R5-2014-0104710000203

Volume II: Chapter 8

Methods for Estimating Air Emissions from Paint, Ink, and Other Coating Manufacturing Facilities

February 2005

STAPPA•ALAPCO•EPA
emission inventory improvement program

Disclaimer

As the Environmental Protection Agency has indicated in Emission Inventory Improvement Program (EIIP) documents, the choice of methods to be used to estimate emissions depends on how the estimates will be used and the degree of accuracy required. Methods using site-specific data are preferred over other methods. These documents are non-binding guidance and not rules. EPA, the States, and others retain the discretion to employ or to require other approaches that meet the requirements of the applicable statutory or regulatory requirements in individual circumstances.

R5-2014-0104710000203

Table of Contents

Section **Page**

1.0 Introduction 8.1-1

2.0 Source Category Description 8.2-1
- 2.1 Process Description 8.2-1
  - 2.1.1 Premix and Premix 8.2-1
  - 2.1.2 Pigment Grinding or Milling 8.2-2
  - 2.1.3 Product Finishing 8.2-3
  - 2.1.4 Product Filling 8.2-3
  - 2.1.5 Basic Flow Sheets for Coating Manufacturing Processes 8.2-3
- 2.2 Emission Sources 8.2-6
  - 2.2.1 Process Operations 8.2-6
  - 2.2.2 Miscellaneous Operations 8.2-7
  - 2.2.3 Material Storage 8.2-7
  - 2.2.4 Equipment Leaks 8.2-8
  - 2.2.5 Spills 8.2-8
- 2.3 Process Design and Operating Factors Influencing Emissions 8.2-8
  - 2.3.1 VOC Control Systems 8.2-9
  - 2.3.2 PM/PM10 Control Systems 8.2-11
  - 2.3.3 Equipment or Process Modifications 8.2-11

3.0 Overview of Available Methods 8.3-1
- 3.1 Emission Estimation Methods 8.3-1
  - 3.1.1 Emission Factors 8.3-1
  - 3.1.2 Source-Specific Models 8.3-2
  - 3.1.3 Material (Mass) Balance Calculations 8.3-2
  - 3.1.4 Test Data 8.3-3
- 3.2 Comparison of Available Emission Estimation Methodologies 8.3-4

4.0 Modeling Methods for Estimating Emissions 8.4-1
- 4.1 Emission Model for Material Loading 8.4-3
- 4.2 Heat-Up Losses 8.4-9
  - 4.2.1 Option 1 . . . . . 8.4-10
  - 4.2.2 Option 2 . . . . . 8.4-15
- 4.3 Emission Model for Spills 8.4-19
- 4.4 Emission Model for Surface Evaporation 8.4-22
- 4.5 Gas Sweep or Purge 8.4-26
  - 4.5.1 Option 1 . . . . . 8.4-26
  - 4.5.2 Option 2 . . . . . 8.4-28
- 4.6 Solvent Reclamation 8.4-36
- 4.7 Emission Model for Liquid Material Storage 8.4-40

4.8 Emission Model for Wastewater Treatment 8.4-41

5.0 Other Methods for Estimating Emissions 8.5-1
5.1 Emission Calculations Using Emission Factors 8.5-1
5.1.1 Total VOC Emissions from Paint Manufacturing Facilities 8.5-1
5.1.2 VOC Emissions from Paint Mixing Operations 8.5-5
5.1.3 VOC Emissions from Ink Manufacturing Facilities 8.5-7
5.1.4 Total and Speciated VOC Emissions from Solvent Reclamation 8.5-9
5.1.5 VOC Emissions from Parts Cleaning 8.5-11
5.1.6 VOC Emissions from Equipment Leaks 8.5-13
5.1.7 PM/PM_{10} Emissions from a Paint or Ink Manufacturing Facility 8.5-14
5.2 VOC and PM Emissions Calculations Using Material Balance 8.5-15
5.3 Emissions Calculations Using Test Data 8.5-16

6.0 References 8.6-1

R5-2014-0104710000203

List of Figures

Figure **Page**

8.2-1. Basic paint manufacturing process flowdiagram 8.2-4
8.2-2. Basic ink manufacturing process flowdiagram 8.2-5

List of Tables

Table Page

8.3-1. Estimated VOC Emissions Summary for the Bright Blue Paint Company 8.3-6
8.4-1. List of Variables and Symbols 8.4-2
8.5-1. List of Variables and Symbols 8.5-2
8.5-2. Emission Factors for Equipment Components at Coatings Manufacturing Facilities 8.5-13

R5-2014-0104710000203

[This page is intentionally left blank.]

R5-2014-0104710000203

1.0 Introduction

The purpose of this guideline is to describe emission estimation techniques for point sources in an organized manner and to provide concise example calculations to aid in the preparation of emission inventories. While emissions estimates are not provided, the information presented in this document may be used to select an emission estimation technique best suited to a particular application. This chapter describes the procedures and recommended approaches for estimating emissions from paint, ink, and other coating manufacturing operations, and it is intended to assist industry as well as regulatory agency personnel.

As EPA has indicated in this and other EIIP documents, the choice of methods to be used to estimate emissions depends on how the estimate will be used and the degree of accuracy required and methods using site-specific data are preferred over other methods. Because this document provides non-binding guidance and is not a rule, EPA, the States, and others retain the discretion to employ or require other approaches that meet the specific requirements of the applicable regulations in individual circumstances.

Section 2 of this chapter provides a brief overview of the types of coating manufacturing processes, emission sources, and factors that affect emissions. Section 3 of this chapter provides an overview of available emission estimation methods and an example showing the application of different techniques to estimate emissions for a paint manufacturing facility. Note that the use of site-specific emissions data is always preferred over the use of default values developed through use of industry emission averages.

Section 4 of this chapter presents mathematical models and equations for estimating emissions from several paint, ink, and other coating manufacturing operations. Section 5 of this chapter describes other techniques for estimating emissions such as the use of emission factors and material balances. Section 6 of this chapter presents references.

R5-2014-0104710000203

[This page is intentionally left blank.]

2.0 Source Category Description

2.1 Process Description

This section provides a brief overview of paint, ink, and other coating manufacturing operations. The reader is referred to Control of VOC Emissions from Ink and Paint Manufacturing Processes, April 1992, for additional background information. 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 (e.g., finishes for automobiles, machinery, metal and wood furniture, and appliances), and special purpose coatings (e.g., industrial new construction and maintenance paints, traffic marking paints, and marine paints). Approximately 80 percent of architectural coatings are water-based (Census Bureau, 1997). However, solvent-based paint is still predominantly used for product finishes and special-purpose coatings. Inks that are currently manufactured include letterpress, lithographic and 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 (NAPIM, 1996). Specialty ink products include textile and silk screen ink, invisible inks, powder inks, carbon paper, typewriter, and duplicating inks. Paint, ink, and other coating manufacturing can be classified as a batch process and generally involves the blending/mixing of resins, pigments, solvents, and additives. Traditional paint, ink, and other coating manufacturing consists of four major steps:

- Preassembly and premix;
- Pigment grinding/milling/dispersing;
- Product finishing/blending; and
- Product filling/packaging.

These steps are described in more detail in the sections below.

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, plasticizers, dry pigment, 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 driers. 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 step depends on the batch size and the type of coating being

produced. Drums equipped with a portable mixer may be used for drum-sized batches. These mixers normally 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. Coating 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/milling step described below.

2.1.2 Pigment Grinding or Milling

Pigment grinding or milling entails the incorporation of the pigment into the liquid base of the coating to yield a fine particle dispersion. The three stages of this process include 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 (Noyes, 1993). More commonly used equipment include the following: roller mills, ball and pebble mills, attritors, sand mills, bead and shot mills, high-speed stone and colloid 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 methods in current pigment base manufacturing technology. Additionally, these types of equipment are usually associated with elevated levels of volatile organic compound (VOC) emissions due to their more open design. Roller mills may have from one to five rolls that grind pigments into vehicles. Most coating manufacturing facilities that use roller mills operate with conventional three-roll mills. Roller mills are labor intensive, requiring 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 and inks and viscous pigmented products that require fine dispersion and clean color (EPA, 1992a).

High-speed dispersion is the most universally used method of mixing in the paint, ink, and other coating manufacturing 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 such as undercoats and primers, it may not be appropriate for high-quality paints and inks. It can, however, be used for premix operations of high-quality paints and inks, thus reducing the number of passes in a media mill or reducing the amount of time spent in a ball mill.

R5-2014-0104710000203

2.1.3 Product Finishing

Final product specifications for color, viscosity, and other coating characteristics are achieved in the product finishing step. This process generally consists of thinning, tinting, and blending. Most of the solvents, tints, and shades are added during this operation (Fisher et al., 1993). Product finishing activities for solvent-based paints and inks involve adding various combinations of pigments, organic solvents, and resins. For water-based coatings, a preservative, an antifoaming agent, a polyvinyl acetate emulsion, and water are added at this step 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/high-speed disperser setup.

2.1.4 Product Filling

The final step in the paint, ink, and other coating 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. Coatings 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 (Fisher et al, 1993). Once the material has been filtered, it can be transferred into pails, drums, totes, tank wagons, or other containers for shipment. Filling may be accomplished either manually or mechanically depending on the number and size of the containers to be filled.

2.1.5 Basic Flow Sheets for Coating Manufacturing Processes

Figures 8.2.1 and 8.2.2 present basic paint and ink manufacturing process diagrams.

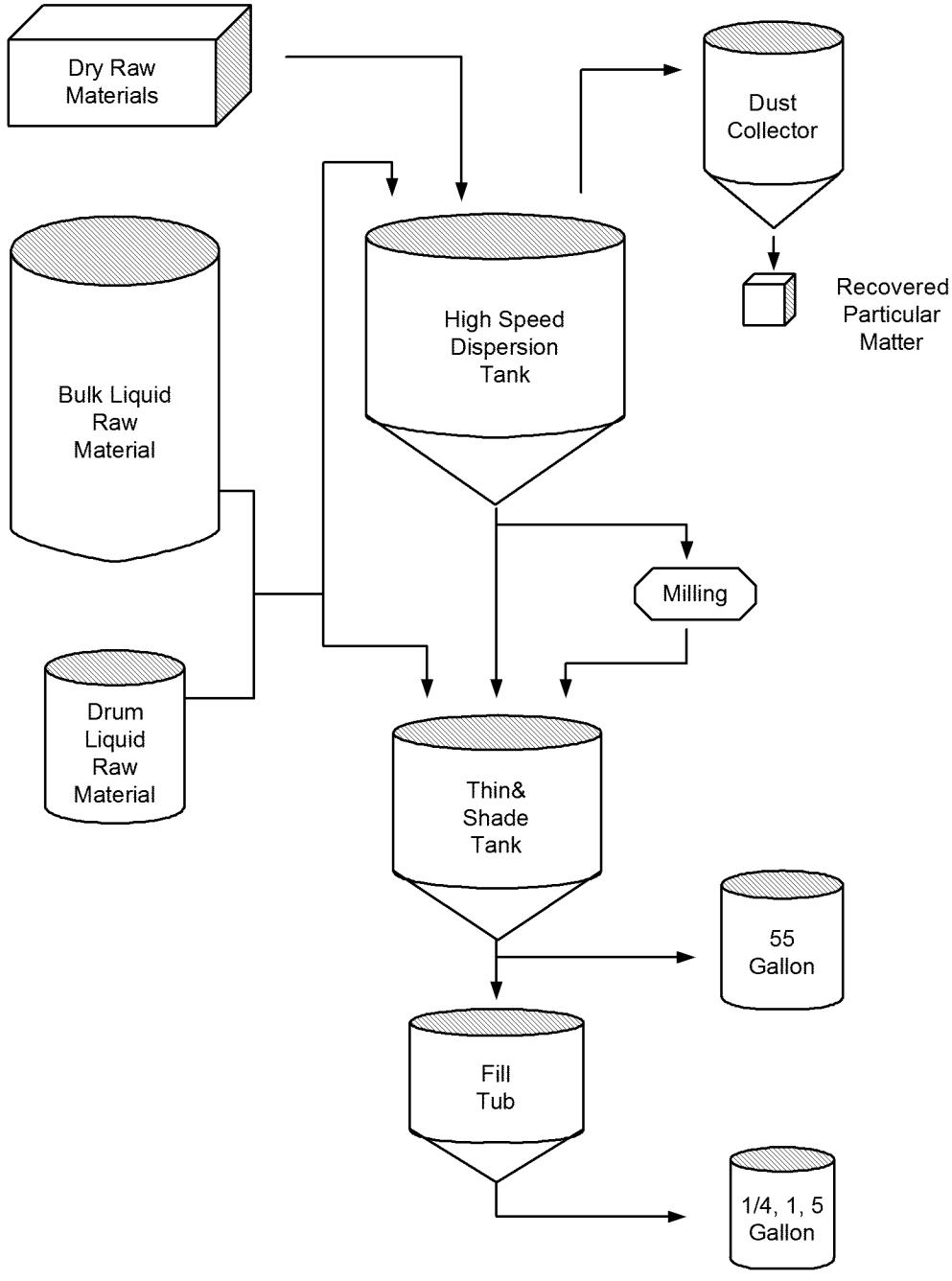

Figure 8.2-1. Basic paint manufacturing process flow diagram.

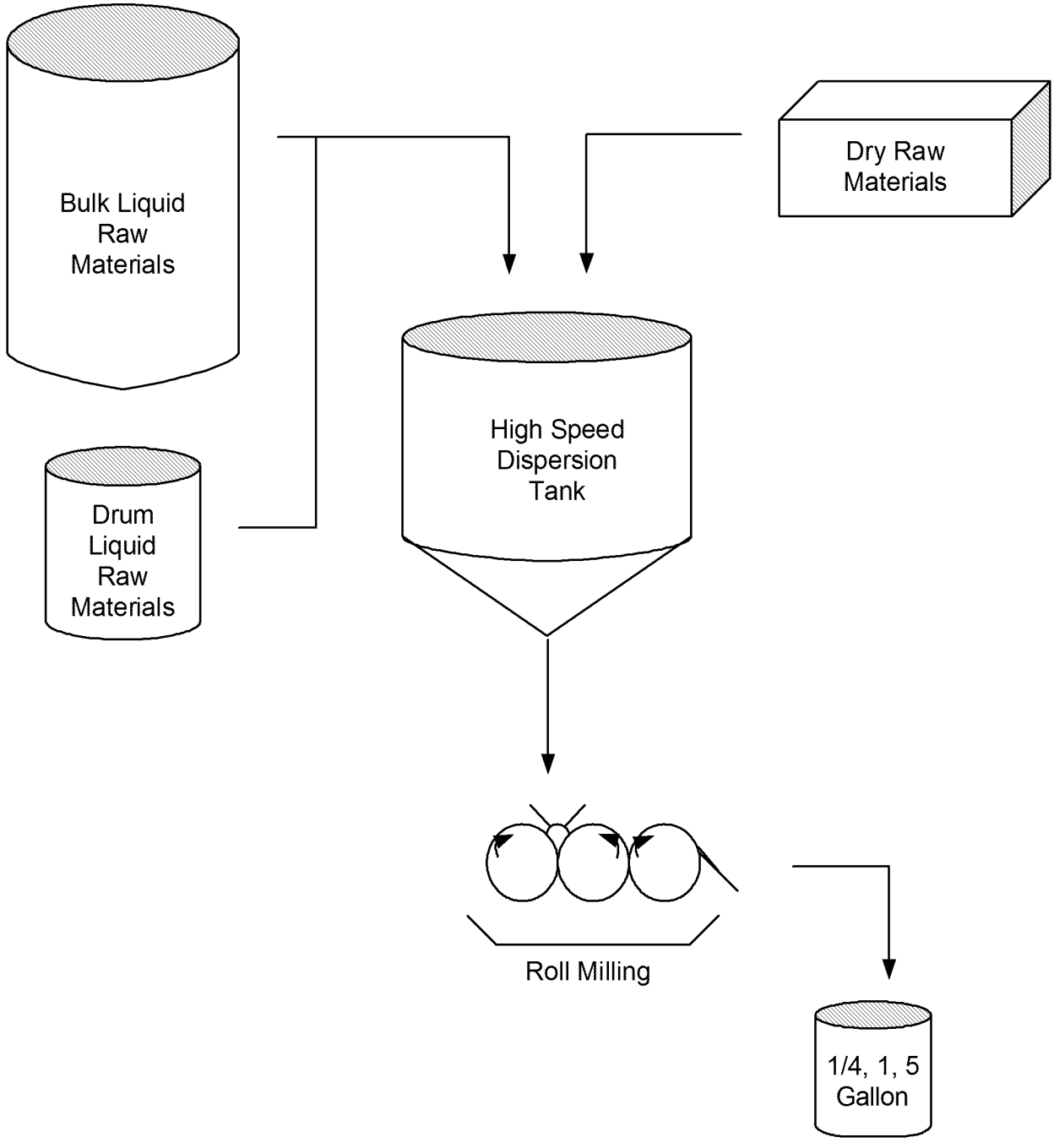

Figure 8.2-2. Basic Inks manufacturing process flow diagram.

2.2 Emission Sources

The majority of emissions that occur from paint, ink, and other coating manufacturing operations are from volatile organic compounds (VOCs) that evaporate during manufacturing. Particulate matter emissions may also occur from the handling of solid powders that are used in manufacturing.

Several air emission sources have been identified for paint, ink, and other coating manufacturing operations; they are as follows:

- Process operations
- Related miscellaneous operations
- Material storage
- Equipment leaks
- Spills and other abnormalities

2.2.1 Process Operations

Process operations cover emissions 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 may occur during material loading of mixing and grinding equipment due to the displacement of organic vapors. 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 released from the chute through which ingredients are added.

Particulate matter (PM) and PM equal to or less than 10 micrometers in diameter (PM10) emissions may also occur during the material loading process from handling of pigments and other solids. VOC and PM emissions during material loading emissions may occur as point source or fugitive, depending on whether a PM emissions 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 mixing energy is converted to thermal energy. This rise in temperature in many cases is controlled through the use of cold water jackets on the process vessel. As the VOCs in the mixers heat up, the vapor in the headspace expands and leads to solvent emissions from the equipment. Emissions that escape the process equipment through loose fittings or duct connections and enter the room air are considered to be fugitive emissions. Emissions that exit the process equipment through the vent duct to the emissions handling system are considered to be process emissions. (Fisher et al, 1993)

Surface Evaporation. Surface evaporation may occur during mixing, dispersing, and blending operations if the vessel contents are exposed to the atmosphere. For 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 (e.g., sand mills, bead mills, and shot mills) may occur from the exposed filtering screen.

Filling Losses. Emissions from product filling occur during transfer and free-fall into the receiving container.

2.2.2 Miscellaneous Operations

In addition to typical process operations associated with paint, ink, and other coating manufacturing, miscellaneous operations can generate emissions (primarily in the form of VOCs). These operations are discussed below:

Solvent Reclamation. Solvent reclamation refers to the purification of dirty or spent solvent through use of a distillation device. VOC emissions occur from loading solvent into the distillation equipment, operation of the distillation equipment, and spillage. Emissions from loading and spilling are classified as fugitive, while emissions from operation of the equipment are generally discharged through a condenser vent and are thus classified as point source.

Cleaning. Cleaning is an important ancillary part of paint, ink, and other coating manufacturing processes. 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 characterized as fugitive. In addition to this type of cleaning, small items used in the process may be cleaned by washing with solvents in a cold cleaner or open-top vapor degreaser. Of the two technologies, the use of a cold cleaner is more common. VOC emissions from this type of cleaning are classified as fugitive.

Wastewater Treatment. A paint, ink, or other coating manufacturing facility may use a wastewater treatment system to treat contaminated water generated during the process (e.g., water that has been used to clean equipment used in the production of water-based coating). Wastewater treatment systems generally consist of a series of surface impoundments that are used for equalization, neutralization, 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 Volume II, Chapter 5, Preferred and Alternative Methods for Estimating Air Emissions from Wastewater Collection and Treatment.

2.2.3 Material Storage

Various types and sizes of storage tanks are used to store solvents and resins used in the paint, ink, and other coating manufacturing processes. Most of these tanks have a fixed-roof design (Fisher et al., 1993). The two significant types of emissions from fixed-roof tanks are breathing and working losses. Breathing loss is the expulsion of vapor from a tank through vapor 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 vapors are expelled from the tank. Evaporative emissions during emptying occur when air drawn into the tank during liquid removal becomes saturated with organic vapor and expands, expelling vapor through the vapor relief valve (EPA, 1995a). Emissions from tanks are characterized as a point source because VOCs are released through a vent.

2.2.4 Equipment Leaks

In order to transport stored materials (e.g., organic solvents and resins) from storage tanks to the paint, ink, or other coating 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 (process line components) may develop leaks over time. When leaks occur, volatile components in the transported material are released to the atmosphere. This generally occurs from the following process line components:

- Pump seals
- Valves
- Compressor seals
- Safety relief valves
- Flanges
- Open-ended lines
- Sampling connections.

Emissions from equipment leaks can be characterized as fugitive and are described in detail in Volume II, Chapter 4, Preferred and Alternative Methods for Estimating Fugitive Emissions from Equipment Leaks. Emission factors for pumps, valves, and connectors at coating manufacturing facilities are also discussed in section 5.1.6 of this chapter.

2.2.5 Spills

Solvents, resins, or product may be accidentally spilled during manufacturing or cleaning activities. Materials that are spilled onto the ground may spread over an area, vaporize, and thus result in an air emission (EPA, 1987). Such an emission would be characterized as fugitive.

2.3 Process Design and Operating Factors Influencing Emissions

VOC and PM emissions from paint, ink, and other coating manufacturing may be reduced through the use of add-on control systems or through equipment and process modifications.

2.3.1 VOC Control Systems

A VOC control system typically consists of a capture device and a removal device. The capture device (such as a hood or enclosure) captures the VOC-laden air from the emission area and ducts the exhaust air stream to removal equipment such as a recovery device or a destructive control device. In either case, the purpose of the control device is to remove VOCs from the exhaust air stream. The overall efficiency of a control system is a function of the specific removal efficiency for each device in the system.

Example recovery devices:

1. Condensers are one of the most frequently used control devices in industry. They work by reducing the temperature of the emission exhaust gas to a cold enough temperature so that VOC vapors are recovered through condensation. One problem that is frequently encountered in the coating manufacturing industries is that the solvent vapors in the emission exhaust gas may have a fairly low dew point temperature. This is because normal processing temperatures are generally low and many exhaust systems provide a high level of dilution from outside air that further reduces the dew point temperature of the gas.

2. Adsorption Devices that incorporate activated carbon are capable of removing VOC vapors from exhaust emission streams to very low levels in the final gas stream. Large scale adsorption based recovery systems normally have two or more activated carbon adsorption chambers. One carbon chamber is being used to remove VOCs from an emission stream while the spent carbon chamber is being regenerated. VOCs are recovered from the system during the regeneration phase. Steam is routed into the saturated carbon bed to cause the VOCs to desorb from the carbon and condense at the condenser. Once VOC liquids have been collected then they may be recycled or further purified prior to reuse in the manufacturing operation.

3. Dust collectors are used to collect particulate matter from the emission stream. Dust collectors are constructed in many different designs. However, one style that is commonly used in the coating manufacturing industry is a bag house design. A bag house consists of a large rectangular housing with many internal banks of vertically mounted filter bags. The emission stream enters the bag house through the side inlet, passes through the bag filter media, and exits the unit through the discharge port at the top. Particulate matter builds up on the filter media until it is shaken off by pulses of compressed air from within each bag. The dust that falls from the bags during the pulsing process is collected at the lower section of the bag house and finally discharged through the solids outlet to a drum or other container. When designing a bag house for an installation it is important to select the appropriate filter media and surface area for the particulate matter to be collected. The pore size of the filter cloth will determine the removal efficiency of the overall unit.

4. A floating roof on a storage tank helps to reduce solvent emissions by eliminating the headspace that is present in conventional storage tanks. For the conventional storage tank, air that is saturated with solvent vapors exits the vessel as the surrounding temperature increases during the day. Outside air then reenters the vessel during the evening hours as the surrounding temperature decreases and the daily cycle prepares to be repeated. Additionally, when a conventional storage tank is filled periodically then emissions occur by way of displacement. A floating roof moves up and down the vessel vertical walls as the level of the storage tank changes. Since the vessel contains no headspace all breathing and filling losses are avoided.

Example destructive control devices:

1. Catalytic Incinerators are used to reduce VOCs from process exhaust gases from paint spray booths, ovens, and other process operations. The catalyst section operates at between 315/C to 400/C to convert VOC to CO_2 and H_2O. A properly designed and installed system can achieve a VOC destruction efficiency of greater than 95%.

2. Thermal Incinerators control VOC levels in a gas stream by passing the stream through a combustion chamber where the VOCs are burned in air at temperatures between 700/C to 1,300/C. Fuel is burned in the unit to supply the necessary heat for decomposition of the VOC's. Heat exchangers may also be installed as part of the unit to conserve energy by warming the inlet air stream with the hot exhaust gases.

3. Venturi Scrubbers are used to remove particulate material from vent exhaust streams. These units normally incorporate a spray nozzle section where liquid is discharged at a high velocity, a mixing section where liquid droplets contact the incoming emission gas stream, and a settling/separation section where scrubber fluid is recycled to the inlet spray nozzle and the exit gas is discharged to the atmosphere or to a secondary control device.

4. Enclosed Oxidizing Flares convert VOCs into CO_2 and H_2O by way of direct combustion. Normally an enclosed oxidizing flare is used when the waste gas is rich enough in organic content to be its own fuel source. If the process gas stream does not contain an adequate level of combustible VOCs then additional fuel must be supplied for effective operation.

The removal efficiency for each control device is a function of the specific design of the unit and how well its capability matches the intended application. Before selecting pollution equipment one should consult different manufacturers and/or engineering firms to determine the most appropriate control device solution for a given application.

2.3.2 PM/PM10 Control Systems

PM/PM10 control systems for the paint, ink, and other coatings manufacturing industry consist of a capture device paired with a control device that is typically a fabric filter (bag house). These systems are typically employed to reduce PM emissions from charging pigments and other solids into mixing and grinding devices. The captured dust may be recycled or sent for off-site disposal or treatment.

Bag houses remove particulate material from an emission gas stream by passing the emission stream through engineered fabric filter tubes, envelopes, or cartridges. Particulate material is retained on the filter media as the clean air is discharged to the atmosphere. Vibrators or timed air blast are used for removing and discharging the dust that has been collected in the unit. When identifying a bag house for an application it is important to consider the particle size in the emission stream, the particle size control requirements, the air flow rate of the emission stream, and the bag filter surface area requirements. Additionally, it is important to identify the appropriate chemical resistance requirements for the materials of construction in the unit.

Fabric filters are least efficient with particles 0.1 to 0.3 : m in diameter and with emission streams of high moisture content. When operated under optimum conditions, they can generally achieve control efficiencies of up to 99+ percent (EIIP, 2000). However, typical control efficiencies range from 95 to 99 percent.

2.3.3 Equipment or Process Modifications

Most coatings manufacturing facilities reduce VOC emissions through equipment or process modifications. Some of these techniques will also reduce PM emissions. Modifications include those discussed below.

Tank Lids. Tank lids are the most common equipment modification used during paint, ink, and other coating manufacturing activities to control VOC emissions.

Modified Milling Equipment. VOC and PM emissions may be reduced by converting older milling equipment to closed systems.

Use of Pigments in Paste Form. PM emissions may be reduced by using pigments that have been wetted or mixed with resins. Since these pigments are wet, dust is not generated when the package is opened and as pigment is dumped into mixing vessels (Noyes, 1993).

Product Reformulation. Production of coatings that contain reduced or no VOCs will reduce VOC emissions from coatings manufacturing facilities. High-solids and water-based coatings contain less VOCs than traditional solvent-based products. Powder coatings and the majority of radiation-curable paints and inks contain no VOCs.

R5-2014-0104710000203

[This page intentionally left blank.]

3.0 Overview of Available Methods

3.1 Emission Estimation Methods

Several methods are available for calculating emissions from paint, ink, and other coating manufacturing operations. The best method to use depends upon the emission source being evaluated, available data, how the estimates will be used, and the degree of accuracy required in the estimate. Although multiple methods are identified for some operations, this document does not mandate any emission estimation method. Industry personnel using this manual should contact the appropriate state or local air pollution control agency regarding suggested methods prior to their use.

This section discusses the methods available for calculating emissions from paint, ink, and other coating manufacturing operations. A discussion of the sampling and analytical methods available for monitoring each pollutant is provided in Chapter 1 of this volume, *Introduction to Point Source Emission Inventory Development*.

Estimation techniques for storage tank emissions are discussed in Chapter 1 of this volume, and procedures for estimating emissions from wastewater are described in Chapter 5. This chapter focuses on estimating emissions from process operations, miscellaneous operations, and spills. This chapter also presents equipment leak emission factors for coating manufacturing; additional equations and factors for calculating emissions from equipment leaks are discussed in Chapter 4.

3.1.1 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 plant or at one or more facilities within an industry. Chapter 1 of this volume contains a detailed discussion of the reliability/quality of available emission factors.

Emission factors may be used to calculate total VOC and PM emissions from a paint and ink manufacturing facility, 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.

EPA-approved emission factors for these sources may be found in *AP-42*, the *Locating and Estimating* series of documents, the Factor Information and REtrieval (FIRE) System, and/or *Protocol for Equipment Leak Emission Estimates* (EPA, 1995g). Emission factors may also be available through trade associations such as the National Association of Printing Ink Manufacturers, Inc. (NAPIM).

Use of paint manufacturing emission factors from Section 6.4 of *AP-42* and ink manufacturing emission factors from Section 6.7 of *AP-42* is generally accepted by regulatory agencies, and their use in calculating total facility or process-specific emissions is more cost-effective than collection and analysis of air samples or use of emission models. Additionally, there are potentially significant limitations with the material balance approach.

3.1.2 Source-Specific Models

Theoretical, more complex "models" or equations can be used for estimating emissions. Use of emission models/equations to estimate emissions from paint, ink, and other coating manufacturing facilities is a more complex and time-consuming process than the use of emission factors. Emission models/equations require more detailed inputs than use of emission factors; however, they provide emission estimates based on site-specific conditions.

Emission estimating models/equations are available for the following types of emissions found at paint, ink, or other coating manufacturing facilities:

- Material loading
- Heat-up losses from dispersion/grinding activities
- Surface evaporation during mixing/blending operations
- Filling
- Gas sweep or purge
- Cleaning solvent loading
- Solvent reclamation
- Material storage
- Spills
- Wastewater treatment.

Inputs for theoretical models/equations generally fall into the following categories: chemical/physical properties of the material(s) involved (e.g., vapor pressure, vapor molecular weight), operating data (e.g., amount of material processed, operating hours) and physical characteristics/properties of the source (e.g., tank color, tank diameter).

3.1.3 Material (Mass) Balance Calculations

The material balance approach to emissions estimation considers the given facility as a sort of "black box," where one compares the total quantity of raw materials consumed versus amounts of materials leaving the facility as product or waste. Waste can consist of used filter bags or

cartridges, spent solvent or still bottoms, dust collector material, pigment bags and/or drum residue, and wastewater (NPCA, 1995).

Calculating emissions from a paint or ink manufacturing facility using material balance appears to represent a straightforward approach to emissions estimations. However, few facilities 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 to each material handling step often accumulate into large deviations. Because emissions from specific materials are typically below 1.5 percent of gross consumption, an error of only ± 5.0 percent in any one step of the operation can significantly skew emissions calculations. Potential sources of error in the material balance calculation method include the following:

- The delivery of bulk raw materials at a paint or ink manufacturing facility is often tracked by volume, not by weight. Since density will vary with temperatures, the actual mass per unit volume of materials delivered in the summer may be less than that received in the winter.

- Raw materials received by paint or ink manufacturing facilities may potentially be used in hundreds or thousands of finished products. In order to complete the material balance, it is crucial that the exact quantity and speciation of each material shipped off-site in the product be known. For many facilities, it is extremely difficult, to accurately track the distribution of specific raw materials across their entire product line.

- The amount of raw material contained in waste must also be considered. This may involve precise analysis of the concentration of the material of interest in each waste stream.

- Batch production of paint or ink often requires the manual addition of raw materials. Sometimes these additions are not accurately measured or recorded (NPCA, 1995).

3.1.4 Test Data

Testing can be performed to quantify point source or fugitive emissions. In point source testing, effluent gas samples are usually collected from a stack using probes inserted through a port in the stack wall. Pollutants in the gas sample 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 such tests.

Industrial hygiene data (concentrations) can be used in conjunction with exhaust system flow rates to calculate fugitive emissions from a room, floor, or building. Direct-reading instruments

R5-2014-0104710000203

that may be used to obtain an instantaneous reading of vapor concentrations include photoionization detectors, portable infrared spectrophotometers, and portable gas chromatographs (NPCA, 1995).

Use of stack and/or industrial hygiene test data is likely to be the most accurate method of quantifying air emissions from paint, ink, and other coating manufacturing operations. However, collection and analysis of air samples from manufacturing facilities can be very expensive and especially complicated for coating manufacturing facilities where a variety of VOCs are emitted and where most of the emissions may be fugitive in nature. Test data from one specific process may not be representative of the entire manufacturing operation and may provide only one example (a snapshot) of the facility's emissions.

To be representative, test data would need to be collected over a period of time that covers production of multiple coating formulations. It may be necessary to sample multiple production areas. In addition, these methods do not address fugitive emissions that occur outside of a building. If testing is performed, care should be taken to ensure that a representative operational cycle has been selected. If possible, full cycles should be monitored as opposed to portions of cycles.

VOC losses from certain operations (e.g., filling of containers) may also be measured by performing a study using a gravimetric analysis such as American Society for Testing and Materials (ASTM) Standard D2369: *Test Method for Volatile Content of Coatings*.

Chapter 1 of Volume II in this series provide information regarding test data quality.

3.2 Comparison of Available Emission Estimation Methodologies

The best method to use depends upon the emission source being evaluated, available data, how the estimates will be used, and the degree of accuracy required in the estimate. In general, a more accurate method will require greater resources than a less accurate method. Case study 8.3-1 presents estimates for all of the operation at a paint manufacturing facility. For some operations, multiple estimates are provided showing the impact of different techniques on the results.

Case Study 8.3-1: The Bright Blue Paint Company

Description

The Bright Blue Paint Company produces a variety of related paint products that can be considered to have similar formulations. The total production rate is about 2,500,000 gal/yr.

The four main manufacturing operations at the Bright Blue Paint Company are:

- Preassembly and premix;
- Pigment grinding/milling;
- Product finishing/blending; and
- Product filling/packaging.

The batch begins with mixing of raw materials in a high speed disperser. The material from the disperser is then transformed to a thindown tank where additional solvent is added. The final product is then transferred to shipping containers. Total batch size is about 1,700 gallons.

Liquid storage of paint ingredients and cleaning compounds is in bulk tanks ranging from 2,500 to 10,000 gallons and in 55-gallon drums. Powder ingredients are stored in paper sacks or fiber drums ranging from 10 to 200 pounds.

Equipment is cleaned after each batch. Approximately 75,000 gallons of cleaning solvents are used for equipment cleaning each year. Small parts are also cleaned as necessary using an open-top vapor degreaser.

Emission Sources

Emission sources for this facility include:

- Mixing (material loading, heat-up, gas sweep, and surface evaporation);
- Filling losses;
- Cleaning (parts, mixers/tanks);
- Solvent reclamation;
- Material storage;
- Equipment leaks; and
- Spills.

Emissions

Emissions, the emission estimation method selected, and supporting data for this facility are summarized in Table 8.3-1.

Table 8.3-1. Estimated VOC Emissions Summary for the Bright Blue Paint Company

Emission Event	VOC Emissions, lb/yr			Data and Assumptions
	A	B	C	
Filling dispersion vessels A: Saturation factor = 0.6 B: Saturation factor = 1.0 C: Saturation factor = 1.45 (Equation 8.4-1)	2683	4472	6485	C 1,008,000 gal toluene C 564,000 gal MEK C 2,200,000 gal mixture of solvents and solids C All materials added simultaneously C T = 77°F (537°R) C VP (toluene) = 0.58 psia C VP (MEK) = 1.93 psia C MW (toluene) = 92.1 C MW (MEK) = 72.1
Gas sweep through dispersion vessels while loading solids A: Option 2 S=0.774 for toluene S=0.788 for MEK (Equation 8.4-32) C: Option 1 (Equation 8.4-23)	11600		14814	C Average liquid mole fractions are same as for filling the vessels C Sweep rate = 10 ft^3/min C Diameter of vessels = 7 ft C T = 77°F (537°R) C Sweep time = 1 hr/batch C 1,500 batches/yr
Heat up in dispersion vessels due to mixing A: Option 2 (Equation 8.4-15) C: Option 1 (Equation 8.4-10)	412		417	C Initial T = 77°F (537°R) C Final T = 105°F (565°R) C Average liquid mole fractions are same as for filling the vessels C VP_{T2} (toluene) = 1.16 psia C VP_{T2} (MEK) = 3.75 psia C Sum of partial pressure for toluene and MEK at 105°F = 2.195 psia
Mixing in dispersion vessels after sweep is turned off (surface evaporation) B: K based on gas velocity (Equations 8.4-21 and 8.4-22)		2089		C batch time after sweep is turned off = 5 hours C final temperature has been reached by the time the gas sweep is turned off (thus, T = 105°F [565°R]) C gas velocity above the vessel is determined to be 0.25 mph C area of annulus in cover around the agitator shaft = 3 ft^2.

Table 8.3-1. (continued)

Emission Event	VOC Emissions, lb/yr			Data and Assumptions
	A	B	C	
Transfer contents of dispersion vessels to thindown tanks A: Saturation factor = 0.6 B: Saturation factor = 1.0 C: Saturation factor = 1.45 (Equation 8.4-1)	5011	8352	12111	C T = 105°F (565°R) C quantity transferred = 2,200,000 gal
Add Toluene to thindown tanks A: saturation factor = 0.6 B: saturation factor = 1.0 C: saturation factor = 1.45 (Equation 8.4-1)	355	592	859	C T = 77°F (537°R) C quantity added = 200 gal/batch
Holding/mixing in thindown tank B: K based as gas velocity (Equations 8.4-21 and 8.4-22)		1048		C hold for 5 hours C T = 77°F (537°R) C gas velocity above vessel estimated to be 0.25 mph C area of annulus in cover around the agitator shaft = 3ft^2
Product loading A: saturation factor = 0.6 B: saturation factor = 1.0 C: saturation factor = 1.45 (Equation 8.4-1)	2870	4784	6937	C total volume loaded = 2,500,000 gal/yr C T = 77°F (537°R) C sum of partial pressures from VOC's at 77°F = 1.0375 psia
Cleaning (solvent flush) A: saturation factor = 0.6 B: saturation factor = 1.0 C: saturation factor = 1.45 (Equation 8.4-1)	56	93	135	C total amount of solvent used = 75,000 gal/yr C solvent is toluene C T = 77°F (537°R)
Small parts cleaning B: AP-42 emission factor (Equation 8.5-13)		660		C one open top vapor degreaser C AP-42 emission factor = 0.33 ton/yr/unit

Table 8.3-1. (continued)

Emission Event	VOC Emissions, lb/yr			Data and Assumptions
	A	B	C	
Solvent reclamation A: Modeling (Equations 8.4-1 and 8.4-34) C: AP-42 emission factor (Equation 8.4-8)	319		990	C 300 tons of waste toluene cleaning solvent processed annually C see example 8.4-10
Material storage B: using TANKS program		6000		
Equipment leaks B: Emission factors in section 5.1.6		949		C 15 valves C 10 pumps C 50 connectors C 8760 hr/yr C see example 8.5-8
Spills B: Equation 8.4-19		18		C One MEK spill outdoors C T = 77°F (537°R) C Area of spill = 15 ft^2 C windspeed at 10 m above the surface = 8 mph C cleanup time = 1 hr
Totals	34,070 to 53,512			

4.0 Modeling Methods for Estimating Emissions

Models/equations for estimating VOC emissions, including HAP, from paint, ink, and other coating manufacturing operations are presented in this section. This section describes these methodologies and provides examples to illustrate the use of each calculation technique.

Source-specific emission models/equations are presented for estimating VOC emissions from:

- Mixing operations (material loading, heat-up losses, and surface evaporation),
- Product filling,
- Vessel cleaning operations,
- Gas sweep or purge,
- Wastewater treatment processes,
- Solvent reclamation,
- Material storage, and
- Spills.

Models for these operations are discussed with examples given below. For additional guidance on estimating emissions from wastewater collection and treatment, see Chapter 5 of this volume. See also Chapter 1 of this volume for additional guidance on material storage.

It is not recommended that paint, ink, and other coating manufacturing facilities apply these models to each of the hundreds or even thousands of different formulations. Rather, formulations should be grouped based on composition and production rate, and a representative recipe and composition should be defined for each group. The emission calculations are then performed for each of the group representatives. In general, there are no specific guidelines for defining product groups except that each product group composition should be fairly characteristic of its components (Fisher et al., 1993).

Table 8.4-1 lists the variables used in Equations 8.4-1 through 8.4-27.

Table 8.4-1. List of Variables and Symbols

Variable	Symbol	Units
Total VOC emissions	E_{VOC}	lb/yr
Saturation factor	S	dimensionless
Vapor pressure of the material loaded	P	pounds per square inch absolute (psia)
Vapor molecular weight	M	lb/lb-mole
Volume of material loaded	Q	1,000 gal/yr
Temperature	T	°R
Partial vapor pressure of VOC species x	P_x	psia
Liquid mole fraction of VOC species x	m_x	mole/mole
True vapor pressure of VOC species x	VP_x	psia
Henry's Law constant for VOC species x	H_x	psia
Liquid mass fraction of VOC species x	z_x	lb/lb
Molecular weight of VOC species x	M_x	lb/lb-mole
Vapor mole fraction of VOC species x	y_x	mole/mole
Loading emissions of VOC species x	E_x	lb/yr
Vapor mass fraction of VOC species x	x_x	lb/lb
Initial partial pressure of VOC species x	$(P_x)_{T1}$	psia
Final partial pressure of VOC species x	$(P_x)_{T2}$	psia
Number of pound-moles of gas displaced	) n	lb-mole/cycle
Vapor molecular weight, average	M_a	lb/lb-mole
Number of cycles/year	CYC	cycles/yr
Volume of free space in vessel	V	ft^3
Universal gas constant at 1 atmosphere of pressure	R	10.73 psia- ft^3/ °R-lb mole
Initial noncondensable gas partial pressure in vessel	Pa_1	psia
Final noncondensable gas partial pressure in vessel	Pa_2	psia
Initial temperature of vessel	T1	°R
Final temperature of vessel	T2	°R
Moles of VOC species x leaving vessel per batch	$N_{x,out}$	lb-mole

Table 8.4-1. (continued)

Variable	Symbol	Units
Average molar volume in gas space during heating	N_{avg}	lb-mole
Initial moles of VOC species x in gas space	$n_{x,1}$	lb-mole
Final moles of VOC species x in gas space	$n_{x,2}$	lb-mole
Initial system pressure	P_1	psia
Final system pressure	P_2	psia
Initial total moles in gas space	n_1	lb-mole
Final total moles in gas space	n_2	lb-mole
Gas-phase mass transfer coefficient for VOC species x	K_x	ft/sec
Surface area (of spill or tank)	A	ft^2
Duration of spill	HR	hr/event
Wind speed	U	mile/hr
Diffusion coefficient for VOC species x in air	D_x	ft^2/sec
Batch time	H	hr/batch
Number of batches per year	B	batches/yr
Flow rate of noncondensable gas into vessel	F_{nc}	ft^3/min
Total system pressure	P_T	psia
Flow rate of VOC species x out of vessel at saturated vapor pressure	F_x^{sat}	ft^3/min
Partial pressure of VOC species x in a saturated gas stream	P_x^{sat}	psia
Mass transfer coefficient for a reference compound	K_o	cm/s
Mass transfer coefficient for VOC species x	K_x	cm/s
Molecular weight of reference compound	M_o	lb/lb-mole
Operating Hours	OH	hr/yr

4.1 Emission Model for Material Loading

VOC emissions resulting from the addition of materials to mixers, grinding equipment, and thindown tanks may be calculated using a modification of the loading loss equation (which is presented in Section 5.2 of *AP-42*; EPA, 1995c). This equation, shown below as Equation 8.4-1, is related to tank car or tank truck loading, but can be applied to any tank or vessel loading (NPCA, 1995). This equation may also be applied to estimate product filling losses.

$$E_{VOC} = 12.46 \times \frac{S \times P \times M \times Q}{T} \quad (8.4\text{-}1)$$

where

E_{VOC}	=	total VOC loading emissions (lb/yr)
S	=	saturation factor (dimensionless; see Table 5.2-1 in *AP-42*)
P	=	vapor pressure of the material loaded at temperature T (psia)
M	=	vapor molecular weight (lb/lb-mole)
Q	=	volume of material loaded (1,000 gal/yr)
T	=	temperature of liquid loaded (°R).

The constant in equation 8.4-1 is a function of the units used for other variables in the equation. The table below shows the constant that would apply if some of the variables are available in other units.

Constant	P	M	Q	T
12.46	psia	lb/lb-mole	1,000 gal	°R
0.241	mm Hg	lb/lb-mole	1,000 gal	°R
6.92	psia	lb/lb-mole	1,000 gal	°K

Calculation of VOC emissions using Equation 8.4-1 is based on the following assumptions:

- The vapors displaced from the process vessel are identical to the vapors from the materials being loaded;
- The volume of vapor displaced is equal to the volume of material loaded into the vessel; and
- All solvent additions are coincident at a constant temperature (in reality, solvent additions may be phased) (Fisher et al., 1993).

An alternative to using the AP-42 saturation factor when material is added by submerged loading is to assume the vapor space in the vessel is saturated with the solvent vapors (i.e., equivalent to S = 1). This assumption is a conservative approach that would ensure that emissions are not underestimated.

If multiple solvents are used, the vapor pressure (P) will need to be calculated using Equation 8.4-2:

$$P = \Sigma P_x \quad (8.4\text{-}2)$$

where

P	=	vapor pressure of material loaded (psia)
P_x	=	partial pressure of VOC species x (psia).

P_x may be calculated using Raoult's Law (for ideal solutions) or using Henry's Law constants (when gases are dissolved at low concentrations in water). Raoult's Law is given in Equation 8.4-3:

$$P_x = m_x \times VP_x \tag{8.4-3}$$

where

P_x	=	partial vapor pressure of VOC species x (psia)
m_x	=	liquid mole fraction of VOC species x (mole/mole)
VP_x	=	true vapor pressure of VOC species x (psia).

P_x may be calculated using Henry's Law constants and Equation 8.4-4:

$$P_x = m_x \times H_x \tag{8.4-4}$$

where

P_x	=	partial vapor pressure of VOC species x (psia)
m_x	=	liquid mole fraction of VOC species x (mole/mole)
H_x	=	Henry's Law constant for VOC species x.

The liquid mole fraction of VOC species x (m_x) may be calculated if the liquid weight fractions of all species are known. Equation 8.4-5 is used:

$$m_x = \frac{z_x/M_x}{\Sigma(z_x/M_x)} \tag{8.4-5}$$

where

m_x	=	liquid mole fraction of VOC species x (mole/mole)
z_x	=	liquid mass fraction of VOC species x (lb/lb)
M_x	=	molecular weight of VOC species x (lb/lb-mole).

The vapor molecular weight (M) will also need to be calculated if multiple solvents are used for a single cleaning event. Equation 8.4-6 may be used:

$$M = \Sigma(y_x \times M_x) \tag{8.4-6}$$

where

M	=	vapor molecular weight (lb/lb-mole)
y_x	=	vapor mole fraction of VOC species x (mole/mole)
M_x	=	molecular weight of VOC species x (lb/lb-mole).

The vapor mole fraction (y_x) is calculated using Equation 8.4-7:

$$y_x = \frac{P_x}{P} \tag{8.4-7}$$

where

y_x	=	vapor mole fraction of VOC species x (mole/mole)
P_x	=	partial pressure of VOC species x (calculated using Equation 8.4-3 or 8.4-4) (psia)
P	=	vapor pressure of the material loaded (calculated using Equation 8.4-2).

Speciated VOC emissions are calculated using Equation 8.4-8:

$$E_x = E_{VOC} \times x_x \tag{8.4-8}$$

where

E_x	=	loading emissions of VOC species x (lb/yr)
E_{VOC}	=	total VOC loading emissions, calculated using Equation 8.4-1 (lb/yr)
x_x	=	vapor mass fraction of VOC species x (lb/lb).

The vapor mass fraction of VOC species x (x_x) is calculated using Equation 8.4-9:

$$x_x = \frac{y_x \times M_x}{M} \tag{8.4-9}$$

where

x_x	=	vapor mass fraction of VOC species x (lb/lb)
y_x	=	vapor mole fraction of VOC species x, calculated using Equation 8.4-7 (mole/mole)
M_x	=	molecular weight of VOC species x (lb/lb-mole)
M	=	vapor molecular weight, calculated using Equation 8.4-6 (lb/lb-mole).

Example 8.4-1

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 gal;
- The cleaning solvent is a 50/50 mixture (by weight) of toluene and heptane;
- The solvent mixture is splash loaded into the vessel (S = 1.45); and
- The temperature of the solvent is 77°F or 537°R (°R = °F + 460).

Example 8.4-1 illustrates the use of the loading equation (Equation 8.4-1) and the supplemental equations (Equations 8.4-2 through 8.4-9).

Emissions are calculated by following Steps 1 through 8 below.

Step 1: Apply Equation 8.4-5 - Calculation of Liquid Mole Fraction (m_x)

Component	Liquid Mass Fraction, z_x (lb of x/lb of liquid)	Molecular Weight, M_x (lb of x/lb-mole of x)	Liquid Mole Fraction, m_x (mole of x/mole of liquid)
Toluene	0.5	92	$\frac{z_x/M_x}{G(z_x/M_x)} = \frac{(0.5 / 92)}{[(0.5/92) + (0.5/100)]}$ = 0.52
Heptane	0.5	100	$\frac{z_x/M_x}{G(z_x/M_x)} = \frac{(0.5 / 100)}{[(0.5/92) + (0.5/100)]}$ = 0.48

Step 2: Apply Equation 8.4-3 - Calculation of Partial Vapor Pressure (P_x)

Component	Liquid Mole Fraction, m_x (mole of x/mole of liquid)	Vapor Pressure, VP_x (psia)	Partial Vapor Pressure, P_x (psia)
Toluene	0.52	0.58	$m_x \times VP_x = 0.52 \times 0.58$ $= 0.30$
Heptane	0.48	0.9	$m_x \times VP_x = 0.48 \times 0.90$ $= 0.43$

Step 3: Apply Equation 8.4-2 - Calculation of Vapor Pressure (P)

$$P = \Sigma P_x = 0.30 + 0.43 = 0.73 \text{ psia}$$

Step 4: Apply Equation 8.4-7 - Calculation of Vapor Mole Fraction (y_x)

Component	Partial Vapor Pressure, P_x (psia)	Total Vapor Pressure, P (psia)	Vapor Mole Fraction, y_x (mole of x/mole of vapor)
Toluene	0.3	0.73	$\frac{P_x}{P} = \frac{0.30}{0.73} = 0.41$
Heptane	0.43	0.73	$\frac{P_x}{P} = \frac{0.43}{0.73} = 0.59$

Step 5: Apply Equation 8.4-6 - Calculation of Vapor Molecular Weight (M)

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

Step 6: Apply Equation 8.4-9 - Calculation of Vapor Mass Fraction (x_x)

Component	Vapor Mole Fraction, y_x (mole of x/mole of vapor)	Molecular Weight, M_x (lb of x/lb-mole of x)	Vapor Molecular Weight, M (lb of vapor/lb-mole of vapor)	Vapor Mass Fraction, x_x (lb of x/lb of vapor)
Toluene	0.41	92	97	$\frac{y_x \times M_x}{M} = \frac{0.41 \times 92}{97} = 0.39$
Heptane	0.59	100	97	$\frac{y_x \times M_x}{M} = \frac{0.59 \times 100}{97} = 0.61$

Step 7: Apply Equation 8.4-1 - Calculate Total VOC Emissions (E_{VOC})

$$E_{VOC} = 12.46 \times \frac{S \times P \times M \times Q}{T}$$

$$= 12.46 \times \frac{1.45 \times 0.73 \times 97 \times 600}{537}$$

$$= 1{,}429 \text{ lb VOCs/yr}$$

Step 8: Apply Equation 8.4-8 - Calculate Speciated VOC Emissions (E_x)

Component	VOC Emissions, E_{VOC} (lb VOCs)	Vapor Mass Fraction, x_x (lb of x/lb of VOCs)	Speciated VOC Emissions, E_x (lb x)
Toluene	1,429	0.39	$E_{VOC} \times x_x = 1{,}429 \times 0.39 = 557$
Heptane	1,429	0.61	$E_{VOC} \times x_x = 1{,}429 \times 0.61 = 872$

4.2 Heat-Up Losses

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

- Covers are closed during operation, but it is possible for vapors to be vented during operation;
- No material is added during heat-up;
- The displaced gas is always saturated with VOC vapor 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 vapor pressure; and
- The vapor pressure of the mixers never rises above 1 atmosphere (Fisher et al., 1993).

This section presents two equations for estimating heatup emissions. The first is from *Control of Volatile Organic Compound Emissions from Batch Processes* (EPA, 1994c). The second was derived by performing moderate balances around the vessel headspace for the noncondensable component and for condensable component x during the heating (Hatfield, 1998a).

The two approaches yield similar results when the amount of heat-up is small, and the final temperature is well below the boiling point of the liquid mixture. However, the disparity between the results from the two options increases as the final temperature approaches the boiling point. Under these conditions Option 1 gives unrealistically high estimates, and Option 2 is the better choice.

4.2.1 Option 1

The equation for calculating heat-up emissions that is in *Control of Volatile Organic Compound Emissions from Batch Processes* is shown in Equation 8.4-10 (EPA, 1994c).

$$E_{VOC} = \frac{\left(\frac{\Sigma(P_x)_{T1}}{14.7 - \Sigma(P_x)_{T1}}\right) + \left(\frac{\Sigma(P_x)_{T2}}{14.7 - \Sigma(P_x)_{T2}}\right)}{2} \times \Delta n \times M_a \times CYC \qquad (8.4\text{-}10)$$

where

E_{VOC}	=	VOC emissions from material heat-up in the process equipment (lb/yr)
$(P_x)_{T1}$	=	initial partial pressure of each VOC species x in the vessel headspace at the initial temperature T1 (psia); see Equations 8.4-3 and 8.4-4
$(P_x)_{T2}$	=	final partial pressure of each VOC species x in the vessel headspace at the final temperature T2 (psia); see Equations 8.4-3 and 8.4-4
)n	=	number of pound-moles of gas displaced (lb-mole/cycle)
M_a	=	average vapor molecular weight (lb/lb-mole)
CYC	=	number of cycles per year (cycles/yr).

The term)n may be calculated using Equation 8.4-11:

$$\Delta n = \frac{V}{R} \times \left(\frac{Pa_1}{T1} - \frac{Pa_2}{T2} \right) \qquad (8.4\text{-}11)$$

where

)n	=	number of pound-moles of gas displaced (lb-mole/cycle)
V	=	volume of free space in the vessel (ft^3)
R	=	universal gas constant at 1 atmosphere of pressure, 10.73 psia " ft^3/lb-mole " °R
Pa_1	=	initial gas pressure in vessel (psia)
Pa_2	=	final gas pressure in vessel (psia)
T1	=	initial temperature of vessel (°R)
T2	=	final temperature of vessel (°R).

Pa_1 and Pa_2 may be calculated using Equations 8.4-12 and 8.4-13:

$$Pa_1 = 14.7 - \Sigma(P_x)_{T1} \qquad (8.4\text{-}12)$$

$$Pa_2 = 14.7 - \Sigma(P_x)_{T2} \qquad (8.4\text{-}13)$$

where

Pa_1	=	initial gas pressure in vessel (psia)
Pa_2	=	final gas pressure in vessel (psia)
$(P_x)_{T1}$	=	partial pressure of each VOC_x in the vessel headspace (psia) at the initial temperature T1; see Equations 8.4-3 and 8.4-4
$(P_x)_{T2}$	=	partial pressure of each VOC_x in the vessel headspace (psia) at the final temperature T2; see Equations 8.4-3 and 8.4-4.

Speciated VOC emissions would be calculated using a modified version of Equation 8.4-10 as shown in Equation 8.4-14:

$$E_x = \frac{\left(\frac{(P_x)_{T1}}{14.7 - \sum(P_x)_{T1}} \right) + \left(\frac{(P_x)_{T2}}{14.7 - \sum(P_x)_{T2}} \right)}{2} \times \Delta n \times M_a \times CYC \qquad (8.4\text{-}14)$$

where

E_x	=	VOC species x emissions from material heat-up in the process equipment (lb/yr)
$(P_x)_{T1}$	=	partial pressure of VOC species x in the vessel headspace at the initial temperature T1 (psia); see Equations 8.4-3 and 8.4-4
$(P_x)_{T2}$	=	partial pressure of VOC species x in the vessel headspace at the final temperature T2 (psia); see Equations 8.4-3 and 8.4-4
) n	=	number of pound-moles of gas displaced (lb-mole/cycle); see Equation 8.4-11
M_a	=	average vapor molecular weight (lb/lb-mole)
CYC	=	Number of cycles/year.

Example 8.4-2 illustrates the use of Equations 8.4-10 through 8.4-13. Emissions are calculated by following Steps 1 through 6 presented on the next few pages.

Example 8.4-2

This example shows how heat-up losses from a disperser are calculated using Equations 8.4-10 through 8.4-13. Supporting equations from Section 4.1.1 (Equations 8.4-3 and 8.4-5) are also used in this example.

A 3,000-gallon, high-speed disperser contains 2,000 gallons of paint. The following data are given:

- The paint consists of 30 percent by weight toluene, 20 percent by weight methyl ethyl ketone (MEK), and 50 percent by weight insoluble pigments and nonvolatile resins;
- The initial temperature (T1) of the mixture is 77°F or 537°R (°R = °F + 460);
- The final temperature (T2) is 105°F (565°R);
- The average vapor molecular weight (M_a) is 77 lb/lb-mole (calculated using Equation 8.4-6); and
- The mixer goes through the given temperature cycle with this paint formulation 25 times/yr (CYC).
- The volume of free space in the vessel is 3,000 - 2,000 gal = 1,000 gal or 133.68 ft^3.

Step 1: Apply Equation 8.4-5, Calculation of Liquid Mole Fraction (m_x)

Component x	Liquid Mass Fraction, z_x (lb of x/lb of liquid)	Molecular Weight, M_x (lb of x/lb-mole of x)	Liquid Mole Fraction, m_x (mole of x/mole of liquid)
Toluene	0.3	92	$\frac{z_x/M_x}{G(z_x/M_x)} = \frac{0.3/92}{(0.3/92 + 0.2/72)} = 0.54$
MEK	0.2	72	$\frac{z_x/M_x}{G(z_x/M_x)} = \frac{0.2/72}{(0.3/92 + 0.2.72)} = 0.46$

Step 2: Apply Equation 8.4-3, Calculation of Partial Vapor Pressure at Initial Temperature [$(P_x)_{T1}$]

Component x	Liquid Mole Fraction, m_x (mole of x/mole of liquid)	Vapor Pressure, VP_x @ 77°F (psia)	Partial Pressure at T1, $(P_x)_{T1}$ (psia)
Toluene	0.54	0.58	$m_x \times VP_x = 0.54 \times 0.58 = 0.313$
MEK	0.46	1.93	$m_x \times VP_x = 0.46 \times 1.93 = 0.888$

Step 3: Apply Equation 8.4-3, Calculation of Partial Pressure at Final Temperature [$(P_x)_{T2}$]

Component x	Liquid Mole Fraction, m_x (mole/mole)	Vapor Pressure, VP_x @ 105°F (psia)	Partial Pressure at T2, $(P_x)_{T2}$ (psia)
Toluene	0.54	1.16	$m_x \times VP_x = 0.54 \times 1.16 = 0.626$
MEK	0.46	3.75	$m_x \times VP_x = 0.46 \times 3.75 = 1.73$

Step 4: Apply Equations 8.4-12 and 8.4-13, Calculation of Initial Pressure (Pa_1) and Final Pressure (Pa_2)

$$Pa_1 = 14.7 - E(P_x)_{T1} = 14.7 - (0.313 + 0.888) = 13.5 \text{ psia}$$

$$Pa_2 = 14.7 - E(P_x)_{T2} = 14.7 - (0.626 + 1.73) = 12.34 \text{ psia}$$

Step 5: Apply Equation 8.4-11, Calculation of lb-moles Gas Displaced ( ) n)

The volume of free space in the vessel (V) is 3,000 gal - 2,000 gal = 1,000 gal or 133.68 ft^3.

$$\Delta n = \frac{V}{R} \times \left(\frac{Pa_1}{T_1} - \frac{Pa_2}{T_2} \right)$$

$$= \frac{133.68}{10.73} \times \left(\frac{13.5}{537} - \frac{12.3}{565} \right)$$

$$= 0.042 \text{ lb-moles/CYC}$$

Step 6: Apply Equation 8.4-10, Calculation of Total VOC Emissions (E_{VOC})

$$E_{VOC} = \frac{\left(\frac{\Sigma (P_x)_{T1}}{14.7 - \Sigma (P_x)_{T1}} \right) + \left(\frac{\Sigma (P_x)_{T2}}{14.7 - \Sigma (P_x)_{T2}} \right)}{2} \times \Delta n \times M \times CYC$$

$$= \frac{\left(\frac{(0.313 + 0.888)}{14.7 - (0.313 + 0.888)} \right) + \left(\frac{(0.626 + 1.73)}{14.7 - (0.626 + 1.73)} \right)}{2} \times 0.042 \times 77 \times 2$$

$$= 11.3 \text{ lb VOCs/yr}$$

Step 7: Apply Equation 8.4-14, Calculation of Toluene Emissions (E_{VOC})

$$E_{VOC} = \frac{\left(\frac{(P_x)_{T1}}{14.7 - \sum(P_x)_{T1}}\right) + \left(\frac{(P_x)_{T2}}{14.7 - \sum(P_x)_{T2}}\right)}{2} \times \Delta n \times M \times CYC$$

$$= \frac{\left(\frac{0.313}{14.7-(0.313+0.888)}\right) + \left(\frac{0.626}{14.7-(0.626+1.73)}\right)}{2} \times 0.042 \times 92 \times 25$$

$$= 3.6 \text{ lb toluene/yr}$$

4.2.2 Option 2

In this heating model, rising vapors from the vessel liquid contents displace the noncondensable gas components from the headspace through the process vessel vent. As the liquid mixture reaches the boiling point, all of the noncondensable component is purged from the vapor space. This model assumes that the average molar headspace volume remains constant relative to changes in the molar composition of the vessel headspace. Equation 8.4-15 is derived from performing material balances around the vessel headspace for the noncodensable component and for condensable component x during the heating (Hatfield, 1998a).

$$N_{x,out} = N_{avg} \ln\left[\frac{Pa_1}{Pa_2}\right] - \left(n_{x,2} - n_{x,1}\right)_{vessel} \qquad (8.4\text{-}15)$$

where

$N_{x,out}$	=	moles of volatile component x leaving the vessel per batch
N_{avg}	=	average gas space molar volume during the heating process
Pa_1	=	partial pressure of noncondensable in the vessel headspace at initial temperature
Pa_2	=	partial pressure of noncondensable in the vessel headspace at final temperature
$n_{x,2}$	=	moles of volatile component x in the vessel headspace at the final temperature
$n_{x,1}$	=	moles of volatile component x in the vessel headspace at the initial temperature.

Note that when the liquid in the vessel contains more than one volatile component, Equation 8.4-15 estimates the total moles of volatile components emitted, and $n_{x,1}$ and $n_{x,2}$ are the total moles of all volatile components in the vessel headspace.

The term N_{avg} may be calculated using equation 8.4-16:

$$N_{avg} = \frac{1}{2}\left(n_1 + n_2\right) \qquad (8.4\text{-}16)$$

where

n_1	=	total moles of gas in the vessel headspace at the initial temperature
n_2	=	total moles of gas in the vessel headspace at the final temperature.

The total number of moles (n_1 and n_2) may be calculated using the ideal gas law as shown in equation 8.4-17 and 8.4-18.

$$n_1 = \frac{P_1 V}{R T_1} \qquad (8.4\text{-}17)$$

$$n_2 = \frac{P_2 V}{R T_2} \qquad (8.4\text{-}18)$$

where

P_1	=	total system pressure at initial temperature
P_2	=	total system pressure at final temperature
V	=	volume of gas space in the vessel
R	=	gas constant
T_1	=	initial temperature of vessel contents
T_2	=	final temperature of vessel contents.

The total number of moles of volatile component x in the vessel headspace at the initial and final temperatures ($n_{x,1}$ and $n_{x,2}$) are also calculated using equations 8.4-17 and 8.4-18, except the partial pressures of the volatile component are used instead of the total system pressure.

Example 8.4-3

For the same disperser described in example 8.4-2, what heat-up emissions would be estimated using option 2?

Step 1: Apply Equations 8.4-17 and 8.4-18, Determine Total Moles in the Vessel Headspace at Initial and Final Temperatures

$$n_1 = \frac{P_1 V}{RT_1} = \frac{(14.7\ \text{psia})(133.68\ \text{ft}^3)}{\left(\frac{10.73\ \text{ft}^3\ \text{psia}}{\text{lbmole}\,°\text{R}}\right)(537\,°\text{R})}$$

$$= 0.341\ \text{lbmole}$$

$$n_2 = \frac{P_2 V}{RT_2} = \frac{(14.7\ \text{psia})(133.68\ \text{ft}^3)}{\left(\frac{10.73\ \text{ft}^3\ \text{psia}}{\text{lbmole}\,°\text{R}}\right)(565\,°\text{R})}$$

$$= 0.324\ \text{lbmole}$$

Step 2: Apply Equation 8.4-16, Determine N_{avg}

$$N_{avg} = \frac{1}{2}(n_1 + n_2) = \frac{1}{2}(0.341 + 0.324) = 0.333\ \text{lbmole}$$

Step 3: Apply Equations 8.4-12 and 8.4-13, Calculation of Noncondensable Partial Pressures and Initial and Final Temperatures

These calculations are shown in Step 4 of example 8.4-2.

$$Pa_1 = 13.5\ \text{psia}$$

$$Pa_2 = 12.34\ \text{psia}$$

Step 4: Determine Partial Pressures of Volatile Components

These values were determined in Steps 2 and 3 of example 8.4-2:

Component x	$(P_x)_{T1}$, psia	$(P_x)_{T2}$, psia
Toluene	0.313	0.626
MEK	0.888	1.73

Step 5: Apply Equations 8.4-17 and 8.4-18, Determine Moles of Condensable Compounds in the Vessel Headspace at Initial and Final Temperatures

$$n_{x,1} = \frac{(\Sigma(P_x)_{T1})(V)}{RT_1} = \frac{(0.313 + 0.888 \text{ psia})(133.68 \text{ ft}^3)}{\left(\frac{10.73 \text{ ft}^3 \text{ psia}}{\text{lbmole}^\circ\text{R}}\right)(537^\circ\text{R})}$$

$$= 0.0279 \text{ lbmole}$$

$$n_{x,2} = \frac{(\Sigma(P_x)_{T2})(V)}{RT_2} = \frac{(0.626 + 1.73 \text{ psia})(133.68 \text{ ft}^3)}{\left(\frac{10.73 \text{ ft}^3 \text{ psia}}{\text{lbmole}^\circ\text{R}}\right)(565^\circ\text{R})}$$

$$= 0.0520 \text{ lbmole}$$

Step 6: Apply Equation 8.4-15, Calculate Total Moles of VOC Emissions

$$n_{x,out} = N_{avg} \ln\left(\frac{Pa_1}{Pa_2}\right) - (n_{x,2} - n_{x,1})_{vessel}$$

$$= (0.333) \ln\left(\frac{13.5}{12.34}\right) - (0.0520 - 0.0279)$$

$$= 0.00582 \text{ lbmole VOC/ batch}$$

Using the average vapor molecular weight from example 8.4-2, the total mass of VOC emitted per batch is:

$$E_{VOC} = \left(0.00582 \frac{\text{lbmole}}{\text{batch}}\right)\left(\frac{77 \text{ lb}}{\text{lbmole}}\right) = 0.448 \text{ lb/batch}$$

For 25 batches per year, the annual emissions are:

$$E_{VOC} = (0.448 \text{ lb/batch})(25 \text{ batches/yr}) = 11.2 \text{ lb/yr}$$

This estimate is essentially the same as the emissions estimated using option 1 in example 8.4-2.

Step 7: Determine the Amount of Each Volatile Species in the Total VOC Emissions

Compound	Average Partial Pressure, psia	Average Vapor Phase Mole Fraction	Number of lbmole Emitted	Molecular Weight	Mass Emission	
					lb/batch	lb/yr
Toluene	0.47	0.26	0.0015	92	0.138	3.45
MEK	1.31	0.74	0.0043	72	0.31	7.74
Totals	1.78		0.0058		0.448	11.2

4.3 Emission Model for Spills

The evaporation rate and VOC emissions that result from a liquid chemical spill can be estimated using a simple model if the size (area) of the spill is known or can be estimated. Other more complex spill models are also available, but they may require more input data (EPA, 1987). Equation 8.4-19, used for the simple model, is as follows:

$$E_x = \frac{M_x \times K_x \times A \times P_x \times 3600 \times HR}{R \times T} \qquad (8.4\text{-}19)$$

where

E_x	=	emissions of VOC species x from the spill (lb/event)
M_x	=	molecular weight of VOC species x (lb/lb-mole)
K_x	=	gas-phase mass transfer coefficient for VOC species x (ft/sec)
A	=	surface area of spill (ft^2)
P_x	=	vapor 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 (psia)[1]
3600	=	3600 sec/hr
HR	=	duration of spill (hr/event)
R	=	universal gas constant at 1 atmosphere of pressure, 10.73 psia-ft^3/°R- lb-mole
T	=	temperature of the liquid spilled, °R (°F + 460).

[1] The vapor pressures of VOC species are listed in AP-42 on Table 7.1-3 (EPA, 1997b). The partial pressure of VOC species x (P_x) may be calculated using Equation 8.4-3 or Equation 8.4-4.

The gas-phase mass transfer coefficient (K_x) may be calculated using Equation 8.4-20:

$$K_x = 0.00438 \times U^{0.78} \times \left(\frac{D_x}{3.1 \times 10^{-4}} \right)^{2/3} \quad (8.4\text{-}20)$$

where

K_x	=	gas-phase mass transfer coefficient for VOC species x (ft/sec)
U	=	wind speed (mile/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 centimeters per second (cm^2/sec). If a diffusion coefficient is not available for a particular chemical, the gas-phase mass transfer coefficient (K_x) may be estimated using Equation 8.4-21:

$$K_x = 0.00438 \times U^{0.78} \times \left(\frac{18}{M_x} \right)^{1/3} \quad (8.4\text{-}21)$$

where

K_x	=	gas-phase mass transfer coefficient for VOC species x (ft/sec)
U	=	wind speed (mile/hr)
M_x	=	molecular weight of VOC species x (lb/lb-mole).

Equations 8.4-20 and 8.4-21 and other similar correlations that are used in more complex models were developed to estimate evaporation from liquid surfaces exposed to natural wind effects. The standard practice when using these equations is that the wind speed is the value at a height 10 meters above the surface (EPA, 1994a). Thus, the equations should be acceptable for estimating mass transfer coefficients for spills that are outdoors. If the spill is indoors, however, the equation should be used with caution. The wind profile inside a building likely differs from the profile outside, so the velocity at a height of 10 meters (even if that much open space exists above the spill) will not have the same meaning as it would outdoors. At a minimum, when applying the equation to a spill indoors, the user should develop site-specific estimates of the air velocity above the spill and recognize the potential that using this approach may underestimate the emissions. An alternative approach for estimating gas-phase mass transfer coefficients is discussed in Section 4.5 of this chapter. The alternative replaces the windspeed variable with a constant reference mass transfer coefficient. This approach likely overstates the emissions, particularly in a room with little air movement, because it assumes the gas above the liquid is well mixed. Thus, equation 8.4-21 generally is preferable to the alternative for estimating emissions from spills and other surface evaporation scenarios.

Example 8.4-4 illustrates the use of equations 8.4-19 and 8.4-21.

Example 8.4-4

Methyl ethyl ketone (MEK) is spilled onto the ground outside of a building. The following data are 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 8 mile/hr.
- The ambient temperature (T) is 77°F or 537°R (°R = °F +460).
- The surface area of the spill (A) is 100 ft^2.
- The molecular weight of MEK (M_x) is 72.10 lb/lb-mole.
- The vapor pressure of MEK (P_x) at 77°F is approximately 1.93 psia.

Step 1: Using Equation 8.4-21, calculate the Gas-phase Mass Transfer Coefficient (K_x)

$$K_x = 0.00438 \times U^{0.78} \times \left(\frac{18}{M_x}\right)^{1/3}$$

$$= 0.00438 \times 8^{0.78} \times \left(\frac{18}{72.1}\right)^{1/3}$$

$$= 0.01397 \text{ ft/sec}$$

Step 2: Using Equation 8.4-19, Calculate Emissions (E_x)

$$E_x = \frac{M_x \times K_x \times A \times P_x \times 3600 \times HR}{R \times T}$$

$$= \frac{72.1 \times 0.01397 \times 100 \times 1.93 \times 3600 \times 3}{10.73 \times 537}$$

$$= 364 \text{ lb MEK/spill}$$

4.4 Emission Model for Surface Evaporation

Emissions from surface evaporation of VOCs from open or partially covered mixing tanks during coating mixing operations can be estimated using Equation 8.4-22, which is also based on the simple vaporization model for spills.

$$E_x = \frac{M_x \times K_x \times A \times P_x \times 3600 \times H}{R \times T} \times B \qquad (8.4\text{-}22)$$

where

E_x	=	emissions of VOC species x (lb/yr)
M_x	=	molecular weight of VOC species x (lb/lb-mole)
K_x	=	gas-phase mass transfer coefficient for VOC species x (ft/sec)
A	=	surface area of exposure or opening of tank (ft^2)
P_x	=	true vapor 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 (psia)[2]
3600	=	3600 sec/hr
H	=	batch time (hr/batch)
R	=	universal gas constant at 1 atmosphere of pressure, 10.73 psia-ft^3/°R-lb mole;
T	=	temperature of the liquid, °R (°F+460)
B	=	number of batches per year (batches/yr).

Equations 8.4-20 or 8.4-21 can be used to estimate K_x. Total VOC emissions would equal the sum of all VOC species emissions. Note that using these equations to estimate mass transfer coefficients for VOC in a tank inside a building is subject to the same uncertainty discussed in Section 4.3 for spills inside a building because such applications differ from the situation for which the equation was developed.

[2] The partial pressure of VOC species x (P_x) may be calculated using Equation 8.4-3 or Equation 8.4-4.

Examples 8.4-5 and 8.4-6 illustrate the use of Equation 8.4-22.

Example 8.4-5

A covered tank is used to mix toluene and various insoluble materials. What are the toluene emissions due to surface evaporation? The following data are given:

- Toluene is the only compound that is a liquid
- The batch time (H) is 4 hours.
- The number of batches per year (B) is 550.
- The average air velocity through the building above the tank (U) is 0.1 miles/hr.
- The ambient temperature (T) is 77°F or 537°R (°R = °F + 460).
- The opening in the cover of the mixing tank (A) for the agitator shaft is 4 ft^2.
- The molecular weight of toluene (M_x) is 92 lb/lb-mole.
- The partial vapor pressure of toluene (P_x) at 77°F is approximately 0.55 psia.

Step 1: Using Equation 8.4-21, calculate the Gas-phase Mass Transfer Coefficient (K_x)

$$K_x = 0.00438 \times U^{0.78} \times \left(\frac{18}{M_x}\right)^{1/3}$$

$$= 0.00438 \times 0.1^{0.78} \times \left(\frac{18}{92}\right)^{1/3}$$

$$= 0.000422 \text{ ft/sec}$$

Step 2: Using Equation 8.4-22, calculate annual emissions (E_x)

$$E_x = \frac{M_x \times K_x \times A \times P_x \times 3600 \times H}{R \times T} \times B$$

$$= \frac{92 \times 0.000422 \times 4 \times 0.55 \times 3600 \times 4}{10.73 \times 537} \times 550$$

$$= 117 \text{ lb toluene/yr}$$

Example 8.4-6

An ink manufacturer uses a three roll mill to ensure that the finished ink product meets particle size and uniformity standards. Material is fed to the rollers between the feed and center rolls. Material is then transferred from the center roll to the apron roll where it is removed by a stationary knife blade. What are the emissions due to surface evaporation? The following data are given:

- The roller elements are 14 inches in diameter and 30 inches long;
- The printing ink being processed contains a light petroleum distillate oil with a molecular weight of 254;
- The rollers operate at ambient temperature of 77°F;
- The MSDS shows that the vapor pressure for the light petroleum distillate oil at 77°F is 0.097 psia;
- The mole fraction of petroleum distillate oil in the ink mixture is estimated to be 0.3;
- Each batch takes 1.5 hours; and
- 400 batches are processed annually.

Step 1: Determine Liquid Surface Area on the Rollers

For this illustration, it is assumed that liquid covers the entire surface area of each roller.

$$A = \pi \times d \times L \times N_{rollers}$$
$$= \pi \times 14 \times 30 \times 3$$
$$= 3{,}956 \text{ in}^2 \left(27.5 \text{ ft}^2\right)$$

Step 2: Apply Equation 8.4-3, Determine Partial Pressure of Light Petroleum Distillate Oil

$$P_x = m_x \times VP_x$$
$$= 0.3 \times 0.097$$
$$= 0.0291 \text{ psia}$$

Step 3: Apply Equation 8.4-29, Determine Mass Transfer Coefficient

Note that this example illustrates use of the alternative procedure described in Section 4.5. Equation 8.4-21 may be used if a site-specific estimate of air velocity over the rollers can be estimated.

$$K_x = 0.83 \times \left[\frac{18}{M_x}\right]^{1/3}$$
$$= 0.83 \times \left[\frac{18}{254}\right]^{1/3}$$
$$= 0.343 \text{ cm/s} \left(0.0113 \text{ ft/s}\right)$$

Step 4: Apply Equation 8.4-22, Calculate Annual Emissions

$$E_x = \frac{M_x \times K_x \times A \times P_x \times 3600 \times H}{R \times T} \times B$$

$$= \frac{254 \times 0.0113 \times 7.5 \times 0.0291 \times 3600 \times 1.5}{10.73 \times 537} \times 400$$

$$= 861 \text{ lb/ yr}$$

4.5 Gas Sweep or Purge

This section presents two models for estimating emissions from a gas sweep or purge through a partially filled process vessel. The first model (option 1) is from *Control of Volatile Organic Emissions from Batch Processes* (EPA, 1994c). The second model (option 2) is a modified version of the first model in that it includes a procedure based on site-specific conditions for estimating the degree to which the exhaust gas is saturated with organic compounds (Hatfield, 2003). Note that option 2 is recommended only for applications where the headspace exchange rate is less than 5 per minute because available data suggest it may underestimate emissions at higher exchange rates (Watson, 2004).

Applying the surface evaporation model to estimate emissions from a gas sweep or purge is inappropriate. As noted in section 4.3, the wind speed correlation for estimating the mass transfer coefficient was developed for scenarios where the flow is uniform across a relatively quiescent liquid surface, and the wind speed is taken at 10 meters above the surface. Flow inside a tank is not uniform, sweep air may be impinging on the liquid surface, the liquid surface is likely turbulent from agitation, material added while loading the vessel may be dropped on the liquid surface causing splashes, and the wind speed cannot be determined at 10 meters above the surface. Furthermore, even if the general correlation is still valid under these conditions, the gas velocity is not uniform across the surface of the liquid, and there is no consensus regarding the value to use or the point at which the velocity should be determined for use in the correlation.

4.5.1 Option 1

The equation for calculating gas sweep or purge emissions that is in *Control of Volatile Organic Compound Emission from Batch Processes* is shown in Equation 8.4-23 (EPA, 1994c).

$$E_x = \frac{P_x \times F_{nc} \times M_x \times 60 \times OH}{R \times T} \times \frac{P_T}{P_T - \Sigma P_x} \qquad (8.4\text{-}23)$$

where

E_x	=	emissions of VOC species x, lb/yr
P_x	=	partial pressure of VOC species x, psia
F_{nc}	=	flow rate into the vessel, ft^3/min
M_x	=	molecular weight of VOC species x, lb/lbmole
60	=	60 min/hr
OH	=	hours that the gas sweep or purge operates, hr/yr
R	=	universal gas constant (10.73 psia ft^3/lbmole °R)
T	=	temperature of the exhaust gas, °R
P_T	=	total system pressure, psia.

Note that to use this model, the exhaust gas stream is assumed to be in equilibrium with the liquid if the flow rate into the vessel is less than 100 ft^3/min (i.e., the partial pressure is equal to the vapor pressure for a tank with one compound in the liquid phase). The exhaust stream is assumed to be 25 percent saturated if the flow is greater than 100 ft^3/min.

Example 8.4-7 illustrates the use of Equation 8.4-23.

Example 8.4-7

A gas sweep is operated while material is added to a high-speed disperser. What are the annual VOC emissions during purges? The following data are provided:

- The average composition of the material in the high-speed disperser while the sweep operates is 30% by weight toluene, 20% by weight MEK, and 50% by weight insoluble pigments and nonvolatile resins;
- The temperature of the material in the vessel and the exhaust gas is 77°F (537°R);
- The partial pressures of toluene and MEK at 77°F are 0.313 psia and 0.888 psia, respectively (see Example 8.4-2, Step 2);
- The inlet purge flow rate is 5 ft^3/min;
- The molecular weight of toluene is 92.1 lb/lbmole;
- The molecular weight of MEK is 72.1 lb/lbmole; and
- The purge operates for 1,000 hr/yr.

Step 1: Apply Equation 8.4-23 to Calculate Toluene Emissions

Note that since te purge flow is <100 ft^3/min, the exhaust gas stream is assumed to be saturated with toluene and MEK.

$$E_x = \frac{P_x \times F_{nc} \times M_x \times 60 \times OH}{R \times T} \times \frac{P_T}{P_T - \Sigma P_x}$$

$$= \frac{0.313 \times 5 \times 92.1 \times 60 \times 1{,}000}{10.73 \times 537} \times \frac{14.7}{14.7 - (0.313 + 0.888)}$$

$$= 1{,}634 \text{lb/yr}$$

Step 2: Apply Equation 8.4-23 to calculate MEK Emissions

$$E_x = \frac{0.888 \times 5 \times 72.1 \times 60 \times 1{,}000}{10.73 \times 537} \times \frac{14.7}{14.7 - (0.313 + 0.888)}$$

$$= 3{,}630 \text{ lb/ yr}$$

Step 3: Sum the Emissions from Steps 1 and 2

$$E_{VOC} = 1{,}634 + 3{,}630$$

$$= 5{,}264 \text{ lb/ yr}$$

4.5.2 Option 2

This model is the same as the model in Option 1 except that it adds a site-specific saturation factor for each VOC species in the exit gas stream. Equation 8.4-24 is used to calculate the saturation factor.

$$S_x = \frac{P_x}{P_x^{Sat}} = \frac{K_x A}{F + K_x A} = \frac{K_x A}{K_x A + F_{nc} + S_x F_x^{Sat}} \qquad (8.4\text{-}24)$$

where

S_x	=	saturation factor for VOC species x
K_x	=	mass transfer coefficient for VOC species x
A	=	surface area of the liquid
F_{nc}	=	volumetric flow rate of the noncondensable purge (e.g., air, nitrogen)
F_x^{Sat}	=	volumetric flow rate of VOC species x at the saturated partial pressure.

Equation 8.4-24 was developed based on the following relationships and assumptions. Equation 8.4-25 relates the evaporation rate for a VOC species x within a vessel to its molecular weight, mass transfer coefficient, surface area, and other known variables [Crowl & Louvar, 2002].

$$E_m = \frac{M_x K_x A}{RT}\left(P_x^{Sat} - P_x\right) \qquad (8.4\text{-}25)$$

where

E_m	=	evaporation rate (lb/min)
M_x	=	molecular weight of VOC species x
K_x	=	mass transfer coefficient (ft/min)
A	=	surface area (ft^2)
R	=	ideal gas constant
T	=	temperature of liquid
P_x^{Sat}	=	partial pressure of VOC species x in a saturated gas stream (true vapor pressure if the liquid is pure species x)
P_x	=	actual partial pressure of VOC species x next to the liquid surface.

Equation 8.4-26 is the basic equation for calculating the emission rate for VOC species x from a gas sweep or purge operation based on the exit gas flow rate, partial pressure of VOC species x, molecular weight, and other known variables.

$$E_v = \frac{FP_T}{RT}\frac{P_x}{P_T}M_x = \frac{M_x F P_x}{RT} \qquad (8.4\text{-}26)$$

where

E_v	=	emissions from vessel vent (lb/min)
F	=	exit gas flow rate (ft^3/min)
P_T	=	overall system pressure
R	=	ideal gas constant
T	=	temperature of liquid
P_x	=	actual partial pressure of VOC species x
M	=	molecular weight of VOC species x.

For a vessel at steady state conditions, the emission rate from the gas sweep activity is equal to the evaporation rate of VOC species x from the liquid within the vessel [Hatfield, 2003]. These two equations can be set equal and solved for the saturation level S_x (i.e., P_x/P_x^{Sat}), resulting in Equation 8.4-24.

Calculation of VOC emissions using Equation 8.4-24 is based on the following assumptions:

- The vessel is at steady state so that the evaporation reate equals the discharge rate in the exit gas stream.
- The vapor space is perfectly mixed so that once the VOC evaporates there is no additional resistence to mass transfer to the exit gas stream (this means the reference mass transfer coefficient, as discussed below, is also assumed to be for a perfectly mixed system).

.

- The equation is recommended only for headspace exchange rates up to 5 per minute.

The ratio of the mass transfer coefficients between the compound of interest (K_x) and the reference compound (K_o) is expressed using Equation 8.4-27 (Crowl and Louvar, 2002):

$$\frac{K_x}{K_o} = \left[\frac{D_x}{D_o}\right]^{2/3} \qquad (8.4\text{-}27)$$

where

K_x	=	mass transfer coefficient for VOC species x
K_o	=	mass transfer coefficient for a reference compound
D_x	=	diffusion coefficient for VOC species x in air
D_o	=	diffusion coefficient for a reference compound in air.

The gas-phase diffusion coefficient D for a compound is estimated from the ratio of the molecular weight of the compound of interest and a known compound (normally water) using Equation 8.4-28:

$$\frac{D_x}{D_o} = \left[\frac{M_o}{M_x}\right]^{1/2} \qquad (8.4\text{-}28)$$

where

M_o	=	molecular weight of a reference compound
M_x	=	molecular weight of VOC species x.

Combining Equations 8.4-27 and 8.4-28 results in a relationship that can be used to estimate the mass transfer coefficient of a given volatile compound:

$$K_x = K_o \left(\frac{M_o}{M_x} \right)^{1/3} \tag{8.4-29}$$

Water is commonly used as a base reference for estimating the mass transfer coefficient for many compounds of interest. The mass transfer coefficient of water at 77°F and 14.7 psia is 0.83 cm/s (0.0272 ft/s) (Matthiesen, 1986).

The saturated partial volumetric flow rate of VOC species x can be estimated from the saturated partial pressure of the VOC species x, the inlet gas purge rate, and the partial pressure of the non-condensable gas at saturated conditions using Equation 8.4-30:

$$F_x^{Sat} = F_{nc} \times \frac{P_x^{Sat}}{P_T - \Sigma P_x^{Sat}} \tag{8.4-30}$$

where

F_x^{Sat}	=	volumetric flow rate of VOC species x at the saturated partial pressure
F_{nc}	=	volumetric flow rate of the noncondensable gas (i.e., air, nitrogen)
P_x^{Sat}	=	partial pressure of VOC species x in a saturated gas stream (true vapor pressure if the liquid is pure species x)
P_T	=	total system pressure.

The saturation factor (S_x) may be solved using the standard quadratic solution. Although the standard quadratic equation contains two roots, only the one solution shown in Equation 8.4-31 produces a realistic value since S_x must be a positive number between 0 and 1.0.

$$S_x = \frac{-(K_x A + F_{nc}) + \sqrt{(K_x A + F_{nc})^2 + 4F_x^{Sat} K_x A}}{2F_x^{Sat}} \tag{8.4-31}$$

Finally, the emission rate for VOC species x may be calculated using Equation 8.4-32, which is similar to Equation 8.4-23, except that the saturated partial pressure is multiplied by the saturation factor.

$$E_x = \frac{M_x \times S_x \times P_x^{Sat} \times F_{nc} \times 60 \times OH}{R \times T} \times \frac{P_T}{P_T - \Sigma P_x^{Sat}} \tag{8.4-32}$$

For multi-component liquid mixtures, Equation 8.4-24 may be expanded to include partial volumetric flow rates for each VOC species in the liquid, as shown in Equation 8.4-33:

$$S_{x+1} = \frac{K_x A}{K_x A + F_{nc} + S_x F_x^{Sat} + S_j F_j^{Sat} + K + S_n F_n^{Sat}} \qquad (8.4\text{-}33)$$

In equation 8.4-33, the subscript x identifies the VOC species for which the saturation level is being calculated, and terms j through n represent the other VOC species in the liquid. Equation 8.4-33 is solved in an iterative trial and error manner with the initial value of S for each VOC species assigned to 1.0. The value of S that is calculated for each VOC species is then used as the starting point for the next iteration. Finally, when the saturation level S of each VOC species remains the same for subsequent iterations, the calculation process is stopped.

Examples 8.4-8 and 8.4-9 illustrate the use of Equations 8.4-29 through 8.4-33 to estimate emissions from purging a partially filled vessel.

Example 8.4-8

A high-speed disperser operates with a gas sweep while material is added to the vessel. What are the annual VOC emissions? The following data are given:

- Mineral spirits are the only material in the liquid phase;
- The molecular weight of mineral spirits is 145 lb/lbmole;
- The contents of the vessel and the purge are at a temperature of 77°F (537°R);
- Vapor pressure of mineral spirits at 77°F is 0.0032 psia;
- The gas sweep is 5 acfm;
- The diameter of the tank is 5 ft; and
- The gas sweep operates for 1,000 hr/yr.

Step 1: Apply Equation 8.4-29, Estimate Mass Transfer Coefficient

Using water as the reference compound results in the following equation:

$$K_x = 0.83 \times \left[\frac{18}{M_x}\right]^{1/3}$$

$$= 0.83 \times \left[\frac{18}{145}\right]^{1/3}$$

$$= 0.414 \text{ cm/s } (0.815 \text{ ft/min})$$

Step 2: Determine Surface Area of Liquid in the Tank

$$A = \frac{\pi \times d^2}{4} = \frac{\pi \times (5)^2}{4}$$

$$= 19.6 \text{ ft}^2$$

Step 3: Apply Equation 8.4-30, Determine Saturated Partial Volumetric Flow Rate of Mineral Spirits in Exit Gas Stream

$$F_x^{Sat} = F_{nc} \times \frac{P_x^{Sat}}{P_T - \Sigma P_x^{Sat}}$$

$$= 5 \times \frac{0.0032}{14.7 - 0.0032}$$

$$= 0.00109 \text{ ft}^3/\text{min}$$

Step 4: Apply Equation 8.4-31, Calculate Saturation Factor For Mineral Spirits in the Exit Gas Stream

$$S_x = \frac{-(K_x A + F_{nc}) + \sqrt{\left((K_x A + F_{nc})^2 + 4F_x^{Sat} K_x A\right)}}{2\, F_x^{Sat}}$$

$$= \frac{-((0.815)(19.6) + 5) + \sqrt{\left(((0.815)(19.6) + 5)^2 + (4)(0.00109)(0.815)(19.6)\right)}}{(2)(0.00109)}$$

$$= \frac{-20.974 + \sqrt{439.909 + 0.06965}}{0.00218}$$

$$= 0.76$$

Step 5: Apply Equation 8.4-32, Calculate Annual Emissions

$$E_x = \frac{M_x \times S_x \times P_x^{Sat} \times F_{nc} \times 60 \times OH}{R \times T} \times \frac{P_T}{P_T - \Sigma P_x^{Sat}}$$

$$= \frac{145 \times 0.76 \times 0.0032 \times 5 \times 60 \times 1{,}000}{10.73 \times 537} \times \frac{14.7}{14.7 - 0.0032}$$

$$= 18 \text{lb/yr}$$

Example 8.4-9

Determine the annual emissions from purging the high-speed disperser in example 8.4-7 using Option 2. The following additional information is provided:

The diameter of the tank is 5 ft.

Step 1. Apply Equation 8.4-29, Estimate Mass Transfer Coefficients for Toluene and MEK

For toluene:

$$K_x = 0.83 \times \left(\frac{18}{92.1}\right)^{1/3} = 0.482 \text{ cm/s}\left(0.948 \text{ ft/min}\right)$$

For MEK:

$$K_x = 0.83 \times \left(\frac{18}{72.1}\right)^{1/3} = 0.523 \text{ cm/s}\left(1.029 \text{ ft/min}\right)$$

Step 2: Determine Surface Area of Liquid in the Tank

$$A = \frac{\pi \times d^2}{4} = \frac{\pi \times (5)^2}{4} = 19.6 \text{ ft}^2$$

Step 3: Determine Saturated Partial Pressures of VOC Species

See Example 8.4-2, Step 2 for the calculations of the following:

VOC	VP at 77°F, psia	Liquid Mole Fractions	P_x^{Sat}, psia
Toluene	0.58	0.54	0.313
MEK	1.93	0.46	0.888

Step 4: Apply Equation 8.4-30, Determine Saturated Partial Volumetric Flowrate of Each VOC Species

$$F_x^{Sat} = F_{nc} \times \frac{P_x^{Sat}}{P_T - \Sigma P_x^{Sat}}$$

$$F_x^{Sat}(\text{for toluene}) = 5 \times \frac{0.313}{14.7 - (0.313 + 0.888)}$$
$$= 0.1160 \text{ ft}^3/\text{min}$$

$$F_x^{Sat}(\text{for MEK}) = 5 \times \frac{0.888}{14.7 - (0.313 + 0.888)}$$
$$= 0.3288 \text{ ft}^3/\text{min}$$

Step 5. Apply Equation 8.4-33, Calculate the Saturation Factors for Each VOC Species

Using trial and error, the following results are obtained:

VOC	K_xA	F_x^{Sat}, ft^3/min	S_x (iteration 0)	S_x (iteration 1)	S_x (iteration 2)	S_x (iteration 3)
Toluene	18.617	0.116	1	0.77372	0.77682	0.77678
MEK	20.200	0.3288	1	0.78769	0.79065	0.79061

For example, the S_x (iteration 1) for toluene is calculated as follows:

$$S_x = \frac{K_xA}{K_xA + F_{nc} + S_xF_x^{Sat} + S_jF_j^{Sat}}$$

$$= \frac{18.617}{18.617 + 5 + (1)(0.116) + (1)(0.3288)}$$

$$= 0.77372$$

Step 6: Apply Equation 8.4-32, Calculate Annual Emissions

$$E_x = \frac{M_x \times S_x \times P_x^{Sat} \times F_{nc} \times 60 \times OH}{R \times T} \times \frac{P_T}{P_T - \Sigma P_x^{Sat}}$$

$$E_x \text{ (toluene)} = \frac{92.1 \times 0.777 \times 0.313 \times 5 \times 60 \times 1000}{10.73 \times 537} \times \frac{14.7}{14.7 - (0.313 + 0.888)}$$

$$= 1{,}270 \text{ lb/ yr}$$

$$E_x \text{ (MEK)} = \frac{72.1 \times 0.791 \times 0.888 \times 5 \times 60 \times 1000}{10.73 \times 537} \times \frac{14.7}{14.7 - (0.313 + 0.888)}$$

$$= 2{,}871 \text{ lb/ yr}$$

Step 7: Sum Emissions From Step 6

$$E_{VOC} = 1{,}270 + 2{,}871$$
$$= 4{,}141 \text{ lb/yr}$$

4.6 Solvent Reclamation

After being collected from coating manufacturing operations, waste cleaning solvents may be purified and reused. Distillation is one of the most common methods of purifying a solvent. Many forms of distillation are used including batch, simple continuous, or steam distillation.

A batch distillation process consists of at least four separate activities including: (1) charging waste solvent into the still, (2) heating the batch to its boiling point, (3) collecting the distillate in a receiver, and (4) filling a container or vessel with the collected distillate for storage. Steps 1, 3 and 4 can be modeled using the filling model described earlier in this section (Equation 8.4-1).

Emissions from heating to boiling (Step 2) cannot be modeled using either of the equations for heatup described in Section 4.2 of this chapter because the equations are mathematically invalid when the partial pressure of air is zero. However, the emissions can be estimated using Equation 8.4-34.

$$E_{VOC} = \frac{(Px)_o}{Pa_1} \times \Delta n \times M_x \qquad (8.4\text{-}34)$$

where

$(Px)_o$	=	partial pressure of VOC species x at the condenser outlet temperature (also the vapor pressure of the pure compound because only one compound is condensing)
)n	=	moles of air in the vessel headspace at the initial temperature
M_x	=	molecular weight of VOC species x
Pa_1	=	partial pressure of air at the condenser outlet temperature.

Calculation of VOC emissions using Equation 8.4-34 is based on the following assumptions:

- all of the air in the vessel headspace at the initial temperature has been expelled when the liquid in the vessel begins to boil
- the heated vapors leaving the still pass through a condenser
- air leaving the condenser is saturated with VOC vapors at the exit gas temperature of the condenser.

Furthermore, while the liquid in the vessel is boiling, emissions are assumed to be zero because only VOC vapor is expelled from the vessel and it all condenses in the condenser.

Example 8.4-10 illustrates the use of the filling and heating equations to estimate VOC emissions from solvent reclamation.

Example 8.4-10

The Bright Blue Paint Company in Case Study 8.3-1 recovers toluene from 300 tons/yr of waste cleaning solvent using a batch distillation unit. What are the estimated annual VOC emissions? The following data are given:

- The still is half filled for each distillation operation (i.e., the vessel vapor space equals the volume of waste solvent for each batch);
- The expelled air and VOC vapors are routed to a condenser that operates with an outlet temperature of 20°C (68°F);
- The still bottoms at the end of the distillation contain 3 percent of the initial waste solvent;
- Analysis shows the waste solvent is about 99 percent toluene (on a molar basis), and the remaining 1 percent is dissolved solids and nonvolatile liquids;
- Typical initial temperature of the waste solvent is 25°C (77°F);
- Toluene density is 7.21 lb/gal;
- Final temperature (toluene boiling point) is 111°C (232°F); and
- Displaced air from all filling steps is assumed to be saturated with toluene vapors (i.e., the saturation factor is 1.0).

Step 1: Determine Volume of Waste Solvent Charged to the Still

$$Q = \left[300\frac{\text{tons solvent}}{\text{yr}}\right] \times \left[\frac{2{,}000\text{ lb}}{\text{ton}}\right] \times \left[\frac{\text{gal}}{7.21\text{ lb}}\right]$$
$$= 83{,}218\,\text{gal/yr}$$

Step 2: Determine the Toluene Vapor Pressure at the Initial Temperature

Numerous resources are available for estimating vapor pressures. This example uses the Antoine equation (Dean, 1992).

$$\log(VP_x) = A - \frac{B}{T + C} \qquad (8.4\text{-}35)$$

where

VP_x	=	vapor pressure of VOC species x, mm Hg
T	=	temperature, °C
A,B,C	=	Antoine Constants.

For toluene at the initial temperature of the still (25°C), the Antoine equation gives the following results:

$$\log(VP_x) = 6.954 - \frac{1{,}344.8}{25 + 219.48}$$

$$VP_x = 28.4 \text{ mm Hg} (0.549 \text{ psia})$$

Step 3: Apply Equation 8.4-3, Determine Toluene Partial Pressure at the Initial Temperature

$$P_x = M_x \times VP_x$$

$$= (0.99) \times (0.549)$$

$$= 0.544 \text{ psia}$$

Step 4: Apply Equation 8.4-1, Calculate Toluene Emissions From Charging Waste Solvent to the Still

$$E_{VOC} = \frac{12.46 \times S \times P_x \times M_x \times Q}{T}$$

$$= \frac{12.46 \times 1 \times 0.544 \times 9.21 \times 83.2}{537}$$

$$= 97 \text{ lb/yr}$$

Step 5: Apply Equations 8.4-11 and 8.4-12, Determine Amount of Noncondensable Gas in the Vessel Headspace When Heating Begins.

Although the description of the problem doesn't specify the size of each batch or the size of the still, it says the headspace volume for each batch is equal to the volume of waste solvent. Thus, the total volume of free space in the still at the start of heatup for all of the batches during the year equals the total volume of waste solvent processed (i.e., 83,218 gal).

$$Pa_1 = 14.7 - \Sigma(P_x)_{T1}$$
$$= 14.7 - 0.544$$
$$= 14.16 \text{ psia}$$

$$\Delta n = \frac{(Pa_1) \times (V)}{(R) \times (T)}$$
$$= \frac{(14.16) \times (83{,}218) \times \left[ft^3 / 7.48 \text{ gal}\right]}{(10.73) \times (537)}$$
$$= 27.3 \text{lbmoleof airexpelled/yr}$$

Step 6: Apply Equation 8.4-35, Determine Vapor Pressure and Partial Pressure of Toluene at 20°C (Condenser Outlet Temperature)

$$\log(VP_x) = A - \frac{B}{T + C}$$
$$= 6.954 - \frac{1{,}344.8}{20 + 219.48}$$
$$VP_x = P_x = 21.80 \text{ mmHg}(0.422 \text{ psia})$$

Step 7: Apply Equation 8.4-34, Determine Amount of Toluene Emitted With the Expelled Air During Heatup

$$E_{VOC} = \frac{(P_x)_o}{Pa_1} \times \Delta n \times M_x$$
$$= \frac{(0.422)}{(14.7 - 0.422)} \times (27.3) \times (92.1)$$
$$= 74 \text{ lb / yr}$$

Step 8: Apply Equation 8.4-1, Calculate Emissions From Filling the Receiver with Distilled Toluene at 20°C (68°F)

Note that since 3 percent of the initial waste solvent remains in the still, the total volume of recovered toluene is 97 percent of the total waste solvent processed.

$$E_{VOC} = \frac{12.46 \times S \times P_x \times M_x \times Q \times 0.97}{T}$$
$$= \frac{12.46 \times 1 \times 0.422 \times 92.1 \times 83.2 \times 0.97}{528}$$
$$= 74 \text{lb/yr}$$

Step 9: Apply Equation 8.4-1, Calculate Emissions From Filling a Storage Vessel or Drums With Distilled Toluene From the Receiver

Assume the distilled toluene is still at 20°C (68°F)

$$E_{VOC} = \frac{12.46 \times S \times P_x \times M_x \times Q \times 0.97}{T}$$
$$= \frac{12.46 \times 1 \times 0.422 \times 92.1 \times 83.2 \times 0.97}{528}$$
$$= 74 \text{lb/yr}$$

Step 10: Sum the Emissions from Steps 4, 7, 8, and 9

$$E_{VOC} = 97 + 74 + 74 + 74$$
$$= 319 \text{ lb/yr}$$

4.7 Emission Model for Liquid Material Storage

The preferred method for calculating emissions from storage tanks is the use of equations presented in *AP-42*. EPA has developed a software package (TANKS) for calculating these types of emissions. The reader is referred to Chapter 1 of this volume, *Introduction to Stationary Point Source Emissions Inventory Development*, for more information on using the TANKS program. Additionally, the reader should consult their state agency and/or the EPA's Clearinghouse for Inventories and Emission Factors (CHIEF) Website for the most recent version of TANKS.

4.8 Emission Model for Wastewater Treatment

VOC emissions from a wastewater treatment system may be estimated using equations presented in *Air Emissions Models for Waste and Wastewater* (EPA, 1994a), and Chapter 5, *Preferred and Alternative Methods for Estimating Air Emissions from Wastewater Collection and Treatment Facilities*, of this volume. These documents, as well as models such as WATER9 are available on the EPA's CHIEF Website.

5.0 Other Methods for Estimating Emissions

Section 4 presented models for estimating emissions from specific coating manufacturing activities. This section presents other types of methods for calculating emissions from manufacturing facilities. The other methods described in this section include emission factors, material balances, and testing.

5.1 Emission Calculations Using Emission Factors

Emission factors have long been used to calculate emissions from coating manufacturing facilities. EPA maintains a compilation of approved emission factors in *AP-42* for criteria pollutants and hazardous air pollutants (HAPs). Available emission factors for paint manufacturing can be found in Section 6.4 of *AP-42* and in a technical memorandum from EPA to the National Paint and Coatings Association (EPA, 1995f). Emission factors for ink manufacturing can be found in Section 6.7 of *AP-42*. The National Association of Printing Ink Manufacturers, Inc. (NAPIM), has also developed ink manufacturing emission factors (NAPIM, 1996). The most comprehensive source for toxic air pollutant emission factors is the Factor Information and REtrieval (FIRE) data system, which also contains criteria pollutant emission factors (EPA, 1999).

VOC emission factors are available in *AP-42* for calculating total plant emissions and mixing operation emissions from a paint manufacturing facility and for vehicle cooking and pigment mixing emissions from an ink manufacturing facility. In addition, emission factors are available for estimating VOC emissions from the following types of sources found in a coating manufacturing facility:

- Solvent reclamation systems;
- Parts washing equipment; and
- Process piping (i.e., equipment leaks).

Emission factors are also available for estimating PM/PM_{10} emissions from coating manufacturing facilities.

5.1.1 Total VOC Emissions from Paint Manufacturing Facilities

A VOC emission factor can be used for calculating total VOC emissions from paint manufacturing facilities. The emission factor presented in *AP-42* is essentially a loss factor that represents an emission rate to be applied to a production rate (NPCA, 1995). The VOC emission factor presented in *AP-42* for paint manufacturing is 30 lb total VOCs/ton product (EPA, 1995b). To calculate total VOCs using this emission factor, see Equation 8.5-1:

$$E_{VOC} = EF_{VOC} * Q_p \quad (8.5\text{-}1)$$

where

E_{VOC} = total emissions of VOCs from the facility (lb/yr)
EF_{VOC} = VOC emission factor (lb VOCs/ton product)
Q_p = amount of product produced (ton/yr).

Table 8.5-1. List of Variables and Symbols

Variable	Symbol	Units
Total VOC emissions	E_{VOC}	lb/yr
VOC emission factor	EF_{VOC}	various
Amount of product produced	Q_{prod}	ton/yr
Emissions of VOC or PM species x	E_x	lb/yr
Amount of VOC species x used by the facility	Q_x	lb/yr
Total amount of solvents used	Q_s	lb/yr
Amount of VOC in spent solvent processed	Q_{VOC}	ton/yr
Concentration of VOC or PM/PM_{10} species x in solvent or pigment x, respectively	C_x	mass %
Mass percent of species x 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
Flow rate through exhaust vent	FR	ft^3/min
Molecular weight of total mixture	M	lb/lb-mole
Molecular weight of VOC or PM species x	M_x	lb/lb-mole
Operating hours	OH	hr/yr
Surface area of solvent exposed to the atmosphere	A	ft^2
Number of cleaning units in use	NU	cleaning units
PM/PM_{10} emissions	E_{PM}	lb/yr
PM/PM_{10} emission factor	EF_{PM}	lb/ton
Amount of pigment containing species x used by the facility	Q_x	lb/yr, ton/yr
Quantity of VOC or PM species x that is received as a raw material	Q_r	lb/yr

Table 8.5-1. (continued)

Variable	Symbol	Units
Quantity of VOC or PM species x shipped out in final product	Q_p	lb/yr
Quantity of VOC or PM species x recovered by all methods	Q_{rec}	lb/yr
Quantity of VOC or PM species x contained in all waste generated	Q_w	lb/yr
Quantity of VOC or PM species x remaining in raw material inventory	Q_{xi}	lb/yr
Concentration of VOC or PM species x	C_{xt}	ppmv or $ft^3/MMft^3$

Because the VOC emissions calculated in Equation 8.5-1 are plantwide emissions, speciated emissions can be estimated based on total solvent used. Speciated VOC emissions are calculated using Equation 8.5-2:

$$E_x = E_{VOC} \times Q_x/Q_s \qquad (8.5\text{-}2)$$

where

E_x = Emissions of VOC species x from the facility (lb/yr);
E_{VOC} = VOC emissions from the facility, calculated using Equation 8.5-1 (lb/yr);
Q_x = Amount of VOC species x used by the facility (lb/yr); and
Q_s = Total amount of solvents used by the facility (lb/yr).

With no other information available, one important assumption made in Equation 8.5-2 is that all solvents evaporate at the same rate. The amount of VOC species x used by a facility (Q_x) can be obtained by reviewing purchase and inventory records and appropriate technical data sheets. Purchase and inventory records can be used to estimate the amount of a particular material consumed.

The sum of speciated emissions for all VOC components calculated using Equation 8.5-2 cannot exceed the total VOC emissions calculated in Equation 8.5-1. The use of Equations 8.5-1 and 8.5-2 is demonstrated in Example 8.5-1.

Example 8.5-1

This example shows how total and speciated VOC emissions may be calculated for a paint manufacturing facility using the production-based VOC emission factor from *AP-42*, Table 6.4-1, and Equations 8.5-1 and 8.5-2.
Given:

EF_{VOC} = 30 lb VOC/ton product
Q_{prod} = 1,250 ton of paint/yr
Q_{xylene} = 250,000 lb used by the facility/yr
Q_s = 1,500,000 lb solvents used by the facility/yr

Total VOC emissions would be calculated using Equation 8.5-1:

$$E_{VOC} = EF_{VOC} \times Q_{prod}$$
$$= 30 \times 1{,}250$$
$$= 37{,}500 \text{ lb VOCs/yr}$$

The amount of xylenes used by the facility (Q_{xylene}) was estimated by conducting a review of purchase and inventory records and technical data sheets.

Xylenes emissions would be calculated using Equation 8.5-2:

E_{VOC} = 37,500 lb VOCs emitted/yr
Q_{xylene} = 250,000 lb xylenes used by the facility/yr
Q_s = 1,500,000 lb solvents used by the facility/yr

$$E_{xylene} = E_{VOC} \times Q_x/Q_s$$
$$= 37{,}500 \times 250{,}000/1{,}500{,}000$$
$$= 6{,}250 \text{ lb xylenes/yr}$$

In addition to the 30 lb VOCs/ton product emission factor, EPA has recently restated the emission factor for total VOC emissions for overall operations from a paint manufacturing facility based on the amount of solvent used (EPA, 1995f). Development of the new proposed factor, 0.034 lb VOCs emitted/lb solvent used, is based on the following information and assumptions:

- The emission estimates used to develop the 30 lb VOCs/ton coating emission factor appear to be based on the formulation of conventional coatings that were prevalent in the late 1950s and early 1960s.

- Densities for conventional coatings were typically 10 to 15 lb/gal (an average density of 12.5 lb/gal was used) during the late 1950s and early 1960s.

- An average solvent content of 5.5 lb VOCs/gal coating was assumed for conventional coatings (EPA, 1995f).

Use of the proposed factor by facilities that primarily manufacture water-based, low-solvent, or high-solids coatings should result in more accurate emissions than use of the 30 lb VOCs/ton coating factor.

To calculate total VOCs using this proposed emission factor, use Equation 8.5-3:

$$E_{VOC} = EF_{VOC} \times Q_s \qquad (8.5\text{-}3)$$

where

E_{VOC}	=	total VOC emissions from a facility (lb/yr)
EF_{VOC}	=	VOC emission factor (lb VOCs/lb solvent used)
Q_s	=	total amount of solvents used (lb/yr).

Speciated emissions are then calculated using Equation 8.5-4:

$$E_x = EF_{VOC} \times Q_x \qquad (8.5\text{-}4)$$

where

E_x	=	emissions of VOC species x from a facility (lb/yr)
EF_{VOC}	=	VOC emission factor (lb VOCs/lb solvent used)
Q_x	=	amount of VOC species x used by the facility (lb/yr).

The sum of speciated emissions for all VOC components calculated in Equation 8.5-4 cannot exceed the total VOC emissions calculated in Equation 8.5-3. The use of Equations 8.5-3 and 8.5-4 is demonstrated in Example 8.5-2.

5.1.2 VOC Emissions from Paint Mixing Operations

VOC emissions from paint mixing equipment may be calculated using emission factors. *AP-42* suggests that "about 1 or 2 percent of solvent is lost even under very well controlled conditions" (EPA, 1995b). This percentage range can be translated into an emission factor range of 0.01 to 0.02 lb solvent lost/lb solvent used. Review of background information indicates that this emission factor range applies specifically to paint mixing operations (i.e., operations where solvents are added as raw materials) (EPA, 1995f).

AP-42 states that the consumption-based emission factor of 0.01 to 0.02 lb VOCs lost/lb solvent used applies even to facilities that have emission sources that are well controlled. If a facility

contains mixers or other process vessels that are uncovered or otherwise poorly controlled, an emission factor greater than 0.02 lb solvent lost/lb solvent used may need to be applied (NPCA, 1995).

Example 8.5-2

This example shows how total and speciated VOC emissions may be calculated for a paint manufacturing facility using the proposed solvent-based VOC emission factor, as shown in Equation 8.5-3.

EF_{VOC} = 0.034 lb VOCs/lb solvent used
Q_s = 350,000 lb solvents used by the facility/yr

E_{VOC} = $EF_{VOC} \times Q_s$
= $0.034 \times 350{,}000$
= 11,900 lb VOCs/yr

Xylene emissions would be calculated using Equation 8.5-4:

EF_{VOC} = 0.034 lb VOCs/lb solvent
Q_x = 15,000 lb xylenes contained in solvents used by the facility/yr

E_x = $EF_{VOC} \times Q_x$
= $0.034 \times 15{,}000$
= 510 lb xylenes/yr

Total VOC emissions can also be calculated by summing the speciated VOC emissions.

Use Equation 8.5-5 for calculating speciated VOC emissions from mixers using the consumption-based emission factor.

$$\mathbf{E_x = EF_{VOC} \times Q_x} \qquad (8.5\text{-}5)$$

where

E_x = emissions of VOC species x from mixing equipment (lb/yr)
EF_{VOC} = VOC emission factor (lb VOCs/lb solvent used)
Q_x = amount of VOC species x added to mixing equipment as a raw material (lb/yr).

The amount of VOC species x used in mixing equipment (Q_x) refers to the total amount of VOC species x that is added to mixing equipment as a raw material. Once the solvent is mixed with other materials, it is no longer considered a raw material.

The use of Equation 8.5-5 is also demonstrated in Example 8.5-3.

Example 8.5-3

This example shows how speciated VOC emissions from mixing equipment may be calculated using Equation 8.5-5 and the emission factor from Section 6.4.1 of *AP-42*. This example assumes an average level of VOC control on process equipment. Consequently, the average of the range (1 to 2 percent) reported in *AP-42* is used.

EF_{VOC} = 0.015 lb xylenes emitted/lb xylenes used
Q_x = 15,000 lb xylenes added to mixing equipment/yr

$E_x = EF_{VOC} \times Q_x$
$= 0.015 \times 15{,}000$
$= 225$ lb xylenes/yr

5.1.3 VOC Emissions from Ink Manufacturing Facilities

Emission factors are also available for VOC sources from ink manufacturing facilities. Section 6.7 of *AP-42* presents VOC emission factors for vehicle cooking. NAPIM has also developed VOC emission factors for mixing, milling, and tub wash processes for both paste and liquid inks (NAPIM, 1996). Emission factors are available for sheetfed three-roll mill and heatset paste inks, and for low-VOC and high-VOC liquid inks. Equation 8.5-6 can be used to estimate emissions using emission factors.

$$E_{VOC} = EF_{VOC} \times Q_p \qquad (8.5\text{-}6)$$

where

E_{VOC} = VOC emissions (lb/yr)
EF_{VOC} = VOC emission factor (lb VOC/ton product)
Q_p = amount of product produced (ton/yr).

Speciated emissions can be calculated using Equation 8.5-7:

$$E_x = E_{VOC} \times Q_x / Q_s \quad (8.5\text{-}7)$$

where

E_x	=	emissions of VOC species x (lb/yr)
E_{VOC}	=	VOC emissions calculated using Equation 8.5-6 (lb/yr)
Q_x	=	amount of VOC species x used (lb/yr)
Q_s	=	total amount of solvent used (lb/yr).

With no other information available, one important assumption made in Equation 8.5-7 is that all solvents evaporate at the same rate. The amount of VOC species x used by a facility (Q_x) can be obtained by reviewing purchase and inventory records and appropriate technical data sheets. Purchase and inventory records can be used to estimate the amount of a particular material consumed.

Example 8.5-4 illustrates the use of these equations.

Example 8.5-4

This example shows how VOC and speciated VOC emissions may be calculated for general vehicle cooking at an ink manufacturing facility using the production-based VOC emission factor from *AP-42*, Table 6.7-1, and Equations 8.5-6 and 8.5-7.

Given:

EF_{VOC}	=	120 lb VOC/ton product
Q_p	=	500 tons of ink/yr
$Q_{toluene}$	=	100,000 lb used/yr
Q_s	=	1,000,000 lb solvents used/yr

VOC emissions would be calculated using Equation 8.5-6:

$$E_{VOC} = EF_{VOC} \times Q_p = 120 \times 500 = 60{,}000 \text{ lb VOCs/yr}$$

The amount of toluene used ($Q_{toluene}$) was estimated by conducting a review of purchase and inventory records, batch records, and technical data sheets.

Toluene emissions would be calculated using Equation 8.5-7:

E_{VOC}	=	60,000 lb VOCs emitted/yr
$Q_{toluene}$	=	100,000 lb toluene used/yr
Q_s	=	1,000,000 lb solvents used/yr
$E_{toluene}$	=	$E_{VOC} \times Q_x/Q_s$
	=	$60{,}000 \times 100{,}000/1{,}000{,}000$
	=	6,000 lb toluene/yr

5.1.4 Total and Speciated VOC Emissions from Solvent Reclamation

VOC emissions from the loading and operation of a distillation device may be calculated using emission factors (EPA, 1995d).

To calculate total VOCs from loading or operation of the distillation device, use Equation 8.5-8:

$$E_{VOC} = EF_{VOC} \times Q_{VOC} \tag{8.5-8}$$

where

E_{VOC}	=	VOC emissions from loading or operation of the distillation device (lb/yr)
EF_{VOC}	=	VOC emission factor for loading of the distillation device or for the distillation column condenser vent (lb VOCs emitted/ton VOCs processed)
Q_{VOC}	=	amount of VOC in spent solvent processed through the distillation device (ton/yr).

Speciated VOC emissions are then calculated using Equation 8.5-9:

$$E_x = E_{VOC} \times C_x/100 \tag{8.5-9}$$

where

E_x	=	emissions of VOC species x from loading or operation of the distillation device (lb/yr)
E_{VOC}	=	VOC emissions from loading or operation of the distillation device, calculated using Equation 8.5-9 (lb/yr)
C_x	=	concentration of VOC species x in the solvent processed through the distillation system (mass %).

Example 8.4-5 illustrates the use of Equations 8.5-8 and 8.5-9.

If the species x concentration is provided on a volume basis, 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 8.5-10:

$$X_x = Y_x \times \frac{M_x}{M} \times 100 \tag{8.5-10}$$

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 molecular weight of the total mixture is not known, the volume percent can be converted to mass percent using Equation 8.5-11:

$$M = \sum_{x=1}^{n} \left(\frac{Y_x}{100} \times M_x \right) \qquad (8.5\text{-}11)$$

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.

Example 8.5-5

First, total VOC emissions from operation of a distillation device may be calculated using an emission factor from *AP-42*, Table 4.7-1 and Equation 8.5-8.

EF_{VOC} = 3.30 lb VOCs/ton solvent processed
Q_{VOC} = 5 tons spent solvent processed/yr

$E_{VOC} = EF_{VOC} \times Q_{VOC}$
$= 3.30 \times 5$
$= 16.5$ lb VOCs emitted/yr

Next, total VOC emissions are speciated using the concentration of VOC species x (mass %) and Equation 8.5-9.

E_{VOC} = 16.5 lb VOCs/yr (calculated above);
C_x = 99% toluene in spent solvent

$E_x = E_{VOC} \times C_x/100$
$= 16.5 \times 99/100$
$= 16.3$ lb toluene emitted/yr

5.1.5 VOC Emissions from Parts Cleaning

VOC emission factors for parts cleaning in cold cleaners, open-top vapor degreasers, or conveyorized degreasers are presented in *AP-42*. Emission factors for cold cleaners and vapor degreasers are in units of tons VOC/yr/unit or lb VOC/hr/ft^2. Emission factors for vapor and nonboiling conveyorized degreasers are presented only in units of ton VOC/yr/unit. If using emission factors based on the surface area of the exposed solvent, use Equation 8.5-12.

$$E_{VOC} = EF_{VOC} \times A \times OH \qquad (8.5\text{-}12)$$

where

E_{VOC}	=	VOC emissions from a cold cleaner or open-top vapor degreaser (lb/yr)
EF_{VOC}[3]	=	VOC emission factor for cold cleaners or open-top vapor degreasers (lb/hr/ft^2)
A	=	surface area of solvent exposed to the atmosphere (ft^2)
OH	=	hours per year that the cold cleaner or vapor degreaser is in operation (hr/yr).

If using emission factors based on the number of cleaning units, use Equation 8.5-13.

$$E_{VOC} = EF_{VOC} \times NU \times 2000 \qquad (8.5\text{-}13)$$

where

E_{VOC}	=	VOC emissions from a cold cleaner, an open-top vapor degreaser, or a conveyorized degreaser (lb/yr)
EF_{VOC}	=	VOC emission factor for cold cleaners, open-top vapor degreasers, or conveyorized degreasers (ton/yr/unit)
NU	=	number of cleaning units in use (units)
2000	=	2,000 lb/ton.

Speciated VOC emissions from parts cleaning may be calculated using Equation 8.5-14:

$$E_x = EF_{VOC} \times C_x/100 \qquad (8.5\text{-}14)$$

[3] Certain halogenated solvents that are widely used for solvent cleaning (e.g., 1,1,1-trichloroethane) have been categorized as "VOC-exempt" by various state and federal regulations. However, the emission factors reported in *AP-42* are still applicable for these solvents (EPA, 1995e).

where

E_x	=	emissions of VOC species x from parts cleaning (lb/yr)
E_{VOC}	=	VOC emissions calculated using Equation 8.5-11 or 8.5-12 (lb/yr)
C_x	=	concentration of VOC species x in cleaning solvent (mass %).

Examples 8.5-6 and 8.5-7 show the application of Equations 8.5-12, 8.5-13, and 8.5-14.

Example 8.5-6

This example shows how total and speciated VOC emissions from a cold cleaner may be calculated using Equations 8.5-12 and 8.5-14 and an emission factor (from *AP-42*, Table 4.6-2) that is based on the surface area of the exposed solvent. First, total VOC emissions are calculated using
Equation 8.5-12.

EF_{VOC} = 0.08 lb/hr/ft^2
A = 5.25 ft^2
OH = 3,000 hr/yr

$E_{VOC} = EF_{VOC} \times A \times OH$
$= 0.08 \times 5.25 \times 3{,}000$
$= 1{,}260$ lb VOC/yr

Next, total VOC emissions are speciated using the concentration of VOC species x (mass %) and Equation 8.5-14.

E_{VOC} = 1,260 lb VOCs/yr (calculated above)
C_x = 99% trichloroethylene in cleaning solvent

$E_x = EF_{VOC} \times C_x/100$
$= 1{,}260 \times 99/100$
$= 1{,}247$ lb trichloroethylene/yr

Example 8.5-7

This example shows how total VOC emissions are calculated from several cold cleaners using Equation 8.5-13 and an emission factor from Table 4-6.2 of *AP-42*.

EF_{VOC} = 0.33 ton/yr/unit
NU = 5 units

E_{VOC} = $EF_{VOC} \times NU \times 2{,}000$
= $0.33 \times 5 \times 2{,}000$
= 3,300 lb VOC/yr

5.1.6 VOC Emissions from Equipment Leaks

Emissions factors for equipment leaks from pumps, valves, and connectors in the coating manufacturing industry were developed from a bagging study conducted to develop equations correlating total organic carbon readings as methane (obtained using Method 21) to VOC emission rate. Using these equations and method 21 screening data for facilities in the industry, average uncontrolled VOC emission factors, on a per component basis, were developed and are presented in the following table (Shine, 2003):

Table 8.5-2. Emission Factors for Equipment Components at Coatings Manufacturing Facilities

Component	Average Emission Factor	
	kg/hr/component	lb/hr/component
Pumps	0.004219	0.009301
Valves	0.000412	0.000908
Connectors	0.000015	0.000033

Additional information regarding various techniques for estimating equipment leak emissions is provided in Chapter 4 of this volume. Example 8.5-8 shows application of the emission factors in Table 8.5-2 to the equipment components for the Bright Blue Paint Company described in Case Study 8.3-1 of this chapter.

Example 8.5-8

The Bright Blue Paint Company in Case Study 8.3-1 uses 15 valves, 10 pumps, and 50 connectors in paint manufacturing operations. Assuming these equipment components are in service 8,760 hr/yr, what are the estimated annual VOC emissions from equipment leaks?

E_{VOC} = (15 values × 0.000908 lb/hr/valve +
10 pumps × 0.009301 lb/hr/pump +
50 connectors × 0.000033 lb/hr/connector) × 8,760 hr/yr
= 949 lb/yr

5.1.7 PM/PM_{10} Emissions from a Paint or Ink Manufacturing Facility

AP-42 also presents PM emission factors from paint and ink manufacturing, which are based on the amount of pigment used by a facility. The *AP-42* factor for paint manufacturing is 20 lb PM/ton pigment. The *AP-42* factor for pigment mixing at an ink manufacturing facility is 2 lb PM/ton pigment. To calculate PM emissions using these emission factors, use Equation 8.5-15.

$$E_{PM} = EF_{PM} \times \Sigma Q_x \qquad (8.5\text{-}15)$$

where

E_{PM} = total PM emissions (lb/yr)
EF_{PM} = PM emission factor (lb PM/ton pigment)
GQ_x = total pigment (ton/yr).

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

Speciated PM emissions are calculated using Equation 8.5-16:

$$E_x = EF_{PM} \times Q_x \times C_x/100 \qquad (8.5\text{-}16)$$

where

E_x = total emissions of PM species x (lb/yr)
EF_{PM} = PM emission factor from *AP-42*, Table 6.4-1 or Table 6.7-1 (lb PM/ton pigment)
Q_x = amount of pigment containing species x used by the facility (ton/yr)
C_x = Concentration of PM species x in pigment x (mass %).

Use of Equation 8.5-16 is demonstrated in Example 8.5-9.

Example 8.5-9

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 6.7-1 of *AP-42* and Equation 8.5-16:

EF_{PM} = 2 lb PM/ton pigment
Q_x = 5 tons ZnO/yr
C_x = 80% Zn in ZnO

$E_x = EF_{PM} \times Q_x \times C_x/100$
$= 2 \times 5 \times 80/100$
$= 8$ lb Zn/yr

5.2 VOC and PM Emission Calculations Using Material Balance

The material balance method requires the totaling of all materials received at the plant and then subtracting out all of the known losses or transfers of the material off-site (including finished product and waste material). The difference is assumed to have been emitted to the atmosphere. The quantity received and the quantity lost or used should be for the same time period, typically January 1 to December 31 for the year of the inventory (NPCA, 1995).

Use Equation 8.5-17 for calculating emissions using the material balance approach.

$$E_x = Q_r - Q_p - Q_{rec} - Q_w - Q_{xi} \quad (8.5\text{-}17)$$

where

E_x = emissions of VOC or PM species x (lb/yr)
Q_r = quantity of VOC or PM species x that is received as a raw material (lb/yr)
Q_p = quantity of VOC or PM species x that is shipped out in the final product (lb/yr)
Q_{rec} = quantity of VOC or PM species x that is recovered by all methods (e.g., solvent recovery) (lb/yr)
Q_w = quantity of VOC or PM species x that is contained in all waste generated during the evaluation period (e.g., wastewater, sludge, drum residue) (lb/yr)
Q_{xi} = quantity of VOC or PM species x that remains in the raw material inventory (lb/yr).

The use of Equation 8.5-17 is demonstrated in Example 8.5-10.

Example 8.5-10

This example shows how total ethylene glycol emissions for a paint manufacturing facility may be calculated using Equation 8.5-17. Data are as follows:

- In a given year, a paint facility receives 100,000 lb of ethylene glycol (Q_r).
- Based on the total amount of product shipped off-site and records of product composition, the facility estimates that the amount of ethylene glycol shipped out in final product (Q_p) is 69,000 lb;
- Based on waste composition analyses, the amount of waste sent off-site, and wastewater discharge rates, the facility estimates that the amount of ethylene glycol that was found in all wastes generated during the year (Q_w) is 5,000 lb; and
- The amount of ethylene glycol that was found to be in the facility's inventory at the end of the evaluation period (Q_{xi}) is 15,000 lb.

Emission of ethylene glycol are calculated as follows:

$$E_x = Q_r - Q_p - Q_{rec} - Q_{xi}$$

$$= 100{,}000 - 69{,}000 - 10{,}000 - 5{,}000 - 15{,}000$$

$$= 1{,}000 \text{ lb ethylene glycol/yr}$$

5.3 Emission Calculations Using Test Data

Because vent or stack testing is relatively uncommon for paint and ink manufacturing facilities, emissions test data for these plants are typically in the form of exposure monitoring results. Industrial hygiene data may be used in conjunction with exhaust system flow rates to calculate fugitive emissions from a room, floor, or building (NPCA, 1995). Use Equation 8.5-18 for calculating these emissions.

$$E_x = \frac{FR \times 60 \times OH \times C_{xt} \times 0.0026 \times M_x}{1 \times 10^6} \qquad (8.5\text{-}18)$$

where

E_x = emissions of VOC or PM species x (lb/yr)
FR = flow rate through exhaust ventilation system (ft^3/min)

60	=	60 min/hr
OH	=	hours per year that the exhaust system is operational (hr/yr)
C_{xt}	=	concentration of VOC or PM species x (ppmv or $ft^3/MMft^3$)
0.0026	=	molar volume of gas at 68°F ($mole/ft^3$)
M_x	=	molecular weight of VOC or PM species x (lb/lb-mole)
1×10^6	=	1×10^6 $ft^3/MMft^3$.

Example 8.5-11 illustrates the use of Equation 8.5-18.

VOC losses from certain operations (e.g., filling of containers) may also be measured by performing a study using a gravimetric analysis such as American Society For Testing and Materials (ASTM) Standard D2369, *Test Method for Volatile Content of Coatings*. The operation under evaluation could be simulated on a small scale, and VOC analysis would be conducted on samples taken before and after the simulated activity (EPA, 1992b).

Example 8.5-11

This example shows how Equation 8.5-18 is used to calculate fugitive emissions of xylenes from a building where several mixing vessels are located. The following data are given:

- The building exhaust flow rate (FR) is 20,000 ft^3/min;
- The exhaust system operates for 7,920 hr/yr (OH);
- Industrial hygiene data indicate that the concentration of mixed xylenes in the building (C_{xt}) is 0.1 ppmv; and
- The molecular weight of mixed xylenes (M_x) is 106 lb/lb-mole.

Xylenes emissions are calculated as follows:

$$E_x = \frac{FR \times 60 \times OH \times C_{xt} \times 0.0026 \times M_x}{1 \times 10^6}$$

$$= \frac{20{,}000 \times 60 \times 7{,}920 \times 0.1 \times 0.0026 \times 106}{1 \times 10^6}$$

$$= 262 \text{ lb xylenes/yr}$$

R5-2014-0104710000203

[This page intentionally left blank.]

6.0 References

Bureau of the Census. 1997. *The Current Industrial Report for Paint, Varnish, and Lacquer* (MA28F) - 1996. United States Department of Commerce. Pages 2 and3.

Crowl, Daniel and Louvar, Joseph. 2002. Chemical Process Safety, Fundamentals With Applications. Second Edition. Practice Hall PTR, Upper Saddle River, NJ 07458. www.phptr.com. ISBN: 0-13-018176-5.

Dean, John, Editor. 1992. Lange's Handbook of Chemistry. Fourteenth Edition. McGraw-Hill.

EIIP. 1996. *Preferred and Alternative Methods for Estimating Air Emissions from Hot-Mix Asphalt Plants, Final Report*. Prepared for the Point Sources Committee, Emission Inventory Improvement Program under EPA Contract No. 68-D2-0160, Work Assignment No. 82. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina.

EIIP. 2000. *How to Incorporate The Effects of Air Pollution Control Device Efficiencies and Malfunctions Into Emission Inventory Estimates*. Chapter 12 in *EIIP Volume II. Point Sources Preferred and Alternative Methods*. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina. (EIIP Internet address http://www.epa.gov/ttn/chief/eiip).

EPA. 1987. *Estimating Releases and Waste Treatment Efficiencies for the Toxic Chemical Release Inventory Form*. U.S. Environmental Protection Agency, Office of Pesticides and Toxic Substances, EPA-560/4-88-002. Washington, D.C.

EPA. 1991. *Control Technologies for Hazardous Air Pollutants Handbook*. U.S. Environmental Protection Agency, Air and Energy Engineering Research Laboratory, EPA-625/6-91/014. Research Triangle Park, North Carolina.

EPA. 1992a. *Control of VOC Emissions from Ink and Paint Manufacturing Processes*. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, EPA-450/3-92-013. Research Triangle Park, North Carolina.

EPA. 1992b. *Protocol for Determining Emissions from Paint and Coating Mixing Processes*. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

EPA. 1994a. *Air Emissions Models for Waste and Wastewater.* U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, EPA-453/R-94-080a. Research Triangle Park, North Carolina.

EPA. 1994b. *Quality Assurance Handbook for Air Pollution Measurements Systems: Volume III, Stationary Source Specific Methods*. U.S. Environmental Protection Agency, Office of Research and Development, EPA-600/R-94-038c. Washington, D.C.

EPA. 1994c. *Control of Volatile Organic Compound Emissions from Batch Processes - Alternate Control Techniques*. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, EPA-453/R-93-017. Research Triangle Park, North Carolina.

EPA. 1995a. *Compilation of Air Pollutant Emission Factors. Volume I: Stationary Point and Area Sources, Fifth Edition, AP-42. Section 7.1, Organic Liquid Storage Tanks*. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina.

EPA. 1995b. *Compilation of Air Pollutant Emission Factors. Volume I: Stationary Point and Area Sources, Fifth Edition, AP-42. Section 6.4, Paint and Varnish*. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina.

EPA. 1995c. *Compilation of Air Pollutant Emission Factors. Volume I: Stationary Point and Area Sources, Fifth Edition, AP-42. Section 5.2, Transportation and Marketing of Petroleum Liquids*. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina.

EPA. 1995d. *Compilation of Air Pollutant Emission Factors. Volume I: Stationary Point and Area Sources, Fifth Edition, AP-42. Section 4.7, Waste Solvent Reclamation*. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina.

EPA. 1995e. *Compilation of Air Pollutant Emission Factors. Volume I: Stationary Point and Area Sources, Fifth Edition, AP-42. Section 4.6, Solvent Degreasing.* U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina.

EPA. 1995f. Memorandum on *AP-42* Emission Factors for the Paint and Varnish Industry from Dennis Beauregard, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, to Robert J. Nelson, National Paint and Coatings Association. Washington, D.C.

R5-2014-0104710000203

EPA. 1995g. *Protocol for Equipment Leak Emission Estimates*. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, EPA-453/R-95-017. Research Triangle Park, North Carolina.

EPA. 1995h. *Survey of Control Technologies for Low Concentration Organic Vapor Gas Streams*. U.S. Environmental Protection Agency, Office of Research and Development, EPA-456/R-95-003. Research Triangle Park, North Carolina. (Internet address, http://www.epa.gov/ttn/catc/dir1/low_vo.pdf)

EPA. 1997a. Toxic Release Inventory System.

EPA. 1997b. *Compilation of Air Pollutant Emission Factors. Volume I: Stationary Point and Area Sources, Fifth Edition, AP-42.* Section 7.1, Organic Liquid Storage Tanks. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina.

EPA. 1999. *Factor Information and Retrieval (FIRE) Database System, Version 6.22.* Updated annually. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. (Internet address, http://www.epa.gov/ttn/chief/fire.html)

EPA. 2000. Source Classification Codes for Point and Area Sources. Updated April 6, 2000. USEPA Technology Transfer Network. http://www.epa.gov/ttn/chief/scccodes.html

Fisher, Perry W., Steven A. Frey, and Kaushik Deb. 1993. *Emission Estimation Methodologies - Paint Manufacturing Industry*, Paper 93-TP-57.07, Air and Waste Management Association, presented at the 86th Annual Meeting and Exhibition, Denver, Colorado, June 13-18, 1993.

Hatfield, Allen. *Improved Algorithum for Estimating Process Emissions From Batch Heating*, Environmental Progress, Vol. 17, No. 3, pp. 190-194. (Fall 1998)

Hatfield, Allen. *A Model for Estimating Process Emissions from Purge Operations in Batch and Continuous Chemical Operations*, Environmental Progress. March 2003.

Mathiessen, R.C. *Estimating Chemical Exposure Levels in the Workplace*, Chemical Engineering Progress. April 1986. p. 30.

NAPIM. 1996. *National Association of Printing Ink Manufacturers Guide to Estimating VOC Emissions from Printing Ink Manufacturing*. National Association of Printing Ink Manufacturers, Inc. Hasbrouk Heights, New Jersey.

NPCA. 1995. *Emission Estimation Guidance Manual for the Paint and Coatings Industry (Second Edition)*. National Paint and Coatings Association, Inc., Washington, D.C.

R5-2014-0104710000203

Noyes, Robert, Editor. 1993. *Pollution Prevention Technology Handbook*. Noyes Publications, Park Ridge, New Jersey.

Shine, Brenda. Development of Equipment Leak Emission Factors at Coatings Manufacturing Facilities. Memorandum to MON Coatings Project Fiel in EPA Docket No. OAR-2003-0178. Docket Item No. IV-B-03. April 30, 2003.

Watson, Douglas. Greenfield Environmental, Inc. Letter to R. McDonald, EPA. Response to Proposed Venting Emission Methodology. September 29, 2004.

R5-2014-0104710000203

COPY

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

OCT 19 1995

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

Mr. Robert J. Nelson
Director
National Paint and Coatings Association
1500 Rhode Island Avenue, Northwest
Washington, D.C. 20005-5597

Dear Mr. Nelson:

This is in response to our meetings on June 9 and August 29, 1995 and your letter of June 14, 1995, regarding Section 6.4 of AP-42 for Paint and Varnish Manufacturing. Based upon information presented at the June 9 meeting by Mr. Frederick Ullrich of Benjamin Moore and Co. and Mr. Robert Ripley of Guardsman Products, Inc., NPCA believes the 30 lbs of volatile organic compound (VOC)/ton of coating emission factor for paint manufacturing in Table 6.4-1 is incorrect and should be expressed in terms of solvent used to formulate coatings.

As I discussed during our meeting on August 29, 1995, I have reviewed the background files for Section 6.4 to document the derivation of the emission factor in Table 6.4-1 and the estimate of solvent losses in the text. The following summarizes the results of my findings:

The 30 lbs of VOC/ton of coating emission factor in Table 6.4-1 of AP-42 is discussed in Reference 1 to the Section. Pages 4-45 and 4-46 of Reference 1 indicate that the factor is based upon material balances and represents "all atmospheric losses." Although the emission factor in Table 6.4-1 is identified as "uncontrolled", it apparently reflects the use of "good housekeeping" practices such as keeping lids closed during mixing. This is supported by Reference 2 to the Section which states on Page 13 that "Although some plants use open vat mixing with certain solvents, the volatilility of most thinners requires that mixing be done in totally enclosed tanks to prevent appreciable losses of these expensive products."

Another estimate of VOC emissions from paint manufacturing is found in the text of Section 6.4. The estimate is from Reference 2 on Page 13 which states that "In general, the loss of solvents to atmosphere from such mixing amounts to no more than 1 or 2% of the solvent used." This statement indicates that the 1 to 2% loss estimate applies only to mixing at paint manufacturing and does not include other operations.

The emission estimates used to develop the emission factor in Table 6.4-1 appear to be based upon formulation of "conventional" coatings that were prevalent during the late 1950's and early 1960's. At that time, coating densities were typically 10 to 15 lbs/gallon (Reference 2, Page 4-47). Assuming an average coating density of 12.5 lbs/gallon, a ton of coatings would yield 160 gallons. Assuming an average solvent content for "conventional" coatings of 5.5 lbs of VOC/gallon of coating ("Control of Volatile Organic Compound Emissions from Existing

Stationary Sources - Volume VI: Surface Coating of Miscellaneous Metal Parts and Products," EPA-450-2-78-015, Page 1-10), 880 lbs of the coatings would be solvent. The 30 lbs of VOC/ton of coating emission factor would therefore be equivalent to a loss rate of 30 lbs of VOC/880 lbs of VOC or 3.4% on the basis of solvent used. This seems to compare favorably with the 1 to 2% loss estimate in the text which only accounts for losses from mixing.

In summary, it appears that the 30 lbs of VOC/ton of coating emission factor in Section 6.4 is expressed as the author intended. It was likely developed based upon the formulation of conventional coatings and represents use of good housekeeping practices. An alternative to using this factor for the formulation of waterborne or high solids coatings would be use of the equivalent solvent loss rate of 3.4% for the overall operation.

As we discussed during our meeting on August 29, 1995, I have enclosed the August 1992 redraft of the AP-42 section for paint and varnish manufacturing. At that time, we were not able to identify any new emissions information to update the emission factors in AP-42. Although the narrative portion of the section was updated and expanded, NPCA commented that additional efforts were needed to adequately address newer coating technologies. Any comments that NPCA and its members may be able to provide regarding the technical adequacy of the information and specific areas needing improvement would be appreciated.

Finally, as we discussed, the Point Sources Committee of the Emission Inventory Improvement Program (EIIP) is developing a document for estimating emissions from paint manufacturing operations. I will forward a copy of the draft document for your review and comment upon its availability. The EIIP guidance document will establish a hierarchy of emission estimation techniques based primarily upon the accuracy of the methods and will allow users to select a method best suited to their needs.

Please contact me (919) 541-5512 with any questions or comments regarding this matter.

Sincerely,

Dennis Beauregard

Dennis Beauregard
Environmental Engineer
Emission Factor and Inventory Group

Enclosure