National Pollutant Inventory

Emission Estimation Technique Manual

for

Paint and Ink Manufacturing

First published in August 1998

EMISSION ESTIMATION TECHNIQUES FOR PAINT AND INK MANUFACTURING

TABLE OF CONTENTS

1.0 INTRODUCTION 3

2.0 PROCESS DESCRIPTION 4

2.1 The Manufacturing Process 4
2.1.1 Preassembly and Premix 5
2.1.2 Pigment Grinding or Milling 6
2.1.3 Product Finishing 7
2.1.4 Product Filling 7

2.2 Emission Sources 8
2.2.1 Process Operation Emissions 8
2.2.2 Miscellaneous Operation Emissions 9
2.2.3 Material Storage Emissions 10
2.2.4 Equipment Leaks 10
2.2.5 Spills 11

2.3 Design and Operating Factors Influencing Emissions 11
2.3.1 VOC Control Systems 11
2.3.2 PM and PM_{10} Control Systems 12
2.3.3 Equipment or Process Modifications 13

3.0 OVERVIEW OF AVAILABLE EMISSION ESTIMATION TECHNIQUES 14

3.1 Emission Factors 14

3.2 Source-Specific Equations 15

3.3 Sampling or Direct Measurement 16

3.4 Mass Balance 16

4.0 ESTIMATING EMISSIONS 17

4.1 Using Equations 18
4.1.1 Equations for Material Loading Emissions 20
4.1.2 Equations for Heat-Up Emissions 25
4.1.3 Equations for Spill Emissions 29
4.1.4 Equations for Surface Evaporation Emissions 31
4.1.5 Liquid Storage Tank Emissions 32

4.2 Using Emission Factors 32
4.2.1 Emissions from Solvent Reclamation 33
4.2.2 Emissions from Parts Cleaning 35
4.2.3 Emissions from Equipment Leaks 38
4.2.4 Emissions of Particulate Matter (PM/PM_{10}) 38

5.0 EMISSION FACTOR RATING 40

6.0 REFERENCES 42

PAINT AND INK MANUFACTURING

LIST OF FIGURES AND TABLES

Figure 1. Basic Process Steps and Emission Points in Paint Manufacturing..... 5

Table 1. Typical Paint and Ink Manufacturing Facility Control Techniques 11

Table 2. List of Variables and Symbols 19

Table 3. Saturation (S) Factors for Calculating Organic Liquid Loading Emissions..... 20

Table 4. Emission Factors for Solvent Reclamation [1] 34

Table 5. Solvent Emission Factors..... 36

Table 6. Emission Factors for Paint and Varnish Manufacturing [a]..... 39

Table 7. Emission Factors for Printing Ink Manufacturing [a] 39

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 paint and ink manufacturing.

The paint manufacturing activities covered in this Manual apply to facilities primarily engaged in the manufacture of paints (in paste and ready-mixed form), varnishes, lacquers, enamels and shellacs, putties, wood fillers and sealants, paint and varnish removers, paint brush cleaners, and allied paint products.

The ink manufacturing activities apply to facilities primarily engaged in the manufacture of inks including carbon ink, drawing ink, indelible ink, India ink, printing ink, silk screen ink, and writing ink.

EET MANUAL : Paint and Ink Manufacturing

HANDBOOK : Paint and Ink Manufacturing

ANZSIC CODE : 254 (including 2542 and 2547)

This Manual was drafted by the NPI Unit of the Queensland Department of Environment 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

This section details the major industrial processes relating to the paint and ink industries, including the raw materials and equipment used, the by-products produced and NPI listed substances emitted, and the substances either recycled or transferred off-site. It is designed to help you gain a general understanding of the industries, and the interrelationship between the industrial processes and the nature and levels of emissions discussed in subsequent sections of the Manual. It should also provide you with an overview of the available emission estimation techniques, and the methods used in applying these techniques.

Schematic representations are used for identified processes in order to highlight the points where emissions may be produced. This section also describes the potential fate - to air, water, or land pathways - of these emissions and waste products.

Paint and ink are suspensions of finely separated pigment particles in a liquid that when spread over a surface in a thin layer will form a solid, cohesive, and adherent film. Types of paints that are currently manufactured include architectural coatings, product finishes (eg. for motor vehicles, machinery, wood and metal furniture, and white-goods), and special-purpose coatings (eg. traffic marking and marine paints). More than 80 percent of architectural paints sold in Australia today are water-based. Solvent-based paint is predominantly used for product finishes and special-purpose coatings.

Inks currently manufactured include letterpress, lithographic, offset, gravure, and flexographic inks. Letterpress and lithographic inks are typically classified as paste inks. Gravure and flexographic inks are typically water or solvent-based and are classified as liquid inks. Specialty ink products include textile and silk screen ink, invisible inks, powder inks, carbon paper, typewriter and toners, and duplicating inks.

2.1 The Manufacturing Process

Paint and ink manufacturing can be classified as a batch process and generally involves the blending/mixing of resins, pigments, solvents, and additives. Traditional paint and ink manufacturing consists of four major processes:

- preassembly and premix;
- pigment grinding, milling, and dispersing;
- product finishing and blending; and
- product filling and packaging.

These steps, including emissions points, are illustrated in Figure 1 and described in more detail below.

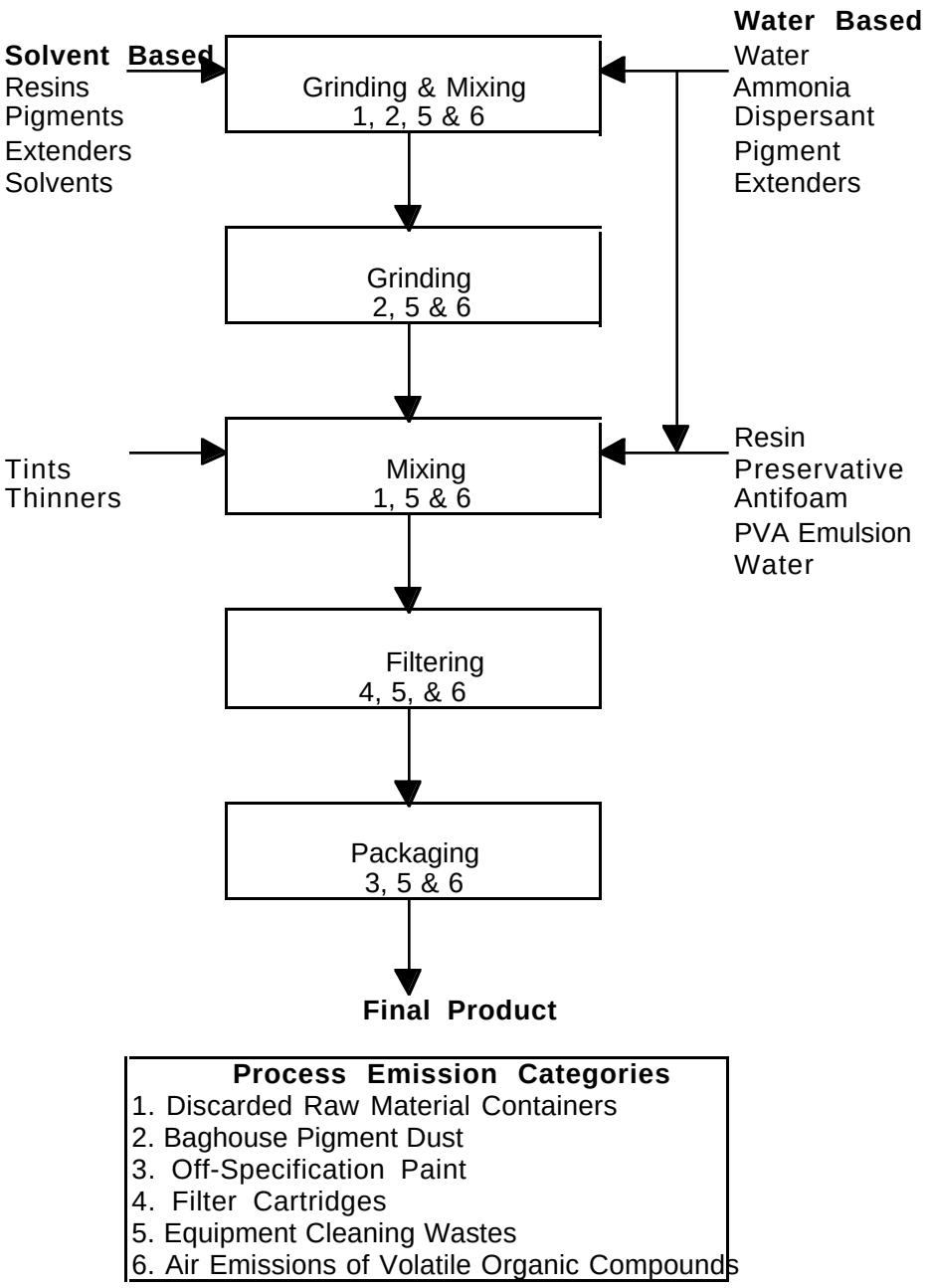

Figure 1. Basic Process Steps and Emission Points in Paint Manufacturing

Queensland Department of Environment, 1998

2.1.1 Preassembly and Premix

In the preassembly and premix step, liquid raw materials are assembled and then mixed in containers to form a viscous material to which pigments are added. For solvent-based paints, the raw ingredients include resins, organic solvents, plasticisers, dry pigments, and pigment extenders.

Raw materials used in the preassembly and premix step for water-based paints include water, ammonia, dispersant, pigment, and pigment extenders. Raw materials for ink manufacturing include pigments, oils, resins, solvents, and dryers. Many of these materials are, or contain, NPI pollutants. The premix stage results in the formation of an intermediate product that is referred to as the base, or mill base.

The type of equipment used in the premix stage depends on the batch size and the type of paint and ink being produced. Drums equipped with a portable mixer may be used for drum-sized batches. These mixers generally have an impeller with three or four blades. Other materials made in portable mix tanks may be blended using larger, permanent high-speed dispersers, or variable-speed mixers fitted with paddle, propeller, turbine, or disc-type agitators.

Paint and ink manufacturing facilities may use typical grinding equipment to accomplish the premix operations. This approach, common with water-based paints and inks, eliminates the need to transfer the material to another type of equipment for the grinding or milling step described below.

2.1.2 Pigment Grinding or Milling

Pigment grinding or milling entails the incorporation of the pigment into the paint and ink vehicle to yield a fine particle dispersion. The three stages of this process are wetting, grinding, and dispersion, which may overlap in any grinding operation. The wetting agent, normally a surfactant, wets the pigment particles by displacing air, moisture, and gases that are adsorbed on the surface of the pigment particles. Grinding is the mechanical breakup and separation of pigment clusters into isolated particles, and may be facilitated by the use of grinding media such as pebbles, balls, or beads. Finally, dispersion is the movement of wetted particles into the body of the liquid vehicle to produce a particle suspension.

There is a wide array of milling equipment. The type of equipment used depends on the types of pigments being handled. More commonly used equipment include the following: roller mills, ball and pebble mills, high-speed dispersers, high-speed impingement mills, and horizontal media mills. However, it should be noted that roller and ball mills are somewhat outdated technologies in current pigment base manufacturing. In addition, these types of equipment are usually associated with elevated levels of volatile organic compound (VOC) emissions because of their more open design.

Roller mills may have from one to five rolls that grind pigments into vehicles. Most paint and ink facilities that use rollermills operate with conventional three-roll mills. Roller mills are labour intensive and require highly skilled operators. Their lack of speed and high operating cost make them unsuitable for large-volume production. The use of roller mills is confined to the manufacture of very high quality paint, inks, and viscous pigmented products that require fine dispersion and clean colour.

High-speed dispersers are the most commonly used method of dispersion in the paint and ink industry. Some paint and ink blends are manufactured entirely in one piece of equipment using high-speed, disk-type impellers. Because no grinding media are present in the mixing vat, pigment disperses on itself and against the surfaces of the rotor. While high-speed disk dispersion may work well for some products including undercoats and primers, it may not be appropriate for high-quality paints and inks. It can, however, be used for the premix operations of high-quality paints and inks, thereby reducing the number of movements in a medial mill, or reducing the amount of time spent in a ball mill.

2.1.3 Product Finishing

Final product specification for colour, viscosity, and other coating characteristics are achieved in the product finishing step. This process normally consists of thinning, coating, and blending. Most of the solvents, tints, and shades are added during this operation.

Product finishing activities for solvent-based paints and inks involve adding various combinations of pigments, organic solvents, and resins. For water-based paints and inks, a preservative, an anti-foaming agent, a polyvinyl acetate emulsion, and water are added at this stage of the manufacturing process.

Blending is the process of mixing the added ingredients to meet product specifications. Blending may consist of additional milling in a ball mill, or added mixing and dispersing in a portable mix tank or high-speed disperser setup.

2.1.4 Product Filling

The final step in the paint and ink manufacturing process is the product filling operation. During the filling step, filtration is performed to remove impurities and to catch small particles of grinding media. Paints and inks may be filtered in a variety of ways and the end use of the product determines the type of filtration required. Some products require only a cloth bag filter; other products require filtering equipment such as strainers or sieves.

Once the material has been filtered, it can be transferred into pails, drums, totes, tank wagons, or other containers for shipment. Filling may be carried out either manually or mechanically depending on the number and size of the containers to be filled.

2.2 Emission Sources

Several emission sources have been identified for paint and ink manufacturing operations:

- process operations;
- miscellaneous operations;
- material storage;
- equipment leaks; and
- spills.

Each of the above emission sources is described in more detail in the following sections.

2.2.1 Process Operation Emissions

Process operation emissions occur during from mixing, grinding, blending, and filling activities. Emissions from these operations can generally be classified in one of the following four categories:

Material Loading Emissions
VOC emissions to air may occur during material loading of mixing and grinding equipment due to displacement of organic vapours. VOCs may be emitted from a mixing tank when the device is uncovered, or when a lid is open. For certain grinding equipment, VOCs may be emitted from the chute into which ingredients are added.

Air emissions of particulate matter (PM) and PM less than or equal to 10μm in diameter (PM_{10}) may also occur during the material loading process from the handling of pigments and other solids. VOC and PM_{10} emissions that occur during material loading may be either point source or fugitive depending on whether a PM emission collection system is in place.

Heat-up Losses
Heat-up losses occur during the operation of high-speed dispersers, ball and pebble mills, and similar types of dispersing equipment. During the grinding/dispersing process, there is a rise in temperature as some of the kinetic energy resulting from mixing is converted to thermal energy. This rise in temperature is controlled through the use of cold water jackets. As the VOCs in the mixers heat up, the vapour in the headspace expands

forcing emissions from the equipment. Heat-up losses are classified as fugitive for NPI reporting purposes.

Surface Evaporation
Surface evaporation can occur during mixing, dispersing, and blending operations if the vessel contents are exposed to the atmosphere. With certain types of mixing and grinding equipment, VOCs may be emitted through agitator shaft openings, or around the edges of a vessel lid. VOC emissions from older vertical media mills (eg. sand, bead, and shot mills) may occur from the exposed filtering screen. Surface evaporation emissions are generally fugitive in nature.

Filling Losses
Emissions from product filling occur during transfer and free-fall into the receiving container. Resultant losses during the filling operations are considered as fugitive.

2.2.2 Miscellaneous Operation Emissions

Miscellaneous operations can also generate emissions primarily in the form of VOCs. These operations are outlined below:

Solvent Reclamation
Solvent reclamation refers to the purification of dirty or spent solvent through the use of a distillation device. VOC emissions can occur from loading solvent into the distillation equipment, operation of the distillation equipment, and spillage. Emissions resulting from loading and spilling are classified as fugitive, while emissions from the operation of equipment generally occur through a condenser vent and are classified as point source. NPI reporting requires the partitioning of both air and water emissions as fugitive and point source.

Cleaning
Cleaning is an important auxiliary part of the paint and ink manufacturing process. Process equipment may be cleaned with solvent as often as after each batch. VOC emissions result from charging the mixer or disperser with solvent and can be characterised as fugitive. In addition to this type of cleaning, small items used in the paint and ink manufacturing process may be cleaned by washing them with solvents in a cold cleaner or open-top vapour degreaser. Of the two technologies, the use of a cold cleaner is more common. VOC emissions from this type of cleaning are also classified as fugitive.

Wastewater Treatment
A paint and ink manufacturing facility may use a wastewater treatment system to treat contaminated water generated during the paint and ink

manufacturing process (eg. water that has been used to clean equipment used in the production of water-based paint and ink). Wastewater treatment systems usually consist of a series of surface impoundments that are used for equalisation, neutralisation, aeration, and clarification of the waste stream. Fugitive VOC emissions may occur from each type of basin. Procedures used to estimate emissions from wastewater treatment facilities are described in detail in the *Sewage and Wastewater Treatment* Manual.

2.2.3 Material Storage Emissions

Various types and sizes of storage tanks are used to store solvents and resins required in the paint and ink manufacturing process. Most of these tanks have a fixed-roof design. The two significant types of emissions from fixed-roof tanks are breathing and working losses. Breathing loss is the expulsion of vapour from a tank through vapour expansion and contraction that result from changes in ambient temperature and barometric pressure. This loss occurs without any liquid level change in the tank.

The combined loss from filling and emptying tanks is called working loss. Evaporation during filling operations results from an increase in the liquid level in the tank. As the liquid level increases, the pressure inside the tank exceeds the relief pressure and vapours are expelled from the tank. Evaporative emissions during the emptying process occur when air, drawn into the tank during liquid removal, becomes saturated with organic vapour and expands, expelling vapour through the vapour relief valve.

Emissions from tanks are characterised as a point source because VOCs are emitted through a vent. The *Fuel and Organic Liquid Storage* Manual should be used when estimating emissions from liquid storage facilities.

2.2.4 Equipment Leaks

In order to transport stored materials (ie. organic solvents and resins) from storage tanks to the paint and ink manufacturing operation, a network of pipes, pumps, valves, and flanges is employed. As liquid material is pumped from the storage tanks to the particular process area, the pipes and supporting hardware (ie. process line components) may develop leaks over time. When leaks occur, volatile components in the transported material are emitted into the atmosphere.

This generally occurs from the following process line components:

- pump seals;
- valves;
- compressor seals;
- safety relief valves;
- flanges;
- open-ended lines; and
- sampling connections.

Emissions from equipment leaks can be characterised as fugitive and are described in detail in the Manual *Estimating Fugitive Emissions from Equipment Leaks*.

2.2.5 Spills

Solvents, resins, or production batches may be accidentally spilled during manufacturing or cleaning activities. Materials that are spilled onto the ground may spread over an area, vaporise, and result in emissions to air, water, and land.

2.3 Design and Operating Factors Influencing Emissions

VOC and PM_{10} emissions from paint and ink manufacturing can be reduced through the use of add-on control systems, or through equipment and process modifications. Control devices and techniques commonly used at paint and ink manufacturing facilities are presented in Table 1.

Table 1. Typical Paint and Ink Manufacturing Facility Control Techniques

Emission Source	Pollutant	Control Technique	Typical Efficiency (%)
material loading	PM and PM_{10}	Fabric Filter	95 - 99
mixing operations	VOCs	Tank Lid	40 - 96

Noyes, 1993.

2.3.1 VOC Control Systems

A VOC control system consists of a capture device and a removal device. The capture device (eg. a hood or enclosure) captures the VOC-laden air from the emission area and ducts the emission stream to the removal equipment. The overall efficiency of a control system is calculated by multiplying the capture system efficiency by the removal device efficiency.

Removal equipment available for removing VOCs from the air includes recovery devices (ie. carbon adsorption, absorption, and condensation), and combustion devices (ie. thermal incinerators, catalytic incinerators, industrial boilers and process heaters). Control efficiencies for this equipment can range from 50 to 99 percent. Carbon adsorbers, absorbers (scrubbers), condensers, and catalytic incinerators are generally not appropriate for paint and ink manufacturing facilities, because these devices are not designed to treat low VOC inlet concentrations that are typical for this industry. In addition, the wide variety of organics that may be emitted at a paint and ink facility will tend to reduce the efficiency of these types of control devices. Industrial and process heaters are capable of effectively treating the types and levels of VOCs generated by the paint and ink industry, but are uncommon in Australian plants.

Thermal incineration is an applicable control technique for the paint and ink industry, but is less likely to be used by larger facilities. Thermal incinerators channel the emission stream through a combustion chamber where VOCs are burned at temperatures ranging from 700 to 1 300 ßC. VOC removal efficiencies of 98 percent or greater are achievable depending on the design of the equipment.

The majority of paint and ink manufacturing facilities use equipment and process modifications to reduce VOC emissions. These are discussed in more detail later in Section 2.3.3.

2.3.2 PM and PM_{10} Control Systems

PM and PM_{10} control systems for the paint and ink industries consist of a capture device paired with a control device, generally a fabric filter (baghouse). These systems are typically employed to reduce PM_{10} emissions from charging pigments and other solids into mixing and grinding devices.

With fabric filter systems, particles are caught on the surface of the bags while the cleaned gaseous stream passes through. To minimise pressure drop, the bags must be cleaned periodically as the dust layer builds up. The captured dust may be recycled, or sent for off-site disposal or treatment.

Fabric filters are least efficient with particles 0.1 to 0.3µm in diameter and with emission streams of high moisture content. When operated under optimum conditions, they can achieve control efficiencies of up to 99+ percent. However, typical control efficiencies range from 95 to 99 percent.

2.3.3 Equipment or Process Modifications

Most paint and ink manufacturing facilities reduce VOC emissions through equipment or process modifications. Some of these techniques will also reduce PM_{10} emissions. Modifications include the following:

Tank Lids
Tank lids are the most common equipment modification used (during paint and ink manufacturing activities) to control VOC emissions. Lids reduce the amount of VOCs emitted during mixing operations, and range in control efficiency from 40 to 96 percent.

Modified Milling Equipment
VOC and PM_{10} emissions may be reduced by converting older milling equipment to newer, more efficient closed systems such as horizontal media mills. Typically, horizontal media mills are charged by pumping material from containers or premix equipment through an enclosed piping system. Material discharge also occurs through enclosed pipes or hoses. VOC emissions during operation of the horizontal media mill are controlled because the filtering screen is enclosed by a sheet metal cover.

Equipment Cleaning Devices
Several types of equipment can be used to reduce amounts of solvents used during vessel cleaning and therefore lessen VOC emissions. These equipment types include the following:

- rubber wipers (used to scrape the clinging paint and ink from the sides of the tank);
- high-pressure spray heads (used to clean process tanks);
- tanks lined with Teflon™ (Teflon™ reduces the ability of paint and ink to cling to the sides of the tank);
- plastic or foam *pigs* (a *pig* is moved through the pipes and pushes leftover paint and ink from previous batches through the pipe from the pipe walls); and
- automatic tank washers.

The degree to which VOC emissions are reduced during cleaning activities depends on the frequency of use of one or more of the cleaning devices listed above. It has been reported that high-pressure spray heads can reduce cleaning material use by 80 to 90 percent.

Use of Pigments in Paste Form
PM_{10} emissions can be reduced by using pigments that have been wetted or mixed with resins. Using wet pigments means that, little or no dust is

generated when the package is opened, and as pigment is dumped into mixing vessels.

Product Reformulation
Production of paints and inks that contain little or no VOCs will minimise VOC emissions from paint and ink manufacturing facilities. High-solids and water-based paints and inks contain less VOCs than these that are solvent-based. Powder coatings, and the majority of radiation-curable paints and inks, contain no VOCs.

3.0 Overview of Available Emission Estimation Techniques

Several methods are available for calculating emissions of NPI listed substances from paint and ink manufacturing operations. The best emission estimation technique (EET) to use depends on the emission source being evaluated, available data, and resources, and the degree of accuracy required by the facility in conducting the estimate. Although the NPI does not favour the use of any particular EET by source or pollutant, this section does attempt to identify the most appropriate and reliable EETs for the pollutants and processes.

This Manual, addresses EETs applying to paint and ink manufacturing process operations, miscellaneous operations, and spills. For information regarding EETs for a range of other sources, other Manuals are available including *Fuel and Organic Liquid Storage* (storage tanks), *Estimating Fugitive Emissions from Equipment Leaks*, and *Sewage and Wastewater Treatment Plants (wastewater).* EETs for storage tank emissions are discussed in the *Fuel and Organic Liquid Storage* Manual, EETs for calculating emissions from equipment leaks are outlined in the *Estimating Fugitive Emissions from Equipment Leaks* Manual, and EETs for estimating emissions from wastewater are described in the EET Manual *Sewage and Wastewater Treatment Plants.*

3.1 Emission Factors

An emission factor can be defined as a pollutant emission rate relative to a level of source activity. Emission factors are typically based on the results of source tests performed at an individual facility, or at one or more facilities within the same or similar industries.

Emission factors may be used to calculate total VOC and PM_{10} emissions from paint and ink manufacturing facilities, as well as emissions from

specific types of equipment typically found at such a facility. These types of equipment include the following:

- process equipment;
- solvent reclamation systems;
- parts washing equipment; and
- process piping.

Emission factors for paint and ink manufacturing processes are provided at Section 4.0. Using emission factors is more cost-effective than collection and analysis of air and water samples, or use of emission equations. There can also be significant limitations with the mass balance approach for several paint and ink manufacturing activities.

3.2 Source-Specific Equations

Theoretical and complex equations, or models can be used for estimating emissions from paint and ink manufacturing processes. EET equations are available for the following types of emissions common to paint or ink manufacturing facilities:

- material loading;
- heat-up losses from dispersion/grinding activities;
- surface evaporation during mixing/blending operations;
- filling;
- cleaning solvent loading;
- material storage;
- spills; and
- wastewater storage.

Inputs for theoretical equations generally fall into the following categories: the chemical/physical properties of the material involved (eg. vapour pressure, vapour molecular weight); operating data, (eg. the amount of material processed and operating hours); and, the physical characteristics and properties of the source, (eg. tank colour and diameter).

Use of emission equations to estimate emissions from paint and ink manufacturing facilities is a more complex and time-consuming process than the use of emission factors. Emission equations require more detailed inputs than the use of emission factors, but they do provide an emission estimate that is based on facility-specific conditions.

3.3 Sampling or Direct Measurement

Sampling can be performed to quantify point source or fugitive emissions. In 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 perform the tasks.

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 photo-ionisation detectors, portable infrared spectrophotometres, and portable gas chromatographs. VOC emissions from some operations, such as filling lines, can also be measured by performing a gravimetric analysis.

Use of stack and/or workplace health and safety sampling data is likely to be the most accurate method of estimating air emissions from paint and ink manufacturing facilities. However, collection and analysis of air samples from facilities can be very expensive, and especially complicated for facilities where a variety of NPI listed VOCs are emitted, and where most of these emissions are fugitive in nature. Sampling data from one 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 would need to be collected over a period of time covering production of multiple paint and ink formulations.

3.4 Mass Balance

The mass balance approach to emissions estimation considers a facility as a sort of *black box* where the total quantity of listed substances in the raw materials consumed as opposed to the amounts of listed substances leaving the facility as product and waste, is compared and analysed. NPI pollutants can be contained in wastes, such as used filter bags or cartridges, spent solvent or still bottoms, dust collector material, pigment bags, drum residue, and wastewater.

Calculating emissions using mass balance initially appears to be a straightforward approach to emission estimation. However, few Australian paint and ink manufacturing facilities consistently track material usage and waste generation with the overall accuracy needed for application of this method, and inaccuracies associated with individual material tracking or other activities inherent in each material handling stage often accumulate into large deviations of total facility emissions. Because emissions from specific materials are typically below two percent of gross consumption, an error of only ± 5 percent in any one step of the operation can significantly skew estimations.

Potential sources of error in the mass balance EET include the following:

- The delivery of bulk raw materials to a 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.

- The raw materials received by a facility may be used in hundreds of finished products. 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 pollutants is known. This involves precise analysis of the concentration of the listed pollutant of interest in each product, waste, or recycling stream.

- Batch production of paint or ink often requires the manual addition of raw materials. Sometimes these additions are not accurately measured or recorded.

4.0 Estimating Emissions

This section provides guidance for estimating emissions of VOCs and PM_{10} from paint and ink manufacturing 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 Equations (1) through (27).

4.1 Using Equations

Source specific equations are the most accurate EET for estimating VOC emissions from:

- Mixing operations (material loading, heat-up losses, and surface evaporation);
- Product filling;
- Vessel cleaning operations;
- Wastewater treatment processes;
- Material storage; and
- Spills.

Table 2. List of Variables and Symbols

Variable	Symbol	Units
Total VOC emissions	E_{VOC}	kg/yr
Saturation factor	S	dimensionless
Vapour pressure of the material loaded	P	kPa
Vapour molecular weight	M	kg/kg-mole
Volume of material loaded	Q	1 000/yr
Temperature	T	° C
Partial vapour pressure of VOC species x	P_x	kPa
Liquid mole fraction of VOC species x	m_x	mole/mole
True vapour pressure of VOC species x	VP_x	kPa
Henry's Law constant for VOC species x	H_x	kPa
Liquid mass fraction of VOC species x	z_x	kg/kg
Molecular weight of VOC species x	M_x	kg/kg-mole
Vapour mole fraction of VOC species x	y_x	mole/mole
Loading emissions of VOC or PM_{10} species x	E_x	kg/yr
Vapour mass fraction of VOC species x	x_x	kg/kg
Inirtial partial pressure of VOC species x	$(P_x)_{T1}$	kPa
Final partial pressure of VOC species x	$(P_x)_{T2}$	kPa
Number of kg-moles of gas displaced	Δn	kg-moles/cycle
Vapour molecular weight, average	M_a	kg/kg-mole
Number of cycles/year	CYC	cycles/yr
Volume of free space in vessel	V	m^3
Universal gas constant at 1 atmosphere of pressure	K	8.314 (kPa) (m^3)/(kg mole) (K)
Initial gas pressure in vessel	Pa_1	kPa
Final gas pressure in vessel	Pa_2	kPa
Initial temperature of vessel	T1	° K
Final temperature of vessel	T2	° K
Molecular weight of liquid mixture	M_1	kg/kg-mole
Gas-phase mass transfer coefficient for VOC species x	K_x	m/sec
Surface area (of spill or tank)	A	m^2
Duration of spill	HR	hr/event
Wind speed	U	kg/hr
Diffusion coefficient for VOC species x in air	D_x	m^2/sec
Batch time	H	hr/batch
Number of batches per year	B	batches/yr
VOC emission factor	EF_{VOC}	various
Amount of VOC in spent solvent processed	Q_{VOC}	tonnes/yr
Concentration of VOC or PM_{10} species x in solvent or pigment x, respectively	C_x	mass %
Mass percent of species in total mixture	X_x	mass %
Volume percent of species x in total mixture	Y_x	volume %
Number of species in total mixture	n	number
Operating hours	OpHrs	hr/yr
Number of cleaning units in use	NU	cleaning units
PM_{10} emissions	E_{PM10}	kg/yr
PM_{10} emission factor	EF_{PM10}	kg/tonne
Amount of pigment containing species x used by the NPI reporting facility	Q_x	kg/yr, tonne/yr

4.1.1 Equations for Material Loading Emissions

VOC emissions resulting from the addition of materials to mixers, grinding equipment, and thinning tanks can be calculated using a loading loss equation. The equation, (shown below as Equation (1)), is related to tank loading, but can be applied to any tank or vessel loading (NPCA, 1995). This equation can also be applied to estimate product filling losses.

$$E_{VOC} = 0.1203 * (S * P * M * Q) / T \quad (1)$$

where:

E_{VOC} = total VOC loading emissions, kg/yr
S = saturation factor (dimensionless); see Table 3.
P = vapour pressure of the material loaded at temperature T, kPa
M = vapour molecular weight, kg/kg-mole
Q = volume of material loaded, 1 000 litres/yr
T = temperature, K

Calculation of VOC emissions using Equation (1) is based on the following assumptions:

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

Table 3. Saturation (S) Factors for Calculating Organic Liquid Loading Emissions

Transport Carrier	Mode of Operation	S Factor
Road and Rail Tankers	Submerged loading of a clean cargo tank	0.50
	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

USEPA, 1995 AP-425.2 *Transportation and Marketing of Petroleum Liquids.*

If multiple NPI listed solvents are used in a paint or ink formulation, the vapour pressure (P) will need to be calculated using Equation (2).

$$P = \Sigma P_x \quad (2)$$

where:

P = vapour pressure of material loaded, kPa
P_x = partial pressure of VOC species x, kPa

P_x 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 (3).

$$P_x = m_x * VP_x \quad (3)$$

where:

P_x = partial vapour pressure of VOC species x, kPa
m_x = liquid mole fraction of VOC species x, mole/mole
VP_x = true vapour pressure of VOC species x, kPa

P_x may be calculated using Henry's Law constants and Equation (4).

$$P_x = m_x * H_x \quad (4)$$

where:

P_x = partial vapour pressure of VOC species x, kPa
m_x = liquid mole fraction of VOC species x, mole/mole
H_x = Henry's Law constant for VOC species x, kPa

The liquid mole fraction of VOC species x (m_x) may be calculated if the liquid weight fractions of all species are known using Equation (5).

$$m_x = (z_x / M_x) / \Sigma (z_x / M_x) \quad (5)$$

where:

m_x = liquid mole fraction of VOC species x, mole/mole
z_x = liquid mass fraction of VOC species x, kg/kg
M_x = molecular weight of VOC species x, kg/kg-mole

The vapour molecular weight (M) will also need to be calculated if multiple solvents are used for a single cleaning event. Equation (6) shows this calculation.

$$M = \Sigma (y_x * M_x) \quad (6)$$

where:

M = vapour molecular weight, kg/kg-mole
y_x = vapour mole fraction of VOC species x, mole/mole
M_x = molecular weight of VOC species x, kg/kg-mole

The vapour mole fraction is calculated using Equation (7).

$$y_x = P_x / P \quad (7)$$

y_x = vapour mole fraction of VOC species x, mole/mole
P_x = partial pressure of VOC species x (calculated using Equations (3) or (4), kPa
P = vapour pressure of the material loaded (calculated using Equation (2))

Speciated VOC emissions are calculated using Equation (8).

$$E_x = E_{VOC} * x_x \quad (8)$$

where:

E_x = loading emissions of VOC species x, kg/yr
E_{VOC} = total VOC loading emissions (calculated using Equation (1)), kg/yr
x_x = vapour mass fraction of VOC species x, kg/kg

The vapour mass fraction of VOC species x (x_x) is calculated using Equation (9).

$$x_x = y_x * M_x / M \quad (9)$$

where:

x_x = vapour mass fraction of VOC species x, kg/kg
y_x = vapour mole fraction of VOC species x (calculated using Equation (7)), mole/mole
M_x = molecular weight of VOC species x, kg/kg-mole
M = vapour molecular weight (calculated using Equation (6)), kg/kg-mole

Example 4.1-1 illustrates the use of Equations (1) through (9). Emissions are calculated by following Steps 1 through 8.

Example 4.1-1 Calculating Material Loading Emissions
A mixing vessel is cleaned with a solvent mixture at the end of each day. The following data are 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 (only toluene is a NPI listed substance);
- the solvent mixture is splash loaded into the vessel (S=1.45 from Table 3.); and
- the temperature of the solvent is 298 K (25 °C).

The following Steps 1 through 8 below calculate emissions.

Step 1: Apply Equation (5) - Calculation of Liquid Mole Fraction (m_x)

Component x	Liquid Mass Fraction, z_x (kg of x/kg of liquid)	Molecular Weight, M_x (kg of x/kg-mole of x)	Liquid Mole Fraction, m_x (mole of x/mole of liquid)
Toluene	0.50	92	$(z_x / M_x) / \Sigma (z_x / M_x)$ $(0.5/92)/[(0.5/92) + (0.5/100)]$ = 0.52
n-Heptane	0.50	100	$(z_x / M_x) / \Sigma (z_x / M_x)$ $(0.5/100)/[(0.5/92) + (0.5/100)]$ = 0.48

Step 2: Apply Equation (3) - Calculation of Partial Vapour Pressure (P_x)

Component x	Liquid Mole Fraction, m_x (mole of x/mole of liquid)	Vapour Pressure, VP_x (kPa)	Partial Vapour Pressure, P_x (kPa)
Toluene	0.52	4.0	$m_x * VP_x = 0.52 * 4 = 2.08$
n-Heptane	0.48	6.2	$m_x * VP_x = 0.48 * 4 = 2.98$

Step 3: Apply Equation (2) - Calculation of Vapour Pressure (P)

$$P = \Sigma P_x = 2.08 + 2.98 = 5.06 \text{ kPa}$$

Step 4: Apply Equation (7) - Calculation of Vapour Mole Fraction (y_x)

Component x	Partial Vapour Pressure, P_x (kPa)	Total Vapour Pressure, P (kPa)	Vapour Mole Fraction, y_x (mole of x/mole of vapour)
Toluene	2.08	5.06	$P_x / P = 2.08 / 5.06 = 0.41$
n-Heptane	2.98	5.06	$P_x / P = 2.98 / 5.06 = 0.59$

Step 5: Apply Equation (6) - Calculation of Vapour Molecular Weight (M)

$$M = \Sigma (y_x * M_x) = (0.41 * 92) + (0.59 * 100) = 97 \text{ kg/kg-mole}$$

Step 6: Apply Equation (9) - Calculation of Vapour Mass Fraction (x_x)

Component x	Vapour Mole Fraction, y_x (mole of x/mole of vapour)	Molecular Weight, M_x (kg of x/kg-mole of x)	Vapour Molecular Weight, M (kg of vapour /kg mole of vapour	Vapour Mass Fraction, x_x (kg of x/kg of vapour)
Toluene	0.41	92	97	$Y_x * M_x / M = 0.41 * 92/97 = 0.39$
n-Heptane	0.59	100	97	$Y_x * M_x / M = 0.59 * 100/97 = 0.61$

Step 7: Apply Equation (1) - Calculate Total VOC Emissions (E_{VOC})

$$E_{VOC} = 0.1203 * (S * P * M * Q) / T$$
$$= 0.1203 * (1.45 * 5.06 * 97 * 600) / 298$$
$$= 172.4 \text{ kg VOC/yr}$$

Step 8: Apply Equation (8) - Calculate Speciated VOC Emissions (E_x)

Component x	VOC Emissions, E_{VOC} (kg VOCs)	Vapour Mass Fraction, x_x (kg of x/kg of VOCs)	Speciated VOC Emissions, E_x (kg x)
Toluene	172.4	0.39	$E_{VOC} * x_x = 172.4 * 0.39 = 67.2$
n-Heptane	172.4	0.61	$E_{VOC} * x_x = 172.4 * 0.61 = 105.2$

4.1.2 Equations for Heat-Up Emissions

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

- that covers are closed during operation, but it is possible for vapours to be vented during operation;
- that no material is added during heat-up;
- that the displaced gas is always saturated with VOC vapour in equilibrium with the liquid mixture;
- that 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
- that the vapour pressure of the mixers never rises above 1 atmosphere.

Equation (10) calculates emissions from heat-up operations.

$$E_{VOC} = \{([\Sigma(P_x)_{T1} / 101.3 - \Sigma(P_x)_{T1}] + [\Sigma(P_x)_{T2} / 101.3 - \Sigma(P_x)_{T2}]) / 2\} * (\Delta n * M_a * CYC) \quad (10)$$

where:

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

$(P_x)_{T1}$ = initial partial pressure of each VOC species x in the vessel headspace at the initial temperature T1, kPa (calculated using Equations (3) and (4))

$(P_x)_{T2}$ = final partial pressure of each VOC species x in the vessel headspace at the final temperature T2, kPa; (calculated using Equations (3) and (4))

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

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

CYC = number of cycles per year, cycles/yr

The term Δn may be calculated using Equation (11).

$$\Delta n = V/R * (Pa_1 / T1 - Pa_2 / T2) \quad (11)$$

where:

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

V = volume of free space in the vessel, m^3

R = universal gas constant at 1 atmosphere of pressure, 8.314 (kPa) (m^3) / (kg mol) (K)

Pa_1 = initial gas pressure in vessel, kPa

Pa_2 = final gas pressure in vessel, kpa

T1 = initial temperature of vessel, °K

T2 = final temperature of vessel, °K

Pa_1 and Pa_2 can be calculated using Equations (12) and (13).

$$Pa_1 = 101.3 - \Sigma (P_x)_{T1} \quad (12)$$

$$Pa_2 = 101.3 - \Sigma (P_x)_{T2} \quad (13)$$

where:

Pa_1 = initial gas pressure in vessel, kPa

Pa_2 = final gas pressure in vessel, kPa

$(P_x)_{T1}$ = partial pressure of each VOC_x in the vessel headspace, kPa, at the initial temperature T1 (calculated using Equations (3) and (4))

$(P_x)_{T2}$ = partial pressure of each VOC_x in the vessel headspace, kPa, at the final temperature T2 (calculated using Equations (3) and (4))

Speciated VOC emissions would be calculated using a modified version of Equation (10), as shown in Equation (14).

$$E_x = \{[(P_x)_{T1} / 101.3 - (P_x)_{T1}] + [(P_x)_{T2} / 101.3 - (P_x)_{T2}] / 2\} * (* \Delta n * M_a * CYC) \quad (14)$$

where:

E_x = VOC species x emissions from material heat-up in the process equipment, kg/yr

$(P_x)_{T1}$ = partial pressure of VOC species x in the vessel headspace at the initial temperature T1, kPa; see Equations (3) and (4)

$(P_x)_{T2}$ = partial pressure of VOC species x in the vessel headspace at the final temperature T2, kPa; see Equations (3) and (4)

Δn = number of kg-moles of gas displaced, kg-mole/cycle; see Equation (11)

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

CYC = number of cycles per year, cycles/yr

Example 4.1-2 illustrates the use of Equations (10) through (13). Emissions are calculated by following Steps 1 through 6.

Example 4.1-2 Calculating Material Loading Emissions

This example shows how heat-up losses from a disperser are calculated using Equations (10) through (13). Supporting equations from Section 4.1.1 (Equations (3) and (4)) 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 30 percent by weight toluene, 20 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 (M_a) is 77 kg/kg-mole, calculated using Equation (6);
- 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 litres = 1 000 litres or 1 m^3

Step 1: Apply Equation (5), Calculation of Liquid Mole Fraction (m_x)

Component x	Liquid Mass Fraction, z_x (kg of x/kg of liquid)	Molecular Weight, M_x (kg of x/kg-mole of x)	Liquid Mole Fraction, m_x (mole of x/mole of liquid)
Toluene	0.2	92	$(z_x / M_x) / \Sigma (z_x / M_x)$ = 0.28
MEK	0.3	72	$(z_x / M_x) / \Sigma (z_x / M_x)$ = 0.24

[a] if the molecular weight of the paint mixture is known, the following expression can be used:

$$m_x = (z_x / M_x) / \Sigma (z_x / M_x)$$
$$= (z_x / M_x) / (1 / M_1)$$

where:

M_1 = molecular weight of the liquid mixture, and all other terms are defined as in Equation (5)

Step 2: Apply Equation (3), Calculation of Partial Vapour Pressure at Initial Temperature [$(P_x)_{T1}$]

Component x	Liquid Mole Fraction, m_x (mole of x/mole of liquid)	Vapour Pressure, VP_x @ 25 °C (kPa)	Partial Pressure at T1, $(P_x)_{T1}$ (kPa)
Toluene	0.28	4	$m_x * VP_x$ = 1.12
MEK	0.24	13.31	$M_x * VP_x$ = 3.19

Step 3: Apply Equation (3), Calculation of Partial Pressure at Final Temperature [$(P_x)_{T2}$]

Component x	Liquid Mole Fraction, m_x (mole/mole)	Vapour Pressure, VP_x @ 40 °C (kPa)	Partial Pressure at T2, $(P_x)_{T2}$ (kPa)
Toluene	0.28	8	$m_x * VP_x$ = 2.240
MEK	0.24	25.86	$m_x * VP_x$ = 6.206

Step 4: Apply Equations (12) and (13), Calculation of Initial Pressure (Pa_1) and Final Pressure (Pa_2)

$Pa_1 = 101.3 - \Sigma (P_x)_{T1}$
$= 101.3 - (1.12 + 3.19)$
$= 96.99$ kPa

$Pa_2 = 101.3 - \Sigma (P_x)_{T2}$
$= 101.3 - (2.24 + 6.206)$
$= 92.84$ kPa

Step 5: Apply Equation (11), 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 m^3.

$\Delta n = V / R * (Pa_1 / T1 - Pa_2 / T2)$
$= (1 / 8.314)*((96.99 / (298) – ((92.84 / (313)$
$= 3.35x10^{-3}$ kg-moles / CYC

Step 6: Apply Equation (10), Calculation of Total VOC Emissions (E_{VOC})

$E_{VOC} = \{[\Sigma(P_x)_{T1} / 101.3 - \Sigma(P_x)_{T1}] + [\Sigma(P_x)_{T2} / 101.3 - \Sigma(P_x)_{T2}] / 2\}*(\Delta n * M_a * CYC)$
$= \{(4.31 / (101.3-4.31))+(8.446 / (101.3-8.446)) / 2\}*3.35x10^{-3} *25*77$
$= 0.45$ kg VOCs / yr

Step 7: Apply Equation (14), Calculation of Toluene Emissions ($E_{toluene}$)

$E_{toluene} = \{[(P_x)_{T1} / 101.3 - (P_x)_{T1}] + [(P_x)_{T2} / 101.3 - (P_x)_{T2}] / 2\}*(* \Delta n * M_a * CYC)$
$= \{((1.12 / (101.3-1.12)+(3.19 / 101.3-3.19))) / 2\}*3.35x10^{-3}*25*77$
$= 0.113$ kg toluene / yr

4.1.3 Equations for 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. This is a simple equation and is illustrated by Equation (15).

$E_x = (M_x * K_x * A * P_x * 3\,600 * HR) / R * T$ (15)

where:

E_x = emissions of VOC species x from the spill, kg/event
M_x = molecular weight of VOC species x, kg/kg-mole
K_x = gas-phase mass transfer coefficient for VOC species x, m/sec
A = surface area of spill, m^2
P_x = partial pressure of VOC species x (if a pure chemical is spilled) or the partial pressure of chemical x (if a mixture of VOCs is spilled) at temperature T, kPa; the partial pressure of VOC species x (P_x) may be calculated using Equations (3) or (4)
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_x) may be calculated using Equation (16).

$$K_x = (0.00438 * U^{0.78} * (D_x / 3.1 \times 10^{-4})^{2/3}) / 3.208 \qquad (16)$$

where:

K_x = gas-phase mass transfer coefficient for VOC species x, m/sec
U = wind speed, miles/hr
D_x = diffusion coefficient for VOC species x in air, ft^2/sec

Diffusion coefficients (D_x) 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_x) may be estimated using Equation (17).

$$K_x = (0.00438 * U^{0.78} * (18 / M_x)^{1/3}) / 3.208 \qquad (17)$$

where:

K_x = gas-phase mass transfer coefficient for VOC species x, m/sec
U = wind speed, miles/hr
M_x = molecular weight of VOC species x, kg/kg-mole

Example 4.1-3 illustrates the use of Equations (15) through (17). Emissions are calculated by following Steps 1 and 2.

Example 4.1-3 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, and 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 21 km/hr (13 miles/hr);
- the ambient temperature (T) is 298 K (25 °C);
- the surface area of the spill (A) is 11 m^2;
- the molecular weight of MEK (M_x) is 72 kg/kg-mole
- the partial pressure of MEK (P_x) at 298 K (25 °C) is approximately 13.31 kPa

Step 1: Using Equation (17), Calculate the Gas-Phase Mass Transfer Coefficient (K_x)

$$K_x = (0.00438 * U^{0.78} * (18 / M_x)^{1/3}) / 3.208$$
$$= (0.00438 * 21^{0.78} * (18 / 72)^{1/3}) / 3.208$$
$$= 0.095 \text{ m/sec}$$

Step 2: Using Equation (15), Calculate Emissions (E_x)

$$E_x = (M_x * K_x * A * P_x * 3\,600 * HR) / R * T$$
$$= (72 * 0.095 * 11 * 3\,600 * 3) / (8.314 * 298)$$
$$= 327.98 \text{ kg MEK/spill}$$

4.1.4 Equations for Surface Evaporation Emissions

Emissions from surface evaporation during paint and ink mixing operations can be estimated using Equation (18).

$$E_x = [(M_x * K_x * A * P_x * 3\,600 * H) / R * T] * B \quad (18)$$

where:

E_x = emissions of VOC species x, kg/yr
M_x = molecular weight of VOC species x, kg/kg-mole
K_x = gas-phase mass transfer coefficient for VOC species x, m/sec
A = surface area of tank, m^2
P_x = vapour pressure of VOC x (if a pure chemical is used) or the partial pressure of chemical x (if a mixture of VOCs is used) at temperature T, kPa; the partial pressure of VOC species x (P_x) may be calculated using Equations (3) or (4))
3 600 = 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

Equations (16) or (17) can be used to estimate K_x. Total VOC emissions would equal the sum of all VOC species emissions.

Example 4.1-4 illustrates the use of Equations (18). Emissions are calculated by following Steps 1 and 2.

Example 4.1-4 Calculating Surface Evaporation Emissions
This example estimates emissions from a mixing operation due to surface evaporation. The following data are given:

- the batch time (H) is 4 hours;
- the number of batches per year (B) is 550;
- the average wind speed (U) is 08 km/hr (0.5 miles/hr);
- the ambient temperature (T) is 298 K (25 °C);
- the surface area of the mixing tank (A) is 8.75 m^2;
- the molecular weight of toluene (M_x) is 92 kg/kg-mole; and
- the partial vapour pressure of toluene (P_x) at 298 K (25 °C) is approximately 4 kPa

Step 1: Using Equation (17), Calculate the Gas-Phase Mass Transfer Coefficient (K_x)

$K_x = (0.00438 * U^{0.78} * (18 / M_x)^{1/3}) / 3.208$
$= (0.00438 * 0.8^{0.78} * (18 / 92)^{1/3}) / 3.208$
$= 6.66 \times 10^{-4}$ m/sec

Step 2: Using Equation (18), Calculate Emissions (E_x)

$E_x = [(M_x * K_x * A * P_x * 3\,600 * H) / R * T] * B$
$= [(92 * 6.66 \times 10^{-4} * 8.75 * * 3\,600 * 4) / 8.314 * 298] * 550$
$= 1\,713.84$ kg toluene/yr

4.1.5 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* Manual which containing the software package AUSTanks.

4.2 Using Emission Factors

Emission factors can be used for estimating emissions from paint and ink manufacturing facilities for the following processes:

- solvent reclamations systems;
- parts washing equipment;
- process piping;
- total facility and mixing operations at a paint manufacturing facility; and
- vehicle cooking and pigment mixing from an ink manufacturing facility.

4.2.1 Emissions from Solvent Reclamation

VOC emissions from the loading and operation of a distillation device may be calculated using the emission factors from Table 4, and the application of Equation (19).

$$E_{VOC} = EF_{VOC} * Q_{VOC} \quad (19)$$

where:

E_{VOC} = VOC emissions from loading or operations 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 (20).

$$E_x = E_{VOC} * C_x / 100 \quad (20)$$

where:

E_x = emissions of VOC species x from loading or operation of the distillation device, kg/yr

E_{VOC} = VOC emissions from loading or operation of the distillation device, calculated using Equation (20), kg/yr

C_x = concentration of VOC species x in the solvent processed through the distillation system, mass %

Table 4. Emission Factors for Solvent Reclamation[1]

Emission Source	Pollutant	Emission Factor Average (kg/tonne)
Storage tank vent [b]	Volatile organics	0.01 (0.002 - 0.04)
Condenser vent	Volatile organics	1.65 (0.26 - 4.17)
Incinerator stack [c]	Volatile organics	0.01
Incinerator stack	Particulates	0.72 (0.55 - 1.0)
Fugitive emissions		
Spillage [c]	Volatile organics	0.10
Loading	Volatile organics	0.36 (0.00012 - 0.71)
Leaks	Volatile organics	ND
Open sources	Volatile organics	ND

[1] USEPA, 1995. 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 4.2-1 illustrates the use of Equations (19) and (20).

Example 4.2-1 Calculating Solvent Reclamation Emissions

First, total VOC emissions from operation of a distillation device may be calculated using an emission factor from Table 4 and Equation (19).

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

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

Next, total VOC emissions are speciated using the concentration of VOC species x, mass %, and Equation (20).

E_{VOC} = 6.6 kg VOCs/yr
C_x = 99% toluene in spent solvent

$E_x = E_{VOC} * C_x / 100$
$= 6.6 * 99/100$
$= 6.5$ kg toluene emitted/yr

If the species x 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 total mixture is known, the volume percent of species x in the total mixture can be converted to mass percent using Equation (21).

$$X_x = Y_x * M_x / M * 100 \quad (21)$$

where:

X_x = mass percent of species x in total mixture
Y_x = volume percent of species x in total mixture
M_x = molecular weight of species x
M = molecular weight of total mixture

If the molecular weight of the total mixture is not known, the volume percent can be converted to mass percent using Equation (22).

$$M = \sum_{x=1}^{n} (Y_x / 100 * M_x) \quad (22)$$

where:

M = molecular weight of total mixture
n = number of species in total mixture
Y_x = volume percent of species x in total mixture
M_x = molecular weight of species x

4.2.2 Emissions from Parts Cleaning

VOC emissions factors for parts cleaning in cold cleaners, open-top vapour degreasers, or conveyor degreasers are presented in Table 5. Emission factors for cold cleaners and vapour degreasers are in units of tonnes VOC/yr/unit, or kg VOC/hr/m^2. Emission factors for vapour and non-boiling conveyor degreasers are presented only in units of tonnes VOC/yr/unit. If you are using emission factors based on the surface area of the exposed solvent, use Equation (23).

$$E_{VOC} = EF_{VOC} * A * OpHrs \quad (23)$$

where:

E_{VOC} = VOC emissions from a cold cleaner or open-top vapour degreaser, kg/yr

EF_{VOC} = VOC emission factor for cold cleaners or open-top vapour degreasers, kg/hr/m^2

A = surface are of solvent exposed to the atmosphere, m^2

OpHrs = hours per year that the cold cleaner or vapour degreaser is in operation, hr/yr

If using emission factors based on the number of cleaning units, use Equation (24).

$$E_{VOC} = EF_{VOC} * NU * 1\,000 \qquad (24)$$

where:

E_{VOC} = VOC emissions from a cold cleaner, an open-top vapour degreaser, or a conveyor degreaser, kg/yr

EF_{VOC} = VOC emission factor for cold cleaners, open-top vapour degreasers, or conveyor degreasers, tonne/hr/unit

NU = number of cleaning units in use, units

1 000 = 1 000 kg/tonne

Speciated VOC emissions from parts cleaning may be calculated using Equation (25).

$$E_x = E_{VOC} * C_x / 100 \qquad (25)$$

where:

E_x = emissions of VOC species x from parts cleaning, kg/yr

E_{VOC} = VOC emissions, calculated using Equations (22) or (23), kg/yr

C_x = concentration of VOC species x in the cleaning solvent, mass %

Table 5. Solvent Emission Factors

Type of Degreasing	Activity Measure	Uncontrolled Organic Emission Factor [a] (kg/tonne)
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		0.06 tonne/yr/unit
Entire unit	Surface area and duty cycle [d]	0.4 kg/hr/m^2
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

[1]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 5.0)

Example 4.2-2 illustrates the use of Equations (23), (24) and (25).

Example 4.2-2 Calculating Parts Cleaning Emissions

This example shows how total and speciated VOC emissions from a cold cleaner may be calculated using Equations (23) to (25) and an emission factor from Table 5 based on the surface area of the exposed solvent. First, total VOC emissions are calculated using Equation (23).

EF_{VOC} = 0.4 kg/hr/m^2
A = 1.2 m^2
OpHrs = 3 000 hr/yr

E_{VOC} = EF_{VOC} * A * OpHrs
= 0.4 * 1.2 * 3 000
= 1 440 kg VOC/yr

Next, total VOC emissions are speciated using the concentration of VOC species x (mass %) and Equation (25).

E_{VOC} = 1 440 kg VOC/yr
C_x = 99% tetrachloroethylene (TCE) in cleaning solvent

E_x = E_{VOC} * C_x /100
= 1 440 * 99/100
= 1 425.6 kg TCE/yr

VOC emissions are calculated from several cold cleaners using Equation (24) and an emission factor from Table 5.

EF_{VOC} = 0.30 tonnes/yr/unit
NU = 5 units

E_{VOC} = EF_{VOC} * NU * 1 000
= 0.30 * 5 * 1 000
= 1 500 kg VOC/yr

4.2.3 Emissions from Equipment Leaks

Emissions from equipment leaks may be calculated using the EETs detailed in the *Emissions from Fugitive Sources and Equipment Leaks* Manual. This Manual covers emissions from various fugitive sources including valves, pumps, seals, connectors, and open-ended lines.

4.2.4 Emissions of Particulate Matter (PM/PM_{10})

Table 6. presents PM/PM_{10} emission factors from paint and ink manufacturing, based on the amount of pigment used by a facility. The factor for paint manufacturing is 10 kg PM/tonne pigment. Table 7 shows

that the emission factor for pigment mixing at an ink manufacturing facility is 1 kg PM/tonne pigment. To calculate PM emissions using these emission factors, use Equation (26).

$$E_{PM} = EF_{PM} * \Sigma Q_x \quad (26)$$

where:

E_{PM} = total PM emissions, kg/yr
EF_{PM} = PM emission factor, kg PM/tonne pigment
ΣQ_x = total pigment, tonne/yr

Table 6. Emission Factors for Paint and Varnish Manufacturing [a]

Type of Product	Emission Factors		Emission Factor Rating Code
	Volatile Organic Compounds [b] (kg/tonne of product)	PM/PM_{10} (kg/tonne of pigment)	
Paint [c]	15	10	C
Varnish			
Bodying oil	20	NA	C
Oleoresinous	75	NA	C
Alkyd	80	NA	C
Acrylic	10	NA	C

[1] USEPA, 1995.
Units are kg of substance emitted per tonne of product or pigment used.
[a] Afterburners can reduce VOC emissions by 99% and particulates by about 90%. A water spray and oil filter system can reduce particulates by about 90%.
[b] Expressed as undefined organic compounds whose composition depends on the type of solvents used in the manufacture of paint and varnish.
[c] Particulate matter (0.5 - 1.0%) is emitted from pigment handling.

Table 7. Emission Factors for Printing Ink Manufacturing [a]

Type of Product	Emission Factors		Emission Factor Rating Code
	Volatile Organic Compounds [b] (kg/tonne of product)	PM/PM_{10} (kg/tonne of pigment)	
Vehicle Cooking			
General	60 [1]	NA	E
Oils	20 [1]	NA	E
Oleoreinous	75 [1]	NA	E
Alkyds	80 [1]	NA	E
Pigment Mixing	NA	1	E

[a] USEPA, 1995.
[b] The non-methane VOC emissions are a mix of volatilised vehicle components, cooking decomposition products, and ink solvent.
Units are kg of substance emitted per tonne of product or pigment used.

PM_{10} can conservatively be estimated by assuming that all the PM emitted is PM_{10}.

PM emissions containing listed metals requires speciation into individual metal species where thresholds for the metal are triggered. Speciated PM emissions are calculated using Equation (27).

$$E_{PM} = EF_{PM} * Q_x * C_x / 100 \quad (27)$$

where:

E_{PM} = total emissions of PM species x, kg/yr
EF_{PM} = PM emission factor, kg PM/tonne pigment
Q_x = amount of pigment containing species x used by the facility, tonne/yr
C_x = concentration of PM species x in pigment x, mass %

The application of Equation (27) is illustrated in Example 4.2-4.

Example 4.2-4 Calculating Speciated PM Emissions

This example demonstrates how speciated PM emissions from pigment mixing at an ink manufacturing facility may be calculated using the consumption-based PM emission factor from Table 7 and Equation (27):

EF_{PM} = 1 kg PM/tonne pigment
Q_x = 5 tonnes ZnO/yr
C_x = 80% Zn in ZnO

$E_{Zn} = EF_{PM} * Q_x * C_x / 100$
$= 1 * 5 * 80/100$
$= 4$ kg Zn/yr

5.0 Emission Factor Rating

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 the references section of this document. 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

Estimating your facility's emissions based on emission factors only, and without taking into account any control measures, may have an uncertainty as high as 100%.

Other EETs, such as release calculations based on mass balance of solvent consumption and without taking into account control measures, may have an uncertainty of 50%.

An EET based on an audit or direct measurement, and taking into account control measures, may have an uncertainty of 20%.

6.0 References

Eastern Research Group. July 1997. *Introduction To Stationary Point Source Emission Inventory Development Volume II: Chapter 1.* Morrisville, NC, USA.

Eastern Research Group. March 1998. *Preferred and Alternative Methods for Estimating Air Emissions from Paint and Ink Manufacturing Facilities Volume II: Chapter 1.* Morrisville, NC, USA.

EMEP/CORINAIR. (1996) *AIR - Atmospheric Emission Inventory Guidebook.* European Environment Agency, Copenhagen, Denmark.

Noyes, Robert, Editor. 1993. *Pollution Prevention Technology Handbook.* Noyes Publications, Park Ridge, NJ, USA.

NPCA. 1995. *Emissions Estimation Guidance Manual for the Paint and Coatings Industry (Second Edition).* National Paint and Coatings Association, Inc., Washington, DC, USA.

USEPA. March 1988. *Title III Section 313 Release Reporting Guidance, Estimating Chemical Releases From Formulation of Aqueous Solutions, Office of Pesticides and Toxic Substances,* EPA 560/4-88-004f. Washington, DC, USA.

USEPA. January 1995a. *Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources, fifth edition, AP-42. Section 6.4 Paint and Varnish.* United States Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC, USA.

USEPA. January 1995a. *Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources, fifth edition, AP-42. Section 6.7 Printing Ink.* United States Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC, USA.

USEPA. January 1995a. *Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources, fifth edition, AP-42. Section 5.2 Transportation and Marketing Of Petroleum Liquids.* United States Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC, USA.