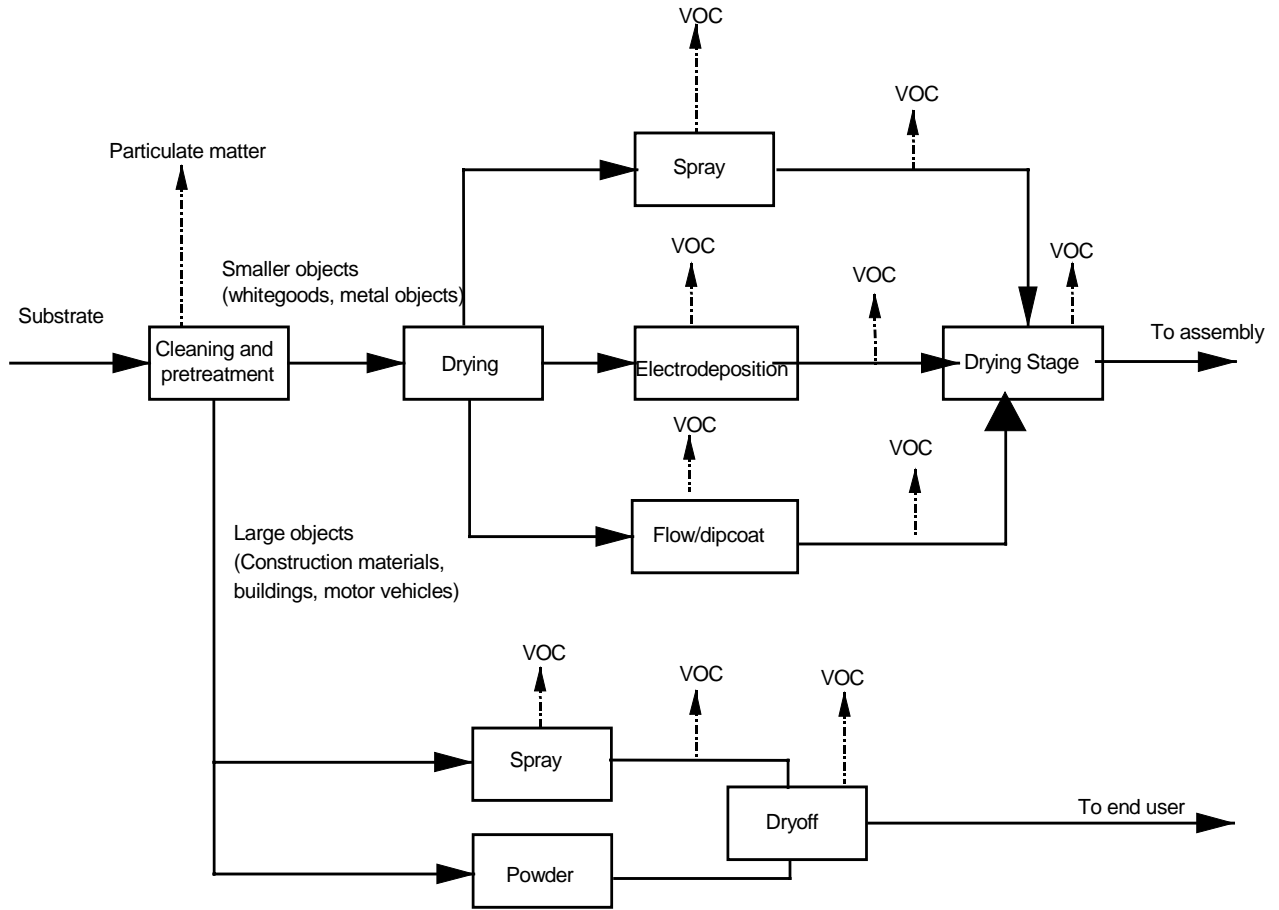


Figure 1 - General Processes in Surface Coating Operations

Adapted from: USEPA AP-42 Section 4.2 1996.

3.0 Estimating Emissions

After all the NPI-listed substances and emission sources at the reporting facility have been identified, the procedures for estimating emissions can proceed. The usual approach initially entails estimating emissions from emission sources across a facility for all substances triggering a threshold and then, based on the disposal method used, determining whether emissions from a particular emission source are to air, water, land, or an off-site disposal facility. (The off-site transfer of NPI-listed substances, including listed substances contained in wastes, does not require reporting, but may nevertheless require characterisation and estimation if emissions are being estimated from a mass balance).

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.

Table 2 lists the variables and symbols used in the equations and examples throughout this Section. It indicates the level of information required in applying the EETs illustrated.

Table 2 - List of Variables and Symbols

| Variable | Symbol | Units |
|--|-------------|--|
| Annual emissions of pollutant i | $E_{kpy,i}$ | kg/yr |
| Total emissions of pollutant i per hour | E_i | kg/hr |
| Concentration of pollutant i | C_i | parts per million volume dry, ppmvd, or mg/m^3 |
| Vapour molecular weight | MW | kg/kg-mole |
| Overall control efficiency for pollutant i | CE_i | % |
| Flow rate through exhaust ventilation system | FR | dry cubic metres per second, m^3/s |
| Molar volume | M | cubic metres (m^3)/kg-mole |
| Total quantity of substance used in the reporting year | Q | L/yr |
| Density of product | ρ | kg/L |
| Emission factor for pollutant i | EF_i | kg/units |
| Gas-phase mass transfer coefficient for VOC species i | K_i | m/sec |
| Vapour pressure of material loaded | P | kPa |
| Partial vapour pressure of VOC species i | P_i | kilopascals, kPa |
| Liquid mole fraction of VOC species i | m_i | mole/mole |
| True vapour pressure of VOC species i | VP_i | kPa |
| Liquid mass fraction of VOC species i | z_i | kg/kg |
| Molecular weight of VOC species i | MW_i | kg/kg-mole |
| Average molecular weight | MW_a | kg/kg-mole |
| Vapour mass fraction of VOC species i | x_i | kg/kg |

Table 2 - List of Variables and Symbols cont'

| Variable | Symbol | Units |
|--|--------|---------------|
| Vapour mole fraction of VOC species i, | y_i | mole/mole |
| Saturation factor | S | dimensionless |

| | | |
|---|-------------------|---|
| Initial partial pressure of VOC species i | $(P_i)_{T1}$ | kPa |
| Final partial pressure of VOC species i | $(P_i)_{T2}$ | kPa |
| Activity factor | AF | units/hr |
| Number of kg-moles of gas displaced | Δn | kg-moles/cycle |
| Number of cycles per year | CYC | cycles/yr |
| Volume of free space in the vessel | V | m ³ |
| Initial gas pressure in vessel | P_{a1} | kPa |
| Final gas pressure in vessel | P_{a2} | kPa |
| Evaporation rate of pollutant i | W_i | kg/sec |
| Duration of spill | HR | hr/event |
| Surface area of spill or tank | area | m ² |
| Vapour pressure of pollutant i | $P_{vap,i}$ | kPa |
| Universal gas constant | R | 8.314 kPa * m ³ /(kgmol * K) |
| Mass percent of species i in total mixture | X_i | mass % |
| Volume percent of species i in total mixture | Y_i | volume % |
| Number of cleaning units in use | NU | cleaning units |
| Diffusion coefficient for VOC species i | D_i | ft ² /sec |
| Batch time | H | hr/batch |
| Initial temperature of vessel | T1 | degrees K |
| Final temperature of vessel | T2 | degrees K |
| Wind speed | U | km/hr |
| Annual operating hours | OpHrs | hr/year |
| Concentration of VOC species i in the cleaning solvent | C_{is} | mass % |
| Gas-phase mass transfer coefficient for VOC species i | K_i | m/sec |
| Number of batches per year | B | batches/yr |
| Amount of pollutant i entering the process, | Amount in_i | kg/yr |
| Amount of pollutant i leaving the process as a waste stream, article or product | Amount out_i | kg/yr |

Source: Queensland Department of Environment and Heritage, 1998.

Table 3 summarises the most reliable EETs to use for specific NPI-listed substances from surface coating operations.

Table 3 - Summary of EET Reliability for Surface Coating Processes

| Process (and Likely Emissions) | Most Reliable EET | Alternative EETs Available |
|---|--------------------------|--|
| Surface Preparation (PM ₁₀ containing lead and other NPI-listed metals) | Emission Factors | Source Testing Engineering Calculations |
| Painting (Total VOCs and speciated organics (including toluene, xylenes, ethylbenzene) | Mass Balance | Source Testing Engineering Calculations Emission Factors |
| Equipment Cleanup (Total VOCs and speciated organics (including toluene, xylenes, ethylbenzene) | Mass Balance | Source Testing Engineering Calculations Emission Factors |

Source: Queensland Department of Environment and Heritage, 1998.

3.1 Emissions from Surface Preparation

Abrasive materials contain small amounts of NPI listed metals. Table 4 gives typical metal content of some abrasives used in Australia. . The use of such abrasives must be included in the threshold determinations for the use of these substances (see the NPI Guide for threshold information). The waste material may be transferred to an appropriate facility in which case it is not reportable, but the metal content of any spills will be reportable as an emission to land. When using such abrasives information on the metal content should be sought from the supplier.

It is uncertain how much of the abrasive and the abraded surface coating materials actually become airborne during the abrasive blasting process. Conservative estimates are 10% for both abrasive material and abraded paint. The total amount of old paint removed by abrasive blasting can be estimated from the thickness of the coating (possibly in the range 0.1 to 0.6 mm) and the surface area treated. The amount of a metal species in the abraded material can be estimated from data on the composition of the original surface coating material.

Equation 1 is used to calculate emissions using Table 4.

Equation 1

$$E_{kpy,i} = A * OpHrs * (C_i/10^6) * (PEM/100)$$

where:

- $E_{kpy,i}$ = emissions of pollutant i emitted as particulate matter, kg/yr
- A = activity rate of usage of abrasive material, kg/hr
- OpHrs = total annual hours of abrasive blasting operations, hr/yr
- C_i = content of metal species i in abrasive material, ppm
- 10^6 = conversion for the proportion of species i in the abrasive material used, ppm
- PEM = assumed percentage of abrasive material emitted to air as particulate matter

Table 4 - Metal Content of Common Australian Abrasives

| Abrasive | Metal (ppm) | | | | | | |
|-----------------------------|-------------|------|------|-------|-----|-----|------|
| | Pb | As | Cr | Zn | Co | Ni | Cu |
| GMA Garnet | 6 | 10 | 3 | 5 | 4 | 2 | 2 |
| Steel Grit | 68 | 62 | 1315 | 110 | 51 | 830 | 2750 |
| Copper Slag Ex Mt Isa | 263 | 690 | 66 | 1480 | 715 | 1 | 6630 |
| Copper Slag Ex Whyalla | 286 | 10 | 26 | 3600 | 635 | 210 | 5310 |
| Copper Slag Ex Pt Kembla | 2690 | 95 | 315 | 12400 | 140 | 74 | 4880 |
| Copper Slag Ex Newcastle | 3680 | 1230 | 225 | 15500 | 140 | 30 | 4070 |

Source: Morris and Salome, 1996.

Example 1 illustrates the use of Equation 1.

Example 1 - Calculating Emissions from Abrasive Blasting

This example illustrates how Equation 5 can be used to calculate emissions of particulate lead from a ship's compartment where abrasive blasting activities are being conducted. The following data is given:

Abrasive material containing 2690 ppm of lead (from Table 4) is used at the rate of 10 kg/hr for a total of 500 hours in a year. Approximately 10% of the abrasive material becomes airborne during the abrasive blasting process.

Lead emissions to atmosphere are then calculated as follows:

$$\begin{aligned} E_{kpy,Pb} &= A * OpHrs * (C_{Lead}/10^6) * (PEM/100) \\ &= 10 * 500 * (2690/10^6) * (10/100) \\ &= 1.34 \text{ kg/yr of lead emitted as particulate matter} \end{aligned}$$

Vent or other outlet testing is relatively uncommon for abrasive blasting activity at port facilities or on vessels in Australia. As a result, emissions test data for these facilities and vessels is generally only available in the form of monitoring results conducted by the port or shipping operator for compliance with Worksafe Australia Exposure Standards for Atmospheric Contaminants in the Workplace Environment. This data may be used in conjunction with exhaust system flow rates to calculate particulate metal emissions from a room, building, ship, or other vessel.

Equation 2 uses data from Table 5 to calculate emissions of materials (eg. metals).

Equation 2

$$E_{kpy,i} = (FR * 3\ 600 * OpHrs * C_i)/10^9$$

where:

$$\begin{aligned} E_{kpy,i} &= \text{emissions of listed metal or PM}_{10} \text{ species } i, \text{ kg/yr} \\ FR &= \text{flow rate through exhaust ventilation system, m}^3/\text{sec} \\ 3\ 600 &= \text{conversion factor, sec/hr} \\ OpHrs &= \text{exhaust system operating hours, hr/yr} \\ C_i &= \text{concentration of metal or PM}_{10} \text{ species in } \mu\text{g/m}^3 \\ 10^9 &= \text{conversion factor, } \mu\text{g/kg} \end{aligned}$$

Example 2 illustrates the application of Equation 2.

Example 2 - Calculating Emissions from Abrasive Blasting

This example illustrates how Equation 2 is used to calculate emissions of particulate lead from a ship's compartment where abrasive blasting activities are being conducted. The following data is given:

the building exhaust flow rate (FR) is 5.1 m³/sec

the exhaust system operates (OpHrs) for 500 hr/yr,

Occupational hygiene data indicates that the concentration of lead in the building (C_i) is 5 880 µg/m³ (Air monitor result from the use of a personal sampler while abrasive blasting using Copper Slag from Port Kembla containing 2690 ppm. Data taken from Table 5).

Lead emissions to atmosphere are then calculated as follows:

$$\begin{aligned}
 E_{\text{kpy,Pb}} &= (\text{FR} * 3\,600 * \text{OpHrs} * C_i) / 10^9 \\
 &= (5.1 * 3\,600 * 500 * 5\,880) / 10^9 \\
 &= 54.0 \text{ kg Pb/yr}
 \end{aligned}$$

Table 5 - Lead Content of Abrasives and Atmospheric Lead Exposures

| Abrasive | Lead Content of Abrasive (ppm) | Lead Exposure from Personal Air Samplers (µg/m ³) | Lead Exposure from TSP High Volume Samplers (µg/m ³) |
|--|--------------------------------|---|--|
| GMA Garnet | < 6 | < 480 [†] | < 27 [†] |
| Steel Grit | 68 | < 480 [‡] | 175 |
| Copper Slag Ex Mt. Isa | 263 | 2720 | na |
| Copper Slag Ex SA | 286 | < 480 [‡] | 632 |
| Copper Slag Ex Pt Kembla | 2690 | 5880 | na |
| Zinc Slag Ex Newcastle | 3680 | 9160 | na |
| Zinc Slag Ex Newcastle [§] | 3680 | 3240 | na |

[†] Detection limit using High Volume TSP sampler

[‡] Detection limit using Personal sampler.

[§] The zinc-slag run was repeated with the blast room air extraction system turned on.

It would be expected that this uncontrolled emission figure would be considerably reduced by appropriate control devices such as bag filters.

3.2 Emissions from Painting

Painting operations emit VOCs to the atmosphere through evaporation of the paint vehicle, thinner, or solvent used to facilitate the application of the coatings. The main factor affecting VOC emissions from painting operations is the volatile content of the coatings, which averages around 15 percent for water-based coatings, and over 50 percent for solvent-based coatings. Most, if not all, of the volatile portion of the coating evaporates during or following application. To diminish these emissions, paint manufacturers have reduced the VOC content of coatings in recent years. In addition, air pollution control equipment, (eg. activated carbon adsorption of hydrocarbon emissions, or destruction of hydrocarbons in an afterburner), is available for use in some applications.

The technique for calculating VOC emissions from painting operations is quite straightforward. For each type of coating fluid used in painting, the quantity of coating used is multiplied by the VOC content of the coatings to obtain the total VOC emissions from the use of that coating. If any types of air pollution control equipment are in use, then the VOC emissions estimated are reduced, reflecting the efficacy of the control device. To report speciated VOCs such as toluene or xylenes, the same technique is used, although only the quantity of coating used is multiplied by the individual content of the VOC being reported.

The technique is expressed by Equation 3.

Equation 3

$$E_{\text{kpy,VOC}} = \Sigma [Q * \rho_{\text{VOC}_i} * (\text{VOC}_i/100) * (1 - \text{CE}_i / 100)]$$

where:

| | | |
|-----------------------|---|---|
| $E_{\text{kpy,VOC}}$ | = | total emissions of VOCs from painting operations, kg/yr |
| Q | = | total quantity of coating used in the reporting year, L/yr |
| ρ_{VOC_i} | = | density of VOC type i, kg/L (from Table 6) |
| VOC_i | = | proportion of VOC type i in total VOC, weight % (from Table 7 to Table 10) |
| CE_i | = | control efficiency for pollutant i, % |
| i | = | pollutant type |

Example 3 illustrates the application of this equation.

Example 3 - Estimating VOC Emissions from Painting

Purchasing records indicate that a surface coating operation consumed 9 300 litres of one particular type of primer during the NPI reporting year. The MSDS for the primer shows that the product density is 1 kg/L with 28 percent by weight toluene and 54 percent by weight methyl ethyl ketone (MEK). The facility estimates that 80 percent of the primer was used in a paint booth with an afterburner fitted that typically destroys 98 percent of VOCs. The remaining 20 percent of primer was applied for retouching and other work outside the booth. Emissions can be estimated using Equation 3. The VOC content data is expressed in weight percent hence the density of the coating liquid needs to be taken into account in calculating the VOC_i figure.

$$\begin{aligned}
 Q &= 9\,300 \text{ L/yr} \\
 VOC_{\text{toluene}} &= 28\% \\
 VOC_{\text{MEK}} &= 54\% \\
 \rho &= 1 \text{ kg/L} \\
 CE &= 98\% \\
 \\
 E_{\text{kpy,toluene}} &= \Sigma [Q * \rho_{VOC_i} * (VOC_i/100) * (1 - CE_i / 100)] \\
 &= [(9\,300 * 1 * (80/100)) * (28/100) * (1 - (98/100))] + \\
 &\quad [(9\,300 * 1 * (20/100)) * (28/100) * (1 - (0/100))] \\
 &= [(2\,083) * (1 - (98/100))] + [(521) * (1 - (0/100))] \\
 &= 563 \text{ kg toluene/yr} \\
 \\
 E_{\text{kpy,MEK}} &= \Sigma [Q * \rho_{VOC_i} * (VOC_i/100) * (1 - CE_i / 100)] \\
 &= [(9\,300 * 1 * (80/100)) * (54/100) * (1 - (98/100))] + \\
 &\quad [(9\,300 * 1 * (20/100)) * (54/100) * (1 - (0/100))] \\
 &= [(4\,018) * (1 - (98/100))] + [(1\,004) * (1 - (0/100))] \\
 &= 1\,084 \text{ kg MEK/yr} \\
 \\
 E_{\text{kpy,VOC}} &= E_{\text{kpy,toluene}} + E_{\text{kpy,MEK}} \\
 &= 563 + 1\,084 \\
 &= 1\,647 \text{ kg VOC/yr}
 \end{aligned}$$

Painting Emissions - Data Inputs

To estimate total and speciated VOC emissions from painting operations, four data inputs are required:

- (1) the type of coating used;
- (2) the quantity of coating used;
- (3) an uncontrolled emission factor; and
- (4) an air pollution control efficiency factor (if applicable).

Coatings include paint, varnish and shellac, lacquer, enamel, and primer. The paint shop operator and purchasing records should be able to provide information on the types of coatings used, and the paint manufacturer could provide details on the VOC content and VOC speciation profile of paint products used.

Air pollution emission control equipment, such as activated carbon adsorption or afterburner destruction of the vapours, is sometimes used in painting operations. Information on the demonstrated effectiveness of these control methods should be obtained from the equipment manufacturer, before calculating emissions for NPI reporting.

The quantities of each type of coating used are usually available in litres. Material and Safety Data Sheets (MSDS) or coating manufacturers and suppliers should be consulted to obtain the volatile content, expressed in terms of kilograms per litre of organic solvent or VOC. If this information is not available, the default values in Table 6 should be used to obtain total VOC content, and Table 7, Table 8, Table 9, and Table 10 to obtain the speciation profiles for various surface coatings.

Table 6 - VOC Content of Common Surface Coatings

| Surface Coating | VOC Content (kg/L) |
|-----------------------|--------------------|
| Paint (solvent-based) | 0.672 |
| Paint (water-based) | 0.156 |
| Enamel | 0.420 |
| Lacquer | 0.732 |
| Primer | 0.792 |
| Varnish and Shellac | 0.396 |
| Thinner | 0.883 |
| Adhesive | 0.528 |

Source: Queensland Department of Environment and Heritage, 1998.

Table 7 - VOC Speciation Profile for Solvent-Based Paints

| CASR No. | NPI-Listed Substance | Weight % (total = 100%) |
|-----------|------------------------|-------------------------|
| 110-82-7 | Cyclohexane | 0.52 |
| 141-78-6 | Ethyl acetate | 2.04 |
| 67-64-1 | Acetone | 1.27 |
| 78-93-3 | Methyl ethyl ketone | 0.54 |
| 108-10-1 | Methyl isobutyl ketone | 0.36 |
| 1330-20-7 | Isomers of xylene | 8.17 |
| 108-88-3 | Toluene | 37.87 |
| 100-41-4 | Ethylbenzene | 0.54 |
| | All other VOCs | 48.69 |

Source: USEPA 1992. VOC / PM Speciation Data System - Version 1.50

Table 8 - VOC Speciation Profile for Primers

| CASR No. | NPI-Listed Substance | Weight % (total = 100%) |
|-----------|----------------------|-------------------------|
| 1330-20-7 | Isomers of xylene | 2.68 |
| 108-88-3 | Toluene | 44.31 |
| | All Other VOCs | 52.01 |

Source: USEPA 1992. VOC / PM Speciation Data System - Version 1.50

Table 9 - VOC Speciation Profile for Enamels

| CASR No. | NPI-Listed Substance | Weight % (total = 100%) |
|-----------|------------------------|-------------------------|
| 110-82-7 | Cyclohexane | 2.27 |
| 141-78-6 | Ethyl acetate | 8.96 |
| 67-64-1 | Acetone | 5.57 |
| 78-93-3 | Methyl ethyl ketone | 2.36 |
| 108-10-1 | Methyl isobutyl ketone | 1.57 |
| 1330-20-7 | Isomers of xylene | 23.09 |
| 108-88-3 | Toluene | 15.9 |
| 100-41-4 | Ethylbenzene | 2.36 |
| | All Other VOCs | 37.92 |

Source: USEPA 1992. VOC / PM Speciation Data System - Version 1.50

Table 10 - VOC Speciation Profile for Water-Based Paints

| CASR No. | NPI-Listed Substance | Weight % (total = 100%) |
|----------|-----------------------|-------------------------|
| 71-43-2 | Benzene | 5.52 |
| 75-09-2 | Dichloromethane | 0.36 |
| | Other VOCs not listed | 94.12 |

Source: USEPA 1992. VOC / PM Speciation Data System - Version 1.50

3.3 Emissions from Equipment Cleaning

VOC emission factors for parts cleaning in cold cleaners, open-top vapour degreasers, or conveyor degreasers are presented in Table 11. Emission factors for cold cleaners and vapour degreasers are in units of tonnes VOC/yr/unit or kg VOC/hr/m². Emission factors for vapour and non-boiling conveyor degreasers are presented only in units of tonnes VOC/yr/unit. If using emission factors based on the surface area of the exposed solvent, use Equation 4.

Equation 4

$$E_{kpy,VOC} = EF_{VOC} * \text{area} * \text{OpHrs}$$

where:

$$\begin{aligned} E_{kpy,VOC} &= \text{VOC emissions from a cold cleaner or open-top vapour degreaser, kg/yr} \\ EF_{VOC} &= \text{VOC emission factor for cold cleaners or open-top vapour degreasers, kg/hr/m}^2 \\ \text{area} &= \text{surface area of solvent exposed to the atmosphere, m}^2 \\ \text{OpHrs} &= \text{hours per year that the cold cleaner or vapour degreaser is in operation, hr/yr} \end{aligned}$$

If using emission factors based on the number of cleaning units, use Equation 5.

Equation 5

$$E_{kpy,VOC} = EF_{VOC} * \text{NU} * 1\,000$$

where:

$$\begin{aligned} E_{kpy,VOC} &= \text{VOC emissions from a cold cleaner, an open-top vapour degreaser, or a conveyor degreaser, kg/yr} \\ EF_{VOC} &= \text{VOC emission factor for cold cleaners, open-top vapour degreasers, or conveyor degreasers, tonne/yr/unit} \\ \text{NU} &= \text{number of cleaning units in use, units} \\ 1\,000 &= \text{conversion factor, kg/tonne} \end{aligned}$$

Speciated VOC emissions from parts cleaning may be calculated using Equation 6.

Equation 6

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

where:

$$\begin{aligned} E_{kpy,i} &= \text{emissions of VOC species i from parts cleaning, kg/yr} \\ E_{kpy,VOC} &= \text{VOC emissions, calculated using Equation 4 or Equation 5, kg/yr} \\ C_{is} &= \text{concentration of VOC species i in the cleaning solvent, mass \%} \end{aligned}$$

Table 11 - Solvent Emission Factors

| Type of Degreasing | Activity Measure | Uncontrolled Organic Emission Factor ^a |
|--|--|---|
| All ^b | Solvent consumed | 1 000 kg/tonne |
| Cold cleaner Entire unit ^c | Units in operation | 0.30 tonne/yr/unit |
| Waste solvent loss | | 0.165 tonne/yr/unit |
| Solvent carryout | | 0.075 tonne/yr/unit |
| Bath spray evaporation Entire unit | Surface area and duty cycle ^d | 0.06 tonne/yr/unit |
| Open top vapour Entire unit | Units in operation | 9.5 tonne/yr/unit |
| Entire unit | Surface area and duty cycle ^e | 0.7 kg/hr/m ² |
| Conveyorised vapour Entire unit | Units in operation | 24 tonne/yr/unit |
| Conveyorised non-boiling Entire unit | Units in operation | 47 tonne/yr/unit |

Source: USEPA, 1995.

^a 100% non-methane VOC.

^b Solvent consumption data will provide a more accurate emission estimate than any of the other factors presented here.

^c Emissions generally are higher for manufacturing units and lower for maintenance units.

^d For trichloroethane degreaser.

^e For trichloroethane degreaser. Does not include waste solvent losses.

All emission factors are rated E. See Section 4.4.

Example 4 - Calculating Emissions from Equipment Cleaning

This example shows how total and speciated VOC emissions from a cold cleaner may be calculated using Equation 4, Equation 5, and Equation 6, and the emission factors from Table 11 based on the surface area of the exposed solvent. First, total VOC emissions are calculated using Equation 4.

$$\begin{aligned} \text{EF}_{\text{VOC}} &= 0.4 \text{ kg/hr/m}^2 \\ \text{area} &= 1.2 \text{ m}^2 \\ \text{OpHrs} &= 3\,000 \text{ hr/yr} \\ \\ E_{\text{kpy,VOC}} &= \text{EF}_{\text{VOC}} * \text{area} * \text{OpHrs} \\ &= 0.4 * 1.2 * 3\,000 \\ &= 1\,440 \text{ kg/yr} \end{aligned}$$

Next, total VOC emissions are speciated using the concentration of VOC species i , (mass %) and Equation 6.

$$\begin{aligned} E_{\text{kpy,VOC}} &= 1\,440 \text{ kg/yr} \\ C_i &= 99\% \text{ trichloroethane in cleaning solvent} \\ \\ E_{\text{kpy,TCE}} &= E_{\text{kpy,VOC}} * C_i / 100 \\ &= 1\,440 * 99 / 100 \\ &= 1\,425.6 \text{ kg/yr} \end{aligned}$$

VOC emissions are calculated from several cold cleaners using Equation 5 and an emission factor from Table 11.

$$\begin{aligned} \text{EF}_{\text{VOC}} &= 0.30 \text{ tonnes/yr/unit} \\ \text{NU} &= 5 \text{ units} \\ \\ E_{\text{kpy,VOC}} &= \text{EF}_{\text{VOC}} * \text{NU} * 1\,000 \\ &= 0.30 * 5 * 1\,000 \\ &= 1\,500 \text{ kg/yr} \end{aligned}$$

3.4 Other Surface Coating Emission Sources

As shown in earlier sections, surface coating activities produce other emission sources for NPI-listed substances. These may include:

- emissions from material loading;
- heat-up emissions;
- emissions from spills;
- surface evaporation emissions;
- wash and rinse waters from equipment cleaning; and
- emissions from empty chemical containers.

Emissions from these sources may already have been accounted for, depending on the emission estimation techniques used. These items (and others of a similar facility-specific nature) should be included in the development of a process flow diagram.

The contribution of the above sources of emissions, such as cleaning out vessels or discarding containers, should be small when compared with process losses. If data is unavailable for these sources (or any monitoring data on overall water emissions), facility operators should assume up to 1 percent of total vessel content may be lost during each cleaning event. For example, if a facility discards the *empty* drums that have not been cleaned, calculate the emission as 1 percent of normal drum content. If the drum is transferred off-site to a landfill or to a drum recycler, then the reportable substance is also transferred off-site and therefore does not require reporting. If however, the drums are washed before disposal, this may contribute 1 percent of the content to the facility's wastewater loading.

This section details emission estimation techniques for calculating emissions from some of these sources.

3.4.1 Material Loading Emissions

VOC emissions resulting from the addition of materials to mixers, grinding equipment, and thinning tanks may be calculated using a loading loss equation. The equation, shown below as Equation 7, is related to tank loading but can be applied to any tank or vessel loading (NPCA, 1995). This equation may also be applied to estimate product filling losses.

Equation 7

$$E_{kpy,VOC} = 0.1203 * (S * P * MW * Q) / T$$

where:

| | | |
|---------------|---|--|
| $E_{kpy,VOC}$ | = | total VOC loading emissions, kg/yr |
| S | = | saturation factor (dimensionless); see Table 12. |
| P | = | vapour pressure of the material loaded at temperature T, kPa |
| MW | = | vapour molecular weight, kg/kg-mole |
| Q | = | volume of material loaded, 1 000 L/yr |
| T | = | temperature, K |
| 0.1203 | = | constant, {(kg-mole * K) / (kPa * 1000L)} |

Calculation of VOC emissions using Equation 7 is based on the following assumptions:

- the vapours displaced from the process vessel are identical to the vapours from the materials being loaded;
- the volume of the vapour being displaced is equal to the volume of material being loaded into the vessel;
- the vapour within the headspace of the vessel is saturated at room temperature and remains at room temperature during loading; and
- all solvent additions are coincident at a constant temperature (in reality, solvent is generally added in stages).

Table 12 - Saturation (S) Factors for Calculating Organic Liquid Loading Emissions

| Transport Carrier | Mode of Operation | S Factor |
|-------------------|---|----------|
| Road and Rail | Submerged loading of a clean cargo tank | 0.50 |
| Tankers | Submerged loading: normal service | 0.60 |
| | Submerged loading: vapour balance service | 1.00 |
| | Splash loading of a clean cargo tanker | 1.45 |

| | | |
|----------------|--|------|
| | Splash loading : normal service | 1.45 |
| | Splash loading: vapour balance service | 1.0 |
| Marine Vessels | Submerged loading: ships | 0.2 |
| | Submerged loading: barges | 0.5 |

Source: USEPA AP-42, 1995.

If multiple NPI-listed solvents are used in a paint, or other surface coating, product the vapour pressure (P) will need to be calculated using Equation 8.

Equation 8

$$P = \Sigma P_i$$

where:

P = vapour pressure of material loaded, kPa

P_i = partial pressure of VOC species i, kPa

P_i may be calculated using Raoult's Law (for ideal solutions), or Henry's Law constants (when gases are dissolved at low concentrations in water). Raoult's Law is given in Equation 9.

Equation 9

$$P_i = m_i * VP_i$$

where:

P_i = partial vapour pressure of VOC species i, kPa

m_i = liquid mole fraction of VOC species i, mole/mole

VP_i = true vapour pressure of VOC species i, kPa

P_i may be calculated using Henry's Law constants and Equation 10.

Equation 10

$$P_i = m_i * H_i$$

where:

P_i = partial vapour pressure of VOC species i, kPa

m_i = liquid mole fraction of VOC species i, mole/mole

H_i = Henry's Law constant for VOC species i, kPa

The liquid mole fraction of VOC species i (m_i) may be calculated if the liquid weight fractions of all species are known using Equation 11.

Equation 11

$$m_i = (z_i / MW_i) / \Sigma (z_i / MW_i)$$

where:

m_i = liquid mole fraction of VOC species i, mole/mole

z_i = liquid mass fraction of VOC species i, kg/kg

$MW_i =$ molecular weight of VOC species i, kg/kg-mole

The vapour molecular weight (MW) will also need to be calculated if multiple solvents are used for a single cleaning event. Equation 12 shows this calculation.

Equation 12

$$MW = \Sigma (y_i * MW_i)$$

where:

MW = vapour molecular weight, kg/kg-mole
 y_i = vapour mole fraction of VOC species i, mole/mole
 MW_i = molecular weight of VOC species i, kg/kg-mole

The vapour mole fraction is calculated using Equation 13.

Equation 13

$$y_i = P_i / P$$

where:

y_i = vapour mole fraction of VOC species i, mole/mole
 P_i = partial pressure of VOC species i (calculated using Equation 9 or Equation 10, kPa)
P = vapour pressure of the material loaded (calculated using Equation 8)

Speciated VOC emissions are calculated using Equation 14.

Equation 14

$$E_{kpy,i} = E_{kpy,VOC} * x_i$$

where:

$E_{kpy,i}$ = loading emissions of VOC species i, kg/yr
 $E_{kpy,VOC}$ = total VOC loading emissions (calculated using Equation 7), kg/yr
 x_i = vapour mass fraction of VOC species i, kg/kg

The vapour mass fraction of VOC species i (x_i) is calculated using Equation 15.

Equation 15

$$x_i = y_i * MW_i / MW$$

where:

- x_i = vapour mass fraction of VOC species i, kg/kg
- y_i = vapour mole fraction of VOC species i (calculated using Equation 13), mole/mole
- MW_i = molecular weight of VOC species i, kg/kg-mole
- MW = vapour molecular weight (calculated using Equation 12), kg/kg-mole

Example 5 illustrates the use of Equation 7 through to Equation 15. Emissions are calculated by following Steps 1 through 8.

Example 5 - Calculating Material Loading Emissions

A mixing vessel is cleaned with a solvent mixture at the end of each day. The following data is given:

- the yearly consumption of the solvent mixture (Q) is 600 000 litres;
- the cleaning solvent is a 50/50 mixture (by weight) of toluene and *n*-heptane;
- the solvent mixture is splash loaded into the vessel (S = 1.45 from Table 12); and
- the temperature of the solvent is 298 K (25°C).

The following Steps 1 through 8 below calculate emissions.

Step 1: Apply Equation 11 - Calculation of Liquid Mole Fraction (m_i)

| Component i | Liquid Mass Fraction, z_i (kg of i/kg of liquid) | Molecular Weight, MW_i (kg of i/kg-mole of i) | Liquid Mole Fraction, m_i (mole of i/mole of liquid) |
|-------------------|--|---|--|
| Toluene | 0.50 | 92 | $(z_i / MW_i) / \Sigma (z_i / MW_i)$ $(0.5/92)/[(0.5/92) + (0.5/100)]$ = 0.52 |
| <i>n</i> -Heptane | 0.50 | 100 | $(z_i / MW_i) / \Sigma (z_i / MW_i)$ $(0.5/100)/[(0.5/92) + (0.5/100)]$ = 0.48 |

Step 2: Apply Equation 9 - Calculation of Partial Vapour Pressure (P_i)

| Component i | Liquid Mole Fraction, m_i (mole of i/mole of liquid) | Vapour Pressure, VP_i (kPa) | Partial Vapour Pressure, P_i (kPa) |
|-------------------|--|-------------------------------|--------------------------------------|
| Toluene | 0.52 | 4.0 | $m_i * VP_i = 0.52 * 4.0$ = 2.08 |
| <i>n</i> -Heptane | 0.48 | 6.2 | $m_i * VP_i = 0.48 * 6.2$ = 2.98 |

Step 3: Apply Equation 8 - Calculation of Vapour Pressure (P)

$$P = \Sigma P_i$$

$$= 2.08 + 2.98$$

$$= 5.06 \text{ kPa}$$

Step 4: Apply Equation 13 - Calculation of Vapour Mole Fraction (y_i)

| Component i | Partial Vapour Pressure, P_i (kPa) | Total Vapour Pressure, P (kPa) | Vapour Mole Fraction, y_i (mole of i/mole of vapour) |
|-------------------|--------------------------------------|--------------------------------|--|
| Toluene | 2.08 | 5.06 | $P_i / P = 2.08 / 5.06$ $= 0.41$ |
| <i>n</i> -Heptane | 2.98 | 5.06 | $P_i / P = 2.98 / 5.06$ $= 0.59$ |

Step 5: Apply Equation 12 - Calculation of Vapour Molecular Weight (MW)

$$\text{MW} = \sum (y_i * \text{MW}_i)$$

$$= (0.41 * 92) + (0.59 * 100)$$

$$= 97 \text{ kg/kg-mole}$$

Step 6: Apply Equation 15 - Calculation of Vapour Mass Fraction (x_i)

| Component i | Vapour Mole Fraction, y_i (mole of i/mole of vapour) | Molecular Weight, MW_i (kg of i/kg-mole of i) | Vapour Molecular Weight, MW (kg of vapour /kg mole of vapour) | Vapour Mass Fraction, x_i (kg of i/kg of vapour) |
|-------------------|--|--|---|--|
| Toluene | 0.41 | 92 | 97 | $Y_i * \text{MW}_i / \text{MW}$ $= 0.41 * 92 / 97$ $= 0.39$ |
| <i>n</i> -Heptane | 0.59 | 100 | 97 | $Y_i * \text{MW}_i / \text{MW}$ $= 0.59 * 100 / 97$ $= 0.61$ |

Step 7: Apply Equation 7 - Calculate Total VOC Emissions ($E_{\text{kpy,VOC}}$)

$$E_{\text{kpy,VOC}} = 0.1203 * (S * P * \text{MW} * Q) / T$$

$$= 0.1203 * (1.45 * 5.06 * 97 * 600) / 298$$

$$= 172.4 \text{ kg VOC/yr}$$

Step 8: Apply Equation 14 - Calculate Speciated VOC Emissions ($E_{kpy,i}$)

| Component i | VOC Emissions, $E_{kpy,VOC}$ (kg VOCs) | Vapour Mass Fraction, x_i (kg of i/kg of VOCs) | Speciated VOC Emissions, $E_{kpy,i}$ (kg of i) |
|-------------------|--|--|--|
| Toluene | 172.4 | 0.39 | $E_{kpy,VOC} * x_i = 172.4 * 0.39 = 67.23$ |
| <i>n</i> -Heptane | 172.4 | 0.61 | $E_{kpy,VOC} * x_i = 172.4 * 0.61 = 105.16$ |

3.4.2 Heat-Up Emissions

Heat-up losses that occur during the operation of high-speed paint dispersers and similar types of dispersing equipment may be estimated by application of the Ideal Gas Law and vapour-liquid equilibrium principles. Emissions are calculated using the following assumptions:

- covers are closed during operation, but it is possible for vapours to be vented during operation;
- no material is added during heat-up;
- the displaced gas is always saturated with VOC vapour in equilibrium with the liquid mixture;
- the moles of gas displaced from the vessel result from the expansion of gases during heat-up and an increase in VOC vapour pressure; and,
- the vapour pressure of the mixers never rises above 101.3 kPa.

Equation 16 calculates emissions from heat-up operations.

Equation 16

$$E_{kpy,VOC} = \left(\frac{[\sum(P_i)_{T1} / (101.3 - \sum(P_i)_{T1})] + [\sum(P_i)_{T2} / (101.3 - \sum(P_i)_{T2})]}{2} \right) * (\Delta n * MW_a * CYC)$$

where:

$E_{kpy,VOC}$ = VOC emissions from material heat-up in the process equipment, kg/yr

$(P_i)_{T1}$ = initial partial pressure of each VOC species i in the vessel headspace at the initial temperature T1, kPa
(calculated using Equation 9 or Equation 10)

$(P_i)_{T2}$ = final partial pressure of each VOC species i in the vessel headspace at the final temperature T2, kPa; (calculated using Equation 9 or Equation 10)

Δn = number of kg-moles of gas displaced, kg-mole/cycle

MW_a = average vapour molecular weight, kg/kg-mole

CYC = number of cycles per year, cycles/yr

The term Δn may be calculated using Equation 17.

Equation 17

$$\Delta n = V/R * ((P_{a1} / T1) - (P_{a2} / T2))$$

where:

Δn = number of kg-moles of gas displaced, kg-mole/cycle
 V = volume of free space in the vessel, m³
 R = universal gas constant at 1 atmosphere of pressure, 8.314 kPa * m³/(kg mol * K)
 P_{a1} = initial gas pressure in vessel, kPa
 P_{a2} = final gas pressure in vessel, kPa
 $T1$ = initial temperature of vessel, K
 $T2$ = final temperature of vessel, K

P_{a1} and P_{a2} can be calculated using Equation 18 and Equation 19.

Equation 18

$$P_{a1} = 101.3 - \Sigma (P_i)_{T1}$$

Equation 19

$$P_{a2} = 101.3 - \Sigma (P_i)_{T2}$$

where:

P_{a1} = initial gas pressure in vessel, kPa
 P_{a2} = final gas pressure in vessel, kPa
 $(P_i)_{T1}$ = partial pressure of each VOC_i in the vessel headspace, kPa, at the initial temperature T1 (calculated using Equation 9 or Equation 10)
 $(P_i)_{T2}$ = partial pressure of each VOC_i in the vessel headspace, kPa, at the final temperature T2 (calculated using Equation 9 or Equation 10)

Speciated VOC emissions would be calculated using a modified version of Equation 16 as shown in Equation 20.

Equation 20

$$E_{kpy,i} = \{ [(P_i)_{T1} / (101.3 - (P_i)_{T1})] + [(P_i)_{T2} / (101.3 - (P_i)_{T2})] \} / 2 * (\Delta n * MW_a * CYC)$$

where:

$E_{kpy,i}$ = VOC species i emissions from material heat-up in the process equipment, kg/yr
 $(P_i)_{T1}$ = partial pressure of VOC species i in the vessel headspace at the initial temperature T1, kPa; see Equation 9 or Equation 10
 $(P_i)_{T2}$ = partial pressure of VOC species i in the vessel headspace at the final temperature T2, kPa; see Equation 9 or Equation 10
 Δn = number of kg-moles of gas displaced, kg-mole/cycle; see Equation 17
 MW_a = average vapour molecular weight, kg/kg-mole
 CYC = number of cycles per year, cycles/yr

Example 6 illustrates the use of Equation 16 through to Equation 20. Emissions are calculated by following Steps 1 through 6.

Example 6 - Calculating Heat-Up Emissions

This example shows how heat-up losses from a disperser are calculated using Equation 16 through to Equation 20. Supporting equations from Section 3.4.1 (Equation 9 and Equation 10) are also used in this example.

A 3 000 litre, high-speed disperser contains 2 000 litres of paint. The following data is given:

- the paint consists of 20 percent by weight toluene, 30 percent by weight methyl ethyl ketone (MEK), and 50 percent by weight pigments and non-volatile resins;
- the initial temperature (T1) of the mixture is 298 K (25°C);
- the final temperature (T2) of the mixture is 313 K (40°C);
- the approximate molecular weight of the paint mixture is 85kg/kg-mole;
- the average vapour molecular weight (MW_a) is 75 kg/kg-mole, calculated using Equation 12;
- the mixer goes through the given temperature cycle with this paint formulation 25 times/yr, CYC; and
- the volume of free space in the vessel is 3 000 - 2 000 L = 1 000 L or 1 m³

Step 1: Apply Equation 11 - Calculation of Liquid Mole Fraction (m_i)

| Component i | Liquid Mass Fraction, z _i (kg of i/kg of liquid) | Molecular Weight, MW _i (kg of i/kg-mole of i) | Liquid Mole Fraction, m _i (mole of i/mole of liquid) ^a |
|-------------|--|---|---|
| Toluene | 0.2 | 92 | $(z_i / MW_i) / \Sigma (z_i / MW_i)$ = $(0.2/92)/((0.2/92)+(0.3/72)+(0.5/85))$ = 0.18 |
| MEK | 0.3 | 72 | $(z_i / MW_i) / \Sigma (z_i / MW_i)$ = $(0.3 / 72)/((0.2/92)+(0.3/72)+(0.5/85))$ = 0.34 |

Step 2: Apply Equation 9 - Calculation of Partial Vapour Pressure at Initial Temperature [(P_i)_{T1}]

| Component i | Liquid Mole Fraction, m _i (mole of i/mole of liquid) | Vapour Pressure, VP _i @ 25°C (kPa) | Partial Pressure at T1, (P _i) _{T1} (kPa) |
|-------------|--|---|---|
| Toluene | 0.18 | 4 | m _i * VP _i = 0.72 |
| MEK | 0.34 | 13.31 | m _i * VP _i = 4.53 |

Step 3: Apply Equation 9 - Calculation of Partial Pressure at Final Temperature [(P_i)_{T2}]

| Component i | Liquid Mole Fraction, m _i (mole/mole) | Vapour Pressure, VP _i @ 40°C (kPa) | Partial Pressure at T2, (P _i) _{T2} (kPa) |
|-------------|---|---|--|
|-------------|---|---|--|

| | | | |
|---------|------|-------|------------------------|
| Toluene | 0.18 | 8 | $m_i * VP_i$ = 1.44 |
| MEK | 0.34 | 25.86 | $m_i * VP_i$ = 8.79 |

Step 4: Apply Equation 18 and Equation 19 - Calculation of Initial Pressure (Pa₁) and Final Pressure (Pa₂)

$$\begin{aligned}
 Pa_1 &= 101.3 - \Sigma (P_i)_{T1} \\
 &= 101.3 - (0.72 + 4.53) \\
 &= 96.05 \text{ kPa}
 \end{aligned}$$

$$\begin{aligned}
 Pa_2 &= 101.3 - \Sigma (P_i)_{T2} \\
 &= 101.3 - (1.44 + 8.79) \\
 &= 91.07 \text{ kPa}
 \end{aligned}$$

Step 5: Apply Equation 17 - Calculation of kg-moles Gas Displaced (Δn)

The volume of free space in the vessel (V) is 3 000 litres - 2 000 litres = 1 000 litres or 1 m³.

$$\begin{aligned}
 \Delta n &= V/R * ((Pa_1 / T1) - (Pa_2 / T2)) \\
 &= (1 / 8.314) * ((96.05 / 298) - (91.07 / 313)) \\
 &= 3.77 * 10^{-3} \text{ kg-moles/cycle}
 \end{aligned}$$

Step 6: Apply Equation 16 - Calculation of Total VOC Emissions (E_{VOC})

$$\begin{aligned}
 E_{kpy,VOC} &= \{([\Sigma(P_i)_{T1} / 101.3 - \Sigma(P_i)_{T1}] + [\Sigma(P_i)_{T2} / 101.3 - \Sigma(P_i)_{T2}] / 2\} * \\
 &\quad (\Delta n * MW_a * CYC) \\
 &= \{((5.25 / (101.3 - 5.25)) + (10.23 / (101.3 - 10.23))) / 2\} * \\
 &\quad 3.77 * 10^{-3} * 25 * 75 \\
 &= 0.590 \text{ kg/yr}
 \end{aligned}$$

Step 7: Apply Equation 20 - Calculation of Toluene Emissions (E_{toluene})

$$\begin{aligned}
 E_{kpy, toluene} &= \{([(P_i)_{T1} / (101.3 - (P_i)_{T1})] + [(P_i)_{T2} / (101.3 - (P_i)_{T2})]) / 2\} * \\
 &\quad \Delta n * MW_a * CYC \\
 &= \{((0.72 / (101.3 - 0.72)) + (1.44 / (101.3 - 1.44))) / 2\} * \\
 &\quad 3.77 * 10^{-3} * 25 * 75 \\
 &= 0.076 \text{ kg/yr}
 \end{aligned}$$

3.4.3 Spill Emissions

A vaporisation equation can be used to estimate the evaporation rate of a liquid chemical spill if the size area of the spill is known or can be estimated.

Equation 21

$$E_i = (MW_i * K_i * \text{area} * P_i * 3\,600 * HR) / (R * T)$$

where:

- E_i = emissions of VOC species i from the spill, kg/event
- MW_i = molecular weight of VOC species i, kg/kg-mole
- K_i = gas-phase mass transfer coefficient for VOC species i, m/sec
- area = surface area of spill, m^2
- P_i = partial pressure of VOC species i (if a pure chemical is spilled) or the partial pressure of chemical i (if a mixture of VOCs is spilled) at temperature T, kPa; the partial pressure of VOC species i (P_i) may be calculated using Equation 4 or Equation 5
- 3 600 = 3 600 sec/hr
- HR = duration of spill, hr/event
- R = universal gas constant at 1 atmosphere of pressure,
- T = temperature of the liquid spilled, K

The gas-phase mass transfer coefficient (K_i) may be calculated using Equation 22.

Equation 22

$$K_i = (0.00438 * (0.62138 * U)^{0.78} * (D_i / (3.1 * 10^{-4}))^{2/3}) / 3.2808$$

where:

- K_i = gas-phase mass transfer coefficient for VOC species i, m/sec
- U = wind speed, km/hr
- D_i = diffusion coefficient for VOC species i in air, ft^2/sec

Diffusion coefficients (D_i) can be found in chemical handbooks and are usually expressed in units of square centimetres per second (cm^2/sec). If a diffusion coefficient is not available for a particular NPI-listed chemical, the gas-phase mass transfer coefficient (K_i) may be estimated using Equation 23.

Equation 23

$$K_i = (0.00438 * (0.62138 * U)^{0.78} * (18/MW_i)^{1/3})/3.2808$$

where:

$$\begin{aligned} K_i &= \text{gas-phase mass transfer coefficient for VOC species } i, \\ &\text{m/sec} \\ U &= \text{wind speed, km/hr} \\ MW_i &= \text{molecular weight of VOC species } i, \text{ kg/kg-mole} \end{aligned}$$

Example 7 illustrates the use of Equation 21 and Equation 23. Emissions are calculated by following Steps 1 and 2.

Example 7 - Calculating Spill Emissions

Methyl ethyl ketone (MEK) is spilled onto the ground outside a building. The following data is given:

- the spill is not detected for 1 hour; it takes an additional 2 hours to recover the remaining MEK; the duration of the spill (HR), therefore, is 3 hours;
- the average wind speed (U) is 33.6 km/hr ;
- the ambient temperature (T) is 298 K (25°C);
- the surface area of the spill (area) is 11 m²;
- the molecular weight of MEK (MW_i) is 72 kg/kg-mole
- the partial pressure of MEK (P_i) at 298 K (25°C) is approximately 13.31 kPa

Step 1: Using Equation 23, Calculate the Gas-Phase Mass Transfer Coefficient (K_i)

$$\begin{aligned} K_i &= (0.00438 * (0.62138 * U)^{0.78} * (18 / MW_i)^{1/3})/3.2808 \\ &= (0.00438 * 21^{0.78} * (18/72)^{1/3})/3.2808 \\ &= 0.0093 \text{ m/sec} \end{aligned}$$

Step 2: Using Equation 21, Calculate Emissions (E_i)

$$\begin{aligned} E_{\text{MEK}} &= (MW_i * K_i * \text{area} * P_i * 3\,600 * \text{HR}) / (R * T) \\ &= (72 * 0.0093 * 11 * 13.31 * 3\,600 * 3) / (8.314 * 298) \\ &= 424.80 \text{ kg/spill} \end{aligned}$$

3.4.4 Surface Evaporation Emissions

Emissions from surface evaporation during paint and other coating mixing operations can be estimated using Equation 24.

Equation 24

$$E_{kpy,i} = [(MW_i * K_i * area * P_i * 3\ 600 * H)/(R * T)] * B$$

where:

| | | |
|-------------|---|--|
| $E_{kpy,i}$ | = | emissions of VOC species i, kg/yr |
| MW_i | = | molecular weight of VOC species i, kg/kg-mole |
| K_i | = | gas-phase mass transfer coefficient for VOC species i, m/sec |
| area | = | surface area of tank, m ² |
| P_i | = | vapour pressure of VOC i (if a pure chemical is used) or the partial pressure of chemical i (if a mixture of VOCs is used) at temperature T, kPa; the partial pressure of VOC species i (P_i) may be calculated using Equation 9 or Equation 10) |
| 3 600 | = | conversion factor, sec/hr |
| H | = | batch time, hr/batch |
| R | = | universal gas constant at 1 atmosphere of pressure, |
| T | = | temperature of the liquid, K |
| B | = | number of batches per year, batches/yr |

Equation 22 or Equation 23 can be used to estimate K_i . Total VOC emissions would equal the sum of all VOC species emissions.

Example 8 illustrates the use of Equation 23 and Equation 24. Emissions are calculated by following Steps 1 and 2.

Example 8 - Calculating Surface Evaporation Emissions

This example estimates emissions from a mixing operation due to surface evaporation. The following data is given:

- the batch time (H) is 4 hours;
- the number of batches per year (B) is 550;
- the average wind speed (U) is 1.28 km/hr ;
- the ambient temperature (T) is 298 K (25°C);
- the surface area of the mixing tank (area) is 8.75 m²;
- the molecular weight of toluene (MW_i) is 92 kg/kg-mole; and
- the partial vapour pressure of toluene (P_i) at 298 K (25°C) is approximately 4 kPa

Step 1: Using Equation 23, Calculate the Gas-Phase Mass Transfer Coefficient (K_i)

$$\begin{aligned}
K_i &= (0.00438 * (0.62138 * U)^{0.78} * (18/MW_i)^{1/3}) / 3.2808 \\
&= (0.00438 * 0.8^{0.78} * (18/92)^{1/3}) / 3.2808 \\
&= 6.66 * 10^{-4} \text{ m/sec}
\end{aligned}$$

Step 2: Using Equation 24, Calculate Emissions ($E_{kpy,i}$)

$$\begin{aligned}
E_{kpy,toluene} &= [(MW_i * K_i * \text{area} * P_i * 3\,600 * H)/(R * T)] * B \\
&= [(92 * 6.66 * 10^{-4} * 8.75 * 4 * 3\,600 * 4)/(8.314 * 298)] * 550 \\
&= 6\,855 \text{ kg/yr}
\end{aligned}$$

3.5 Mass Balance

A mass balance approach may be used to estimate emissions when the quantities of a material used, recycled, emitted, and disposed of are known. Emissions from surface coating for an uncontrolled facility can be estimated by assuming that all VOCs in the coatings are emitted. For liquid applications, such as wet chemical stations or coating/solvent application stations, usage figures will generally be in litres. The difference (by mass) of the amount of a coating or liquid used and the amount of the liquid recovered, either through product recovery or disposal, is assumed to equal emissions to atmosphere.

Similarly, estimating emissions for speciated VOCs would require knowledge of the types of coatings and solvents used and the weight percentages of listed materials in the coatings and solvents. Annual usage may be based on gross purchase amount (in cubic metres). When operations have several formulas for different batches, a conservative emissions estimate for each listed substance can be achieved based on the formula with the highest listed substance usage. This approach is suitable for speciated organics (xylenes, toluene) because they are not involved in chemical reactions and their usage rates may already be tracked for purchasing reasons.

Mass balance calculations for estimating emissions to air of NPI-listed substances can be represented conceptually by Equation 25.

Equation 25

$$E_{kpy,i} = \text{Amount in}_i - \text{Amount out}_i$$

where:

$$\begin{aligned}
E_{kpy,i} &= \text{emissions of pollutant } i, \text{ kg/yr} \\
\text{Amount in}_i &= \text{amount of pollutant } i \text{ entering the process, kg/yr} \\
\text{Amount out}_i &= \text{amount of pollutant } i \text{ leaving the process as a waste stream, article or product, kg/yr}
\end{aligned}$$

The term “Amount out_i” may actually involve several different fates for an individual pollutant. This could include the amount recovered or recycled, the amount leaving the process in the manufactured product, the amount leaving the process in wastewater, the amount emitted to the atmosphere, or the amount of material transferred off-site as hazardous waste or to landfill. A thorough knowledge of the different destinations for the pollutant of interest is necessary for an accurate emission estimate to be made using the mass balance approach.

The amount of a particular substance entering or leaving a facility is often mixed within a solution as a formulation component or as a trace element within the raw material. To determine the total weight of the substance entering or leaving the process, the concentration of the substance within

the material is required. Using this concentration data, Equation 26 can be applied as a practical extension of Equation 25.

Equation 26

$$E_{kpy,i} = [Q_{in} * C_{in} - Q_{pr} * C_{pr} - Q_{rec} * C_{rec} - Q_{waste} * C_{waste}] / 10^6$$

where:

| | | |
|--------------------------------------|---|--|
| $E_{kpy,i}$ | = | emissions of pollutant i, kg/yr |
| $Q_{in}, Q_{pr}, Q_{rec}, Q_{waste}$ | = | quantity of raw material, product, recycled material or waste respectively, that is processed annually (generally expressed in kg for solids, L for liquids) |
| $C_{in}, C_{pr}, C_{rec}, C_{waste}$ | = | concentration of substance i in the raw material, product, recycled material or waste respectively, that is processed annually (generally expressed in mg/kg for solids, mg/L for liquids) |
| 10^6 | = | conversion from milligrams to kilograms. |

Example 9 illustrates the application of Equation 26.

Example 9 - Using a Mass Balance for Lead Emissions

A manufacturer uses a particular paint in the production of a specialist product. The paint contains amounts of lead (Pb). The facility uses 110,000 litres of paint per year to manufacture 1,000,000 items, to each of which 0.1 litres of paint is applied. The concentration of lead initially in the paint is 9g/L. A water scrubber is used from which 3,000 litres of sludge is removed annually. The concentration of lead in the sludge from the scrubber is 12 g/L. The sludge is transferred offsite to a treatment facility. 1.5% of the supplied paint is retained in the drums which are returned to the manufacturer. Assuming the paint applied to the items has the same concentration of lead as the source material and there are no other recycling activities taking place, annual emissions to air could be determined using Equation 26:

$$\begin{aligned}
 E_{kpy,Pb} &= [Q_{in} * C_{in} - Q_{pr} * C_{pr} - Q_{rec} * C_{rec} - Q_{waste} * C_{waste}] / 10^6 \\
 &= [110\ 000 * 9000 - 1\ 000\ 000 * 0.1 * 9000 - 110\ 000 * 9000 * \\
 &\quad 1.5 / 100 - 3000 * 12\ 000] / 10^6 \\
 &= 39 \text{ kilograms of Pb emitted to air per year.}
 \end{aligned}$$

Where a facility uses a listed mineral acid or base, with this acid or base being 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 should be reported. If the acid or base is itself transformed into another listed substance, however, 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 and require reporting where annual emissions total 10 tonnes or more.

Wastewater treatment may precipitate the reportable chemical in a sludge. Facilities are often required to obtain data on the concentration of metals or other substances in sludges as part of their licensing requirement and this data can be used to calculate the emissions as kilograms of sludge multiplied by the concentrations of the substance in the sludge. 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 disposed of on-site.

For many chemicals used and emitted during chemical processes, some degradation in treatment may occur so that not all the chemical is transferred to the sludge. Facilities can estimate the amount of reportable 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.

4.0 Emission Estimation Techniques: Acceptable Reliability and Uncertainty

Several techniques are available for calculating emissions of NPI-listed substances from surface coating operations. The best emission estimation technique (EET) to use will depend on the emission source being evaluated, and available data, and resources. Emissions to atmosphere, wastewater, and via solid wastes are likely to be the primary emission points to consider. If water is treated on-site, sludges or other wastes containing listed substances may be created. Other emissions may come from either discarded containers or samples, vessel washings, or from volatilisation to the air. Facility operators should ensure that all emissions are accounted for when reporting.

4.1 Direct Measurement

Because vent or other outlet testing is relatively uncommon for Australian surface coating facilities, emissions test data for these facilities are generally only available in the form of monitoring results for NPI-listed substances conducted for compliance with Worksafe Australia Exposure Standards for Atmospheric Contaminants in the Workplace Environment. However, while this data may be used in conjunction with exhaust system flow rates to calculate total VOCs or speciated organic solvent emissions from a room, floor, or building, concentrations are often below detection limits due to high ventilation flow rates.

4.2 Mass Balance

Calculating emissions from a surface coating facility using mass balance appears to be a straightforward approach to emission estimation. However, it is likely that few Australian surface coating facilities consistently track material usage and waste generation with the overall accuracy needed for application of this method. Inaccuracies associated with individual material tracking, or other activities inherent in each material handling stage, can result in large deviations for 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.

4.3 Engineering Calculations

In the absence of other data, engineering calculations may be used to estimate emissions from some surface coating processes. For example, for any process that involves transfer of a chemical species from the liquid phase to the vapour phase, the saturation (equilibrium) vapour pressure and exhaust flow rate from the process can be used to establish the upper limit of emissions from that process. This is a conservative approach because of the assumption that the airflow is saturated.

4.4 Emission Factors

Emission factors are used to estimate emissions based on known relationships between process rates and emission rates. The use of emission factors to estimate emissions from surface coating operations is an appropriate approach for NPI reporting. Development of an accurate emission factor will require detailed knowledge of the process conditions and chemical usage rates during the time period for which emissions are known.

Emission factors are available for surface preparation, painting, and equipment cleaning operations, and are based on the results of source tests performed on individual facilities. The reader should recognise that, in most cases, emission factors adopted for the NPI are averages of available industry-wide data with varying degrees of reliability. Emission factors are, however, an acceptable technique for estimating emissions for the NPI where estimations of emissions are required to quantify medium to long-term emission trends.

Basically, an emission factor is the pollutant emission rate relative to the level of source activity. It is usually expressed as the weight of a substance emitted multiplied by the unit weight, volume, distance, or duration of the activity emitting the substance, (eg. kilograms of total VOCs emitted to air per square metre of substrate coated).

Every emission factor has an associated emission factor rating (EFR) code. This rating system is common to EETs for all industries and sectors and, therefore, to all Industry Handbooks. They 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 5.0 of this Manual. The emission factor ratings will not form part of the public NPI database.

When using emission factors, you 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/process selected in applying the factor, and the target equipment/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 References

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The following Emission Estimation Technique Manuals referred to in this Manual are available at the NPI website (<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 Galvanizing; and
- Emission Estimation Technique Manual for Electroplating and Anodising.