

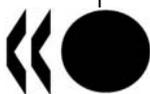
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EMISSION SCENARIO DOCUMENT ON ADHESIVE FORMULATION

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**EMISSION SCENARIO DOCUMENT ON ADHESIVE
FORMULATION**

IOMC

**INTER-ORGANISATION PROGRAMME FOR THE
SOUND MANAGEMENT OF CHEMICALS**

**A cooperative agreement among
UNEP, ILO, FAO, WHO, UNIDO, UNITAR and OECD**

Environment Directorate

ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

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EXPLANATORY NOTES

Purpose and background

This OECD Emission Scenario Document (ESD) is intended to provide information on the sources, use patterns, and potential release pathways of chemicals used in the adhesive formulation industry. The document presents standard approaches for estimating the environmental releases of and occupational exposures to additives and components used in adhesive formulations. These approaches are intended to provide conservative, screening-level estimates resulting in release and exposure amounts that are likely to be higher, or at least higher than average, than amounts that might actually occur in the real world setting.

This ESD may be periodically updated to reflect changes in the industry and new information available, and extended to cover the industry area in countries other than the lead (the United States). Users of the document are encouraged to submit comments, corrections, updates, and new information to the OECD Environment, Health and Safety Division (env.riskassessment@oecd.org) and U.S. Environmental Protection Agency (EPA) (EPA contact: Nhan Nguyen, nguyen.nhan@epa.gov). The comments received will be forwarded to the OECD Task Force on Environmental Exposure Assessment, which will review the comments every two years so that the lead country can update the document. Submitted information will also be made available to users within the OECD web site (www.oecd.org/env/riskassessment).

How to use this document

This document may be used to provide conservative, screening-level estimates of environmental releases of and occupational exposures to both volatile and nonvolatile chemical components contained in an adhesive formulation. Such estimates might result in release and exposure amounts that are likely to be higher, or at least higher than average, than amounts that might actually occur in real world practice.

The users of this ESD should consider how the information contained in the document emulates the specific scenario being assessed. Where specific information is available, it should be used in lieu of the defaults presented in this document, as appropriate. All input values (default or ESD-specific) and the estimated results should be critically reviewed to assure their validity and appropriateness.

Coverage and methodology

EPA developed this ESD using relevant data¹ and information on the adhesives formulation industry, including process descriptions, operating information, chemicals used, wastes generated, waste treatment, worker activities, and exposure information. EPA supplemented the data collected with standard models² to develop the environmental release and occupational exposure estimating approaches presented in this ESD.

The primary sources of information cited in this ESD include the Kirk-Othmer Encyclopedia of Technology, Ullmann's Encyclopedia of Industrial Chemistry, the U.S. Census Bureau's County Business Patterns and Annual Survey of Manufacturers, and various EPA and other government sources (e.g., CEB, Environment Canada, OECD, the Toxic Release Inventory (TRI), and regional/state pollution prevention organizations). Additional information on the sources investigated and the references cited in this document are presented in Section 8. After reviewing these sources, EPA contacted the Adhesives and Sealants Council (ASC)³ to obtain additional input on this ESD.

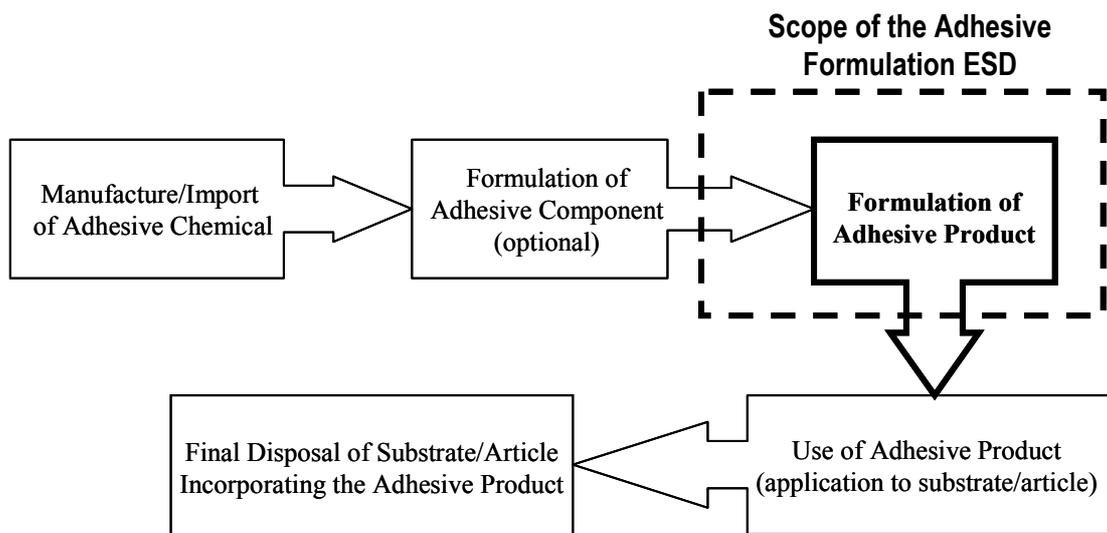
The information in this document is based on U.S. data. Certain aspects of the adhesives formulation process may differ in other countries; therefore, alternate assumptions and parameters may be necessary in some applications of this emission scenario.

This ESD includes methods for estimating the environmental releases of and associated occupational exposures to both volatile and nonvolatile chemical components used to formulate adhesive products. The ESD covers the blending of the components into adhesive formulations. It does not cover the manufacture of chemical raw materials or component products, nor does it cover the application of the formulated adhesive product to a surface or substrate. The EPA is currently developing an ESD on the use of adhesives. An illustration of the scope of this ESD within the context of the life cycle of the chemical of interest is provided below.

¹ Please refer to Section 8 for a list of the specific references used in developing this ESD.

² EPA has developed a series of "standard" models for use in performing conservative release and exposure assessments in the absence of chemical- or industry-specific data. Several of these standard models are described in Appendix B to this ESD.

³ The ASC is the leading trade association for the U.S. adhesives manufacturing industry. Visit <http://www.ascouncil.org/> for more information.



This ESD describes the following general categories and types of adhesives:

- Solution (either water-based or organic solvent-based);
- Solventless (e.g., hot-melts);
- Reactive (e.g., epoxies, urethanes, and silicones); and,
- Pressure-sensitive (may be formulated as solution, solventless, or reactive adhesives before being incorporated into the final product).

The formulation of radiation-curable reactive adhesives is covered under an ESD on the Formulation of Radiation Curable Coatings, Inks, and Adhesives, and is not included in this ESD.

Adhesives are generally composed of a binder material formulated with other components. Binders are typically natural or synthetic high molecular weight polymers. Binders may alternatively contain reactive organic compounds (e.g., prepolymers, oligomers, monomers) that form polymers during the bonding process. Some materials commonly used as binders in adhesive formulations are esters, natural and synthetic rubber, polyvinyl compounds, polyurethanes, epoxy resins, and acrylate polymers. Adhesives may also contain components such as non-reactive resins, plasticizers, fillers, thickeners, solvents, hardeners, and setting retarders (Ullmann, 1985).

To estimate environmental releases, this ESD assumes that volatile chemicals may be released to air at certain points in the process, and that associated inhalation exposures to the chemical vapors may occur as a result of handling those chemicals. Each ESD user will have to decide the definition of what constitutes *volatile* based on the specific objectives of the assessment. For example, EPA often assumes chemicals with a vapor pressure less than 0.001

torr are nonvolatile. Nonvolatile chemicals result in negligible releases to air from volatilization and negligible associated inhalation exposures (CEB, 1991).

Methods for estimating the following releases and exposures to components used to formulate adhesive products, and associated facility operating parameters are discussed in this ESD:

- Number of sites in the United States formulating adhesive products containing the chemical of interest, and the duration of these activities;
- Releases from transport container residue (via container cleaning or direct disposal of empty containers);
- Releases during transfer from the container into the process (storage or mixing vessel);
- Releases of volatile chemicals vented from the equipment during the formulation process;
- Releases during product quality sampling;
- Releases from equipment cleaning;
- Releases of volatile chemicals during packaging;
- Releases from the disposal of off-spec adhesive product;
- Number of workers that may come into contact with the adhesive components;
- Inhalation and dermal exposures during container unloading;
- Inhalation and dermal exposures during container cleaning and disposal;
- Inhalation exposure during unsealed formulation process operations;
- Inhalation and dermal exposures during product quality sampling activities;
- Inhalation and dermal exposures during equipment cleaning; and,
- Inhalation and dermal exposures during packaging.

The estimation methods in this ESD apply to any volatile or nonvolatile adhesive component, regardless of its function within the adhesive formulation.

How this document was developed

The U.S. Environmental Protection Agency (EPA) with support from Eastern Research Group, Inc. (ERG) has developed this ESD. The scope of the ESD is designed to serve the needs of both EPA and OECD programs. The Chemical Engineering Branch (CEB) of EPA's Office of Pollution Prevention and Toxics (OPPT) is responsible for preparing occupational exposure and environmental release assessments of chemicals for a variety of programs under the Toxic Substances Control Act (TSCA), including Premanufacture Notice (PMN) reviews. While OECD ESDs traditionally focus on the potential releases of chemicals from industrial processes, this document also describes approaches for estimating potential occupational exposures to adhesive chemicals. The occupational exposure methods are included so that the ESD may be used to fully support EPA's chemical review programs.

This ESD supersedes the EPA's Chemical Engineering Branch's (CEB) undated and unpublished *CEB Cheat Sheets: Adhesive Manufacturing* document (CEB, no date). This earlier document has been revised and expanded to meet EPA's revised quality standards for generic scenarios (CEB, 2006a).

A first draft ESD was circulated to the Task Force and posted on the OECD website in April 2006. Comments were received from Canada and the United Kingdom and have been incorporated into this document. Comments on an early draft of this ESD were also received in January 2006 from Canada. Data supplied by Canada with their comments were reviewed and found to be comparative to the U.S. data described in the main body of this ESD. These Canadian data have been included in Appendix C to this ESD. A revised version was submitted to OECD in August 2006 and discussed at the meeting of the Task Force in September 2006. Since the aforementioned draft, EPA has also incorporated comments received from the United Kingdom in February 2008, and has made the following modifications to the ESD:

- The August 2006 draft did not provide methodology for estimating dust emissions from unloading solid powder components. EPA has since developed a standard model for estimating dust emissions from transferring solids and added this methodology to the ESD.
- Additional background information on adhesives was added to the ESD based on research conducted by EPA to develop an ESD on the use of adhesives.

This document is published on the responsibility of the Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology of the OECD.

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1 INDUSTRY SUMMARY AND BACKGROUND

The following subsections provide descriptions of the adhesive industry and the types of adhesives produced in the United States.

1.1 Introduction to Adhesives

An adhesive is any substance capable of holding two objects together in a functional manner through non-mechanical means (Kirk-Othmer, 2002). Adhesives are generally composed of a binder material formulated with other components. Binders are typically natural or synthetic high molecular weight polymers. Binders may alternatively contain reactive organic compounds (e.g., prepolymers, oligomers, monomers) that form polymers during the bonding process. Some materials commonly used as binders in adhesive formulations are esters, natural and synthetic rubber, polyvinyl compounds, polyurethanes, epoxy resins, and acrylate polymers. Adhesives may also contain components such as non-reactive resins, plasticizers, fillers, thickeners, solvents, hardeners, and setting retarders (Ullmann, 1985).

Adhesives are capable of producing a strong, lightweight bond at a relatively low cost when compared to screws, bolts, or welds. These materials form a bond between two substrates by wetting the surfaces and subsequently setting, curing, or adhering to form a strong bond. Figure 1-1 presents a cross section of an adhesive bond.

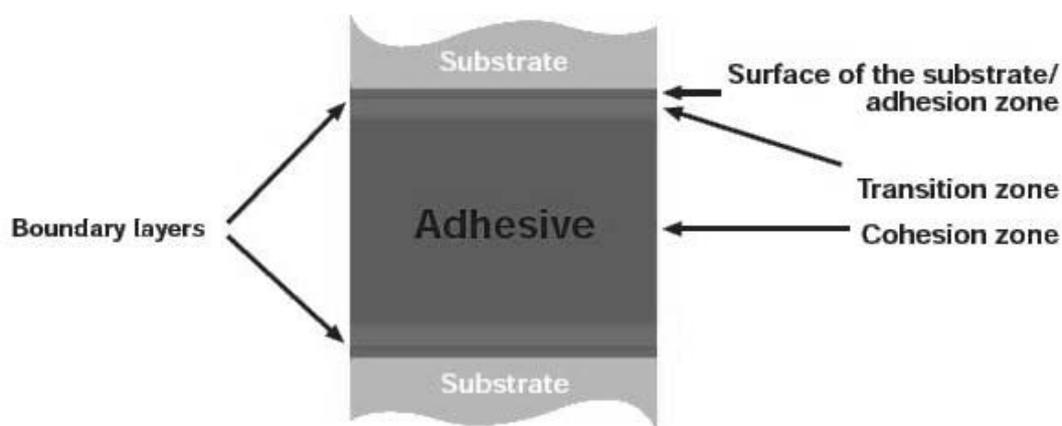


Figure 1-1. Cross Section of an Adhesive Bond

Source: FEICA, 2004.

Adhesive bond strength is dependent on both the cohesion and adhesion properties of the adhesive. Cohesion is the inner strength of the adhesive (i.e., how well the adhesive sticks

to itself based on chemical bonds, crosslinking, and other intermolecular forces). Adhesion is the strength of the bond between the adhesive and the substrate (FEICA, 2004).

Several different theories have been developed to explain the mechanism of adhesion; however, none has been proven to completely explain the adhesion process. The mechanism of adhesion is a complex addition of various effects, not a consistent or isolatable process (Ullmann, 1985). Some theories that may combine to explain the mechanism of adhesion are listed below. These theories may be applicable to all types of adhesives (Ullmann, 1985).

- Mechanical Adhesion Theory – The adhesive polymer mechanically anchors to the pores and irregularities in the substrates.
- Electrostatic Theory of Adhesion – Electron transfer potentials (i.e., the tendency of electrons to flow to positive charges or away from negative charges) cause the buildup of electrostatic forces at the boundary layer between the adhesive and the substrate.
- Adsorption Theory – Secondary valence or van der Waal's forces (i.e., intermolecular attractive forces) between the adhesive and the substrate cause adhesion.
- Diffusion Theory – The adhesive polymer and substrate mutually penetrate then dissolve in each other and cure to form a solid bond.
- Liquid Adhesion – The adhesive polymer creates a thin film of an extremely high viscosity liquid causing surface tension (i.e., the tendency of interior molecules to draw the surface molecules into the bulk of the liquid and minimize the liquid surface area) between the two substances.

1.2 Industry Sector Description

Due to technological advances, the adhesive and sealant industry is rapidly changing and growing. In the late 1990s, the estimated global production of adhesives and sealants was expected to more than double between 1996 and 2002 and to grow by as much as four percent each year through 2005. Adhesives comprise more than 80 percent of the adhesives and sealants industry (Kirk-Othmer, 2002).

The variety of existing adhesives and the increasing number of hybrid adhesives (i.e., multiple types of adhesives combined to utilize the strengths of each type) make it difficult to concisely categorize these compounds; however, three general adhesives classifications are solution, solventless/solid (e.g., hot-melts), and reactive adhesives. Pressure sensitive adhesives (PSAs) are unique in that, while typically formulated as solution adhesives initially, they are inherently tacky and often incorporated as a thin film coated on a continuous web before being sold for use (e.g., tapes, labels). PSAs remain the same chemically throughout their useful life and do not undergo a chemical transformation in order to bond to a substrate. Table 1-1 provides a list of typical binders or polymers that are used in the solution, hot-melt, and PSA adhesive

types. Note that reactive adhesives do not contain polymers; instead they form polymers when used.

Table 1-1. Typical Polymers used in Solution, Hot-melt, and Pressure Sensitive Adhesives

| Adhesive Type | Typical Polymers Used as Binder |
|--------------------------------|--|
| Water-Based Solution | Natural polymers, polyurethane dispersions, polyvinyl alcohol (PVA), polyvinyl acetate (PVAC) emulsions, polychloroprene |
| Organic Solvent-Based Solution | Natural rubber, polychloroprene, polyurethane, styrene-butadiene-styrene block polymers, styrene-butadiene rubber (SBR), butadiene-acrylonitrile rubber, acrylic or vinyl resins |
| Pressure-Sensitive | Natural rubber, polybutadiene, polyorganosiloxanes, SBR, carboxylated styrene-butadiene rubber, halogenated butyl rubber, polyalkyl acrylate homopolymers/ copolymers, polyvinyl ethers, amorphous polyolefins, block polymers based on styrene with isoprene, butadiene, ethylene-propylene, or ethylene-butylene |
| Hot-Melt | Ethylene-vinyl acetate copolymers, styrenic block polymers, synthetic elastomers, ethylene-ethyl acrylate copolymers, amorphous polyolefins, branched polyethylenes, polypropylene, polybutene-1, phenoxy resins, polyamides, polyesters, polyurethanes |

Source: Kirk-Othmer Encyclopedia of Chemical Technology, 2002.

1.2.1 *Solution Adhesives*

Solution adhesives contain a synthetic or natural binder material and other components dispersed within an organic solvent or water. In organic-solvent based solution adhesives, the adhesive polymer is typically dissolved within the solvent. Most water-based solution adhesives are aqueous dispersions. In solution adhesives the adhesive polymers do not cure (i.e., undergo a chemical reaction); rather they set via evaporation of the solvent (with or without heat) once applied to a substrate. Solution adhesives can be used on a wide range of substrates, such as wood, paper, plastic, metal, rubber, silicate-containing materials, moistenable adhesive tapes, and fiberboard (Ullmann, 1985).

Many solution adhesives are used for joining large surface areas. Major end uses of solution adhesives are carpet manufacturing (attaching carpet fibers to backing material), construction (gluing down carpet, tiles, wood flooring, and wall paper), packaging (making envelopes, paper bags, and paper-board cartons and tubes), and furniture manufacturing (woodworking and laminates) (Kusumgar, 2000). Solution adhesives are also used in many consumer products, such as Elmer's® glue (water-based), rubber cement (organic solvent-based), and adhesives to seal envelopes (water-based, but remoistenable). Many PSAs are formulated as solution adhesives, but are subsequently incorporated onto a continuous web without their solvent. PSAs are described in detail in Section 1.2.4.

Due to increasing volatile organic compound (VOC) emission and exposure regulations, the industry has shifted away from the use of organic solvents. For example, in 1985

approximately 50 percent of flooring installation adhesives were water-based and 50 percent organic-solvent based. In 2003, water-based adhesives comprised over 90 percent of the same market (FEICA, 2004).

1.2.2 Hot-Melt Adhesives

Hot-melt adhesives comprise polymeric compounds that are solids at room temperature. When used, they are heated to form a molten liquid, and adhere firmly to surfaces when cooled. They do not set via a chemical reaction. Hot-melt adhesives are most often used in packaging, bookbinding, disposable paper products, shoe making, and textile binding. Consumers may use hot-melt adhesives in hot-glue guns (e.g., in arts and crafts activities). They are considered environmentally friendly, because they are solvent-free and thus, their market share is expected to increase in the early 21st century (Kirk-Othmer, 2002).

1.2.3 Reactive Adhesives

In reactive adhesives, the adhesive polymer is formed after the formulation has been applied to the substrate then cured by one of the following mechanisms.

- Polymerization - A chemical reaction in which two or more molecules combine to form larger molecules that contain repeating structural units. Polymerization adhesives harden through radical or ionic polymerization of the monomers often concurrent with graft polymerization or crosslinking of unsaturated polymers (Ullmann, 1985).
- Polyaddition – A polymerization reaction in which monomers containing multiple-bonds (e.g., C=C) combine through an addition reaction, forming chains of singly bonded atoms (e.g., -C-C-C...) (Silberberg, 2000).
- Polycondensation – A polymerization reaction in which monomers with two functional groups are linked together via a dehydration-condensation reaction (i.e., H- and OH- groups on separate molecules react to form water as a product) (Silberberg, 2000).

These reactive formulations are significantly different from the other categories of adhesives (i.e., solution and hot-melt adhesives) because they do not contain an adhesive polymer. Rather, they contain unreacted prepolymers, oligomers, or monomers that react to form a crosslinked polymer at the point of application. The resulting polymer serves as the adhesive, binding the surfaces together. Reactive adhesive products are typically marketed as one of the following (Ullmann, 1985):

- 2-Part System – Reactive components are kept separate until they are used, at which point they must be mixed together to initiate the curing/crosslinking reaction.

- 1-Part System – Reaction is initiated by exposure to the air, moisture, or heat.
- No-Mix System – Components of the reaction are pre-applied to each surface to be adhered and the bond forms instantly when the two surfaces are brought together.

Reactive adhesives are used to bond metals, plastics, silicate-containing materials, rubber, and wood (high-strength spot or small-area bonds) (Ullmann, 1985). Table 1-2 presents the general classification of reactive adhesives and examples of each category.

Table 1-2. General Classification of Reactive Adhesives

| Curing Mechanism | Examples |
|------------------|--|
| Polymerization | <ul style="list-style-type: none"> • Cyanoacrylates: cure initiated by moisture; type of adhesive in industrial and consumer superglue. • Methyl Methacrylates (MMA): 2-part system; used in automobile and rail vehicle manufacturing. • Anaerobic adhesives (e.g., dimethyl acrylates): cure upon contact with copper or iron in the absence of oxygen. • Radiation-curable adhesives^a: cure upon exposure to ultra-violet or electron beam radiation; can only be used if one substrate allows light to penetrate to the adhesive. |
| Polyaddition | <ul style="list-style-type: none"> • Epoxies: 1-Part heat cured (including reactive hot-melts) or cold curing 2-Part systems; used in many industries, including automotive, aerospace, construction, electronics (with conductive additives), and plastics. • Polyurethanes: cold curing 2-Part, heat curing 1-Part, or moisture-curing 1-Part systems; used across most industries. |
| Polycondensation | <ul style="list-style-type: none"> • Phenol-formaldehyde resins: heat cured; good for high temperature applications (e.g., automotive brake pads, aerospace); also used extensively in furniture manufacturing. • Silicones: cold curing 2-Part or moisture-curing 1-Part systems; excellent resistance to UV light, moisture, and weathering; low adhesive strength; mainly used as sealants. • Polyimides: typically require an autoclave to cure; used in high-quality, high-temperature metal bonds in aerospace applications. |

Source: FEICA, 2004.

a - Radiation-curable adhesives are covered under a separate ESD being developed by EPA.

Two commonly used reactive adhesives are epoxy adhesives and moisture-curable adhesives.

Epoxy adhesives are commonly formulated into 2-part systems. One mixture will primarily contain the epoxy resin; the other will contain the hardener (catalysts and crosslinkers). Typical hardeners are aliphatic and cycloaliphatic amines, adducts of polyamines, phenol-amine combinations, and polyaminoamides (Ullmann, 1985). Epoxies may also be formulated into a one-part, heat-activated mixture, usually requiring temperatures above 100°C to cure. Typical hardeners for heat-activated epoxies are dicarboxylic acid anhydrides, dicyanodiamide, and aromatic amines (Ullmann, 1985).

Moisture-curable adhesives (e.g., silicone- and urethane-based sealants used to line bathroom fixtures) cure when exposed to atmospheric moisture (Ullmann, 1985). The atmospheric moisture neutralizes the acidic stabilizer in the adhesives causing rapid polymerization. Optimal curing conditions for moisture-curable adhesives are room temperature with a relative humidity between 40 percent and 60 percent (Petrie, 2004). Lower humidity slows curing; however, higher humidity may lower the bond strength. The most popular moisture-curable adhesive resins are cyanoacrylates, silicones, and polyurethanes (Petrie, 2004).

1.2.4 Pressure-Sensitive Adhesives

Pressure-sensitive adhesives (PSAs) contain binders that are permanently soft, tacky substances that adhere spontaneously to surfaces with very little pressure. Most PSAs are initially formulated as a water- or organic solvent-based solution, and then applied to a continuous web substrate where the solvent is removed by evaporation before being sold as a component of various industrial and consumer products. PSAs may also be formulated as solventless (e.g., hot-melts) or reactive adhesives but most are solution based (Petrie, 2005). Typical PSA products include duct, masking, or packaging tapes, and self-adhesive labels and stamps. PSA tapes may also be used for industrial applications (e.g., construction and automobile manufacturing).

PSAs differ from other adhesive types because they remain soft, tacky, and ready for use after solvent evaporation. Many PSAs can also be easily removed from one substrate and placed on another (e.g., moving a self-stick note). In contrast, once other adhesives are applied and set, they have hardened and bonded to the substrate (Kirk-Othmer, 2002).

1.3 Market Profile and Adhesive Production

Adhesive manufacturing facilities fall under the North American Industry Classification System (NAICS) code 32552. The U.S. Census Bureau defines this industry as comprising establishments primarily engaged in manufacturing adhesives, glues, and caulking compounds. According to the 2003 County Business Patterns data, 592 establishments within the United States were classified within this NAICS code and employed a total of 21,048 workers (USCB, 2003).

The total U.S. adhesive production in 1999 was estimated at approximately 15 billion pounds, and was anticipated to grow by 2 billion pounds by 2004 (Kirk-Othmer, 2002). Table 1-3 presents a summary of the U.S. production for the various types of adhesives. Table 1-4 and Table 1-5 present a summary of the U.S. PSA and reactive adhesives markets, respectively.

Seven companies dominate the adhesives market, producing 49 percent of the adhesives sold worldwide in 1999. The remainder of the market is highly fragmented with approximately 500 companies operating in the U.S. (Kirk-Othmer, 2002).

Table 1-3. Estimated U.S. Adhesive Production in 1999

| Adhesive Type | Percentage of Production ^a | U.S. Production | |
|-------------------------|---------------------------------------|-----------------------------|--------------------------------|
| | | million pounds ^b | million kilograms ^c |
| Water-Based | 73 | 11,000 | 4,990 |
| Organic Solvent-Based | 6 | 900 | 410 |
| Hot-Melt | 14 | 2,100 | 950 |
| Other Liquid (Reactive) | 7 | 1,000 | 450 |
| Total | 100 | 15,000 | 6,800 |

a - Source: Kusumgar, 2000.

b - Individual adhesive type productions are estimated from the total U.S. adhesive production (15 billion pounds – Kirk-Othmer, 2002) and the relative percentage of the market for each adhesive type. Note: it is not known whether these production amounts include imported adhesive products formulated outside of the U.S. but sold within the U.S. adhesive market.

c - Calculated based on a conversion factor of 2.2046 lbs/kg.

Table 1-4. U.S. PSA Production in 1999

| | Total | Water-Based PSA | Other PSA ^a |
|--------------------------------------|-------|-----------------|------------------------|
| Million dry pounds ^b | 600 | 230 | 370 |
| Million dry kilograms ^c | 270 | 100 | 170 |
| Million “wet” kilograms ^d | 540 | 200 | 340 |

a - PSAs may also be formulated into organic solvent-based or solventless, hot-melt adhesives (Kirk-Othmer, 2002), as well as reactive (Petrie, 2005). “Other” PSAs are assumed to encompass all types of non-water-based PSAs.

b - Source: Kusumgar, 2000. Kusumgar estimated that 38% of all U.S. PSAs are water-based.

c - Calculated based on a conversion factor of 2.2046 lbs/kg.

d - “Wet” quantities are estimated assuming a solids content of 50%. This assumption is based on sources generally estimating 40-60% solids content in water-based adhesives (Ullmann, 1985) and less than 10% in organic solvent-based PSAs (NEWMOA, 1999).

Table 1-5. U.S. Reactive Adhesive Production in 1997

| Adhesive Type | U.S. Production | |
|----------------|-----------------------------|--------------------------------|
| | million pounds ^a | million kilograms ^b |
| Urethanes | 143.1 | 64.9 |
| Cyanoacrylates | 34.9 | 15.8 |
| Epoxies | NA | NA |
| Silicones | NA | NA |

a - Source: USCB, 1997.

b - Calculated based on a conversion factor of 2.2046 lbs/kg.

NA – Not available. U.S. production data for these types of reactive adhesives have not been identified to date.

1.4 Adhesive Application

The application of adhesives is outside the scope of this ESD. Note, however, that the application technique depends greatly on the type of adhesive. Typical application techniques for each adhesive category are:

- Solution adhesives—generally applied via spray, curtain, or roll coating techniques (Ullmann, 1985);
- PSA solutions—generally roll coated onto a paper, plastic, or other substrate backing to manufacture tape and other PSA products (Kirk-Othmer 2002), or applied via a metered “curtain” or extrusion/slot die (for hot-melt/low viscosity formulations) (Mausar, 2005);
- Hot-melt adhesives—must be heated prior to application and are typically applied via a hot-melt gun; however, these adhesives may also be applied via roll coating and spray coating (rarely) (Ullmann, 1985); and,
- Reactive adhesives—applied via roll or spray coating (Ullmann, 1985), often in two solutions that are mixed at the point of application.

EPA is currently developing an ESD on the application of adhesives to substrates.

2 PROCESS DESCRIPTION

This ESD focuses on the formulation of an adhesive product. It does not cover the manufacture of the chemical raw materials or component products or the application of the formulated adhesive product to a surface or substrate.

Adhesives are formulated by mixing together volatile and nonvolatile chemical components, such as binders and components in sealed, unsealed, or heated processes. The specific formulation process used depends on the type of adhesive being produced (ASC, 2005). The three general process types each have distinct sources of release and worker exposure activities. Figures 2-1, 2-2, and 2-3 illustrate these adhesive process types. The following sections describe each type of process in more detail.

2.1 Sealed Mixing/Transfer

Because many adhesives are designed to set or react when exposed to ambient conditions, most are formulated in a sealed process. A sealed process is also likely to be used in cases where environmental or health hazards are associated with the chemicals used to formulate the adhesive (e.g., isocyanates) (ASC, 2005). Figure 2-1 illustrates the sealed adhesive formulation process and the associated release sources and worker exposure activities.

Typically, solid or liquid adhesive binders and components are unloaded from transport containers (tank trucks, totes, drums, sacks) either directly into the mixing equipment or into intermediate storage tanks (Release 3 or Release 4, Exposure A). If the component is in the solid/powdered form, it is assumed that some amount of the component will be lost during the transfer as dusts released into the workspace air that will be subsequently vented to the air outside of the facility or settle out within the workspace. Dusts that collect on vent filters or within the workspace are collected and disposed (Release 4, Exposure A).

No specific information was found regarding the handling of empty transport containers by the adhesives formulation industry. While transport containers may be cleaned off site by a third party, this ESD assumes that the container residues are disposed by the receiving formulating facility, either by being rinsed from the container or the empty container being discarded directly into an off-site landfill (Release 1, Release 2, Exposure B).

In a sealed process, the mixing occurs with no direct contact from the workers in closed vessels. Typically, a high-speed dispenser combines the components using precise settings to avoid overstirring, which may adversely affect the viscosity and other properties of the adhesive (Ullmann, 1985). It is assumed that the sealed system captures the volatile components released during the mixing process and vents them through a stack to air outside the facility (Release 5). Because the process is sealed, worker exposure to the component vapors vented from the mixing vessel is expected to be negligible.

Although no industry-specific data were found regarding product sampling practices at adhesive formulators, it is generally assumed that some amount of product quality analysis/quality control (QA/QC) sampling is performed as part of the formulation process (engineering judgment). Releases and associated exposures are expected to occur as a result of sampling activities (Release 6, Release 7, Exposure D).

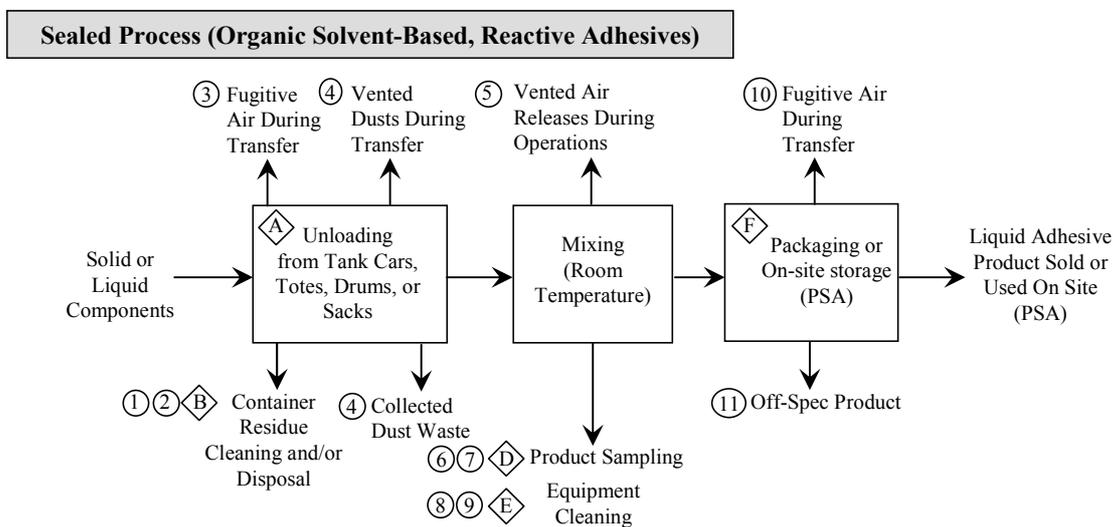
Formulated adhesives are expected to be shipped to the end user in a variety of container sizes, depending on the type of product. For example, consumer adhesive products, such as craft glue, may be sold directly for consumer or commercial use in small containers. In contrast, industrial glues (e.g., those used in carpet or plywood manufacture), may be transported in bulk (e.g., drums, totes, or tank cars). The adhesive product containers may be filled from storage tanks by workers connecting transfer lines to tank cars, totes, or drums (industrial adhesives), or by large automated bottling systems (consumer or commercial adhesives loaded and sold in small quantities) (Release 10, Exposure F).

Limited information was found regarding standard equipment cleaning practices within the adhesives formulation industry. The formulation process equipment is expected to be routinely cleaned and the residues disposed to either water, incineration, or landfill. While some facilities may clean process equipment after a certain number of batches within a formulation campaign, this ESD assumes that the residues from each batch are removed prior to the next one as a conservative estimate (Release 8, Release 9, Exposure E).

A certain amount of off-spec adhesive product is also expected to be released (i.e., disposed) from the formulation site (Release 11). No specific information was found regarding the specific method of disposing off-spec adhesive product for the adhesives formulation industry.

As previously discussed, PSAs are often applied and incorporated into a tape or label prior to their ultimate distribution to end users. In most cases, the application of the PSA to the web substrate is performed at the formulation site prior to packaging and shipping (Kirk-Othmer, 2002); therefore, PSAs are expected to be transferred to on-site storage tanks instead of into transport containers. Note: this ESD addresses the formulation of the PSA and its transfer into the on-site storage only. The application of the PSA to the continuous web substrate is outside the scope of this ESD.

For the purposes of this ESD, it is assumed that organic solvent-based and reactive adhesives (including organic solvent-based PSAs) are formulated in a sealed process.



○ = Environmental Releases:

1. Container residue from adhesive component transport container released to water, incineration, or landfill.
2. Open surface losses of volatile chemicals to air during container cleaning.
3. Transfer operation losses to air of volatile chemicals from unloading the adhesive component.
4. Dust losses vented to outside air from the transfer of a solid/powdered adhesive component into the process. Alternatively, these dusts are captured on vent filters or settle within the workspace, and are subsequently collected and released to water, incineration, or landfill.
5. Vented losses of volatile chemicals to air during mixing operations.
6. Product sampling wastes disposed to water, incineration or landfill (not quantified in this ESD).
7. Open surface losses of volatile chemicals during product sampling.
8. Equipment cleaning releases to water, incineration, or landfill.
9. Open surface losses of volatile chemicals to air during equipment cleaning.
10. Transfer operation losses of volatile chemicals to air from loading adhesive product into transport containers.
11. Off-spec adhesive product released to water, incineration, or landfill.

◇ = Occupational Exposures:

- A. Inhalation and dermal exposure from unloading solid or liquid adhesive components.
- B. Inhalation and dermal exposure to solid or liquid adhesive components during container cleaning.
- D. Inhalation and dermal exposure to liquid adhesive product during sampling activities.
- E. Inhalation and dermal exposure to liquid during equipment cleaning of mixing and other process equipment.
- F. Inhalation and dermal exposure to liquids during the packaging of adhesive formulations into containers.

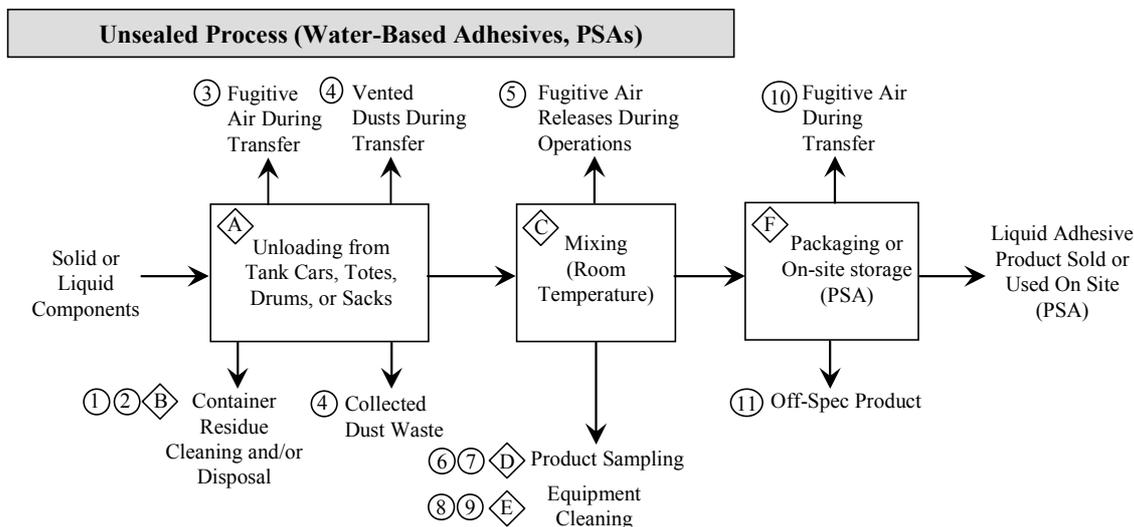
Figure 2-1. Sealed Adhesive Formulation Process

2.2 Unsealed Mixing/Transfer

Adhesives may also be formulated in an unsealed process in which the tanks and transfer operations are open. It is expected that solution adhesives containing low-volatility solvents (i.e., water-based adhesive dispersions) or other components that are relatively stable under ambient conditions are formulated using open mixing tanks and transfer operations (ASC, 2005). Figure 2-2 illustrates the unsealed adhesive formulation process and the associated release sources and worker exposure activities. Each of the release source reference numbers and exposure activity reference letters are consistent with those described in Section 2.1 above for the sealed adhesive formulation process.

The anticipated release sources and associated exposure activities in the unsealed adhesive formulation process are expected to be virtually the same as the releases described for a sealed process in Section 2.1; however, workers have a potential inhalation exposure to the fugitive releases of volatile adhesive components (Exposure C) during the formulation process.

For the purposes of this ESD assessment, it is assumed that water-based adhesives (including water-based PSAs) are formulated in an unsealed process.



○ = Environmental Releases:

1. Container residue from adhesive component transport container released to water, incineration, or landfill.
2. Open surface losses of volatile chemicals to air during container cleaning.
3. Transfer operation losses to air of volatile chemicals from unloading the adhesive component.
4. Dust losses vented to outside air from the transfer of a solid/powdered adhesive component into the process. Alternatively, these dusts are captured on vent filters or settle within the workspace, and are subsequently collected and released to water, incineration, or landfill.
5. Fugitive losses of volatile chemicals to air during mixing operations.
6. Product sampling wastes disposed to water, incineration or landfill (not quantified in this ESD).
7. Open surface losses of volatile chemicals during product sampling.
8. Equipment cleaning releases to water, incineration, or landfill.
9. Open surface losses of volatile chemicals to air during equipment cleaning.
10. Transfer operation losses of volatile chemicals to air from loading adhesive product into transport containers.
11. Off-spec adhesive product released to water, incineration, or landfill.

◇ = Occupational Exposures:

- A. Inhalation and dermal exposure from unloading solid or liquid adhesive components.
- B. Inhalation and dermal exposure to solid or liquid adhesive components during container cleaning.
- C. Inhalation exposure to volatilized adhesive chemical during unsealed mixing operations.
- D. Inhalation and dermal exposure to liquid adhesive product during sampling activities.
- E. Inhalation and dermal exposure to liquid during equipment cleaning of mixing and other process equipment.
- F. Inhalation and dermal exposure to liquids during the packaging of adhesive formulations into containers.

Figure 2-2. Unsealed Adhesive Formulation Process

2.3 Heated Mixing/Transfer

Adhesives may also be formulated in an unsealed process in which the components are melted and mixed into a molten liquid adhesive product, and subsequently extruded, poured, or otherwise formed into a solid hot-melt adhesive product when cooled. Figure 2-3 illustrates the unsealed heated adhesive formulation process and the associated release sources and worker exposure activities. Each of the release source reference numbers and exposure activity reference letters are consistent with those described in Section 2.1 above for the sealed adhesive formulation process.

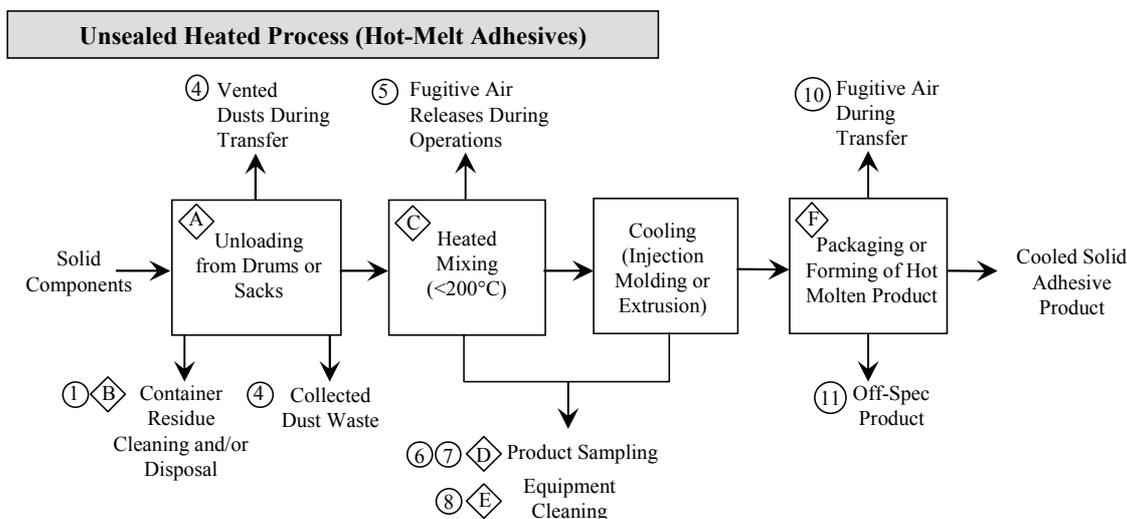
The components are unloaded from transport containers (drums, sacks, etc.) into heated stirring tanks. It is assumed that the components of hot-melt adhesives are nonvolatile at room temperatures. As similarly described in Section 2.1, if the component is in the solid/powdered form, it is assumed that some amount of the component will be lost from the process through dusts that are released into the workspace during the transfer, and that subsequently settle out, are collected, and finally disposed (Release 4, Exposure A). Some components may need to be heated before being pumped from their transport containers. The disposition of the empty container residues are expected to be similar to that described for a sealed formulation process in Section 2.1 (Release 1, Exposure B).

In the heated stirring vessels, the components are melted and mixed to form a blended product. Formulation temperatures are expected to be similar to the application temperature for hot-melt adhesives, which ranges from 150-190°C. Often, at temperatures over 200°C in the presence of air, discoloration, viscosity modification, gelation, and carbonization may adversely affect the quality of the adhesive product (Ullmann, 1985). While most components are expected to remain nonvolatile at these elevated temperatures, some amount may potentially volatilize and be released from the process, resulting in a potential inhalation exposure (Release 5, Exposure C).

Although no industry-specific data were found regarding product sampling practices at hot-melt adhesive formulators, it is generally assumed that some amount of product quality analysis/quality control (QA/QC) sampling is performed as part of the formulation process (engineering judgment). Releases and associated exposures are expected to occur as a result of sampling activities (Release 6, Release 7, Exposure D). It is assumed that sampling will be performed in part on the adhesive product while it is in the molten, liquid form.

The blended hot-melt product is then transferred to shipping containers or otherwise shaped and cooled prior to distribution (Exposure F). Hot-melts may be formed in a variety of ways into the final adhesive product, including (Ullmann, 1985):

- Dripped onto a cooling belt to form a film or pellets;
- Injection molded to produce hot-melt sticks, blocks, or cubes; or
- Extruded to form slugs or rods.



○ = Environmental Releases:

1. Container residue from adhesive component transport container released to water, incineration, or landfill.
4. Dust losses vented to outside air from the transfer of a solid/powdered adhesive component into the process. Alternatively, these dusts are captured on vent filters or settle within the workspace, and are subsequently collected and released to water, incineration, or landfill.
5. Fugitive losses of volatile chemicals to air during operations.
6. Product sampling wastes disposed to water, incineration or landfill (not quantified in this ESD).
7. Open surface losses of volatile chemicals during product sampling.
8. Equipment cleaning releases to water, incineration, or landfill.
10. Transfer operation losses of volatile chemicals to air from loading hot, molten adhesive product into transport containers.
11. Off-spec adhesive product released to water, incineration, or landfill.

◇ = Occupational Exposures:

- A. Inhalation and dermal exposure from unloading solid or liquid adhesive components.
- B. Inhalation and dermal exposure to solid or liquid adhesive components during container cleaning.
- C. Inhalation exposure to volatilized adhesive chemical.
- D. Inhalation and dermal exposure to liquid adhesive product during sampling activities.
- E. Inhalation and dermal exposure to liquid during equipment cleaning of mixing and other process equipment.
- F. Potential Inhalation exposure to volatile chemicals from hot, molten liquid adhesive product during packaging into transport containers.

Figure 2-3. Unsealed Heated Adhesive Formulation Process

Assumptions regarding the frequency and method of disposing of process equipment residues and off-spec adhesive product are the same as those described for a sealed mixing process in Section 2.1 (Release 8, Release 10, Exposure E).

For the purposes of this ESD assessment, it is assumed that hot-melt adhesives (including hot-melt PSAs) are formulated in a heated process.

2.4 Adhesive Formulations

The main components of water-based, organic solvent-based, and hot-melt adhesives are polymers/elastomers and tackifiers; however, other components may include fillers, pigments, plasticizers, stabilizers, viscosity control agents, preservatives, surfactants, antioxidants, and solvents. A summary of available formulation data that has been found to date for solution and hot-melt adhesives is presented in Table 2-1.

Note that some component types are not used in every adhesive type. It is assumed that PSA formulations are similar to water-based and organic solvent-based solution adhesives, as appropriate. In lieu of PSA-specific formulation data, available data for either organic solvent-based or water-based solution adhesives may be used.

Typical components of reactive adhesives are polymers, prepolymers/oligomers, viscosity control agents, plasticizers, tougheners, adhesion promoters, colorants, and solvents. Table 2-2 and Table 2-3 present available formulation data for two common reactive adhesives, moisture-cure reduced temperature vulcanizing (RTV) silicone and urethane adhesives, respectively.

Table 2-1. Summary of Available Information on the Formulation of Solution and Hot-Melt Adhesives

| Component | Weight Fraction of Adhesive Components by Type ^a | Function | Compounds |
|--|---|---|--|
| Elastomer or Adhesive Polymer ^b (Default) | Organic Solvent: 0.11-0.16 Water: 0.55-0.61 Hot-Melt: 0.30 | Elasticity | Styrene-butadiene-styrene block copolymer; nitrile rubber; latex; polychloroprene (Neoprene); ethylene vinyl acetate |
| Tackifier ^b | Organic Solvent: 0.13-0.25 Water: 0.02 Hot-Melt: 0.35 | Increase the tack of the adhesive | Rosin-based resin |
| Filler | Organic Solvent: 0.33 ^c Water: 0.33 ^c Hot-Melt: 0.35 ^b | Increase the cohesive strength; reduce tack; lower cost | Microcrystalline wax; paraffin wax |
| Plasticizer ^c | All: Assume 0.01 | Improve flexibility and plastic flow properties | Chlorinated biphenyl; formamide; phthalates; polyacrylates |
| Solvent ^b | Organic Solvent: 0.60-0.75 Water: 0.29 Hot-Melt: -- | Carrier | Acetone; methylene chloride; heptane; n-propyl bromide; water |
| Stabilizer | Organic Solvent: 0.03 ^b Water: 0.01 ^c Hot-Melt: 0.01 ^c | Prevent unwanted alteration of physical state | 1,2-butylene oxide; 1,3-dioxolane |
| Viscosity Control | Organic Solvent: 0.005 ^c Water: 0.002-0.4 ^d Hot-Melt: 0.005 ^c | Regulate viscosity | Acrylic copolymer; polyurethane |
| Preservative | Organic Solvent: 0.001 ^c Water: 0.001-0.01 ^d Hot-Melt: 0.001 ^c | Protect adhesive from microorganism growth and spoilage | Aldehydes; benzoate; esters; phenolics |
| Surfactant ^d | Organic Solvent: NA Water: 0.001-0.005 Hot-Melt: NA | Reduce surface tension of the liquid; increase spreading and wetting properties | Polycarboxylic acid salt; polyglycolesters; mineral oil; polysiloxane copolymer |
| Antioxidant ^a | Organic Solvent: 0.01 Water: 0.005 Hot-Melt: 0.001 | Retard oxidation | Aromatic amines; substituted phenolic compounds |
| Other Components ^d | All: Assume 0.01 | | |

NA – Not available. Concentration data for surfactants used in these adhesive types have not been identified to date.

a - If a range in concentration is shown, EPA recommends using the high end as a default.

b - Source: Swanson et al. developed “typical” adhesive formulations for various organic solvent- and water-based adhesives used in foam furniture and bedding manufacture (Swanson et al., 2002).

c - Source: *CEB Cheat Sheets: Adhesive Manufacturing* (CEB, no date). These data are based on engineering judgment. No other data for typical concentrations of these component types have been identified to date.

d - Source: Specific component product specification sheets from Ciba Specialty Chemicals and Munzing, available at the *SpecialChem Adhesives & Sealants* web site (SpecialChem, 2006).

Table 2-2. Formulation of Moisture-Curable RTV Silicone Adhesives

| Component | Weight Fraction^a | Function |
|--------------------------------|------------------------------------|--|
| Silicone Polymers (Default) | 0.45-0.85 | Adhesive polymer |
| Calcium Carbonate | 0.20-0.30 | Regulate viscosity and strengthen the bond from shear stress |
| Plasticizer | 0.05-0.20 | Improve flexibility and plastic flow properties |
| Silanes | 0.05-0.07 | Adhesion promoter |
| Fumed Silica | 0.02-0.15 | Regulate viscosity |
| Other | 0.03-0.05 | |

Source: Petrie, 2004.

a - If a range in concentration is shown, EPA recommends using the high end as a default.

Table 2-3. Formulation of Moisture-Curable Urethane Adhesives

| Component | Weight Fraction^a | Function |
|------------------------------|------------------------------------|--|
| NCO Prepolymers (Default) | 0.50-0.55 | Adhesive prepolymer |
| Calcium Carbonate | 0.33 | Regulate viscosity and strengthen the bond from shear stress |
| Carbon Black | 0.04-0.36 | Pigment; adds conductivity |
| Silica | 0.03-0.06 | Regulate viscosity |
| Titanium Dioxide | 0.02 | Pigment |
| Toluene | 0.01-0.02 | Solvent |

Source: Petrie, 2004.

a - If a range in concentration is shown, EPA recommends using the high end as a default.

2.5 Physical Properties of Adhesive Chemicals

Table 2-4 presents the physical properties of example chemical compounds that may be used for each of the adhesive component categories described in this ESD. The specific chemicals within each component category for each adhesive type were identified through available references that discuss adhesive formulations. These references include:

- National Institutes of Health's *Household Products Database*;
- *Kirk-Othmer Encyclopedia of Chemical Technology*;
- *SpecialChem Adhesives & Sealants* web site;
- Web sites of known adhesive formulation companies; and,
- Other references as cited in Tables 2-1, 2-2, and 2-3.

EPA reviewed several sources of physical property data for each of the chemicals identified for the component categories. These sources are cited at the bottom of Table 2-4 and included in the *References* section (Section 8) of this ESD. The example chemicals shown in the table were selected based on the following data quality criteria:

- Available data are characterized as either experimental or extrapolated (estimated/modeled data are not included in Table 2-4);
- Physical property data were found to be relatively consistent among multiple sources; and,
- A complete "set" of Table 2-4 physical property data were found for the chemical.

The physical properties of these chemicals are presented to provide the reader with a general understanding of potential characteristics of certain adhesive components. It should be noted, however, that these chemicals are simply examples of the wide array of chemicals that may be used in specific adhesive formulations.

Table 2-4. Physical Properties of Example Adhesive Component Chemicals

| Component Category | Example Chemical (CAS, if available) | Neat Physical State | Molecular Weight | Vapor Pressure (torr at 25°C) | Boiling Point (°C) | Melting Point (°C) | Water Solubility (mg/L) | Density, LogK _{ow} |
|-------------------------------------|--|--|------------------|-------------------------------|--------------------|--------------------|-------------------------|-----------------------------|
| Elastomer/ Binder/ Adhesive Polymer | <p><u>Organic solvent-based adhesive chemicals:</u></p> <ul style="list-style-type: none"> • Natural rubber • Polychloroprene • Polyurethane • Styrene-butadiene-styrene block polymers • Styrene-butadiene rubber (SBR) • Butadiene-acrylonitrile rubber • Acrylic or vinyl resins <p><u>Water-based adhesive chemicals:</u></p> <ul style="list-style-type: none"> • Natural polymers • Polyurethane dispersions • Polyvinyl alcohol (PVA) • Polyvinyl acetate (PVAC) emulsions • Polychloroprene <p><u>Hot-melt adhesive chemicals:</u></p> <ul style="list-style-type: none"> • Ethylene-vinyl acetate copolymers | | | | | | | |
| | | <p>The polymers used in adhesive formulations may be solids or liquids and possess a wide range of molecular weights, vapor pressures, and other physical properties.</p> <p>Adhesive polymers are generally expected to be of high, variable molecular weight and have a negligible vapor pressure.</p> <p>If the physical state of the polymer is not known, EPA recommends that the polymer be assessed as a solid, which will result in more conservative worker inhalation exposure assessment.</p> | | | | | | |

Table 2-4 (Continued)

| Component Category | Example Chemical (CAS, if available) | Neat Physical State | Molecular Weight | Vapor Pressure (torr at 25°C) | Boiling Point (°C) | Melting Point (°C) | Water Solubility (mg/L) | Density, LogK _{ow} |
|--|---|---|---------------------|-------------------------------|-------------------------------|--------------------|-------------------------|--|
| Elastomer/ Binder/ Adhesive Polymer (Continued) | <u>PSA chemicals:</u> <ul style="list-style-type: none"> Natural rubber Polybutadiene Polyorganosiloxanes SBR Carboxylated styrene-butadiene rubber Halogenated butyl rubber Polyalkyl acrylate homopolymers/copolymers Polyvinyl ethers Amorphous polyolefins Block polymers based on styrene with isoprene, butadiene, ethylene-propylene, or ethylene-butylene | <p>The polymers used in adhesive formulations may be solid or liquid, and possess a wide range of molecular weights, vapor pressures, and other physical properties.</p> <p>Adhesive polymers are generally expected to be of high, variable molecular weight and have a negligible vapor pressure.</p> <p>If the physical state of the polymer is not known, EPA recommends that the polymer be assessed as a solid, which will result in more conservative worker inhalation exposure assessment.</p> | | | | | | |
| | <u>Moisture-curable RTV silicone adhesive:</u> <ul style="list-style-type: none"> Methyltriacetoxysilane (4253-34-3) | NA | 220.26 ^d | 0.135 ^d | NA | 40.5 ^d | 9.22 ^d | log K _{ow} 0.25 ^d |
| | <u>Moisture-curable urethane adhesive:</u> <ul style="list-style-type: none"> Methylene diphenyl diisocyanate (101-68-8) | Solid ^b | 250.26 ^d | 5e-6 ^d | 196 (@ 0.7 torr) ^d | 37 ^b | 0.829 ^d | ρ 1.197 (@ 70°C) ^b log K _{ow} 5.22 ^d |

| Component Category | Example Chemical (CAS, if available) | Neat Physical State | Molecular Weight | Vapor Pressure (torr at 25°C) | Boiling Point (°C) | Melting Point (°C) | Water Solubility (mg/L) | Density, LogK _{ow} |
|--------------------|---|---|---|--|--|------------------------|----------------------------|--|
| Tackifier | <u>Solvent-based and hot-melt adhesive:</u> • Rosin-based resin | The polymers used in adhesive formulations may be solids or liquids and possess a wide range of molecular weights, vapor pressures, and other physical properties. Adhesive polymers are generally expected to be of high, variable molecular weight and have a negligible vapor pressure. If the physical state of the polymer is not known, EPA recommends that the polymer be assessed as a solid, which will result in more conservative worker inhalation exposure assessment. | | | | | | |
| Filler | <u>Solvent-based and hot-melt adhesive:</u> • Paraffin wax (8002-74-2) | Solid ^b | Mixture of solid, high molecular weight hydrocarbons. ^b Vapor pressure is assumed to be negligible. | | 47–65 ^b | Insoluble ^b | ρ 0.880–0.915 ^b | |
| Plasticizer | <u>Solvent-based and hot-melt adhesives:</u> • di-sec-octyl phthalate (i.e., DOP, DEHP) (117-81-7) | Liquid ^b | 390.57 ^d | 1.42e-7 ^d 1.32 (@ 200°C) ^b | 384 ^d 231 (@ 5 torr) ^b | -55 ^d | 0.27 ^d | ρ 0.9861 ^b log K _{OW} 7.60 ^d |
| | <u>Moisture-curable RTV silicone adhesive:</u> • diisodecylphthalate (26761-40-0) | Liquid ^b | 446.68 ^d | 5.28e-7 ^d | 250-257 (@ 4 torr) ^b | -45.6 ^d | 0.28 ^d | ρ 0.966 ^b log K _{OW} 10.36 ^d |
| Solvent | <u>Organic solvent-based adhesive:</u> • n-Heptane (142-82-5) | Liquid ^a | 100.20 ^a | 46 ^d | 98.4 ^a | -90.7 ^a | 3.4 ^d | ρ 0.684 ^a log K _{OW} 4.66 ^d |
| | <u>Water-based adhesive:</u> • Water (7732-18-5) | Liquid ^a | 18.02 ^a | 23.8 ^d 760 (@ 100°C) ^b | 100 ^a | 0 ^a | 1e6 ^d | ρ 0.997 ^a log K _{OW} -1.38 ^d |
| | <u>Moisture-curable urethane adhesive:</u> • Toluene (108-88-3) | Liquid ^a | 92.14 ^a | 28.4 ^d | 110.6 ^a | -95 ^a | 526 ^d | ρ 0.866 ^a log K _{OW} 2.73 ^d |

Table 2-4 (Continued)

| Component Category | Example Chemical (CAS, if available) | Neat Physical State | Molecular Weight | Vapor Pressure (torr at 25°C) | Boiling Point (°C) | Melting Point (°C) | Water Solubility (mg/L) | Density, LogK _{ow} |
|--------------------|--|---|---------------------|--|--|----------------------------------|------------------------------------|---|
| Stabilizer | <u>Solvent-based and hot-melt adhesives:</u> • 1,3-Dioxolane (646-06-0) | Liquid ^b | 74.08 ^d | 70 (@ 20°C) ^b 79 (@ 20°C) ^d | 74 ^b 78 ^d | -95 ^d | 1e6 ^d | ρ 1.065 ^b log K _{OW} -0.37 ^d |
| Pigment | <u>Moisture-curable urethane adhesive:</u> • Titanium dioxide (13463-67-7) | Solid ^a | 79.87 ^a | Metal oxide; Vapor pressure assumed negligible | 2900 ^c | 1855 ^{a,c} | Insoluble ^a | ρ 4.23 (rutile) ρ 3.90 (anatase) ρ 4.13 (brookite) ^a |
| Viscosity Control | <u>Solvent-based and hot-melt adhesive chemicals:</u> • Acrylic copolymer • Polyurethane | The polymers used in adhesive formulations may be solids or liquids and possess a wide range of molecular weights, vapor pressures, and other physical properties. Adhesive polymers are generally expected to be of high, variable molecular weight and have a negligible vapor pressure. If the physical state of the polymer is not known, EPA recommends that the polymer be assessed as a solid, which will result in more conservative worker inhalation exposure assessment. | | | | | | |
| | <u>Moisture-curable reactive adhesives:</u> • Calcium carbonate (471-34-1) | Solid ^a | 100.09 ^a | Metal carbonate; Vapor pressure assumed negligible | NA | 825 (decomposes) ^a | Very slightly soluble ^b | ρ 2.7–2.95 ^b |
| Preservative | <u>Solvent-based and hot-melt adhesives:</u> • Sodium benzoate (532-32-1) | Solid ^a | 144.11 ^a | Salt; Vapor pressure assumed negligible | NA | >300 ^d | 5.56e5 ^d | log K _{OW} -2.27 ^d |

| Component Category | Example Chemical (CAS, if available) | Neat Physical State | Molecular Weight | Vapor Pressure (torr at 25°C) | Boiling Point (°C) | Melting Point (°C) | Water Solubility (mg/L) | Density, LogK _{ow} |
|--------------------|--|---------------------|---------------------|-------------------------------|--------------------|--------------------|-------------------------|---|
| Surfactant | Water-based adhesive: • 2,4,7,9-Tetramethyl-5-decyn-4,7-diol (126-86-3) | Solid ^e | 226.36 ^c | 0.01 (@ 21°C) ^e | 262 ^e | >54 ^e | 0.1 (wt%) ^e | ρ 0.89 ^e log K _{ow} 2.8 ^e |
| Antioxidant | Solvent-based and hot-melt adhesives: • 2,6-Di-tert-butyl-4-methylphenol (BHT) (128-37-0) | Solid ^b | 220.36 ^b | 0.00516 ^d | 265 ^b | 70 ^b | 0.6 ^d | ρ 1.048 ^b log K _{ow} 5.10 ^d |

NA = No data were found in the references reviewed for this ESD.

a – Source: Merck, 1996.

b – Source: Hawley's, 1997.

c – Source: ChemFinder, 2006.

d – Source: SRC, 2006.

e – Source: APC, 2005.

3 OVERALL APPROACH AND GENERAL FACILITY ESTIMATES

This ESD presents EPA's standard approach for estimating environmental releases of and worker exposures to components used in adhesive formulations. The ESD covers the blending of the components into adhesive formulations.

The estimation methods described in this document utilize available industry-specific information and data to the greatest extent possible; however, EPA acknowledges several areas in which additional adhesive formulation industry data are needed. These data needs are summarized in Section 7 of this ESD. It should be noted that the default values cited throughout this ESD are intended to be used only when appropriate site-specific or industry-specific information is not available.

Because this ESD presents several alternative default assumptions or values for some estimation parameters, one must consider carefully how the selection of these defaults will affect the final assessment results.

This section of the ESD presents general facility calculations, which estimate daily use rates of adhesive and component chemicals, the number of adhesive formulation sites using the chemical of interest, and the number of days the chemical is expected to be used in the formulation process.

Section 4 of the ESD presents the environmental release assessment, which uses the general facility estimates to estimate of the quantity of chemical released from various points in the adhesive formulation process and the most likely media of release for each release source.

Section 5 of the ESD presents the occupational exposure assessment, which uses both the general facility estimates and release estimates to estimate the number of workers potentially exposed while performing various process activities and the corresponding potential level (quantity) and routes of those exposures.

3.1 Introduction to the General Facility Estimates

Through the remainder of this section, a method utilizing available adhesive formulation industry data is described to estimate the number of formulation sites that may use a particular adhesive component containing the chemical of interest. The number of sites is estimated using average annual production rates for various types of adhesive products, combined with available formulation data for different components. The average annual production rates are also used with a default batch size to estimate the total annual number of adhesive batches. These default assumptions and calculations are then used to estimate the use rate for the chemical of interest, the number of shipping containers that are transferred into the operation annually, and the number of containers that are filled with the adhesive product annually.

The general facility estimates described in this section are summarized with their associated inputs/bases and corresponding ESD section number in Table 3-1. In addition, Table A-2 in Appendix A presents a detailed summary of the default values used as inputs to each of the general facility estimates, accompanied by their references.

Table 3-1. Summary of General Facility Parameters

| Parameter | Description | ESD Section |
|--------------------------------------|--|--------------------|
| $Q_{\text{adhes_site_yr}}$ | Annual facility production rate for adhesives containing the chemical of interest (kg adhesive/site-yr) | 3.2 |
| $F_{\text{chem_comp}}$ | Mass fraction of the chemical of interest in the adhesive component (kg chemical/kg component) | 3.3 |
| $F_{\text{comp_adhes}}$ | Mass fraction of the component used in the formulated adhesive product (kg component/kg adhesive) | 3.4 |
| N_{sites} | Number of facilities using the chemical of interest to formulate an adhesive product (sites) | 3.5 |
| $N_{\text{bt_site_yr}}$ | Annual number of adhesive formulation batches run at each facility (batches/site-day) | 3.6 |
| $\text{TIME}_{\text{working_days}}$ | Annual number of days the adhesive is formulated at each facility (days/yr) | 3.7 |
| $Q_{\text{chem_site_day}}$ | Daily use rate for the chemical of interest at each facility (kg of chemical/site-day) | 3.8 |
| $N_{\text{cont_empty_site_yr}}$ | Annual number of chemical-containing adhesive component containers emptied per facility (container/site-yr). | 3.9 |
| $N_{\text{cont_fill_site_yr}}$ | Annual number of chemical-containing adhesive product containers filled per facility (container/site-yr). | 3.10 |

The method described in the remaining sections incorporates certain assumptions in cases where industry-specific data were not found. These key assumptions are presented throughout this section and are accompanied by a discussion of their uncertainties and potential effects on the estimates.

3.2 Annual Facility Adhesive Production Rate ($Q_{\text{adhes_site_yr}}$)

Average annual facility production rates for the types of adhesive products discussed in this ESD are estimated using available adhesive production and formulator site data found to date. The industry is highly fragmented; however, seven companies produce 49 percent of the worldwide production (Kirk-Othmer, 2002). These seven companies are 3M, Bostik Findley, H.B. Fuller, Henkel, National Starch and Chemical, Rohm and Hass, and Sika (Kramer, 2000)¹.

To estimate the number of U.S. formulation sites that are represented by these seven companies, data submitted to EPA's Toxics Release Inventory (TRI) were reviewed for sites that identified themselves as adhesive formulators under Standard Industrial Classification (SIC) code 2891 and that listed one of the seven companies as their parent company. Based on the

¹Two of these companies (3M and H.B. Fuller) are also "major" formulating companies in Canada, while four major Canadian formulators (Forbo Adhesives, GE Silicones, Roberts Company Canada, and Tremco) are based in the United States. This information was submitted to EPA by Environment Canada and can be found in Appendix C.

TRI data and through a review of the companies' web sites, it is estimated that the seven dominant companies control approximately 50 sites (TRI, 2000).

U.S. production data for these "large" formulators was not found in the references reviewed for this ESD (refer to Section 8 for a description of the sources reviewed and full citations for those specifically used in these calculations). For the purposes of this ESD, it is therefore assumed that the U.S. market share of the large formulators is 49 percent, equivalent to the 49 percent share they hold in the worldwide market. The remaining 51 percent is assumed to be formulated by other sites. Note these "other" formulators are not necessarily small; they are simply not controlled by one of the major formulators.

A total of 592 adhesive formulators operate in the United States (USCB, 2003). It is assumed that 50 of these U.S. formulators comprise the large sites, as described above and the remaining 542 are classified as "other" formulators for the purposes of the ESD calculations.

Table 3-2 summarizes the estimated annual facility production rate ($Q_{\text{adhes_site_prod_rate}}$) for the various types of adhesives for which data are available. The annual facility production rates are derived from total U.S. production volumes for each adhesive type (initially presented in Tables 1-3, 1-4, and 1-5), as well as the estimated numbers of large and other formulation sites and division of production between these two types of formulators, as described above.

If the specific type of adhesive product is not known, please refer to the decision logic diagram presented in Figure 3-1 to determine the most appropriate adhesive type based on what is known of the chemical of interest. If the type of adhesive product cannot be determined based on the decision logic, use the production rate shown for an *Unknown* adhesive at the bottom of Table 3-2. This production rate is an average of the production rates for the four primary adhesive types for each of the large and other formulator types.

The recommended default value for the annual facility production rate ($Q_{\text{adhes_site_prod_rate}}$) depends on the type of assessment to be performed (release, exposure, or both release and exposure) in the adhesive formulation scenario. Each assessment option presents the recommended conservative choice for the default value for $Q_{\text{adhes_site_prod_rate}}$:

- Option 1 - Release-Only Assessment: The recommended default for $Q_{\text{adhes_site_prod_rate}}$ is the production rate listed in Table 3-2 for "Large" formulators for the desired adhesive type. If the adhesive type is not known, it is recommended that the average production rate listed for an *Unknown* adhesive at large formulators be used as the default (17 million kg/site-yr). This default value will minimize the number of formulation sites that use the chemical of interest, thereby increasing the amount that is released from each site.

Table 3-2. Average Annual Facility Production Rate of Adhesives

| Adhesive Type | Total U.S. Production Volume (million kg/yr)^a | Formulator Type (est. number of U.S. sites)^b | Est. U.S. Production Volume, by Formulator Type (million kg/yr)^c | Average Facility Production Rate (Q_{adhes site prod rate}) (million kg/site-yr)^d |
|--------------------------------|---|--|--|---|
| Water-Based Solution | 4,990 | Large (50 sites) | 2,445 | 49 |
| | | 2 sites) | 2,545 | 4.6 |
| <i>Water-Based PSA</i> | 200 | <i>Large (50 sites)</i> | <i>98</i> | <i>2.0</i> |
| | | <i>Other (542 sites)</i> | <i>102</i> | <i>0.19</i> |
| Organic Solvent-Based Solution | 410 | Large (50 sites) | 201 | 4.0 |
| | | Other (542 sites) | 209 | 0.38 |
| Hot-Melt | 950 | Large (50 sites) | 466 | 9.3 |
| | | Other (542 sites) | 484 | 0.88 |
| Other Liquid (assume Reactive) | 450 | Large (50 sites) | 220 | 4.4 |
| | | Other (542 sites) | 230 | 0.42 |
| <i>Cyanoacrylate</i> | <i>15.8</i> | <i>Large (50 sites)</i> | <i>7.7</i> | <i>0.15</i> |
| | | <i>Other (542 sites)</i> | <i>8.1</i> | <i>0.015</i> |
| <i>Urethane</i> | <i>64.9</i> | <i>Large (50 sites)</i> | <i>31.8</i> | <i>0.64</i> |
| | | <i>Other (542 sites)</i> | <i>33.1</i> | <i>0.060</i> |
| n (Default)^e | NA | Large (50 sites) | NA | 17 |
| | | Other (542 sites) | | 1.6 |

NA – not applicable.

a - Total U.S. production volumes were previously discussed and summarized in Tables 1-3, 1-4, and 1-5.

b - It is estimated that 50 of the total U.S. formulation sites are controlled by the seven top formulators (TRI, 2000) and are assumed to be large. U.S. Census data for the adhesive formulation sector indicate that 592 formulators operated in 2003 (USCB, 2003); therefore, the remaining 542 sites are presented as “other” formulators (i.e., not large).

c - It is assumed that the large formulators collectively produce 49 percent of the total U.S. production (Kirk-Othmer, 2002) and the remaining 51 percent of U.S. production occurs at the other formulator sites.

d - The average facility annual production rate is estimated by the following:

(Estimated U.S. Production Volume, by Formulator Type) ÷ (Estimated Number of U.S. Sites)

It should be noted that no facility-specific production rates were found; therefore, no ranges in the production rates are available to demonstrate their variability.

e - The production rates shown for the *Unknown* adhesive type are averages of the four primary adhesive type rates: Water-Based Solution, Organic Solvent-Based Solution, Hot-Melt, and Other Liquid.

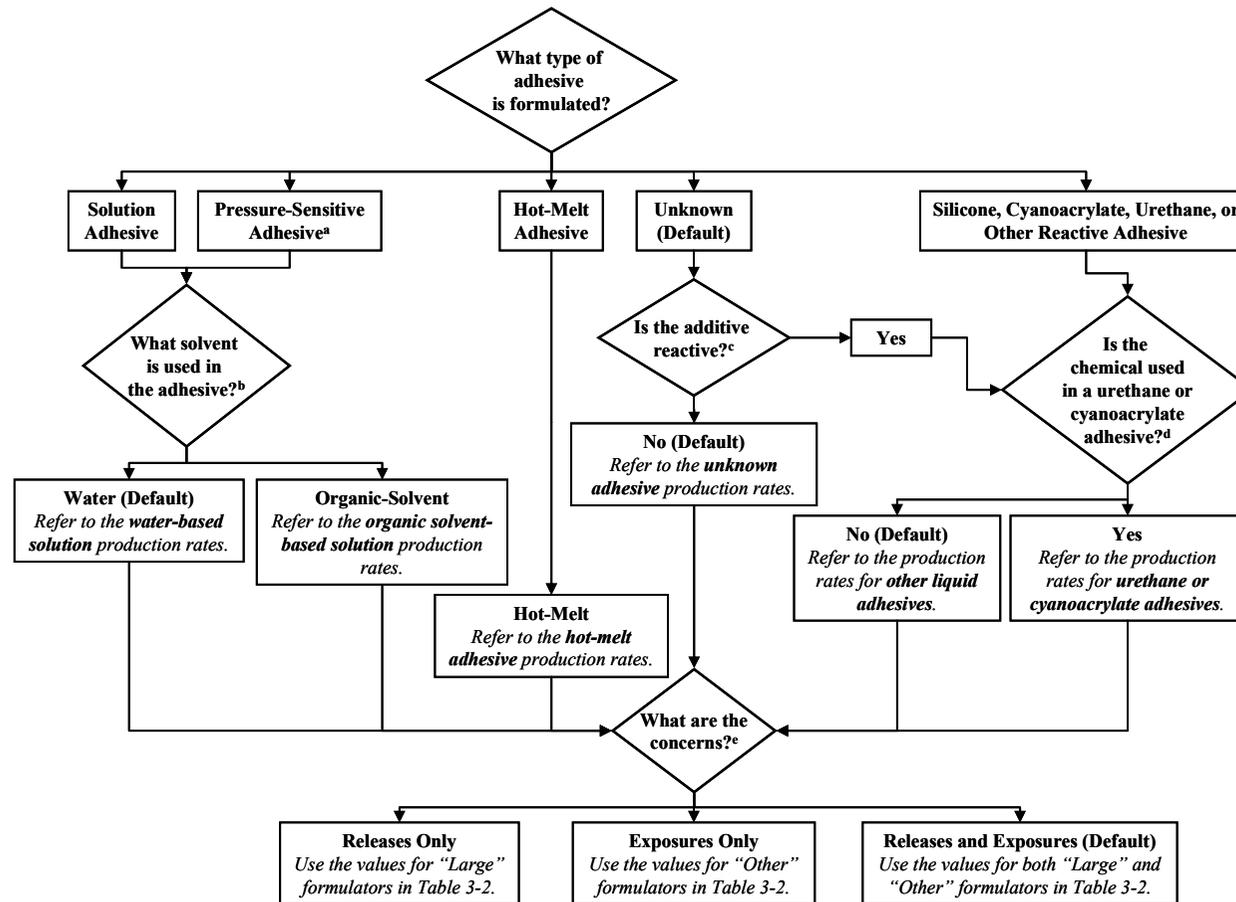


Figure 3-1. Decision Logic Diagram for Determining Appropriate Default Annual Facility Adhesive Production Rate in Table 3-2

(Notes for Figure 3-1 are presented on the following page.)

Notes for Figure 3-1:

- a. PSAs are often initially formulated into a solution before application to a continuous web substrate (e.g., tapes, labels). If specific data are not known for the PSA formulation being assessed, use available solution adhesive data, as appropriate.
- b. If the type of solvent used in the adhesive formulation is not known, assume a water-based adhesive (since most adhesives produced water-based). Also note the use of organic solvent-based adhesives has significantly declined in recent years due to increasing regulations to control the release of various VOCs.
- c. If the type of adhesive formulation being assessed is not known, use the production rate data presented in Table 3-2 for an *Unknown* adhesive. If the function of the chemical or component in the adhesive formulation is reactive in nature (e.g. the chemical is a monomer, oligomer, crosslinker, catalyst), formulation of a reactive adhesive is assumed. These components are typically found only in reactive adhesives.
- d. To date, production data were found only for urethane and cyanoacrylate reactive adhesives. If the chemical of interest is a component of another reactive adhesive type, use the data included for “Other Liquid” adhesives in Table 3-2.
- e. If releases are the primary concern (Option 1 – Release Only Assessment), use the appropriate data for “Large” formulators included in Table 3-2, resulting in larger daily releases from fewer sites.

If worker exposures are the primary concern (Option 2 – Exposure Only Assessment), use the data for “Other” formulators, increasing the number of formulation sites and thus, increasing the number of workers potentially exposed to the chemical of interest.

If both releases and exposures are a concern (default Option 3 – Release and Exposure Assessment), then the assessment should use both the “Large” and “Other” formulator data, as described in the calculation methodology presented in this section.

- Option 2 - Exposure-Only Assessment: The recommended default for $Q_{\text{adhes_site_prod_rate}}$ is the production rate listed in Table 3-2 for “Other” formulators for the desired adhesive type. If the adhesive type is not known, it is recommended that the average production rate listed for an *Unknown* adhesive at other formulators be used as the default (1.6 million kg/site-yr). This default value will maximize the number of formulation sites that use the chemical of interest, thereby increasing the number of workers potentially exposed to the adhesive chemical.
- Option 3 (Default) – Release and Exposure Assessment: The recommended defaults for $Q_{\text{adhes_site_prod_rate}}$ are the production rates listed in Table 3-2 for both “Large” and “Other” formulators for the desired adhesive type. If the adhesive type is not known, it is recommended that the average production rates listed for an *Unknown* adhesive be used as the defaults (Large: 17 million kg/site-yr and Other: 1.6 million kg/site-yr).

For this option, it is recommended that 49 percent of the chemical production volume ($Q_{\text{chem_yr}}$) be assessed using the adhesive production rate at large sites and 51 percent of $Q_{\text{chem_yr}}$ be assessed using the adhesive production rate at other sites. These calculations will be explained further in the appropriate sections of the ESD.

The following calculation may be used to determine the annual facility production rate for the adhesive containing the chemical of interest ($Q_{\text{adhes_site_yr}}$), and includes a factor (F_{adhes}) for adjusting the total adhesive production rate ($Q_{\text{adhes_site_prod_rate}}$) to account for the chemical of interest being used to formulate a portion of the all adhesive products of the specified type. Industry specific information on the number of different adhesives formulated at a site was not available; therefore, this ESD assumes that the chemical of interest is formulated into all adhesive formulations at a particular site. If site-specific information is available, it should be used in lieu of this general assumption. The recommended default value for $Q_{\text{adhes_site_prod_rate}}$ presented in this ESD assumes that the specific adhesive type is not known and that an Option 3 – Release and Exposure assessment will be performed:

$$Q_{\text{adhes_site_yr}} = Q_{\text{adhes_site_prod_rate}} \times F_{\text{adhes}} \quad (3-1)$$

Where:

- | | | |
|--------------------------------------|---|---|
| $Q_{\text{adhes_site_yr}}$ | = | Annual facility adhesive production rate using the chemical of interest (kg adhesive incorporating the chemical/site-yr) |
| $Q_{\text{adhes_site_prod_rate}}$ | = | Total annual facility adhesive production rate (Defaults: 17,000,000 kg total adhesive produced/site-yr for an unknown adhesive formulated at large sites and 1,600,000 kg total adhesive produced/site-yr for an <i>unknown</i> adhesive formulated at <i>other</i> sites. See Figure 3-1 and Table 3-2 for alternative production rates.) |
| F_{adhes} | = | Fraction of the total adhesive type produced that incorporates the chemical of interest (Default: 1 kg adhesive incorporating the chemical/kg total adhesive produced) |

Note that the production rates shown in Table 3-2 represent industry *average* rates based on total annual production amounts and estimated numbers of large and other formulators in the United States. Several key assumptions are inherent in these default production rates:

- Assumption #1: All of the 592 adhesive formulation sites produce all types of adhesives.

This assumption may not be the most conservative for an exposure-based assessment. Some niche-market formulators are likely to be smaller with lower production rates; however, data were not found to date that can be used to estimate the variability in production rates for the various adhesive types.

One resource indicated that most adhesive companies market by industry, not by the adhesive type (Kirk-Othmer, 2002), implying that a single formulator may formulate multiple types of adhesives. However, no information was found to indicate whether sites controlled by these companies tend to be dedicated to a particular type of adhesive, nor whether most companies will formulate all types of adhesives. Lacking more specific data on the numbers of formulation sites that produce each type of adhesive, the assumption is made that the production amounts are evenly distributed across the entire industry.

- Assumption #2: The chemical of interest is used to formulate all of a particular adhesive type at each site (i.e., $F_{\text{adhes}} = 1$ kg adhesive incorporating the chemical/kg total adhesive produced).

It is suspected that some sites may formulate more than one product for a single adhesive type (i.e., they formulate multiple water-based solution adhesive products). No information or data were found that could be used to determine the extent to which this is the case, or that could be used to quantify the fraction of a site's adhesive type product that would incorporate a single component. It is possible that the chemical of interest is not used to formulate all of a particular adhesive type, which would make the default production rates in Table 3-2 tend toward the high end (i.e., less conservative for exposures, more conservative for releases).

- Assumption #3: PSA formulators are represented among the 592 sites included in NAICS 32552 (Adhesive Formulation).

Since PSAs are often formulated and applied to the end product (e.g., tapes, labels) at the same site, there may be sites included within NAICS 322222 (Coated and Laminated Paper Manufacturing) that are likely to be using the chemical of interest to formulate a PSA and apply it to their end product. In other words, PSA formulators may alternately be represented as coated and laminated paper manufacturers within the U.S. Census data; however,

it is not possible to quantify the specific number of PSA formulation sites within this industrial sector or within the Adhesive Formulation data (i.e., for NAICS 32552) used in this ESD.

Since the overlap between the two industry sectors cannot be determined for PSA formulators, EPA assumes that they are among the 592 U.S. adhesive formulation sites for the purposes of this ESD. Note: 528 coated and laminated paper manufacturers operated in the United States in 2003. (USCB, 2003). It is likely that only a subset of the 592 adhesive formulator sites formulate PSAs, which would make the default PSA production rate in Table 3-2 tend toward the low end (i.e., more conservative for exposures, but less conservative for releases).

3.3 **Mass Fraction of the Chemical of Interest in the Adhesive Component** ($F_{\text{chem_comp}}$)

The chemical of interest may be shipped to the formulation site for use in an adhesive component product, or it may be the adhesive component itself. If specific information about the chemical-containing component is not known, EPA recommends assuming 100 percent chemical of interest when performing the calculations in this assessment¹:

$$F_{\text{chem_comp}} = \text{Mass fraction of the chemical of interest in the adhesive component (Default: 1 kg chemical/kg component)}$$

3.4 **Mass Fraction of the Component in the Adhesive Product** ($F_{\text{comp_adhes}}$)

Available adhesive formulation data for solution and hot-melt adhesives are presented in Table 2-1, while Tables 2-2 and 2-3 present formulation data for two types of moisture-curable reactive adhesives.

Table 3-3 summarizes the available formulation data across all adhesive types. It is recommended that this table be reviewed in cases where the adhesive type is unknown. Note: Table 3-3 does not include reactive components, such as prepolymers or silanes, since it is assumed that a reactive component will be specifically used to formulate a reactive adhesive product. It is recommended that Table 2-2 or Table 2-3 be consulted when considering the potential component concentration within a reactive adhesive.

If the component type containing the chemical of interest is known, the mass fraction of the component in the formulated adhesive product may be estimated using the data presented in these tables. If a range in concentration is presented, EPA suggests using the upper bound concentration¹. If the component type is not known, it is recommended that the type having the highest concentration (e.g., the polymer in solution or hot-melts) be assumed.

As illustrated in Figure 3-2, the default concentration data used as the basis for $F_{\text{comp_adhes}}$ should correspond to the adhesive type selected as the basis for the default annual facility production rate in Section 3.2.

$F_{\text{comp_adhes}}$ = Mass fraction of the component used in the formulated adhesive product (Default for the formulation of an unknown adhesive product: 0.85 kg component/kg adhesive for an elastomer/polymer. See Figure 3-2 and Tables 2-1, 2-2, 2-3, or Table 3-3 for alternative fractions, as appropriate.)

¹Using the upper bound concentration will provide a conservative (worst case) assessment for releases, as well as worst case exposure doses; however, it will not provide a conservative result in the total number of workers potentially exposed to the chemical of interest (i.e., the total number of sites, and thus the number or workers will be minimized).

Table 3-3. General Formulation Data Summary for Adhesive Products

| Component^a | Weight Fraction of Adhesive Components^b | Function |
|---|---|---|
| Elastomer or Adhesive Polymer (Default) | 0.11-0.85 | Elasticity |
| Solvent | 0.01-0.75 | Carrier |
| Viscosity Control | 0.002-0.4 | Regulate viscosity |
| Pigment | 0.02-0.36 | Imparts color |
| Tackifier | 0.02-0.35 | Increase the tack of the adhesive |
| Filler | 0.33-0.35 | Increase the cohesive strength; reduce tack; lower cost |
| Plasticizer | 0.01-0.2 | Improve flexibility and plastic flow properties |
| Stabilizer | 0.01-0.03 | Prevent unwanted alteration of physical state |
| Preservative | 0.001-0.01 | Protect adhesive from microorganism growth and spoilage |
| Antioxidant | 0.001-0.01 | Retard oxidation |
| Surfactant | 0.001-0.005 | Reduce surface tension of the liquid; increase spreading and wetting properties |

a - The adhesive component formulation data summarized in this table were derived from the available data shown in Tables 2-1, 2-2, and 2-3. Note: reactive components, such as prepolymers and silanes are not included since it is assumed that reactive components are specifically used in reactive adhesive formulations, such as those summarized in Tables 2-2 and 2-3.

b - If a range in concentration is shown, EPA recommends using the high end as a default.

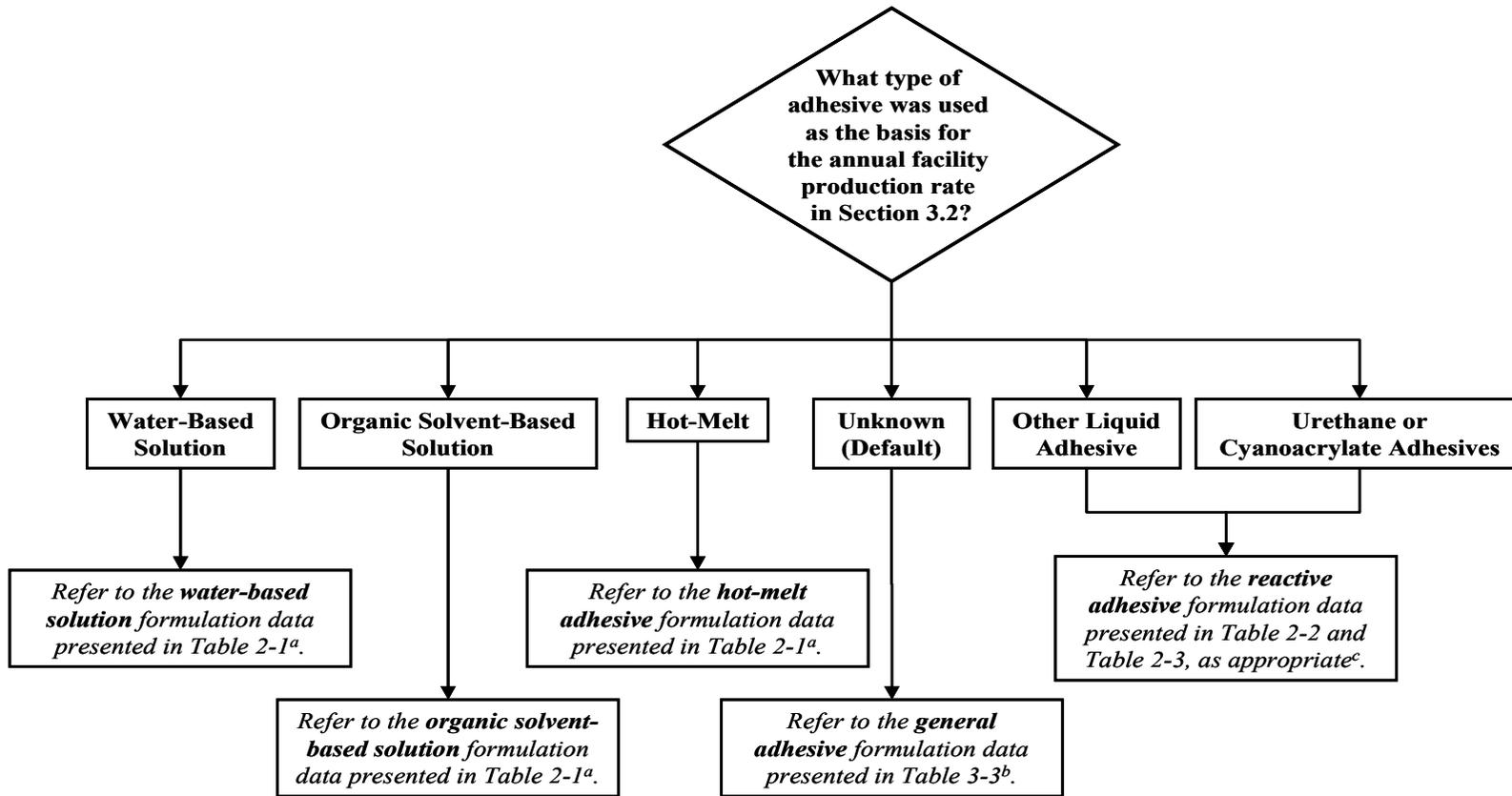


Figure 3-2. Decision Logic Diagram for Determining Appropriate Default Adhesive Component Concentration

(Notes for Figure 3-2 are presented on the following page.)

Notes for Figure 3-2:

- a. If the component function is not known, use the concentration data for “Elastomer or Adhesive Polymer” shown in Table 2-1. If the component type is known but not listed in Table 2-1, use the concentration for Other Components in Table 2-1.
- b. If the component function is not known, use the concentration data for “Elastomer or Adhesive Polymer” shown in Table 3-3. If the component type is known but not listed in Table 3-3, use the concentration for Other Components in Table 2-1.
- c. Tables 2-2 and 2-3 present available formulation data for two specific types of reactive adhesives: moisture-curable RTV silicones and moisture-curable urethanes. If the chemical of interest is a component of another type of reactive adhesive, use the highest concentration from either of these two tables for the chemical-containing component. If the specific function or component type in the reactive adhesive is not known, use the concentration data for the adhesive polymers/prepolymers included in Table 2-2 or Table 2-3, as appropriate. If the component type is known but not listed in Table 2-2 or Table 2-3, use the concentration included for “Other” components in Table 2-2.

3.5 Number of Sites (N_{sites})

The following calculation combines the average adhesive production rate ($Q_{\text{adhes_site_yr}}$) and the fraction of the chemical of interest in the adhesive product ($F_{\text{chem_comp}} \times F_{\text{comp_adhes}}$) to estimate the number of formulator sites expected to utilize the amount of chemical of interest in producing adhesives:

$$N_{\text{sites}} = \frac{Q_{\text{chem_yr}}}{Q_{\text{adhes_site_yr}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}}} \quad (3-2)$$

Where:

| | | |
|------------------------------|---|---|
| N_{sites}^1 | = | Number of adhesive formulators using the component that contains the chemical of interest (sites) |
| $Q_{\text{chem_yr}}$ | = | Annual production volume of the chemical of interest (kg chemical/yr) |
| $Q_{\text{adhes_site_yr}}$ | = | Annual facility adhesive production rate (kg adhesive/site-yr) (See Section 3.2) |
| $F_{\text{chem_comp}}$ | = | Mass fraction of the chemical of interest in the adhesive component (kg chemical/kg component) (See Section 3.3) |
| $F_{\text{comp_adhes}}$ | = | Mass fraction of the component used in the formulated adhesive product (kg component/kg adhesive) (See Section 3.4) |

The number of sites that formulate the chemical of interest into an adhesive product is estimated based on the total amount of the chemical-containing component produced (kg/yr) and the annual facility production rate of the adhesive product (kg/site-yr). The maximum number of sites should not exceed 592, per U.S. Census data (USCB, 2003) (estimated as 50 large formulators and 542 other formulators, per TRI data for top formulators as discussed in Section 3.2).

Note for default Option 3 – Release and Exposure assessment:

It is recommended that Equation 3-2 be calculated using the two default values for $Q_{\text{chem_yr}}$ and $Q_{\text{adhes_site_yr}}$ to estimate the number of large and other formulation sites:

1. Calculation for large formulators: use *49 percent* of the total $Q_{\text{chem_yr}}$ with the default $Q_{\text{adhes_site_yr}}$ for *large* formulators, as described in Section 3.2.

¹The value for N_{sites} , calculated using Equation 3-2 should be rounded up to the nearest integer value. $Q_{\text{adhes_site_yr}}$ should then be adjusted for the N_{sites} integer value (to avoid errors due to rounding):

$$Q_{\text{adhes_site_yr}} = \frac{Q_{\text{chem_yr}}}{N_{\text{sites}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}}}$$

Note: If the number of formulation sites is known, the previous equation may also be used to estimate the resulting average annual production rate for use in subsequent calculations.

2. Calculation for other formulators: use *51 percent* of the total Q_{chem_yr} with the default $Q_{adhes_site_yr}$ for *other* formulators, as described in Section 3.2.

3.6 Annual Number of Batches ($N_{bt_site_yr}$)

The following calculation estimates the number of batches based on the average annual facility production rate and the average batch size:

$$N_{bt_site_yr} = \frac{Q_{adhes_site_yr}}{Q_{adhes_bt}} \quad (3-3)$$

Where:

- | | | |
|-----------------------|---|---|
| $N_{bt_site_yr}$ | = | Annual number of batches of adhesive formulated, per site (batches/site-yr) |
| $Q_{adhes_site_yr}$ | = | Annual facility adhesive production rate (kg adhesive/site-yr) (See Section 3.2) |
| Q_{adhes_bt} | = | Mass of adhesive formulated per batch (Default: 4,000 kg adhesive/batch (CEB, no date) (see below)) |

One of the following three methods may be used to define a default value for the batch size (Q_{adhes_bt}):

- Method 1. If the particular batch size is not known (default method), then assume $Q_{adhes_bt} = 4,000$ kilograms per batch as a default (CEB, no date)

- Method 2. If the density of the formulated adhesive is known, a batch size of 1,000 gallons may be assumed (CEB, no date) and converted to kilograms by multiplying by the adhesive product density:

$$Q_{adhes_bt} = V_{adhes_bt} \times RHO_{adhes} \times 3.785 \frac{L}{gal} \quad (3-3a)$$

Where:

- | | | |
|-----------------|---|--|
| V_{adhes_bt} | = | Volume of adhesive formulated per batch (Default: 1,000 gallons adhesive/batch (CEB, no date)) |
| RHO_{adhes} | = | Density of the formulated adhesive product (kg/L) |

- Method 3. If the number of days of operation ($TIME_{working_days}$) is known, assume one batch is formulated per site per day and estimate the batch size using the following equation:

$$Q_{adhes_bt} = \frac{Q_{adhes_site_yr}}{TIME_{working_days} \times N_{bt_site_day}} \quad (3-3b)$$

Where:

| | | |
|--------------------------------------|---|---|
| $Q_{\text{adhes_site_yr}}$ | = | Annual facility adhesive production rate (kg adhesive/site-yr) (See Section 3.2) |
| $\text{TIME}_{\text{working_days}}$ | = | Annual number of days the adhesive is formulated (days/yr) |
| $N_{\text{bt_site_day}}$ | = | Daily number of adhesive batches formulated at each site (Default: 1 batch/site-day; Alternative default: 3 batches/site-day (See Section 3.7 below)) |

It should be noted that batch sizes vary across the industry. For example, data from a single formulator shows batch sizes ranging from 300 to 5,000 gallons (P2AD, no date). In Method 3 above, the daily number of batches formulated per site may be adjusted based on engineering judgment if the batch size is significantly larger than the default batch size. A maximum default of three batches/site-day may be assumed¹.

Note for default Option 3 – Release and Exposure assessment:

It is recommended that Equation 3-3 be calculated using the two default values for $Q_{\text{adhes_site_yr}}$ to estimate the annual number of batches performed at large and other formulation sites:

1. Calculation for large formulators: use the default $Q_{\text{adhes_site_yr}}$ for *large* formulators, as described in Section 3.2.
2. Calculation for other formulators: use the default $Q_{\text{adhes_site_yr}}$ for *other* formulators, as described in Section 3.2.

In addition, if available information supports alternative defaults for batch size ($Q_{\text{adhes_bt}}$) or daily number of batches ($N_{\text{bt_site_day}}$) at large and other formulators, it is recommended that these alternative values be incorporated into the calculations for the two types of formulators.

3.7 Days of Operation ($\text{TIME}_{\text{working_days}}$)

If the number of days of operation is not known, the following equation may be used to estimate the number of days, based on the annual number of batches formulated per site and the number of batches formulated per day:

$$\text{TIME}_{\text{working_days}} = \frac{N_{\text{bt_site_yr}}}{N_{\text{bt_site_day}}} \quad (3-4)$$

Where:

| | | |
|--------------------------------------|---|--|
| $\text{TIME}_{\text{working_days}}$ | = | Annual number of days the adhesive is formulated (days/yr) |
|--------------------------------------|---|--|

¹For multiple batches per day, assume 8 hours per batch in a 24-hour operating day for a maximum of 3 batches per line, per day (a single line per site is assumed) (engineering judgment).

| | | |
|---------------------|---|---|
| $N_{bt_site_yr}$ | = | Annual number of batches of adhesive formulated, per site (batches/site-yr) (See Equation 3-3) |
| $N_{bt_site_day}$ | = | Daily number of adhesive batches formulated at each site (Default: 1 batch/site-day; Alternative default: 3 batches/site-day (See Equation 3-3b)) |

Assume one batch is formulated per day as a default; however, the number of batches formulated per day should be increased if needed, so the days of operation do not exceed 365 days per year.

Note for default Option 3 – Release and Exposure assessment:

It is recommended that Equation 3-4 be calculated using the two calculated values for $N_{bt_site_yr}$ (Equation 3-3) to estimate the days of operation at large and other formulation sites.

3.8 Daily Use Rate of the Chemical of Interest ($Q_{chem_site_day}$)

The daily use rate for the chemical of interest in formulating adhesives is estimated using the following equation, based on the batch size, the number of batches formulated per day, and the concentration of the chemical of interest in the formulated adhesive product:

$$Q_{chem_site_day} = Q_{adhes_bt} \times N_{bt_site_day} \times F_{chem_comp} \times F_{comp_adhes} \quad (3-5)$$

Where:

| | | |
|-----------------------|---|---|
| $Q_{chem_site_day}$ | = | Daily use rate of the chemical of interest used to formulate the adhesive product (kg chemical/site-day) |
| Q_{adhes_bt} | = | Mass of adhesive formulated per batch (kg adhesive/batch) (See Section 3.6) |
| $N_{bt_site_day}$ | = | Daily number of adhesive batches formulated at each site (batches/site-day) (See Equation 3-4) |
| F_{chem_comp} | = | Mass fraction of the chemical of interest in the adhesive component (kg chemical/kg component) (See Section 3.3) |
| F_{comp_adhes} | = | Mass fraction of the component used in the formulated adhesive product (kg component/kg adhesive) (See Section 3.4) |

Note for default Option 3 – Release and Exposure assessment:

If alternative defaults for the batch size (Q_{adhes_bt}) or daily number of batches ($N_{bt_site_day}$) were used in Equation 3-3, it is recommended that those defaults also be used in Equation 3-5 to estimate the daily use rate of the chemical of interest at large and other formulation sites.

Summary of the Relationship of General Facility Parameters

The values for days of operation, daily use rate of the chemical of interest ($Q_{\text{chem_site_day}}$), and number of sites (N_{sites}) are related. This ESD presents one method for estimating $Q_{\text{chem_site_day}}$ using estimated default values for: 1) the total U.S. production volume of the adhesive; 2) the total number of U.S. formulation sites; 3) batch size ($Q_{\text{adhes_bt}}$); and 4) number of operating days ($\text{TIME}_{\text{working_days}}$).

If N_{sites} and $\text{TIME}_{\text{working_days}}$ are known, $Q_{\text{chem_site_day}}$ can be calculated directly without the use of Equation 3-5. This alternative calculation is:

$$Q_{\text{chem_site_day}} = \frac{Q_{\text{chem_yr}}}{N_{\text{sites}} \times \text{TIME}_{\text{working_days}}}$$

However, it is recommended to calculate the chemical of interest throughput based on the methodology presented in Section 3.8, and compare it to the throughput based on number of sites and operating days, as calculated above.

3.9 Annual Number of Adhesive Component Containers Emptied per Facility ($N_{\text{cont_empty_site_yr}}$)

The number of adhesive component containers unloaded annually per site can be estimated based on the daily use rate, container size, and concentration of the chemical of interest in the component. EPA suggests that a default transportation container size of a 55-gallon drum could be used in the absence of site-specific information. Industry-specific information on the types of containers used by the adhesive formulation industry was not found in the references reviewed for this ESD (refer to Section 8 for a description of the sources reviewed and full citations for those specifically used in these calculations). Engineering judgment should be used to determine if another container type or size is more appropriate (e.g., a 50-pound bag may be more appropriate for a solid component). If the density of a liquid component is not known, the density for water can be used as a default (1 kg/L).

$$N_{\text{cont_empty_site_yr}} = \frac{Q_{\text{chem_site_day}} \times \text{TIME}_{\text{working_days}}}{F_{\text{chem_comp}} \times Q_{\text{cont_empty}}} \quad (3-6)$$

Where:

| | | |
|--------------------------------------|---|---|
| $N_{\text{cont_empty_site_yr}}$ | = | Annual number of containers emptied containing chemical of interest per site (containers/site-yr) |
| $Q_{\text{chem_site_day}}$ | = | Daily use rate of the chemical of interest used to formulate the adhesive product (kg chemical/site-day) (See Equation 3-5) |
| $\text{TIME}_{\text{working_days}}$ | = | Annual number of days the adhesive is formulated (days/yr) (See Equation 3-4) |
| $F_{\text{chem_comp}}$ | = | Mass fraction of the chemical of interest in the adhesive component (kg chemical/kg component) (See Section 3.3) |

$$Q_{\text{cont_empty}}^1 = \text{Mass of the adhesive component in the container (kg component/container)}$$

Note for default Option 3 – Release and Exposure assessment:

It is recommended that Equation 3-6 be calculated using the appropriate default values selected for large and other formulators to estimate the annual number of containers emptied at large and other formulation sites.

3.10 Annual Number of Adhesive Product Containers Filled per Facility ($N_{\text{cont_fill_site_yr}}$)

The number of adhesive product containers filled annually per site can be estimated similar to the methodology described in Section 3.9 above. The calculation is based on the daily use rate, container size, and concentration of the chemical of interest in the formulated adhesive product. EPA suggests that a default transportation container size of a 55-gallon drum could be used in the absence of site-specific information. Industry-specific information on the types of containers used by the adhesive formulation industry was not found in the references reviewed for this ESD (refer to Section 8 for a description of the sources reviewed and full citations for those specifically used in these calculations). Engineering judgment should be used to determine if another container type or size is more appropriate. If the density of an adhesive product is not known, the density for water can be used as a default (1 kg/L).

$$N_{\text{cont_fill_site_yr}} = \frac{Q_{\text{chem_site_day}} \times \text{TIME}_{\text{working_days}}}{F_{\text{chem_comp}} \times F_{\text{comp_adhes}} \times Q_{\text{cont_fill}}} \quad (3-7)$$

Where:

$$\begin{aligned} N_{\text{cont_fill_site_yr}} &= \text{Annual number of containers filled containing chemical of interest per site (containers/site-yr)} \\ Q_{\text{chem_site_day}} &= \text{Daily use rate of the chemical of interest used to formulate the adhesive product (kg chemical/site-day) (See Equation 3-5)} \\ \text{TIME}_{\text{working_days}} &= \text{Annual number of days the adhesive is formulated (days/yr) (See Equation 3-4)} \end{aligned}$$

¹If the mass of the component in each container is not known, it can be calculated using the volume of the container and the density of the component:

$$Q_{\text{cont_empty}} = V_{\text{cont_empty}} \times \text{RHO}_{\text{component}}$$

Where:

$$\begin{aligned} V_{\text{cont_empty}} &= \text{Volume of adhesive component per container (Default: 208 L component/container (55-gallon drum); See Table B-3 in Appendix B for alternative default container volumes)} \\ \text{RHO}_{\text{component}} &= \text{Density of the adhesive component (Default: 1 kg component/L component)} \end{aligned}$$

| | | |
|---------------------------|---|---|
| $F_{\text{chem_comp}}$ | = | Mass fraction of the chemical of interest in the adhesive component (kg chemical/kg component) (See Section 3.3) |
| $F_{\text{comp_adhes}}$ | = | Mass fraction of the component used in the formulated adhesive product (kg component/kg adhesive) (See Section 3.4) |
| $Q_{\text{cont_fill}}^1$ | = | Mass of the adhesive product in the filled container (kg adhesive/container) |

Note for default Option 3 – Release and Exposure assessment:

It is recommended that Equation 3-7 be calculated using the appropriate default values selected for large and other formulators to estimate the annual number of containers filled at large and other formulation sites.

¹If the mass of the adhesive product in each container is not known, it can be calculated using the volume of the container and the density of the adhesive:

$$Q_{\text{cont_fill}} = V_{\text{cont_fill}} \times \text{RHO}_{\text{adhes}}$$

Where:

| | | |
|-----------------------------|---|---|
| $V_{\text{cont_fill}}$ | = | Volume of adhesive product per filled container (Default: 208 L adhesive/container (55-gallon drum); See Table B-3 in Appendix B for alternative default container volumes) |
| $\text{RHO}_{\text{adhes}}$ | = | Density of the formulated adhesive product (Default: 1 kg adhesive/L adhesive) |

4 ENVIRONMENTAL RELEASE ASSESSMENTS

This section presents approaches for estimating the amount of the adhesive chemical of interest released from each process source. The release sources are discussed in the order that they occur in the process (See Figure 2-1, Figure 2-2, and Figure 2-3), and include most likely receiving media (i.e., air, water, landfill, or incineration). The primary sources of release include container residue, process equipment cleaning, and off-spec adhesive product. Key default values used for the release estimates, accompanied by their respective references, are provided in Table A-2 of Appendix A.

It is generally assumed that during adhesive product formulation, the losses of the chemical of interest are minimized in actual practice; however, it is likely that some pre-process or other upstream releases occur. Because losses are assumed to be minimized, the methodology presented in this section for estimating the releases of the chemical of interest from the adhesive formulation process does not include adjustments to account for pre-process or other upstream releases of the chemical (e.g., while some material may remain in the transport container, the entire volume received in the container is assumed when estimating equipment cleaning releases). These omissions of mass balance adjustments should not result in a negative throughput of the chemical of interest in these calculations (i.e., the total amount of chemical released from the process should not exceed the amount that enters the process).

All release equations estimate daily rates for a given site. To estimate annual releases for all sites for a given source, the release rates must be multiplied by the number of days of release and by the total number of adhesive formulation sites using the chemical of interest (N_{sites}) (See Equation 3-2).

Some process releases are expected to be released to the same receiving medium on the same days. Therefore, daily and annual releases to a given medium may be summed to yield total amounts released.

Many of the environmental release estimates presented in this document are based on standard EPA release models, with the exception of the methodology described in Section 4.12 for estimating the amount of release from the disposal of off-spec adhesive product. This release estimate is based on a loss rate for off-spec solution adhesives provided by a Source Reduction Research Partnership (SRRP) study. Table 4-1 summarizes the release estimation methods used in this ESD.

Note that the standard model default values cited are current as of the date of this ESD; however, EPA may update these models as additional data become available. It is recommended that the most current version of the models be used in these calculations.

EPA has developed a software package (ChemSTEER) containing these models as well as all current EPA defaults. Because of the complexity of the air release models, ChemSTEER is recommended for estimating air releases. Appendix B provides additional information on ChemSTEER, including instructions for obtaining the program, as well as background information, model equations, and default values for several parameters for all standard EPA models.

Table 4-1. Summary of Adhesive Formulation Scenario Release Models

| Release Source # | Description | Model Name or Description^a | Standard EPA Model (✓) |
|-------------------------|--|---|-------------------------------|
| 1 | Container residue released to non-air media | Specific model used is based on the type and size of the containers, and on the physical state of the adhesive component: <ul style="list-style-type: none"> • EPA/OPPT Bulk Transport Residual Model • EPA/OPPT Drum Residual Model • EPA/OPPT Small Container Residual Model • EPA/OPPT Solid Residuals in Transport Containers Model | ✓ |
| 2 | Open surface losses of volatile chemical to air during container cleaning | EPA/OPPT Penetration Model | ✓ |
| 3 | Transfer operation losses of volatile chemical to air during unloading | EPA/OAQPS AP-42 Loading Model | ✓ |
| 4 | Dust losses of solid chemical during unloading | EPA/OPPT Dust Emissions from Transferring Solids Model | ✓ |
| 5 | Vented losses of volatile chemical to air during process operations | EPA/OPPT Penetration Model | ✓ |
| 6 | Adhesive product sampling wastes disposed to non-air media | No methodology for quantifying the release from this source has been developed | |
| 7 | Open surface losses of volatile chemical to air during product sampling | EPA/OPPT Penetration Model | ✓ |
| 8 | Equipment cleaning residues released to non-air media | EPA/OPPT Multiple Process Vessel Residual Model | ✓ |
| 9 | Open surface losses of volatile chemical to air during equipment cleaning | EPA/OPPT Penetration Model | ✓ |
| 10 | Transfer operation losses of volatile chemical to air during product container loading | EPA/OAQPS AP-42 Loading Model | ✓ |
| 11 | Off-spec product wastes disposed to non-air media | Loss rate is based on available industry-specific data | |

OPPT – Office of Pollution Prevention and Toxics.

OAQPS – Office of Air Quality Planning and Standards.

a – Additional detailed descriptions for each of the models presented in this section are provided in Appendix B.

Note for default Option 3 – Release and Exposure assessment:

It is recommended that each of the release calculations described in this section be performed using the appropriate default values selected for large and other formulators to estimate the releases from large and other formulation sites.

4.1 Control Technologies

No specific data were found on typical pollution control technologies used by the adhesive formulation industry, although it is likely that some sites may implement pretreatment of their process wastewaters or have controls on their process stacks. EPA suggests that as a default, it should be assumed that all aqueous wastes are discharged directly to a publicly owned treatment works (POTW) for pretreatment prior to discharge to surface waters. The Pacific Northwest Pollution Prevention Resource Center (PPRC) does note that switching from organic-solvent based to water-based solution adhesives may require additional on-site wastewater treatment systems (PPRC, 1998).

4.2 Adhesive Component Container Residue Released to Water, Incineration, or Landfill (Release 1)

The amount of adhesive component remaining in transportation containers depends on the size of the transport container and the physical form of the component product. In the absence of industry-specific data, the following standard EPA models may be used to estimate container residue releases:

- *EPA/OPPT Bulk Transport Residual Model* may be used for large containers (e.g., totes, tank trucks, rail cars) containing greater than or equal to 100 gallons of liquid;
- *EPA/OPPT Drum Residual Model* may be used for drums containing between 20 and 100 gallons of liquid;
- *EPA/OPPT Small Container Residual Model* may be used for liquid containers containing less than 20 gallons; and,
- *EPA/OPPT Solid Residuals in Transport Containers Model* may be used for containers of all sizes containing solids.

The rationale, defaults, and limitations of these models are further explained in Appendix B. The release estimates are based on the current version of the models (as of April 10, 2006). Standard EPA/OPPT models are subject to change; therefore, the current version of the standard EPA/OPPT model should be used.

Adhesive component chemicals may be received as liquids or solids. Note that most components of hot-melt adhesives are expected to be solids. If the physical state of the

component is not known, EPA suggests reviewing the physical property data summarized in Table 2-4 for some example adhesive component chemicals and using engineering judgment to determine if the chemical of interest should be assumed a solid or liquid for the purposes of the assessment.

EPA suggests that a default transportation container size of a 55-gallon drum should be used in the absence of site-specific information. Industry-specific information on the types of containers used by the adhesive formulation industry was not found in the references reviewed for this ESD (refer to Section 8 for a description of the sources reviewed and full citations for those specifically used in these calculations). Engineering judgment should be used to determine if another container type or size is more appropriate (e.g., a 50-pound bag may be more appropriate for a solid component).

Solvent-based adhesive formulators may rinse the containers and add the residual to the next batch (NEWMOA, 1999). Although hot-melt adhesives are expected to be insoluble in water (reducing the likelihood of discharging this release to water), container residue could be released to water. Alternatively, it could be incinerated or landfilled during container cleaning or disposal. Therefore, if additional site-specific information is not available, the entirety of this release is conservatively assessed to each of water, incineration, and landfill.

The annual number of containers emptied ($N_{\text{cont_empty_site_yr}}$) is estimated based on the daily use rate of the component and the container size (see Section 3.9). EPA recommends assuming 55-gallon (208 L) drums and density of 1 kg/L (density of water) as defaults. If the fraction of the chemical in the component is unknown, assume 100 percent concentration.

If the $N_{\text{cont_empty_site_yr}}$ value is fewer than the days of operation ($\text{TIME}_{\text{working_days}}$), the days of release equal $N_{\text{cont_empty_site_yr}}$ (as calculated in Equation 3-6) and the daily release is calculated based on the following equation:

$$E_{\text{local_container_residue_disp}} = Q_{\text{cont_empty}} \times F_{\text{chem_comp}} \times F_{\text{container_residue}} \times N_{\text{cont_empty_site_day}} \quad (4-1a)$$

This release will occur over $[N_{\text{cont_empty_site_yr}}]$ days/year from $[N_{\text{sites}}]$ sites

Where:

| | | |
|--|---|---|
| $E_{\text{local_container_residue_disp}}$ | = | Daily release of chemical of interest from container residue (kg chemical/site-day) |
| $Q_{\text{cont_empty}}$ | = | Mass of the adhesive component in the container (kg component/container) (Default: use the same value used to estimate $N_{\text{cont_empty_site_yr}}$ in Section 3.9) |
| $F_{\text{chem_comp}}$ | = | Mass fraction of the chemical of interest in the adhesive component (kg chemical/kg component) (See Section 3.3) |
| $F_{\text{container_residue}}$ | = | Fraction of adhesive component remaining in the container as residue (Default: 0.03 kg component remaining/kg shipped for drums (CEB, 2002a); See Appendix B for defaults used for other container types) |

$N_{\text{cont_empty_site_day}}^1$ = Number of containers unloaded per site, per day (Default: 1 container/site-day)

If $N_{\text{cont_empty_site_yr}}$ is greater than $\text{TIME}_{\text{working_days}}$, more than one container is unloaded per day (i.e., $N_{\text{cont_empty_site_day}} > 1$). The days of release should equal the days of operation, and the average daily release can be estimated based on the following equation:

$$\text{Elocal}_{\text{container_residue_disp}} = Q_{\text{chem_site_day}} \times F_{\text{container_residue}} \quad (4-1b)$$

This release will occur over [$\text{TIME}_{\text{working_days}}$] days/year from [N_{sites}] sites

Where:

$\text{Elocal}_{\text{container_residue_disp}}$ = Daily release of chemical of interest from container residue (kg chemical/site-day)

$Q_{\text{chem_site_day}}$ = Daily use rate of the chemical of interest used to formulate the adhesive product (kg chemical/site-day) (See Equation 3-5)

$F_{\text{container_residue}}$ = Fraction of adhesive component remaining in the container as residue (Default: 0.03 kg component remaining/kg shipped for drums (CEB, 2002a); See Appendix B for defaults used for other container types)

Note: this equation may also be used if a container size is not assumed in Equations 3-6 and 4-1a, and $N_{\text{cont_empty_site_yr}}$ is unknown.

4.3 Open Surface Losses to Air During Container Cleaning (Release 2)

For nonvolatile chemicals (e.g., the vapor pressure is < 0.001 torr), releases to air are expected to be negligible.

If the chemical is volatile (e.g., the vapor pressure is > 0.001 torr), it may volatilize and be emitted from the process while empty containers are being rinsed and cleaned ($\text{Elocal}_{\text{air_cleaning}}$). The EPA standard model for estimating releases to air from containers cleaned indoors may be used (*EPA/OPPT Penetration Model*).

Table 4-2 lists the model inputs and default values. The models and all current EPA defaults have been programmed into ChemSTEER; EPA recommends using this software to

¹ The daily number of containers unloaded per site may be estimated as (consistent with Section 3.9):

$$N_{\text{cont_empty_site_day}} = \frac{N_{\text{cont_empty_site_yr}}}{\text{TIME}_{\text{working_days}}}$$

($N_{\text{cont_empty_site_day}}$ should be rounded up to the nearest integer.)

Where:

$N_{\text{cont_empty_site_yr}}$ = Annual number of containers emptied containing chemical of interest per site (containers/site-yr) (See Equation 3-6)

$\text{TIME}_{\text{working_days}}$ = Annual number of days the adhesive is formulated (days/yr) (See Equation 3-4)

calculate open surface losses to air during container cleaning. Appendix B provides background information, model equations, and default values for several parameters the model uses to estimate daily releases to air.

Table 4-2. EPA/OPPT Penetration Model Parameter Default Values During Container Cleaning

| Input Parameter | Default Values |
|----------------------------------|--|
| Diameter of Opening | EPA default 2 in. (5.08 cm) for all containers less than 5,000 gallons (CEB, 2002b) (See Appendix B for alternative default diameters) |
| Frequency of Release | Equal to the lesser of $N_{\text{cont_empty_site_yr}}$ or $\text{TIME}_{\text{working_days}}$, consistent with Section 4.2 |
| Molecular Weight | Chemical-specific parameter |
| Number of Sites | Calculated in Section 3.5 |
| Operating Hours for the Activity | Number of containers per site, per day ($N_{\text{cont_empty_site_day}}$, consistent with Release 1) divided by the unload rate (CEB, 2002b) (Default: 20 containers/hr for volumes between 20 and 1,000 gallons (CEB, 1991); Alternative default unload rates are found in Appendix B) |
| Vapor Pressure | Chemical-specific parameter |
| Air Speed | EPA default 100 feet/min for indoor conditions (CEB, 1991) |
| Vapor Pressure Correction Factor | Standard EPA default = 1 |

Note: The model also assumes standard temperature and pressure along with ideal gas interactions.

4.4 Transfer Operation Losses to Air from Unloading the Adhesive Component (Release 3)

For nonvolatile chemicals (e.g., the vapor pressure is < 0.001 torr), releases to air are expected to be negligible.

If the chemical is volatile (e.g., the vapor pressure is > 0.001 torr), releases to air may occur from the displacement of saturated air when the chemical is transferred ($E_{\text{local_air_transfers}}$). The standard EPA estimation model for transfer operations may be used to estimate the release to air (*EPA/OAQPS AP-42 Loading Model*). The transfer operations model provides worst and typical case estimates for releases and exposures during transfer operations (e.g., transferring liquids from transport containers into storage tanks or mixers).

Table 4-3 lists the model inputs and default values. The models and all current EPA defaults have been programmed into ChemSTEER; EPA recommends using this software to calculate air releases and exposures during transfer operations. Appendix B provides background information, model equations, and default values for several parameters the model uses to estimate daily releases to air.

Table 4-3. EPA/OAQPS AP-42 Loading Model Parameter Default Values for Air Releases During Unloading

| Input Parameter | Default Values |
|----------------------------------|---|
| Saturation Factor | EPA defaults 0.5 (typical) and 1 (worst case) for all containers less than 5,000 gallons (CEB, 2002b) (See Appendix B for alternative default saturation factors) |
| Frequency of Release | Equal to the lesser of $N_{\text{cont_empty_site_yr}}$ or $\text{TIME}_{\text{working_days}}$, consistent with Section 4.2 |
| Molecular Weight | Chemical-specific parameter |
| Number of Sites | Calculated in Section 3.5 |
| Operating Hours for the Activity | Number of containers per site, per day (see Table 4-2) divided by the unload rate (CEB, 2002b) (default unload rates are found in Appendix B) |
| Unloading Rate | EPA default 20 containers/hr for volumes between 20 and 1,000 gallons (CEB, 1991) (Alternative default unload rates are found in Appendix B) |
| Container Volume | Default: 55-gallon drum (208 L) (See Appendix B for alternative default container volumes) |
| Vapor Pressure | Chemical-specific parameter |
| Vapor Pressure Correction Factor | Standard EPA default = 1 |

Note: The model also assumes standard temperature and pressure along with ideal gas interactions.

4.5 Dust Generation from Transfer Operations Released to Air, or Collected and Released to Water, Incineration, or Landfill (Release 4)

For liquid adhesive components received at adhesive product formulation site, this release is negligible

For solid adhesive components, dust generation is expected from transferring operations. Industry-specific data was not found on control technologies used to collect and dispose dust generated from unloading or transferring solid powders. The *EPA/OPPT Dust Emissions from Transferring Solids Model* may be used to estimate dust releases. This model assumes that up to 0.5 percent of the transferred quantity may be released to the environment (CEB, 2006b). The rationale, defaults, and limitations of these models are further explained in Appendix B.

No information was available on the media of release for adhesive formulation dust waste; however, in some cases the vented particulate may be small enough as to travel several miles from the facility, resulting in environmental and human exposures to the chemical of interest beyond the boundaries of the site. Dusts that are either collected on the filters or cleaned from workspace surfaces are expected to be disposed to water, incineration, or landfill.

Most facilities utilize some type of control technology to collect fugitive emissions. Many facilities collect fugitive dust emissions from these operations in filters and dispose of the filters in landfills or by incineration. Wet scrubbers are not anticipated for this industry. In some

cases, uncontrolled/uncollected particulate may be small enough to travel several miles from the facility, resulting in environmental and human exposures to the chemical of interest beyond the boundaries of the site. Some amount of the dust particles may alternately settle on the floor or equipment within the workspace and are disposed of during facility cleaning (water if the floors are rinsed or land or incineration if the floors are swept). Therefore, if additional site-specific information is not available, the entirety of this release is conservatively assessed to each of air, water, incineration, and landfill.

The daily release of fugitive dust emissions can be estimated using the daily use rate ($Q_{\text{chem_site_day}}$).

If the facility-specific information states a control technology is employed, the release may be partitioned to the appropriate media. Table 4-4 provides estimated efficiencies for more common control technologies that may be used in the adhesives formulation industry.

Table 4-4. Estimated Control Technology Efficiencies

| Control Technology | Estimated Efficiency (%) | Notes | Default Media of Release for Controlled Release |
|--------------------------------|--------------------------|---------------------------------|---|
| Filter (such as a baghouse) | >99% | For particles >1 μm | Incineration or Land |
| Cyclone/Mechanical Collectors: | 80-99 | For particles >15 μm | Incineration or Land |

Source: CEB, 1991.

The portion of release that may be captured by the control technology may be disposed to incineration or land or may be recycled. If the control technology is not known, it can be assumed that none of the dust generated is captured. If the control technology is known, the quantity captured may be estimated using the following equation:

$$E_{\text{local dust captured}} = Q_{\text{chem_site_day}} \times F_{\text{dust_generation}} \times F_{\text{dust_control}} \quad (4-2)$$

Where:

| | | |
|----------------------------------|---|---|
| $E_{\text{local dust captured}}$ | = | Daily amount captured by control technology from transfers or unloading (kg/site-day) |
| $Q_{\text{chem_site_day}}$ | = | Daily use rate of the chemical of interest used to formulate the adhesive product (kg chemical/site-day) (See Section 3.9) |
| $F_{\text{dust_generation}}$ | = | Loss fraction of chemical during transfer/unloading of solid powders (Default: 0.005 kg released/kg handled) |
| $F_{\text{dust_control}}$ | = | Control technology capture efficiency (kg captured/kg processed) (Default: If the control technology is unknown, assume capture efficiency = 0 kg captured/kg processed, see Table 4-4 for alternative efficiencies). |

The portion of the release that will not be captured by the control technology and may be released to air or settle onto the facility floor may be estimated using the following equation:

$$E_{\text{local}_{\text{dust_fugitive}}} = Q_{\text{chem_site_day}} \times F_{\text{dust_generation}} \times (1 - F_{\text{dust_control}}) \quad (4-3)$$

Where:

| | | |
|--|---|--|
| $E_{\text{local}_{\text{dust_fugitive}}}$ | = | Daily amount not captured by control technology from transfers or unloading (kg/site-day) |
| $Q_{\text{chem_site_day}}$ | = | Daily use rate of the chemical of interest used to formulate the adhesive product (kg chemical/site-day) (See Section 3.9) |
| $F_{\text{dust_generation}}$ | = | Loss fraction of chemical during transfer/unloading of solid powders (Default: 0.005 kg released/kg handled) |
| $F_{\text{dust_control}}$ | = | Control technology capture efficiency (kg captured/kg processed) (Default: If the control technology is unknown, assume capture efficiency = 0 kg captured/kg processed, see Table 4-4). |

This approach is designed for screening-level estimates where appropriate industry-specific or chemical specific information is not available. If the site provided a loss fraction from dust releases, then the site-specific number should be used.

4.6 Vented Losses to Air During Process Operations (Release 5)

For nonvolatile chemicals (e.g., the vapor pressure is < 0.001 torr at the operating temperature), releases to air are expected to be negligible.

If the chemical is volatile (e.g., the vapor pressure is > 0.001 torr) at the operating temperature, chemicals may volatilize and be emitted from the process during mixing ($E_{\text{local}_{\text{air_process_vent}}}$). In an operation where the adhesive product is generally nonvolatile or that incorporates relatively stable, non-reactive components, the mixing vessel and other operations may be open. In this case, volatile chemicals may be emitted into the workspace and subsequently vented to the air outside of the facility.

Because the components in organic solvent-based adhesives and reactive adhesives may volatilize or degrade/react when exposed to ambient conditions, it is expected that their formulation process is sealed and vented to the air outside of the facility (e.g., through a stack), minimizing the losses and fugitive emissions into the workspace. Scrubbers or other pollution control devices may be required to prevent excess VOC emissions; however, pollution control devices are not standard across the industry. One study estimated a three percent loss to air due to evaporation during mixing of volatile solvents; however, the vapor pressure of these solvents was over 70 torr (SRRP, no date).

It should be noted that hot-melt adhesives and some PSAs are processed at temperatures ranging from 150°C to 190°C (Ullmann, 1985). For most components of hot-melt adhesives (polymers and waxes), the elevated temperatures will not cause them to volatilize and be emitted into the air; however, the elevated temperature could result in air releases for some

components. The vapor pressure of the chemical of interest at these elevated temperatures should be estimated to determine whether it should be considered volatile for the purposes of this assessment (e.g., has a vapor pressure > 0.001 torr at 190°C). If the chemical is volatile at these temperatures, the volatile releases should be estimated at the elevated temperature conditions.

The EPA standard model for estimating releases to air from open vessels or process vents may be used (*EPA/OPPT Penetration Model*). The model inputs and default values are listed in Table 4-5. The models and all current EPA defaults have been programmed into ChemSTEER; EPA recommends using this software to calculate open surface losses to air during process operations. Appendix B provides background information, model equations, and default values for several parameters the model uses to estimate daily releases to air.

Table 4-5. EPA/OPPT Penetration Model Parameter Default Values During Process Operations

| Input Parameter | Default Values |
|----------------------------------|---|
| Diameter of Opening | EPA default 4-in vent (10 cm) (engineering judgment) If the mixing vessel is open, see Equation 4-4 |
| Frequency of Release | Equal to $TIME_{\text{working days}}$ (See Section 3.7) |
| Molecular Weight | Chemical-specific parameter |
| Number of Sites | Calculated in Section 3.5 |
| Operating Hours for the Activity | 24 hrs/day or 8 hrs/batch $\times N_{\text{bt_site_day}}$ (See Section 3.7), whichever is less (CEB, 2002b) and consistent with calculations described in Section 3.7 |
| Temperature | For non-heated processes, use the standard EPA default of 298 K (CEB, 1991) For heated processes, use worst-case temperature of 463 K (Ullmann, 1985) |
| Vapor Pressure | Chemical-specific chemical parameter (for heated processes, EPA recommends using the vapor pressure of the chemical at the operating temperature (e.g., worst-case default of 190°C)) |
| Air Speed | EPA default 100 feet/min for indoor conditions (CEB, 1991) |
| Vapor Pressure Correction Factor | Standard EPA default = 1 |

Note: The model generally assumes standard temperature and pressure along with ideal gas interactions.

Two parameters required for using the model are release time and diameter of the opening. EPA suggests assuming the air release occurs over eight hours per batch as a default (CEB, no date). Mixing vessels will likely be closed; therefore, EPA also suggests assuming the vent has an opening diameter of four inches (engineering judgment¹). These defaults should be used in absence of site-specific data for the *EPA/OPPT Penetration Model*.

¹ Note: The 4-inch vent diameter default is based on professional experience in the radiation-curable adhesives formulation, fermentation, and petroleum processing industries. Based on these industries, a 4-inch vent is assumed to provide conservative estimates for potential air releases during operations. Similar vent sizes are anticipated throughout the adhesive formulation industry; however, the applicability of this default to the entire industry is uncertain. Additionally, the vessel may be vented through control technologies (e.g.,

If it is known that the process utilizes an open mixing vessel, the opening diameter should be the diameter of the vessel and not of the vent. EPA recommends assuming that the mixing vessel is cylindrical and capable of holding the known or estimated batch size ($Q_{\text{adhes_bt}}$; See Section 3.6). The following equation can be used to calculate the opening diameter to use in the *EPA/OPPT Penetration Model* based on batch size:

$$D_{\text{opening}} = \left[\frac{4 \times V_{\text{adhes_bt}} \times 3785.44 \text{ (cm}^3 \text{ / gal)}}{\pi} \right]^{1/3} \quad (4-4)$$

Where:

D_{opening} = Diameter of the mixing vessel opening (cm/vessel)
 $V_{\text{adhes_bt}}$ = Volume of adhesive formulated per batch (See Section 3.6)

Note that this equation assumes an aspect ratio (height/diameter) of one, per McCabe, Smith, and Harriott, Unit Operations of Chemical Engineering, 5th Edition to relate mixing time for various types of impellers and Reynolds Number.

4.7 Adhesive Product Sampling Wastes Disposed to Water, Incineration, or Landfill (Release 6)

EPA generally assumes that formulation processes incorporate product sampling activities for quality assurance/quality control (QA/QC) and that some amount of waste from this sampling will be generated and disposed to either water, incineration, or landfill (engineering judgment). If additional site-specific information is not available, the entirety of this release is conservatively assessed to all three media. No industry-specific data were found in the references reviewed for this ESD (refer to Section 8 for a description of the sources reviewed and full citations for those specifically used in these calculations), nor does EPA currently have data on QA/QC sampling waste amounts that can be used to generally quantify the release of these process wastes to non-air media.

It should be noted that EPA expects releases of the chemical from product sampling activities to be relatively low in comparison to the other sources of release in the adhesive formulation process.

4.8 Open Surface Losses to Air During Product Sampling (Release 7)

For nonvolatile chemicals (e.g., the vapor pressure is < 0.001 torr), releases to air are expected to be negligible.

If the chemical is volatile (e.g., the vapor pressure is > 0.001 torr), it may volatilize and be emitted from the process during product QA/QC sampling activities ($E_{\text{local_air_sample}}$). The

scrubber, condenser, thermal oxidizer); however, industry-specific information on vent sizes or control technologies for volatile components was not identified.

EPA standard model for estimating releases to air from sampling activities performed indoors may be used (*EPA/OPPT Penetration Model*). It should be noted that EPA expects releases of the chemical from product sampling activities to be relatively low in comparison to the other sources of release in the adhesive formulation process.

In the case of hot-melt adhesives, it is assumed that the product will be in its hot, molten form for at least a portion of the sampling activity. As previously described in Section 4.6, most components of hot-melt adhesives (polymers and waxes), the elevated temperatures will not cause them to volatilize and be emitted into the air; however, the elevated temperature (ranging from 150°C to 190°C (Ullmann, 1985)) could result in air releases for some components. The vapor pressure of the chemical of interest at these elevated temperatures should be estimated to determine whether it should be considered volatile for the purposes of this assessment (e.g., has a vapor pressure > 0.001 torr at 190°C). If the chemical is volatile at these temperatures, the volatile releases should be estimated at the elevated temperature conditions.

The model inputs and default values are listed in Table 4-6. The models and all current EPA defaults have been programmed into ChemSTEER; EPA recommends using this software to calculate open surface losses to air during container cleaning. Appendix B provides background information, model equations, and default values for several parameters the model uses to estimate daily releases to air.

Table 4-6. EPA/OPPT Penetration Model Parameter Default Values During Product Sampling

| Input Parameter | Default Values |
|----------------------------------|---|
| Diameter of Opening | EPA defaults are 1 in. (2.5 cm) typical; and 4 in. (10 cm) worst case (CEB, 2002b) |
| Frequency of Release | Equal to TIME _{working days} (See Section 3.7) |
| Molecular Weight | Chemical-specific parameter |
| Number of Sites | Calculated in Section 3.5 |
| Operating Hours for the Activity | 1 hour/day (CEB, 1991) |
| Temperature | For non-heated processes, use the standard EPA default of 298 K (CEB, 1991) For heated processes, use worst-case temperature of 463 K (Ullmann, 1985) |
| Vapor Pressure | Chemical-specific chemical parameter (for heated processes, EPA recommends using the vapor pressure of the chemical at the operating temperature (e.g., worst-case default of 190°C)) |
| Air Speed | EPA default 100 feet/min for indoor conditions (CEB, 1991) |
| Vapor Pressure Correction Factor | Standard EPA default = 1 |

Note: The model also assumes standard temperature and pressure along with ideal gas interactions.

4.9 Equipment Cleaning Releases to Water, Incineration or Landfill (Release 8)

The amount of residual adhesive chemical remaining in the process equipment may be estimated using the *EPA/OPPT Multiple Process Vessel Residual Model*. The model assumes that no more than two percent of the batch size or capacity of the process remains in the equipment as residue that is released as equipment cleaning waste. The multiple vessel model is recommended as the default because the mixing vessel, cooling equipment (hot-melt adhesives), and adhesive packaging dispensing equipment will be cleaned. These residues may be released to water, incineration, or landfill. If additional site-specific information is not available, the entirety of this release is conservatively assessed to all three media.

The wide range of adhesives formulated and the limited shelf life of many adhesive products makes equipment cleaning waste minimization a challenge. Companies cannot typically recycle materials into future batches, and it is difficult to schedule longer production runs of a single product (P2AD, no date). Many facilities are expected to clean equipment after each batch. In some cases (e.g., PSA sites), formulators will perform daily equipment cleaning (NEWMOA, 1999). While equipment cleaning may be less frequent at some sites, equipment cleaning after each batch can be assumed as a conservative estimate.

If $N_{bt_site_yr}$ or known number of cleanings is fewer than the days of operation ($TIME_{working_days}$), the days of release equal $N_{bt_site_yr}$ (as calculated in Section 3.6) and the daily release of chemical residue in the process equipment is calculated using the following equation:

$$E_{local_equipment_cleaning} = Q_{adhes_bt} \times F_{chem_comp} \times F_{comp_adhes} \times N_{bt_site_day} \times F_{equipment_cleaning} \quad (4-5a)$$

This release will occur over $[N_{bt_site_yr}]$ days/year from $[N_{sites}]$ sites

If $N_{bt_site_yr}$ is greater than $TIME_{working_days}$, the days of release equal the days of operation, and the daily release of chemical residue in the process equipment is calculated using the following equation:

$$E_{local_equipment_cleaning} = Q_{chem_site_day} \times F_{equipment_cleaning} \quad (4-5b)$$

This release will occur over $[TIME_{working_days}]$ days/year from $[N_{sites}]$ sites

Where:

| | | |
|----------------------------------|---|--|
| $E_{local_equipment_cleaning}$ | = | Daily release of chemical of interest from equipment cleaning (kg chemical/site-day) |
| Q_{adhes_bt} | = | Mass of adhesive formulated per batch (kg adhesive/batch) (See Section 3.6) |
| F_{chem_comp} | = | Mass fraction of the chemical of interest in the adhesive component (kg chemical/kg component) (See Section 3.3) |
| F_{comp_adhes} | = | Mass fraction of the component in the formulated adhesive product (kg component/kg adhesive) (See Section 3.4) |
| $N_{bt_site_day}$ | = | Daily number of adhesive batches formulated at each site (See Equation 3-4) |
| $F_{equipment_cleaning}$ | = | Fraction of adhesive product released as residual in process equipment (Default: 0.02 kg adhesive released/kg batch holding capacity (CEB, 1992a)) |

$Q_{\text{chem_site_day}}$ = Daily use rate of the chemical of interest used to formulate the adhesive product (kg chemical/site-day) (See Equation 3-5)

4.10 Open Surface Losses to Air During Equipment Cleaning (Release 9)

For nonvolatile chemicals (e.g., the vapor pressure is < 0.001 torr), releases to air are expected to be negligible.

If the chemical is volatile (e.g., the vapor pressure is > 0.001 torr) it may be released to the air ($E_{\text{local,air_eqpt_cleaning}}$). This operation is likely to occur indoors; therefore, the *EPA/OPPT Penetration Model* (EPA default for indoor operations) may be used to estimate the release of volatile chemicals during equipment cleaning. Model inputs and default values are listed in Table 4-7. The models and all current EPA defaults have been programmed into ChemSTEER; EPA recommends using this software to calculate open surface losses to air during equipment cleaning. Appendix B provides background information, model equations, and default values for several parameters the model uses to estimate daily releases to air.

Table 4-7. EPA/OPPT Penetration Model Parameter Default Values During Equipment Cleaning

| Input Parameter | Default Values |
|----------------------------------|---|
| Diameter of Opening | EPA default 3-ft manhole (92 cm) (CEB, 2002b) |
| Frequency of Release | Equal to the number of cleanings per year, as determined in Section 4.9 |
| Molecular Weight | Chemical-specific parameter |
| Number of Sites | Calculated in Section 3.5 |
| Operating Hours for the Activity | 24 hrs/day or EPA default 4 hrs/batch $\times N_{\text{bt_site_day}}$ (See Section 3.7), whichever is less (CEB, 2002b) and consistent with calculations described in Section 3.7 |
| Vapor Pressure | Chemical-specific parameter |
| Air Speed | EPA default 100 feet/min for indoor conditions (CEB, 1991) |
| Vapor Pressure Correction Factor | Standard EPA default = 1 |

Note: The model also assumes standard temperature and pressure along with ideal gas interactions.

The default assumption for operating hours for this activity is based on the EPA default of four hours for cleaning multiple vessels. One case study indicated a range of equipment cleaning time between one and three hours (P2AD, no date). EPA suggests that the default of four hours per cleaning be used in lieu of site-specific information (CEB, 2002b).

4.11 Transfer Operation Losses to Air from Loading Adhesive Product into Transport Containers (Release 10)

For nonvolatile chemicals (e.g., the vapor pressure is < 0.001 torr) at the operating temperature, releases to air are expected to be negligible.

If the chemical is volatile (e.g., the vapor pressure is > 0.001 torr) at the operating temperature, chemicals may volatilize and be emitted during adhesive product transfer (e.g., drumming) operations (Elocal_{air_packaging}). In an operation where the adhesive product is generally nonvolatile or that incorporates relatively stable, non-reactive components, the transfer operations may be open. In this case, volatile chemicals may be emitted into the workspace and subsequently vented to the air outside of the facility.

Because of the components in organic solvent-based adhesives and reactive adhesives may volatilize or degrade/react when exposed to ambient conditions, it is expected that the transfer process is sealed and vented to the air outside of the facility (e.g., through a stack), minimizing the losses and fugitive emissions into the workspace. Scrubbers or other pollution control devices may be required to prevent excess VOC emissions; however, pollution control devices are not standard across the industry.

It should be noted that hot-melt adhesives and some PSAs are processed at elevated temperatures (ranging from 150°C to 190°C (Ullmann, 1985)) and may be transferred to the containers as hot, molten liquids. As previously discussed in Section 3.6, most components of hot-melt adhesives (polymers and waxes) are not expected to be volatile even at elevated temperatures; however, the elevated temperature could result in air releases for some components. The vapor pressure of the chemical of interest at these elevated temperatures should be estimated to determine whether it should be considered volatile for the purposes of this assessment (e.g., the vapor pressure is > 0.001 torr at 190°C). If the chemical is volatile at these temperatures, the volatile releases should be estimated at the elevated temperature conditions.

For volatile chemicals (e.g., the vapor pressure is >0.001 torr), the *EPA/OAQPS AP-42 Loading Model* may be used. Model parameter defaults are based on the type and size of the containers. A default transportation container size of a 55-gallon drum should be used in the absence of site-specific information. Industry-specific information on the types of containers used by the adhesive formulation industry was not found in the references reviewed for this ESD (refer to Section 8 for a description of the sources reviewed and full citations for those specifically used in these calculations). Engineering judgment should be used to determine if another container type or size is more appropriate.

Model inputs and default values are listed in Table 4-8. The model and all current EPA defaults have been programmed into ChemSTEER; EPA recommends using this software to calculate open surface losses to air during container loading. Appendix B provides background information, model equations, and default values for several parameters the model uses to estimate daily releases to air.

Table 4-8. EPA/OAQPS AP-42 Loading Model Parameter Default Values During Adhesive Product Packaging

| Input Parameter | Default Values |
|----------------------------------|--|
| Saturation Factor | EPA defaults 0.5 (typical) and 1 (worst case) for all containers less than 5,000 gallons (CEB, 1991) (See Appendix B for alternative default diameters) |
| Frequency of Release | Equal to the lesser of $N_{\text{cont_fill_site_yr}}$ (Section 3.10) or $\text{TIME}_{\text{working_days}}$ (Section 3.7) |
| Molecular Weight | Chemical-specific parameter |
| Number of Sites | Calculated in Section 3.5 |
| Operating Hours for the Activity | Number of containers per site, per day ¹ divided by the fill rate (CEB, 2002b) (Default: 20 containers/hr for volumes between 20 and 1,000 gallons (CEB, 1991); Alternative default fill rates are found in Appendix B) |
| Temperature | For non-heated processes, EPA recommends using the standard EPA default of 298 K (CEB, 1991) For heated processes, EPA recommends using the worst-case temperature of 463 K (Ullmann, 1985) |
| Vapor Pressure | Chemical-specific chemical parameter (for heated processes, EPA recommends using the vapor pressure of the chemical at the operating temperature (e.g., worst-case default of 190°C)) |
| Container Volume | Default: 55-gallon drum (208 L) (See Appendix B for alternative default container volumes) |
| Vapor Pressure Correction Factor | Standard EPA default = 1 |

Note: The model also assumes standard temperature and pressure along with ideal gas interactions.

¹The daily number of containers filled per site may be estimated as:

$$N_{\text{cont_fill_day}} = \frac{N_{\text{cont_fill_site_yr}}}{\text{TIME}_{\text{working_days}}}$$

($N_{\text{cont_fill_day}}$ should be rounded up to the nearest integer.)

Where:

$N_{\text{cont_fill_site_yr}}$ = Annual number of containers filled containing chemical of interest per site (containers/site-yr) (See Equation 3-7)
 $\text{TIME}_{\text{working_days}}$ = Annual number of days the adhesive is formulated (days/yr) (See Equation 3-4)

4.12 Off-Spec Product Released to Water, Incineration or Landfill (Release 11)

This release estimate is based on the loss fraction from off-spec product and the use rate of the component. An SRRP study estimated one percent loss rate in the annual production of solvent-based solution adhesives from off-spec product wastes disposed as solids (SRRP, no date). No information was provided for the likely receiving media for this release. For the purposes of the assessment, if additional site-specific information is not available the entirety of this release is conservatively assessed to each of water, incineration, and landfill. In addition, a report by the Northeast Waste Management Officials' Association (NEWMOA) and the Northeast States for Coordinated Air Use Management (NESCAUM) states that large volumes of unused or off-spec product waste may be generated from tape manufacturers formulating more PSA than needed for a particular product run (NEWMOA, 1999).

It is assumed that off-spec product waste does not generally result in a small, daily release, but a large, infrequent release (e.g., when an entire batch is contaminated). EPA suggests that the days of release should be estimated using the following equation and the result rounded up to the nearest integer:

$$N_{\text{off-spec_days_site_yr}} = \frac{N_{\text{bt_site_yr}} \times F_{\text{off-spec_bt}}}{N_{\text{off-spec_bt_day}}} \quad (4-6)$$

Where:

| | | |
|---------------------------------------|---|--|
| $N_{\text{off-spec_days_site_yr}}$ | = | Number of days per year off-spec adhesive product waste is disposed/released (days/site-yr) |
| $N_{\text{bt_site_yr}}$ | = | Annual number of batches of adhesive formulated, per site (batches/site-yr) (See Equation 3-3) |
| $F_{\text{off-spec_bt}}$ | = | Fraction of the annual number of batches that are disposed as off-spec product waste (Default: 0.01 off-spec batch/annual number of batches (SRRP, no date)) |
| $N_{\text{off-spec_bt_day}}$ | = | Number of off-spec batches per day (Default: 1 off-spec batch/day) |

The release of off-spec product may then be estimated by the following equation:

$$E_{\text{local_off-spec}} = Q_{\text{adhes_bt}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}} \quad (4-7)$$

This release will occur over $[N_{\text{off-spec_days_site_yr}}]$ days/year from $[N_{\text{sites}}]$ sites

Where:

| | | |
|------------------------------|---|--|
| $E_{\text{local_off-spec}}$ | = | Release of chemical of interest on each occurrence of off-spec adhesive batch discharge (kg chemical/site-day) |
| $Q_{\text{adhes_bt}}$ | = | Mass of adhesive formulated per batch (kg adhesive/batch) (See Section 3.6) |
| $F_{\text{chem_comp}}$ | = | Mass fraction of the chemical of interest in the adhesive component (kg chemical/kg component) (See Section 3.3) |
| $F_{\text{comp_adhes}}$ | = | Mass fraction of the component in the formulated adhesive product (kg component/kg adhesive) (See Section 3.4) |

5 OCCUPATIONAL EXPOSURE ASSESSMENTS

The following section presents estimation methods for worker exposures to the chemical of interest. Figure 2-1, Figure 2-2, and Figure 2-3 illustrate the occupational activities performed within a sealed, unsealed, and heated formulation process, respectively, that have the greatest potential for worker exposure to the chemical.

Industry-specific occupational exposure information was not found in the references reviewed for this ESD (refer to Section 8 for a description of the sources reviewed and full citations for those specifically used in these calculations), with the exception of the total number of workers employed by the adhesive formulation industry available from the U.S. Census Bureau. The occupational exposure estimates presented in this document are based on standard EPA exposure models. Table 5-1 summarizes the exposure estimation methods used in this ESD.

Note that the standard model default values cited are current as of the date of this ESD; however, EPA may update these models as additional data become available. It is recommended that the most current version of the models be used in these calculations.

EPA has developed a software package (ChemSTEER) containing these models as well as all current EPA defaults. Because of the complexity of the inhalation exposure to vapor models, ChemSTEER is recommended for estimating these exposures. Appendix B provides additional information on ChemSTEER, including information on obtaining the program, as well as background information, model equations, and default values for several parameters for all standard EPA models.

Note for default Option 3 – Release and Exposure assessment:

It is recommended that each of the exposure calculations described in this section be performed using the appropriate default values selected for large and other formulators to estimate the exposures that occur at large and other formulation sites.

Table 5-1. Summary of Adhesive Formulation Scenario Exposure Models

| Exposure Activity | Description | Route of Exposure / Physical Form | Model Name or Description^a | Standard EPA Model (✓) |
|--------------------------|---|---|---|-------------------------------|
| A | Unloading solid or liquid adhesive components | Inhalation of volatile liquid chemical vapors | EPA/OPPT Mass Balance Model | ✓ |
| | | Inhalation of solid chemical particles | Specific model used is based on daily amount of adhesive component handled: <ul style="list-style-type: none"> • For amounts > 54 kg/day: OSHA PNOR PEL-Limiting Model • For amounts ≤ 54 kg/day: EPA/OPPT Small Volume Solids Handling Model | ✓ |
| | | Dermal exposure to liquid chemical | EPA/OPPT 2-Hand Dermal Contact with Liquid Model | ✓ |
| | | Dermal exposure to solid chemical | EPA/OPPT 2-Hand Dermal Contact with Solids Model | ✓ |
| B | Exposure to solid or liquid adhesive components during container cleaning | Inhalation of volatile liquid chemical vapors | EPA/OPPT Mass Balance Model | ✓ |
| | | Inhalation of solid chemical particles | Specific model used is based on daily amount of adhesive component handled: <ul style="list-style-type: none"> • For amounts > 54 kg/day: OSHA PNOR PEL-Limiting Model • For amounts ≤ 54 kg/day: EPA/OPPT Small Volume Solids Handling Model | ✓ |
| | | Dermal exposure to liquid chemical | EPA/OPPT 2-Hand Dermal Contact with Liquid Model | ✓ |
| | | Dermal exposure to solid chemical | EPA/OPPT 2-Hand Dermal Contact with Solids Model | ✓ |
| C | Exposure to chemical vapors during operation of open mixing vessel | Inhalation of volatile liquid chemical vapors | EPA/OPPT Mass Balance Model | ✓ |
| D | Exposure to liquid adhesive product during sampling | Inhalation of volatile liquid chemical vapors | EPA/OPPT Mass Balance Model | ✓ |
| | | Dermal exposure to liquid chemical | EPA/OPPT 1-Hand Dermal Contact with Liquid Model | ✓ |
| E | Exposure to liquid adhesive product during equipment cleaning | Inhalation of volatile liquid chemical vapors | EPA/OPPT Mass Balance Model | ✓ |
| | | Dermal exposure to liquid chemical | EPA/OPPT 2-Hand Dermal Contact with Liquid Model | ✓ |

| Exposure Activity | Description | Route of Exposure / Physical Form | Model Name or Description ^a | Standard EPA Model (✓) |
|-------------------|--|---|--|------------------------|
| F | Exposure to liquid adhesive product during packaging | Inhalation of volatile liquid chemical vapors | EPA/OPPT Mass Balance Model | ✓ |
| | | Dermal exposure to liquid chemical | EPA/OPPT 2-Hand Dermal Contact with Liquid Model | ✓ |

a – Additional detailed descriptions for each of the models presented in this section are provided in Appendix B to this DSR.

5.1 Personal Protective Equipment

No information on typical personal protective equipment (PPE) specific to adhesive formulation was found; however, a great deal of information is available on typical PPE for the application and use of adhesive formulations. This information mainly focuses on minimizing exposure due to spray application or VOC emissions. General assumptions can be made based on the known hazards of certain adhesive formulation processes: hot-melt adhesives are processed at temperatures over 150°C and solution adhesives generally have VOC concerns. Chemical submissions recently submitted to EPA by adhesive chemical manufacturers show that, at a minimum, all manufacturers recommended the use of gloves and safety glasses with side shields or goggles. Approximately half of the submissions also recommended the use of some kind of ventilation and respirators if necessary. One submission for a hot-melt adhesive chemical also specifically recommended the use of thermal gloves.

5.2 Number of Workers Exposed Per Site

Industry-specific data on the numbers of workers potentially exposed while performing each of the adhesive formulation activities were not found in the references reviewed for this ESD (refer to Section 8 for a description of the sources reviewed and full citations for those specifically used in these calculations). According to the 2002 Economic Census for the adhesives formulation industry (NAICS code 32552), an average of 35 workers are employed at each facility (USCB, 2002); however, not all are expected to work in the production areas. The 2002 Economic Census estimates approximately 62 percent of these workers are *production* workers (USCB, 2002), which are defined by the U.S. Census Bureau to include...

...workers (up through the line-supervisor level) engaged in fabricating, processing, assembling, inspecting, receiving, storing, handling, packing, warehousing, shipping (but not delivering), maintenance, repair, janitorial and guard services, product development, auxiliary production for plant's own use (e.g., power plant), record keeping, and other services closely associated with these production operations at the establishment (USCB, 2002).

All other “non-production” employees include...

...those engaged in supervision above the line-supervisor level, sales (including driver-salespersons), sales delivery (highway truck drivers and their helpers), advertising, credit, collection, installation and servicing of own products, clerical and routine office functions, executive, purchasing, financing, legal, personnel (including cafeteria, medical, etc.), professional, technical employees, and employees on the payroll of the manufacturing establishment engaged in the construction of major additions or alterations utilized as a separate work force (USCB, 2002).

It is therefore assumed that 62 percent of the 35 workers per site, or **up to 22 workers per site**, are potentially exposed to the chemical of interest while performing adhesive formulation process activities. No information was found that would provide bases for estimating the specific numbers of these 22 production workers that perform each of the exposure activities discussed in this section. Therefore, it can be conservatively estimated that all 22 workers per site are exposed during each activity.

Data submitted to EPA by Environment Canada shows that, while the number of Canadian formulation sites is less than U.S. sites, the average number of employed workers is consistent with the U.S. data. This information can be found in Appendix C.

No information was found on the typical hours of operation per day or the number of shifts supporting operations at adhesive formulation facilities; however, an estimate for the duration of exposure for each worker activity are presented in the remainder of this section (based on standard EPA defaults and methodology).

5.3 Exposure from Unloading Solid or Liquid Chemicals (Exposure A)

Workers may connect transfer lines or manually unload chemicals from transport containers into the mixing tanks. If the concentration of the chemical in the component ($F_{\text{chem_comp}}$) is unknown, 100 percent concentration may be assumed as conservative, as previously discussed in Section 3.3. Up to 22 workers per site may be exposed during this activity.

Inhalation Exposure:

Liquids:

The method used to calculate inhalation exposure ($EXP_{\text{inhalation}}$) depends on the volatility and the physical state of the chemical of interest. Inhalation exposure to liquids is assumed negligible for nonvolatile liquids (e.g., the vapor pressure is < 0.001 torr).

The vapor generation rate calculated in Release 3 and the EPA standard model for estimating inhalation exposure due to evaporation of volatile chemicals (*EPA/OPPT Mass Balance Model*) may be used to estimate the associated worker inhalation exposure to the chemical of interest during transfer operations. The model and all current EPA defaults have been programmed into ChemSTEER; EPA recommends using this software to calculate inhalation

exposure to volatile chemicals during transfer operations. Appendix B explains the background and derivation of the model and provides EPA default values for several model parameters.

Table 5-2 lists the model inputs and default values. Note that the exposure hours per day is equivalent to the operating hours per day for this activity (consistent with Section 4.4 calculations), but EPA assumes a maximum exposure duration of eight hours per day. Similarly, the exposure days per site, per year should be consistent with the release days, but EPA assumes a maximum of 250 days per year. These exposure duration maximum defaults are based on full-time employment and considers an individual worker's vacation, sick, and weekend time (i.e., a 40-hour work week over 50 weeks per year).

Table 5-2. EPA/OPPT Mass Balance Model Parameter Default Values During Transfers

| Input Parameter | Default Values |
|----------------------------------|--|
| Inhalation Rate | Default = 1.25 m ³ /hr (CEB, 1991) |
| Exposure Days | Consistent with the Frequency of Release determined in Section 4.4, up to 250 days per year |
| Vapor Generation Rate | Calculated by the <i>EPA/OPPT Penetration Model</i> (Section 4.4) |
| Exposure Duration | Consistent with the Operating Hours determined in Section 4.4, up to 8 hours per day |
| Mixing Factor | EPA defaults 0.5 (typical) and 0.1 (worst case) (CEB, 1991) |
| Molecular Weight | Chemical-specific parameter |
| Number of Sites | Calculated in Section 3.5 |
| Ventilation Rate | EPA defaults 3,000 ft ³ /min (typical) and 500 ft ³ /min (worst case) for indoor conditions (default for containers less than 1,000 gallons (CEB, 1991) (See Appendix B for alternative default ventilation rates) |
| Vapor Pressure | Chemical-specific parameter |
| Vapor Pressure Correction Factor | Standard EPA default = 1 |

Note: The model also assumes standard temperature and pressure along with ideal gas interactions.

Solids:

The transfer of nonvolatile powdered adhesive components from containers to storage or mixing vessels generates particulates. The degree of inhalation exposure to particulates depends on the concentration of the chemical of interest in the component ($F_{\text{chem_comp}}$), the potential concentration of the component in the worker's breathing zone ($C_{\text{particulate}}$), and the total amount of component the worker is exposed to per day in performing this activity ($Q_{\text{comp_site_day}}$).

The daily transfer rate of the adhesive component may be estimated using the following equation:

$$Q_{\text{comp_site_day}} = \frac{Q_{\text{chem_site_day}}}{F_{\text{chem_comp}}} \quad (5-1)$$

Where:

| | | |
|------------------------------|---|---|
| $Q_{\text{comp_site_day}}$ | = | Daily amount of adhesive component transferred into the process (kg component/site-day) |
| $Q_{\text{chem_site_day}}$ | = | Daily use rate of the chemical of interest used to formulate the adhesive product (kg chemical/site-day) (See Equation 3-5) |
| $F_{\text{chem_comp}}$ | = | Mass fraction of the chemical of interest in the adhesive component (kg chemical/kg component) (See Section 3.3) |

Two equations can be used to determine worker exposure. Selection of the appropriate equation should be based on the amount of component the worker is exposed to per day ($Q_{\text{comp_site_day}}$), not the amount of chemical of interest the worker is exposed to ($Q_{\text{chem_site_day}}$). Additional explanation, including the background and model defaults, of the two standard EPA models used to estimate inhalation exposure to solid powder is presented in Appendix B.

If the transfer rate of the solid powder adhesive component containing the chemical of interest ($Q_{\text{comp_site_day}}$) is *greater than* 54 kg/site-day, EPA recommends using the OSHA Total Particulates Not Otherwise Regulated (PNOR) PEL-Limiting Model:

$$EXP_{\text{inhalation}} = C_{\text{particulate}} \times RATE_{\text{breathing}} \times TIME_{\text{exposure}} \times F_{\text{chem_comp}} \quad (5-2a)$$

This exposure will occur over [the lesser of $N_{\text{cont_empty_site_yr}}$ or $TIME_{\text{working_days}}$, up to 250] days/year

Where:

| | | |
|---------------------------|---|---|
| $EXP_{\text{inhalation}}$ | = | Inhalation exposure to the chemical of interest per day (mg chemical of interest/day) |
| $C_{\text{particulate}}$ | = | Concentration of particulate adhesive component in the workers breathing zone (Default: 15 mg component/m ³ ; based on OSHA Total PNOR PEL (8-hr TWA*) (29 CFR 1910.1000)) |
| $RATE_{\text{breathing}}$ | = | Typical worker breathing rate (Default: 1.25 m ³ /hr (CEB, 1991)) |
| $TIME_{\text{exposure}}$ | = | Duration of exposure (Default: 8 hrs/day; Note: because the default value for $C_{\text{particulate}}$ is an 8-hr TWA*, the 8 hrs/day value <u>must</u> be used) |
| $F_{\text{chem_comp}}$ | = | Mass fraction of the chemical of interest in the adhesive component (mg chemical/mg component) (See Section 3.3) |

*TWA = Time-weighted average

The accuracy of solid component inhalation estimates are limited by the estimated airborne concentration of the chemical of interest and the assumed breathing rate.

If the transfer rate of the solid powder adhesive component containing the chemical of interest ($Q_{\text{comp_site_day}}$) is *less than or equal to* 54 kg/site-day, EPA recommends using the EPA/OPPT Small Volume Solids Handling Inhalation Model:

$$EXP_{\text{inhalation}} = Q_{\text{comp_site_day}} \times F_{\text{chem_comp}} \times F_{\text{exposure}} \quad (5-2b)$$

This exposure will occur over [the lesser of $N_{\text{cont_empty_site_yr}}$ or $\text{TIME}_{\text{working_days}}$, up to 250] days/year

Where:

| | | |
|----------------------------------|---|---|
| $\text{EXP}_{\text{inhalation}}$ | = | Inhalation exposure to the chemical of interest per day (mg chemical/day) |
| $Q_{\text{comp_site_day}}$ | = | Daily amount of adhesive component transferred into the process (kg component/site-day) (See Equation 5-1) |
| $F_{\text{chem_comp}}$ | = | Mass fraction of the chemical of interest in the adhesive component (mg chemical/mg component) (See Section 3.3) |
| F_{exposure} | = | Weight fraction of the total particulate adhesive component in the workers breathing zone (Default: 0.0477 (typical) to 0.161 (worst) mg component exposure/kg of component handled (CEB, 1992b)) |

Dermal Exposure:

Dermal exposure is expected for both automated and manual unloading activities. Automated systems may limit the extent of dermal exposure more than manual unloading; however, workers may still be exposed when connecting transfer lines or transferring the liquid chemicals from the transport container to storage or mixing vessels. Workers may manually scoop or pour solid or liquid adhesive chemicals into the process equipment.

The *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* may be used to estimate dermal exposure to the chemical of interest in a liquid formulation during these activities, and the *EPA/OPPT Direct 2-Hand Dermal Contact with Solids Model* may be used to estimate dermal exposure to the chemical of interest in a solid powder formulation. The rationale, defaults, and limitations of these models are further explained in Appendix B.

Liquids:

To estimate the potential worker exposure to the chemical of interest in a liquid adhesive component for this activity, EPA recommends using the following equation:

$$\text{EXP}_{\text{dermal}} = Q_{\text{liquid_skin}} \times \text{AREA}_{\text{surface}} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \quad (5-3a)$$

This exposure will occur over [the lesser of $N_{\text{cont_empty_site_yr}}$ or $\text{TIME}_{\text{working_days}}$ (consistent with Section 4.4), up to 250] days per year

Where:

| | | |
|--------------------------------|---|--|
| $\text{EXP}_{\text{dermal}}$ | = | Potential dermal exposure to the chemical of interest per day (mg chemical/day) |
| $Q_{\text{liquid_skin}}$ | = | Quantity of liquid adhesive component remaining on skin (Defaults: 2.1 mg component/cm ² -incident (high-end) and 0.7 mg component/cm ² -incident (low-end) for routine or incidental contact (CEB, 2000)) |
| $\text{AREA}_{\text{surface}}$ | = | Surface area of contact (Default: 840 cm ² for 2 hands (CEB, 2000)) |

| | | |
|------------------------------|---|--|
| $N_{\text{exp_incident}}^1$ | = | Number of exposure incidents per day (Default: 1 incident/day) |
| $F_{\text{chem_comp}}$ | = | Mass fraction of the chemical of interest in the adhesive component (mg chemical/mg component) (See Section 3.3) |

Solids:

To estimate the potential worker exposure to the chemical of interest in a solid adhesive component for this activity, EPA recommends using the following equation:

$$\text{EXP}_{\text{dermal}} = \text{up to } 3,100 \text{ mg component/incident} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \quad (5-3b)$$

This exposure will occur over [the lesser of $N_{\text{cont_empty_site_yr}}$ or $\text{TIME}_{\text{working_days}}$ (consistent with Section 4.5), up to 250] days per year

Where:

| | | |
|------------------------------|---|--|
| $\text{EXP}_{\text{dermal}}$ | = | Potential dermal exposure to the chemical of interest per day (mg chemical/day) |
| $N_{\text{exp_incident}}$ | = | Number of exposure incidents per day (Default: 1 incident/day) (see footnote to Equation 5-3a) |
| $F_{\text{chem_comp}}$ | = | Mass fraction of the chemical of interest in the adhesive component (mg chemical/mg component) (See Section 3.3) |

5.4 Exposure to Solids or Liquids During Container Cleaning (Exposure B)

Workers may be exposed while rinsing containers used to transport the adhesive component. If the concentration of the chemical in the component ($F_{\text{chem_comp}}$) is unknown, 100 percent concentration may be assumed as a conservative default, as previously discussed in Section 3.3. Up to 22 workers per site may be exposed during this activity.

Inhalation Exposure:

Liquids:

The method used to calculate inhalation exposure ($\text{EXP}_{\text{inhalation}}$) depends on the volatility and the physical state of the chemical of interest. Inhalation exposure to liquids is assumed negligible for nonvolatile liquids (e.g., the vapor pressure is < 0.001 torr).

Using the vapor generation rate calculated in Release 2, the *EPA/OPPT Mass Balance Model* can be used to calculate worker inhalation exposure due to volatilization during cleaning operations. The default ventilation rates and mixing factors provide a typical and worst

¹Only one contact per day ($N_{\text{exp_incident}} = 1$ event/worker-day) is assumed because $Q_{\text{liquid_skin}}$, with few exceptions, is not expected to be significantly affected either by wiping excess chemical material from skin or by repeated contacts with additional chemical material (i.e., wiping excess from the skin does not remove a significant fraction of the small layer of chemical material adhering to the skin and additional contacts with the chemical material do not add a significant fraction to the layer). Exceptions to this assumption may be considered for chemicals with high volatility and/or with very high rates of absorption into the skin.

case estimate of exposure. Table 5-3 lists the model inputs and default values. Note that the exposure hours per day are equivalent to the operating hours per day for this activity (consistent with Section 4.3 calculations), but EPA assumes a maximum exposure duration of eight hours per day. Similarly, the exposure days per site, per year, should be consistent with the release days, but EPA assumes a maximum of 250 days per year, as previously discussed in Section 5.3.

Table 5-3. EPA/OPPT Mass Balance Model Parameter Default Values During Container Cleaning

| Input Parameter | Default Values |
|----------------------------------|--|
| Inhalation Rate | Default = 1.25 m ³ /hr (CEB, 1991) |
| Exposure Days | Consistent with the Frequency of Release determined in Section 4.3, up to 250 days per year |
| Vapor Generation Rate | Calculated by the EPA/OPPT Penetration Model (Section 4.3) |
| Exposure Duration | Consistent with the Operating Hours determined in Section 4.3, up to 8 hours per day |
| Mixing Factor | EPA defaults 0.5 (typical) and 0.1 (worst case) (CEB, 1991) |
| Molecular Weight | Chemical-specific parameter |
| Number of Sites | Calculated in Section 3.5 |
| Ventilation Rate | EPA defaults 3,000 ft ³ /min (typical) and 500 ft ³ /min (worst case) for indoor conditions (default for containers less than 1,000 gallons (CEB, 1991) (See Appendix B for alternative default ventilation rates) |
| Vapor Pressure | Chemical-specific parameter |
| Vapor Pressure Correction Factor | Standard EPA default = 1 |

Note: The model also assumes standard temperature and pressure along with ideal gas interactions.

The models and all current EPA defaults have been programmed into ChemSTEER; EPA recommends this software to calculate inhalation exposure to volatile chemicals during container cleaning. Appendix B explains the background and derivation of the model and provides EPA default values for several model parameters.

Solids:

The cleaning of solid powders from transport containers may generate dust particulate. The degree of inhalation exposure to particulates depends on the concentration of the chemical of interest in the formulation ($F_{\text{chem_comp}}$), the potential concentration of the adhesive chemical in the worker's breathing zone ($C_{\text{particulate}}$), and the total amount of adhesive component residual removed from the containers ($Q_{\text{comp_residue_site_day}}$). EPA recommends using the following equation to estimate the amount of component residual handled by a worker during container cleaning:

$$Q_{\text{comp_residue_site_day}} = \frac{E_{\text{local}}_{\text{container_residue_disp}}}{F_{\text{chem_comp}}} \quad (5-4)$$

Where:

| | | |
|--|---|---|
| $Q_{\text{comp_residue_site_day}}$ | = | Quantity of adhesive component handled during container cleaning (kg component/site-day) |
| $E_{\text{local_container_residue_disp}}$ | = | Daily release of chemical of interest from container residue (kg chemical/site-day) (See Equation 4-1a or 4-1b, consistent with Section 4.2 calculations) |
| $F_{\text{chem_comp}}$ | = | Mass fraction of the chemical of interest in the adhesive component (kg chemical/kg component) (See Section 3.3) |

Two equations can be used to determine worker exposure. Selection of the appropriate equation should be based on the amount of solid adhesive component the worker is exposed to per day ($Q_{\text{comp_residue_site_day}}$), not the amount of chemical of interest the worker is exposed to per day ($E_{\text{local_container_residue_disp}}$). A further explanation, including the background and model defaults, of the two standard EPA models used to estimate inhalation exposure to solid powder is presented in Appendix B.

If the daily amount of the solid powder adhesive component containing the chemical of interest ($Q_{\text{comp_residue_site_day}}$) is *greater than* 54 kg/site-day, EPA recommends using the OSHA Total PNOR PEL-Limiting Model:

$$EXP_{\text{inhalation}} = C_{\text{particulate}} \times RATE_{\text{breathing}} \times TIME_{\text{exposure}} \times F_{\text{chem_comp}} \quad (5-5a)$$

This exposure will occur over [the lesser of $N_{\text{cont_empty_site_yr}}$ or $TIME_{\text{working_days}}$ (consistent with Section 4.2), up to 250] days per year

Where:

| | | |
|---------------------------|---|---|
| $EXP_{\text{inhalation}}$ | = | Inhalation exposure to the chemical of interest per day (mg chemical/day) |
| $C_{\text{particulate}}$ | = | Concentration of particulate adhesive component in the workers breathing zone (Default: 15 mg component/m ³ ; based on OSHA Total PNOR PEL (8-hr TWA*) (29 CFR 1910.1000)) |
| $RATE_{\text{breathing}}$ | = | Typical worker breathing rate (Default: 1.25 m ³ /hr (CEB, 1991)) |
| $TIME_{\text{exposure}}$ | = | Duration of exposure (Default: 8 hrs/day; Note: because the default value for $C_{\text{particulate}}$ is an 8-hr TWA*, the 8 hrs/day value <u>must</u> be used) |
| $F_{\text{chem_comp}}$ | = | Mass fraction of the chemical of interest in the adhesive component (mg chemical/mg component) (See Section 3.3) |

*TWA = Time-weighted average

The accuracy of solid component inhalation estimates are limited by the estimated airborne concentration of the chemical of interest and the assumed breathing rate.

If the daily amount of the solid powder adhesive component containing the chemical of interest ($Q_{\text{comp_residue_site_day}}$) is *less than or equal to* 54 kg/site-day, EPA recommends using the EPA/OPPT Small Volume Solids Handling Inhalation Model:

$$EXP_{\text{inhalation}} = Q_{\text{comp_residue_site_day}} \times F_{\text{chem_comp}} \times F_{\text{exposure}} \quad (5-5b)$$

This exposure will occur over [the lesser of $N_{\text{cont_empty_site_yr}}$ or $TIME_{\text{working_days}}$ (consistent with Section 4.2), up to 250] days per year

Where:

| | | |
|---------------------------------------|---|---|
| $EXP_{\text{inhalation}}$ | = | Inhalation exposure to the chemical of interest per day (mg chemical/day) |
| $Q_{\text{comp_residue_site_day}}$ | = | Quantity of adhesive component handled during container cleaning (kg component/site-day) (See Equation 5-4) |
| $F_{\text{chem_comp}}$ | = | Mass fraction of the chemical of interest in the adhesive component (mg chemical/mg component) (See Section 3.3) |
| F_{exposure} | = | Weight fraction of the total particulate adhesive component in the workers breathing zone (Default: 0.0477 (typical) to 0.161 (worst) mg component exposure/kg of component handled (CEB, 1992b)) |

Dermal Exposure:

Dermal exposure is expected during the cleaning of transport containers. The *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* may be used to estimate dermal exposure to the chemical of interest in a liquid formulation during these activities, and the *EPA/OPPT Direct 2-Hand Dermal Contact with Solids Model* may be used to estimate dermal exposure to the chemical of interest in a solid powder formulation. The rationale, defaults, and limitations of these models are explained in Appendix B.

Liquids:

To estimate the potential worker exposure to the chemical of interest in a liquid adhesive component for this activity, EPA recommends using the following equation:

$$EXP_{\text{dermal}} = Q_{\text{liquid_skin}} \times AREA_{\text{surface}} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \quad (5-6a)$$

This exposure will occur over [the lesser of $N_{\text{cont_empty_site_yr}}$ or $TIME_{\text{working_days}}$ (consistent with Section 4.2), up to 250] days per year

Where:

| | | |
|----------------------------|---|--|
| EXP_{dermal} | = | Potential dermal exposure to the chemical of interest per day (mg chemical/day) |
| $Q_{\text{liquid_skin}}$ | = | Quantity of liquid adhesive component remaining on skin (Defaults: 2.1 mg component/cm ² -incident (high-end) and 0.7 mg component/cm ² -incident (low-end) for routine or incidental contact (CEB, 2000)) |
| $AREA_{\text{surface}}$ | = | Surface area of contact (Default: 840 cm ² for 2 hands (CEB, 2000)) |
| $N_{\text{exp_incident}}$ | = | Number of exposure incidents per day (Default: 1 incident/day) (see footnote to Equation 5-3a) |
| $F_{\text{chem_comp}}$ | = | Mass fraction of the chemical of interest in the adhesive component (mg chemical/mg component) (See Section 3.3) |

Solids:

To estimate the potential worker exposure to the chemical of interest in a solid adhesive component for this activity, EPA recommends using the following equation:

$$EXP_{\text{dermal}} = \text{up to } 3,100 \text{ mg component/incident} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \quad (5-6b)$$

This exposure will occur over [the lesser of $N_{\text{cont_empty_site_yr}}$ or $\text{TIME}_{\text{working_days}}$ (consistent with Section 4.2), up to 250] days per year

Where:

| | | |
|----------------------------|---|--|
| EXP_{dermal} | = | Potential dermal exposure to the chemical of interest per day (mg chemical/day) |
| $N_{\text{exp_incident}}$ | = | Number of exposure incidents per day (Default: 1 incident/day) (see footnote to Equation 5-3a) |
| $F_{\text{chem_comp}}$ | = | Weight fraction of the chemical of interest in the adhesive component (mg chemical/mg component) (See Section 3.3) |

5.5 Inhalation Exposure During Operation of Open Mixing Vessels (Exposure C)

During the mixing operation, volatile chemicals may potentially be released to the air. Mixing vessels are generally closed and vented to stack air; in this case, inhalation exposures to vapors are expected to be negligible. However, if the mixing vessel is open, workers may be exposed to vapors from volatile chemicals, particularly if the mixing vessel is heated. Up to 22 workers per site may be exposed during this activity.

The method used to calculate inhalation exposure ($EXP_{\text{inhalation}}$) depends on the volatility and the physical state of the chemical of interest at the operating temperature (e.g., hot-melt adhesives are assumed to be formulated in a heated mixing process at 190°C; see discussion in Section 4.6). Inhalation exposure to liquids is assumed negligible for nonvolatile liquids (e.g., the vapor pressure is < 0.001 torr).

Using the vapor generation rate calculated in Release 5, the *EPA/OPPT Mass Balance Model* can be used to calculate worker inhalation exposure due to volatilization during open mixing operations. The default ventilation rates and mixing factors provide a typical and worst case estimate of exposure. Table 5-4 lists the model inputs and default values. Note that the exposure hours per day are equivalent to the operating hours per day for this activity (consistent with Section 4.6 calculations), but EPA assumes a maximum exposure duration of eight hours per day. Similarly, the exposure days per site, per year should be consistent with the release days, but EPA assumes a maximum of 250 days per year, as previously discussed in Section 5.3.

Table 5-4. EPA/OPPT Mass Balance Model Parameter Default Values During Mixing Operation

| Input Parameter | Default Values |
|----------------------------------|--|
| Inhalation Rate | Default = 1.25 m ³ /hr (CEB, 1991) |
| Exposure Days | Consistent with the Frequency of Release determined in Section 4.6, up to 250 days per year |
| Vapor Generation Rate | Calculated by the <i>EPA/OPPT Penetration Model</i> (Section 4.6) |
| Exposure Duration | Consistent with the Operating Hours determined in Section 4.6, up to 8 hours per day |
| Mixing Factor | EPA defaults 0.5 (typical) and 0.1 (worst case) (CEB, 1991) |
| Molecular Weight | Chemical-specific parameter |
| Number of Sites | Calculated in Section 3.5 |
| Ventilation Rate | EPA defaults 3,000 ft ³ /min (typical) and 500 ft ³ /min (worst case) for indoor conditions (CEB, 1991) (See Appendix B for alternative default ventilation rates) |
| Temperature | Consistent with the Temperature used in Section 4.6 |
| Vapor Pressure | Consistent with the Vapor Pressure used in Section 4.6 |
| Vapor Pressure Correction Factor | Standard EPA default = 1 |

Note: The model generally assumes standard temperature and pressure along with ideal gas interactions.

The models and all current EPA defaults have been programmed into ChemSTEER; EPA recommends using this software to calculate inhalation exposure to volatile chemicals during the mixing operation. Appendix B explains the background and derivation of the model and provides EPA default values for several model parameters.

5.6 Exposure from Sampling Liquid Adhesive Product (Exposure D)

Workers may collect samples of the adhesive product for quality analysis/quality control (QA/QC). Up to 22 workers per site may be exposed during this activity.

Inhalation Exposure:

The method used to calculate inhalation exposure ($EXP_{\text{inhalation}}$) depends on the volatility and the physical state of the chemical of interest at the operating temperature (e.g., EPA assumes that hot-melt adhesives are formulated in a heated mixing process and subsequently sampled/analyzed in part as a molten liquid at 190°C; see discussion in Section 4.8). Inhalation exposure to liquids is assumed negligible for nonvolatile liquids (e.g., the vapor pressure is < 0.001 torr).

Because reactive adhesives may be sensitive to ambient conditions and losses of product are expected to be minimized, this operation may be closed and this exposure may be negligible. However, unless site-specific information is available, EPA recommends assuming

that fugitive emission of volatile chemicals may occur and estimating the associated worker inhalation exposure as a worst-case.

Using the vapor generation rate calculated in Release 7, the *EPA/OPPT Mass Balance Model* can be used to calculate worker inhalation exposure due to volatilization during sampling activities. The default ventilation rates and mixing factors provide a typical and worst case estimate of exposure. Table 5-5 lists the model inputs and default values. Note that the exposure days per site, per year should be consistent with the release days, but EPA recommends a maximum of 250 days per year, as previously discussed in Section 5.3.

The models and all current EPA defaults have been programmed into ChemSTEER; EPA recommends using this software to calculate inhalation exposure to volatile chemicals during packaging/loading activities. Appendix B explains the background and derivation of the model and provides EPA default values for several model parameters.

Dermal Exposure:

Dermal exposure to liquid adhesives is expected during sampling activities. The *EPA/OPPT 1-Hand Dermal Contact with Liquid Model* may be used to estimate dermal exposure to the chemical of interest in a liquid formulation during these activities. The rationale, defaults, and limitations of this model are explained in Appendix B.

Table 5-5. EPA/OPPT Mass Balance Model Parameter Default Values During Sampling

| Input Parameter | Default Values |
|----------------------------------|--|
| Inhalation Rate | Default = 1.25 m ³ /hr (CEB, 1991) |
| Exposure Days | Consistent with the Frequency of Release determined in Section 4.8, up to 250 days per year |
| Vapor Generation Rate | Calculated by the <i>EPA/OPPT Penetration Model</i> (Section 4.8) |
| Exposure Duration | Consistent with the Operating Hours determined in Section 4.8, up to 8 hours per day (default: 1 hour/day (CEB, 1991)) |
| Mixing Factor | EPA defaults 0.5 (typical) and 0.1 (worst case) (CEB, 1991) |
| Molecular Weight | Chemical-specific parameter |
| Number of Sites | Calculated in Section 3.5 |
| Ventilation Rate | EPA defaults 3,000 ft ³ /min (typical) and 500 ft ³ /min (worst case) for indoor conditions (default for containers less than 1,000 gallons (CEB, 1991) (See Appendix B for alternative default ventilation rates) |
| Temperature | Consistent with the Temperature used in Section 4.8 |
| Vapor Pressure | Consistent with the Vapor Pressure used in Section 4.8 |
| Vapor Pressure Correction Factor | Standard EPA default = 1 |

Note: The model also assumes standard temperature and pressure along with ideal gas interactions.

As described for the inhalation exposure to liquid adhesives above, if the adhesive product is sampled/analyzed as a hot, molten liquid (e.g., hot-melt adhesives), EPA recommends

that the dermal exposure to hot materials be assumed negligible when they are handled at temperatures above 60°C (CEB, 1991). EPA typically assumes that dermal exposures to hot materials are mitigated through the use of PPE.

To estimate the potential worker exposure to the chemical of interest in a liquid adhesive component sampled at temperatures less than 60°C, EPA recommends using the following equation:

$$EXP_{\text{dermal}} = Q_{\text{liquid_skin}} \times AREA_{\text{surface}} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}} \quad (5-7)$$

This exposure will occur over [the lesser of $N_{\text{cont_fill_site_yr}}$ or $TIME_{\text{working_days}}$ (consistent with Section 4.8), up to 250] days per year

Where:

| | | |
|----------------------------|---|--|
| EXP_{dermal} | = | Potential dermal exposure to the chemical of interest per day (mg chemical/day) |
| $Q_{\text{liquid_skin}}$ | = | Quantity of liquid adhesive product remaining on skin (Defaults: 2.1 mg adhesive/cm ² -incident (high-end) and 0.7 mg adhesive/cm ² -incident (low-end) for routine or incidental contact (CEB, 2000)) |
| $AREA_{\text{surface}}$ | = | Surface area of contact (Default: 420 cm ² for 1 hand (CEB, 2000)) |
| $N_{\text{exp_incident}}$ | = | Number of exposure incidents per day (Default: 1 incident/day) (see footnote to Equation 5-3a) |
| $F_{\text{chem_comp}}$ | = | Mass fraction of the chemical of interest in the adhesive component (mg chemical/mg component) (See Section 3.3) |
| $F_{\text{comp_adhes}}$ | = | Mass fraction of the component in the formulated adhesive product (mg component/mg adhesive) (See Section 3.4) |

5.7 Exposure to Liquids During the Equipment Cleaning of Mixers and Other Process Equipment (Exposure E)

Workers may be exposed while cleaning the mixing tanks or other process equipment with water or organic solvents. Workers may manually wipe down equipment with rags (NEWMOA, 1999). Because some equipment cleaning may be performed manually, exposures during equipment cleaning should be assessed. Up to 22 workers per site may be exposed during this activity.

Inhalation Exposure:

The method used to calculate inhalation exposure ($EXP_{\text{inhalation}}$) depends on the volatility and the physical state of the chemical of interest. Inhalation exposure to liquids is assumed negligible for nonvolatile liquids (e.g., the vapor pressure is < 0.001 torr).

Using the vapor generation rate calculated in Release 9, the *EPA/OPPT Mass Balance Model* can be used to calculate worker inhalation exposure due to volatilization during equipment cleaning activities. The default ventilation rates and mixing factors provide a typical and worst case estimate of exposure. Table 5-6 lists the model inputs and default values. Note that the exposure hours per day are equivalent to the operating hours per day for this activity

(consistent with Section 4.10 calculations), but EPA assumes a maximum exposure duration of eight hours per day. Similarly, the exposure days per site, per year should be consistent with the release days, but EPA assumes a maximum of 250 days per year, as previously discussed in Section 5.3.

The models and all current EPA defaults have been programmed into ChemSTEER; EPA recommends using this software to calculate inhalation exposure to volatile chemicals during equipment cleaning. Appendix B explains the background and derivation of the model and provides EPA default values for several model parameters.

Table 5-6. EPA/OPPT Mass Balance Model Parameter Default Values During Equipment Cleaning

| Input Parameter | Default Values |
|----------------------------------|--|
| Inhalation Rate | Default = 1.25 m ³ /hr (CEB, 1991) |
| Exposure Days | Consistent with the Frequency of Release determined in Section 4.10, up to 250 days per year |
| Vapor Generation Rate | Calculated by the <i>EPA/OPPT Penetration Model</i> (Section 4.10) |
| Exposure Duration | Consistent with the Operating Hours determined in Section 4.10, up to 8 hours per day |
| Mixing Factor | EPA defaults 0.5 (typical) and 0.1 (worst case) (CEB, 1991) |
| Molecular Weight | Chemical-specific parameter |
| Number of Sites | Calculated in Section 3.5 |
| Ventilation Rate | EPA defaults 3,000 ft ³ /min (typical) and 500 ft ³ /min (worst case) for indoor conditions (CEB, 1991) (See Appendix B for alternative default ventilation rates) |
| Vapor Pressure | Chemical-specific parameter |
| Vapor Pressure Correction Factor | Standard EPA default = 1 |

Note: The model also assumes standard temperature and pressure along with ideal gas interactions.

Dermal Exposure:

Dermal exposure to liquids is expected during the cleaning of process equipment. The *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* may be used to estimate dermal exposure to the chemical of interest in a liquid formulation during these activities. The rationale, defaults, and limitations of this model are explained in Appendix B.

To estimate the potential worker exposure to the chemical of interest in a liquid adhesive component for this activity, use the following equation:

$$EXP_{\text{dermal}} = Q_{\text{liquid_skin}} \times AREA_{\text{surface}} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}} \quad (5-8)$$

This exposure will occur over [the number of cleanings per year (consistent with Section 4.9), up to 250] days per year

Where:

| | | |
|----------------------------|---|--|
| EXP_{dermal} | = | Potential dermal exposure to the chemical of interest per day (mg chemical/day) |
| $Q_{\text{liquid_skin}}$ | = | Quantity of liquid adhesive product remaining on skin (Defaults: 2.1 mg adhesive/cm ² -incident (high-end) and 0.7 mg adhesive/cm ² -incident (low-end) for routine or incidental contact (CEB, 2000)) |
| $AREA_{\text{surface}}$ | = | Surface area of contact (Default: 840 cm ² for 2 hands (CEB, 2000)) |
| $N_{\text{exp_incident}}$ | = | Number of exposure incidents per day (Default: 1 incident/day) (see footnote to Equation 5-3a) |
| $F_{\text{chem_comp}}$ | = | Mass fraction of the chemical of interest in the adhesive component (mg chemical/mg component) (See Section 3.3) |
| $F_{\text{comp_adhes}}$ | = | Mass fraction of the component in the formulated adhesive product (mg component/mg adhesive) (See Section 3.4) |

5.8 Exposure from Packaging Adhesive Product (Exposure F)

Liquid Adhesives:

Workers may connect transfer lines to load chemical into transport containers. Loading processes for consumer and commercial products may be automated, minimizing exposure. Up to 22 workers per site may be exposed during this activity.

Inhalation Exposure:

The method used to calculate inhalation exposure ($EXP_{\text{inhalation}}$) depends on the volatility and the physical state of the chemical of interest at the operating temperature (e.g., EPA assumes that hot-melt adhesives are formulated in a heated mixing process and subsequently packaged as a molten liquid at 190°C; see discussion in Section 4.11). Inhalation exposure to liquids is assumed negligible for nonvolatile liquids (e.g., the vapor pressure is < 0.001 torr).

Because reactive adhesives may be sensitive to ambient conditions and losses of product are expected to be minimized, this operation may be closed and this exposure may be negligible. However, unless site-specific information is available, EPA recommends assuming that fugitive emission of volatile chemicals may occur and estimating the associated worker inhalation exposure as a worst-case.

Using the vapor generation rate calculated in Release 8, the *EPA/OPPT Mass Balance Model* can be used to calculate worker inhalation exposure due to volatilization during packaging activities. The default ventilation rates and mixing factors provide a typical and worst case estimate of exposure. Table 5-7 lists the model inputs and default values. Note that the exposure hours per day are equivalent to the operating hours per day for this activity (consistent with Section 4.11 calculations), but EPA assumes a maximum exposure duration of eight hours per day. Similarly, the exposure days per site, per year, should be consistent with the release days, but EPA assumes a maximum of 250 days per year, as previously discussed in Section 5.3

Table 5-7. EPA/OPPT Mass Balance Model Parameter Default Values During Loading

| Input Parameter | Default Values |
|----------------------------------|--|
| Inhalation Rate | Default = 1.25 m ³ /hr (CEB, 1991) |
| Exposure Days | Consistent with the Frequency of Release determined in Section 4.11, up to 250 days per year |
| Vapor Generation Rate | Calculated by the <i>EPA/OAQPS AP-42 Loading Model</i> (Section 4.11) |
| Exposure Duration | Consistent with the Operating Hours determined in Section 4.11, up to 8 hours per day |
| Mixing Factor | EPA defaults 0.5 (typical) and 0.1 (worst case) (CEB, 1991) |
| Molecular Weight | Chemical-specific parameter |
| Number of Sites | Calculated in Section 3.5 |
| Ventilation Rate | EPA defaults 3,000 ft ³ /min (typical) and 500 ft ³ /min (worst case) for indoor conditions (default for containers less than 1,000 gallons (CEB, 1991) (See Appendix B for alternative default ventilation rates) |
| Temperature | Consistent with the Temperature used in Section 4.11 |
| Vapor Pressure | Consistent with the Vapor Pressure used in Section 4.11 |
| Vapor Pressure Correction Factor | Standard EPA default = 1 |

Note: The model also assumes standard temperature and pressure along with ideal gas interactions.

The models and all current EPA defaults have been programmed into ChemSTEER; EPA recommends using this software to calculate inhalation exposure to volatile chemicals during packaging/loading activities. Appendix B explains the background and derivation of the model and provides EPA default values for several model parameters.

Dermal Exposure:

Dermal exposure to liquid adhesives is expected during packaging activities. The *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* may be used to estimate dermal exposure to the chemical of interest in a liquid formulation during these activities. The rationale, defaults, and limitations of this model are explained in Appendix B.

As described above for the inhalation exposure to liquid adhesives, if the adhesive product is formulated in a heated mixing process (e.g., hot-melt adhesives), it may be transferred into the packaging containers as a hot, molten liquid. However, EPA recommends that the dermal exposure to hot materials be assumed to be negligible when they are handled at temperatures above 60°C (CEB, 1991). EPA typically assumes that dermal exposures to hot materials are mitigated through the use of PPE.

To estimate the potential worker exposure to the chemical of interest in a liquid adhesive component packaged at temperatures less than 60°C, EPA recommends using the following equation:

$$EXP_{\text{dermal}} = Q_{\text{liquid_skin}} \times AREA_{\text{surface}} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}} \quad (5-9)$$

This exposure will occur over [the lesser of $N_{\text{cont_fill_site_yr}}$ or $\text{TIME}_{\text{working_days}}$ (consistent with Section 4.11), up to 250] days per year

Where:

| | | |
|--------------------------------|---|--|
| $\text{EXP}_{\text{dermal}}$ | = | Potential dermal exposure to the chemical of interest per day (mg chemical/day) |
| $Q_{\text{liquid_skin}}$ | = | Quantity of liquid adhesive product remaining on skin (Defaults: 2.1 mg adhesive/cm ² -incident (high-end) and 0.7 mg adhesive/cm ² -incident (low-end) for routine or incidental contact (CEB, 2000)) |
| $\text{AREA}_{\text{surface}}$ | = | Surface area of contact (Default: 840 cm ² for 2 hands (CEB, 2000)) |
| $N_{\text{exp_incident}}$ | = | Number of exposure incidents per day (Default: 1 incident/day) (see footnote to Equation 5-3a) |
| $F_{\text{chem_comp}}$ | = | Mass fraction of the chemical of interest in the adhesive component (mg chemical/mg component) (See Section 3.3) |
| $F_{\text{comp_adhes}}$ | = | Mass fraction of the component in the formulated adhesive product (mg component/mg adhesive) (See Section 3.4) |

Solid Adhesives:

Hot-melt adhesives may also be cooled within the process before being packaged as pellets, sticks, or blocks that consist of large particle sizes. Dust generation is not expected during packaging; therefore, inhalation is negligible. In addition, volatile components (e.g., the vapor pressure is > 0.001 torr) are expected to have evaporated during the formulation process. Recognizing that the adhesive chemical has been incorporated into a solid adhesive product, some dermal contact with the chemical may occur. However, EPA typically considers this type of dermal exposure to be non-quantifiable (CEB, 2000).

6 SAMPLE CALCULATIONS

This section presents an example of how the equations introduced in Sections 3, 4, and 5 might be used to estimate releases of and exposures to a volatile chemical found in a liquid component used to formulate an adhesive product. The default values used in these calculations are presented in Sections 3, 4, and 5 and should be used only in the absence of site-specific information. The following data are used in the example calculations:

1. Chemical of interest production volume ($Q_{\text{chem_yr}}$) is *5,000,000 kg chemical/yr* and is used as part of a solvent component added to the adhesive formulation.
2. Chemical of interest has a molecular weight (MW_{chem}) of 100 g/mol and a vapor pressure (VP_{chem}) of 0.1 torr @ 25°C (i.e., the chemical is volatile for the purposes of the assessment).
3. Chemical of interest is distributed to the adhesive formulators in *liquid* form to be incorporated into an *unknown adhesive product*.
4. The assessment is concerned with exposures only; however, releases are calculated in this section in order to demonstrate the calculations.

6.1 General Facility Estimates

6.1.1 Annual Adhesive Production Rate ($Q_{\text{adhes_site_yr}}$)

Aside from the annual production volume and physical state of the chemical of interest, no other site-specific information or data are known for the Equation 3-2 parameters (i.e., $Q_{\text{adhes_site_yr}}$, $F_{\text{chem_comp}}$, and $F_{\text{comp_adhes}}$) used to estimate the number of formulation sites using the chemical (N_{sites}). Therefore, use of the default assumptions is appropriate. Using the decision logic illustrated in Figure 3-1, the following default assumptions about the type of formulator and adhesive product are made:

Type of adhesive product: *Unknown adhesive*

Type of formulator: *Other*

The resulting default production rate ($Q_{\text{adhes_site_prod_rate}}$) from Table 3-2 is *1,600,000 kg adhesive/site-yr*:

$$Q_{\text{adhes_site_yr}} = Q_{\text{adhes_site_prod_rate}} \times F_{\text{adhes}} \quad [\text{Eqn. 3-1}]$$

$$Q_{\text{adhes_site_yr}} = 1,600,000 \text{ kg total adhesive/site - yr} \times 1 \text{ kg adhes with chem./kg total adhesive}$$

$$Q_{\text{adhes_site_yr}} = 1,600,000 \text{ kg total adhesive/site - yr}$$

6.1.2 Concentration (Mass Fraction) of the Chemical of Interest in the Adhesive Component (F_{chem_comp})

If the concentration of the chemical of interest in the adhesive component (F_{chem_comp}) is not known, assume 100 percent (or *1 kg chemical/kg component*).

6.1.3 Concentration (Mass Fraction) of the Adhesive Component in the Adhesive Product (F_{comp_adhes})

Since the component is used as a *solvent* within the adhesive, and since the concentration of the component in the final product is not known, the high-end solvent concentration (weight fraction) presented in Table 3-3 is assumed. The high-end concentration for solvents used in adhesive products generally (F_{comp_adhes}) is *0.75 kg component/kg adhesive*.

6.1.4 Number of Sites (N_{sites})

$$N_{sites} = \frac{Q_{chem_yr}}{Q_{adhes_site_yr} \times F_{chem_comp} \times F_{comp_adhes}} \quad [\text{Eqn. 3-2}]$$

$$N_{sites} = \frac{5,000,000 \text{ kg chem./yr}}{1,600,000 \text{ kg adhes./site - yr} \times 1 \text{ kg chem./kg comp.} \times 0.75 \text{ kg comp./kg adhes.}}$$

$$N_{sites} = 4.2 \text{ sites}$$

Round N_{sites} up to next integer (*5 formulation sites*) and recalculate $Q_{adhes_site_yr}$:

$$Q_{adhes_site_yr} = \frac{5,000,000 \text{ kg chem./yr}}{5 \text{ sites} \times 1 \text{ kg chem./kg comp.} \times 0.75 \text{ kg comp./kg adhes.}}$$

$$Q_{adhes_site_yr} = 1,330,000 \text{ kg adhes./site - yr}$$

6.1.5 Number of Batches ($N_{bt_site_yr}$ batches/site-year)

If the batch size (Q_{adhes_bt}) is not known, *4,000 kg adhesive formulated per batch* is assumed:

$$N_{batch_site_yr} = \frac{Q_{adhes_site_yr}}{Q_{adhes_bt}} \quad [\text{Eqn. 3-3}]$$

$$N_{batch_site_yr} = \frac{1,330,000 \text{ kg adhes./site - yr}}{4,000 \text{ kg adhes./bt}}$$

$$N_{batch_site_yr} = 333 \text{ bts/site - yr}$$

6.1.6 Days of Operation ($TIME_{working_days}$ days/year)

Since the annual number of batches formulated per site ($N_{bt_site_yr} = 333$ batches/site-year) is less than 365 days per year, the default assumption for the number of batches formulated per day ($N_{bt_site_day} = 1$ batches/site-day) is used:

$$TIME_{working_days} = \frac{N_{bt_site_yr}}{N_{bt_site_day}} \quad [Eqn. 3-4]$$

$$TIME_{working_days} = \frac{333 \text{ bts/site - yr}}{1 \text{ bt/site - day}}$$

$$TIME_{working_days} = 333 \text{ days/yr}$$

6.1.7 Daily Use Rate of the Chemical of Interest ($Q_{chem_site_day}$ kg chemical/site-day)

$$Q_{chem_site_day} = Q_{adhes_bt} \times N_{batch_site_day} \times F_{chem_comp} \times F_{comp_adhes} \quad [Eqn. 3-5]$$

$$Q_{chem_site_day} = \frac{4,000 \text{ kg adhes.}}{\text{bt}} \times \frac{1 \text{ bt}}{\text{site - day}} \times \frac{1 \text{ kg chem.}}{\text{kg comp.}} \times \frac{0.75 \text{ kg comp.}}{\text{kg adhes.}}$$

$$Q_{chem_site_day} = \frac{3,000 \text{ kg chem.}}{\text{site - day}}$$

6.1.8 Annual Number of Component Containers Emptied per Site ($N_{cont_empty_site_yr}$ container/site-year)

It is assumed that the adhesive component (which is 100% chemical of interest, by default) is shipped to the formulators in 55-gallon drums, as a default. A density of 1 kg/L is also assumed for the adhesive component. The mass capacity for each of the drums is calculated as:

$$Q_{cont_empty} = V_{cont_empty} \times RHO_{component} = \frac{208 \text{ L comp.}}{\text{container}} \times \frac{1 \text{ kg comp.}}{\text{L}} = \frac{208 \text{ kg comp.}}{\text{container}}$$

The number of shipping containers that are emptied per site, per year is calculated as:

$$N_{cont_empty_site_yr} = \frac{Q_{chem_site_day} \times TIME_{working_days}}{F_{chem_comp} \times Q_{cont_empty}} \quad [Eqn. 3-6]$$

$$N_{cont_empty_site_yr} = \frac{3,000 \text{ kg chem./site - day} \times 333 \text{ days/yr}}{1 \text{ kg chem./kg comp.} \times 208 \text{ kg comp./container}}$$

$$N_{cont_empty_site_yr} = 4,803 \text{ containers/site - yr}$$

6.1.9 Annual Number of Adhesive Product Containers Filled per Site ($N_{\text{cont_fill_site_yr}}$ container/site-year)

It is assumed that the adhesive product (which is 75 percent chemical of interest, by default) is packaged in 55-gallon drums, as a default. A density of 1 kg/L is also assumed for the adhesive product. The mass capacity for each of the drums is calculated as:

$$Q_{\text{cont_fill}} = V_{\text{cont_fill}} \times \text{RHO}_{\text{adhes}} = \frac{208 \text{ L adhes.}}{\text{container}} \times \frac{1 \text{ kg adhes.}}{\text{L}} = \frac{208 \text{ kg adhes.}}{\text{container}}$$

The number of shipping containers that are filled per site, per year is calculated as:

$$N_{\text{cont_fill_site_yr}} = \frac{Q_{\text{chem_site_day}} \times \text{TIME}_{\text{working_days}}}{F_{\text{chem_comp}} \times F_{\text{comp_adhes}} \times Q_{\text{cont_fill}}} \quad [\text{Eqn 3-7}]$$

$$N_{\text{cont_fill_site_yr}} = \frac{\left(\frac{3,000 \text{ kg chem.}}{\text{site - day}} \times \frac{333 \text{ days}}{\text{yr}} \right)}{\left(\frac{1 \text{ kg chem.}}{\text{kg comp.}} \times \frac{0.75 \text{ kg comp.}}{\text{kg adhes.}} \times \frac{208 \text{ kg adhes.}}{\text{container}} \right)}$$

$$N_{\text{cont_fill_site_yr}} = 6,404 \text{ containers/site - yr}$$

6.2 Release Assessments

6.2.1 Adhesive Component Container Residue Released to Water, Incineration, or Landfill (Release 1)

Since $N_{\text{cont_empty_site_yr}}$ is greater than $\text{TIME}_{\text{working_days}}$, it is assumed that more than one container is emptied on each operating day. The following equation is used to estimate the daily release:

$$\text{Elocal}_{\text{container_residue_disp}} = Q_{\text{chem_site_day}} \times F_{\text{container_residue}} \quad [\text{Eqn. 4-1b}]$$

Since it is known that the adhesive component is in a liquid form when shipped to the formulation site, and the container is assumed to be a 55-gallon drum by default, the *EPA/OPPT Drum Residual Model* is used to estimate this release. The default fraction of liquid chemical that remains in the empty container ($F_{\text{container_residue}}$) is 0.03 kg chemical remaining/kg chemical in full container (see Table B-3 in Appendix B):

$$\text{Elocal}_{\text{container_residue_disp}} = \frac{3,000 \text{ kg chem.}}{\text{site - day}} \times \frac{0.03 \text{ kg chem. remain}}{\text{kg chem. full}}$$

$$\text{Elocal}_{\text{container_residue_disp}} = \frac{90 \text{ kg chem. released}}{\text{site - day}}$$

...over 333 days/year from 5 sites.

6.2.2 Open Surface Losses to Air During Container Cleaning (Release 2)

Since the chemical of interest is volatile, it will be emitted from the process while the emptied containers are cleaned. The *EPA/OPPT Penetration Model* is used to estimate the rate at which the chemical is emitted during this activity:

$$Q_{\text{vapor_generation}} = \frac{(8.24 \times 10^{-8}) \times MW_{\text{chem}}^{0.835} \times F_{\text{correction_factor}} \times VP_{\text{chem}} \times \left(\frac{1}{29} + \frac{1}{MW_{\text{chem}}} \right)^{0.25} \times \text{RATE}_{\text{air_speed}}^{0.5} \times \text{AREA}_{\text{opening}}}{\text{TEMP}_{\text{ambient}}^{0.05} \times D_{\text{opening}}^{0.5} \times P_{\text{ambient}}^{0.5}} \quad [\text{Eqn. B-1}]$$

Table 6-1. Summary of ChemSTEER Inputs for Release 2

| Parameter | Units | ChemSTEER Input |
|-----------------------------------|---------------|-----------------|
| MW_{chem} | g/mol | 100 |
| $F_{\text{correction_factor}}$ | dimensionless | 1 |
| VP_{chem} | torr | 0.1 |
| $\text{RATE}_{\text{air_speed}}$ | ft/min | 100 |
| $\text{AREA}_{\text{opening}}$ | cm^2 | 20.3 |
| $\text{TEMP}_{\text{ambient}}$ | K | 298 |
| D_{opening} | cm | 5.08 |
| P_{ambient} | atm | 1 |

Therefore:

$$Q_{\text{vapor_generation}} = 1.2 \times 10^{-5} \text{ g/s}$$

Using $Q_{\text{vapor_generation}}$ calculated in Equation B-1 and the other standard default values presented in Table 4-2 for container cleaning, the model then estimates the daily release to air using the following equation:

$$\text{Elocal}_{\text{air_cleaning}} = Q_{\text{vapor_generation}} \times \text{TIME}_{\text{activity_hours}} \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}} \quad [\text{Eqn. B-2}]$$

$$\text{Elocal}_{\text{air_cleaning}} = 1.2 \times 10^{-5} \text{ g chem./sec} \times \left(\frac{4,803 \text{ containers/site-yr}}{333 \text{ days/yr} \times 20 \text{ containers/hr}} \right) \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}}$$

$$\text{Elocal}_{\text{air_cleaning}} = 3.1 \times 10^{-5} \text{ kg chem. emitted/site-day}$$

...over 333 days/year from 5 sites.

6.2.3 Transfer Operation Losses to Air from Unloading the Adhesive Component (Release 3)

Since the chemical of interest is volatile, it will be emitted from the process from the displacement of saturated air when the chemical is transferred. The *EPA/OAQPS AP-42 Loading Model* is used to estimate the rate at which the chemical is emitted during this activity:

$$Q_{\text{vapor_generation}} = \frac{F_{\text{saturation_factor}} \times MW_{\text{chem}} \times \left(V_{\text{cont_empty}} \times \frac{3785.4 \text{ cm}^3}{\text{gal}} \right) \times \left(\frac{\text{RATE}_{\text{fill}}}{3600 \text{ sec/hour}} \right) \times F_{\text{correction_factor}} \times \left(\frac{VP_{\text{chem}}}{760 \text{ torr/atm}} \right)}{R \times \text{TEMP}_{\text{ambient}}} \quad [\text{Eqn. B-5}]$$

Table 6-2. Summary of ChemSTEER Inputs for Release 3

| Parameter | Units | ChemSTEER Input |
|--------------------------------|-----------------|---------------------------------|
| MW _{chem} | g/mol | 100 |
| F _{saturation_factor} | dimensionless | Typical = 0.5 Worst Case = 1 |
| VP _{chem} | torr | 0.1 |
| V _{cont_empty} | gal | 55 |
| RATE _{fill} | containers/hour | 20 |
| TEMP _{ambient} | K | 298 |
| F _{correction_factor} | dimensionless | 1 |
| R | atm | 82.05 |

Therefore:

$$Q_{\text{vapor_generation}} = 3.1 \times 10^{-4} \text{ g/s for typical and } Q_{\text{vapor_generation}} = 6.2 \times 10^{-4} \text{ g/s for worst case}$$

Using $Q_{\text{vapor_generation}}$ calculated in Equation B-5 and the other standard default values presented in Table 4-3 for container unloading, the model then estimates the daily release to air using the following equation:

$$\text{Elocal}_{\text{air_transfers}} = Q_{\text{vapor_generation}} \times \text{TIME}_{\text{activity_hours}} \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}} \quad [\text{Eqn. B-7}]$$

$$\text{Elocal}_{\text{air_transfers}} = (3.1 \times 10^{-4} \text{ to } 6.2 \times 10^{-4}) \text{ g chem./sec} \times \left(\frac{4,803 \text{ containers/site - yr}}{333 \text{ days/yr} \times 20 \text{ containers/hr}} \right) \times \frac{3600 \text{ sec/hr}}{1000 \text{ g/kg}}$$

$\text{Elocal}_{\text{air_transfers}} = 8.0 \times 10^{-4} - 0.0016 \text{ g chem. emitted/site-day}$
...over 333 days/year from 5 sites.

6.2.4 *Dust Generation from Transfer Operations Released to Air, or Collected and Released to Water, Incineration, or Landfill (Release 4)*

The chemical is received as a liquid component; therefore, dust generation is not expected.

6.2.5 *Vented Losses to Air During Process Operations (Release 5)*

Since the chemical of interest is volatile, it will be emitted from the process during adhesive product mixing and formulation. Because of the volatility of the chemical, it is also assumed that the vessel is closed with a 4-inch (10 cm) diameter vent. The *EPA/OPPT Penetration Model* is used to estimate the rate at which the chemical is emitted during this activity:

[Eqn. B-1]

$$Q_{\text{vapor_generation}} = \frac{(8.24 \times 10^{-8}) \times MW_{\text{chem}}^{0.835} \times F_{\text{correction_factor}} \times VP_{\text{chem}} \times \left(\frac{1}{29} + \frac{1}{MW_{\text{chem}}} \right)^{0.25} \times RATE_{\text{air_speed}}^{0.5} \times AREA_{\text{opening}}}{TEMP_{\text{ambient}}^{0.05} \times D_{\text{opening}}^{0.5} \times P_{\text{ambient}}^{0.5}}$$

Table 6-3. Summary of ChemSTEER Inputs for Release 5

| Parameter | Units | ChemSTEER Input |
|--------------------------------|-----------------|-----------------|
| MW _{chem} | g/mol | 100 |
| F _{correction factor} | dimensionless | 1 |
| VP _{chem} | torr | 0.1 |
| RATE _{air speed} | ft/min | 100 |
| AREA _{opening} | cm ² | 79 |
| TEMP _{ambient} | K | 298 |
| D _{opening} | cm | 10 |
| P _{ambient} | atm | 1 |

Therefore:

$$Q_{\text{vapor_generation}} = 3.3 \times 10^{-5} \text{ g/s}$$

Using $Q_{\text{vapor_generation}}$ calculated in Equation B-1 and the other standard default values presented in Table 4-4 for adhesive mixing, the model then estimates the daily release to air using the following equation:

$$E_{\text{local air_process_vent}} = Q_{\text{vapor_generation}} \times TIME_{\text{activity_hours}} \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}} \quad [\text{Eqn. B-2}]$$

$$E_{\text{local}}_{\text{air_process_vent}} = 3.3 \times 10^{-5} \text{ g chem./sec} \times (8 \text{ hrs/bt} \times 1 \text{ bt/site} - \text{day}) \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}}$$

$$E_{\text{local}}_{\text{air_process_vent}} = 9.5 \times 10^{-4} \text{ kg chem. emitted/site} - \text{day}$$

...over 333 days/year from 5 sites.

6.2.6 Adhesive Product Sampling Wastes Disposed to Non-air Media (Release 6)

While a release from this source is likely to occur, EPA does not currently have data to support quantifying the release.

6.2.7 Open Surface Losses to Air During Product Sampling (Release 7)

Since the chemical of interest is volatile, it will be emitted from the process during adhesive product QA/QC sampling. The *EPA/OPPT Penetration Model* is used to estimate the rate at which the chemical is emitted during this activity:

[Eqn. B-1]

$$Q_{\text{vapor_generation}} = \frac{(8.24 \times 10^{-8}) \times MW_{\text{chem}}^{0.835} \times F_{\text{correction_factor}} \times VP_{\text{chem}} \times \left(\frac{1}{29} + \frac{1}{MW_{\text{chem}}} \right)^{0.25} \times \text{RATE}_{\text{air_speed}}^{0.5} \times \text{AREA}_{\text{opening}}}{\text{TEMP}_{\text{ambient}}^{0.05} \times D_{\text{opening}}^{0.5} \times P_{\text{ambient}}^{0.5}}$$

Table 6-4. Summary of ChemSTEER Inputs for Release 7

| Parameter | Units | ChemSTEER Input |
|--------------------------------|-----------------|-----------------|
| MW _{chem} | g/mol | 100 |
| F _{correction factor} | dimensionless | 1 |
| VP _{chem} | torr | 0.1 |
| RATE _{air speed} | ft/min | 100 |
| AREA _{opening} | cm ² | 4.9-78.5 |
| TEMP _{ambient} | K | 298 |
| D _{opening} | cm | 2.5-10 |
| P _{ambient} | atm | 1 |

Therefore:

$$Q_{\text{vapor_generation}} = 4.2 \times 10^{-6} - 3.3 \times 10^{-5} \text{ g/s}$$

Using $Q_{\text{vapor_generation}}$ calculated in Equation B-1 and the other standard default values presented in Table 4-5 for adhesive product sampling, the model then estimates the daily release to air using the following equation:

$$E_{\text{local}}_{\text{air_sample}} = Q_{\text{vapor_generation}} \times \text{TIME}_{\text{activity_hours}} \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}} \quad [\text{Eqn. B-2}]$$

$$Elocal_{air_sample} = (4.2 \times 10^{-6} \text{ to } 3.3 \times 10^{-4}) \text{ g chem./sec} \times 1 \text{ hr/site} - \text{day} \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}}$$

$$Elocal_{air_sample} = 1.5 \times 10^{-5} - 1.2 \times 10^{-4} \text{ kg chem. emitted/site} - \text{day}$$

...over 333 days/year from 5 sites.

6.2.8 Equipment Cleaning Releases to Water, Incineration, or Landfill (Release 8)

Since it is assumed that one batch is formulated per day ($N_{bt_site_yr}$ is equivalent to $TIME_{working_days}$), the following equation is used to estimate the daily release:

$$Elocal_{equipment_cleaning} = Q_{adhes_bt} \times F_{chem_comp} \times F_{comp_adhes} \times F_{equipment_cleaning} \quad [\text{Eqn. 4-5a}]$$

$$Elocal_{equipment_cleaning} = \frac{4,000 \text{ kg chem.}}{\text{site} - \text{day}} \times \frac{1 \text{ kg chem.}}{1 \text{ kg comp.}} \times \frac{0.75 \text{ kg comp.}}{\text{kg adhes.}} \times \frac{0.02 \text{ kg chem released}}{\text{kg chem used}}$$

$$Elocal_{equipment_cleaning} = \frac{60 \text{ kg chem. released}}{\text{site} - \text{day}}$$

...over 333 days/year from 5 sites

6.2.9 Open Surface Losses to Air During Equipment Cleaning (Release 9)

Since the chemical of interest is volatile, it will be emitted from the process during process equipment cleaning. The *EPA/OPPT Penetration Model* is used to estimate the rate at which the chemical is emitted during this activity:

[Eqn. B-1]

$$Q_{vapor_generation} = \frac{(8.24 \times 10^{-8}) \times MW_{chem}^{0.835} \times F_{correction_factor} \times VP_{chem} \times \left(\frac{1}{29} + \frac{1}{MW_{chem}} \right)^{0.25} \times RATE_{air_speed}^{0.5} \times AREA_{opening}}{TEMP_{ambient}^{0.05} \times D_{opening}^{0.5} \times P_{ambient}^{0.5}}$$

Table 6-5. Summary of ChemSTEER Inputs for Release 9

| Parameter | Units | ChemSTEER Input |
|--------------------------------|-----------------|-----------------|
| MW _{chem} | g/mol | 100 |
| F _{correction factor} | dimensionless | 1 |
| VP _{chem} | torr | 0.1 |
| RATE _{air speed} | ft/min | 100 |
| AREA _{opening} | cm ² | 6,648 |
| TEMP _{ambient} | K | 298 |
| D _{opening} | cm | 92 |

Therefore:

$$Q_{\text{vapor_generation}} = 9.2 \times 10^{-4} \text{ g/s}$$

Using $Q_{\text{vapor_generation}}$ calculated in Equation B-1 and the other standard default values presented in Table 4-6 for process equipment cleaning, the model then estimates the daily release to air using the following equation:

$$\text{Elocal}_{\text{air_eqpt_cleaning}} = Q_{\text{vapor_generation}} \times \text{TIME}_{\text{activity_hours}} \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}} \quad [\text{Eqn. B-2}]$$

$$\text{Elocal}_{\text{air_eqpt_cleaning}} = 9.2 \times 10^{-4} \text{ g chem./sec} \times (4 \text{ hrs/bt} \times 1 \text{ bt/site} - \text{day}) \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}}$$

$$\text{Elocal}_{\text{air_sample}} = 0.013 \text{ kg chem. emitted/site} - \text{day}$$

...over 333 days/year from 5 sites.

6.2.10 *Transfer Operation Losses to Air from Loading Adhesive Product into Transport Containers (Release 10)*

Since the chemical of interest is volatile, it will be emitted from the process from the displacement of saturated air when the chemical is transferred. The *EPA/OAQPS AP-42 Loading Model* is used to estimate the rate at which the chemical is emitted during this activity:

$$Q_{\text{vapor_generation}} = \frac{F_{\text{saturation_factor}} \times MW_{\text{chem}} \times \left(V_{\text{cont_empty}} \times \frac{3785.4 \text{ cm}^3}{\text{gal}} \right) \times \left(\frac{\text{RATE}_{\text{fill}}}{3600 \text{ sec/hour}} \right) \times F_{\text{correction_factor}} \times \left(\frac{VP_{\text{chem}}}{760 \text{ torr/atm}} \right)}{R \times \text{TEMP}_{\text{ambient}}} \quad [\text{Eqn. B-5}]$$

Table 6-6. Summary of ChemSTEER Inputs for Release 10

| Parameter | Units | ChemSTEER Input |
|---------------------------------|-----------------|---------------------------------|
| MW_{chem} | g/mol | 100 |
| $F_{\text{saturation_factor}}$ | dimensionless | Typical = 0.5 Worst Case = 1 |
| VP_{chem} | torr | 0.1 |
| $V_{\text{cont_empty}}$ | gal | 1 |
| $\text{RATE}_{\text{fill}}$ | containers/hour | 20 |
| $\text{TEMP}_{\text{ambient}}$ | K | 298 |
| $F_{\text{correction_factor}}$ | dimensionless | 1 |
| R | atm | 82.05 |

Therefore:

$$Q_{\text{vapor_generation}} = 3.1 \times 10^{-4} \text{ g/s for typical and } Q_{\text{vapor_generation}} = 6.2 \times 10^{-4} \text{ g/s for worst case}$$

Using $Q_{\text{vapor_generation}}$ calculated in Equation B-5 and the other standard default values presented in Table 4-7 for adhesive packaging, the model then estimates the daily release to air using the following equation:

$$E_{\text{local_air_packaging}} = Q_{\text{vapor_generation}} \times \text{TIME}_{\text{activity_hours}} \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}} \quad [\text{Eqn. B-7}]$$

$$E_{\text{local_air_packaging}} = (3.1 \times 10^{-4} \text{ to } 6.2 \times 10^{-4}) \text{ g chem./sec} \times \left(\frac{6,404 \text{ containers/site - yr}}{333 \text{ days/yr} \times 20 \text{ containers/hr}} \right) \times \frac{3600 \text{ sec/hr}}{1000 \text{ g/kg}}$$

$E_{\text{local_air_packaging}} = 0.0011 - 0.0021 \text{ kg chem. emitted/site-day}$
 ...over 333 days/year from 5 sites.

6.2.11 *Off-spec Product Released to Water, Incineration, or Landfill (Release 11)*

It is assumed that one percent of the annual batches are disposed as off-spec product. The number of batches disposed per year is calculated as:

$$N_{\text{off-spec_release_days}} = \frac{N_{\text{bt_site_yr}} \times F_{\text{off-spec_batch}}}{N_{\text{off-spec_bt_day}}} \quad [\text{Eqn. 4-6}]$$

$$N_{\text{off-spec_release_days}} = \frac{\frac{333 \text{ batches}}{\text{site - yr}} \times \frac{0.01 \text{ off - spec batch}}{\text{batch}}}{\left(\frac{1 \text{ off - spec batch}}{\text{day}} \right)}$$

$$N_{\text{off-spec_release_days}} = \frac{3 \text{ days}}{\text{site - yr}}$$

The release is then calculated as:

$$E_{\text{local_off-spec}} = Q_{\text{adhes_bt}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}} \quad [\text{Eqn. 4-7}]$$

$$E_{\text{local_off-spec}} = \frac{4,000 \text{ kg adhes.}}{\text{bt}} \times \frac{1 \text{ kg chem.}}{\text{kg comp.}} \times \frac{0.75 \text{ kg comp.}}{\text{kg adhes.}}$$

$$E_{\text{local_off-spec}} = \frac{3,000 \text{ kg chem. released}}{\text{site - day}}$$

...over 3 days/year from 5 sites

6.3 Occupational Exposure Assessments

6.3.1 Total Number of Workers Potentially Exposed to the Chemical

It is assumed that 22 adhesive formulation workers are potentially exposed to the chemical at each site; therefore, the total number of workers is calculated as:

$$22 \frac{\text{workers}}{\text{site}} \times N_{\text{sites}} = 22 \frac{\text{workers}}{\text{site}} \times 5 \text{ sites} = 110 \text{ total adhesive formulation workers}$$

Note that all 110 workers are assumed to be exposed during each of the exposure activities performed at the five adhesive formulation sites.

6.3.2 Exposure from Unloading Solid or Liquid Chemicals (Exposure A)

Inhalation Exposure to Liquids:

Using the vapor generation rate calculated in Release 3 and the CEB standard model for estimating inhalation exposure due to evaporation of volatile chemicals (*EPA/OPPT Mass Balance Model*), ChemSTEER calculates the worker exposure using the following equations:

Table 6-7. Summary of ChemSTEER Inputs for Exposure A

| Parameter | Units | ChemSTEER Input |
|--------------------------------|----------------------|---|
| $F_{\text{mixing_factor}}$ | dimensionless | Typical = 0.5 Worst Case = 0.1 |
| $TEMP_{\text{ambient}}$ | K | 298 |
| MW_{chem} | g/mol | 100 |
| $RATE_{\text{ventilation}}$ | ft ³ /min | Typical = 3000 Worst Case = 500 |
| $Q_{\text{vapor_generation}}$ | g/s | Typical = 3.1×10^{-4} Worst Case = 6.2×10^{-4} |
| $RATE_{\text{breathing}}$ | m ³ /hour | 1.25 |
| V_{molar} | L/mol | 24.45 |
| $RATE_{\text{fill}}$ | containers/hr | 20 |
| $TIME_{\text{exposure}}$ | hours/day | 0.72 |

$$C_{\text{chem_volumetric}} = \frac{(1.7 \times 10^5) \times TEMP_{\text{ambient}} \times Q_{\text{vapor_generation}}}{MW_{\text{chem}} \times RATE_{\text{ventilation}} \times F_{\text{mixing_factor}}} \quad [\text{Eqn. B-7}]$$

$$C_{\text{chem_volumetric}} = 0.1 \text{ ppm for typical and } 6.3 \text{ ppm for worst case}$$

Next, the volumetric concentration is converted to a mass concentration ($C_{\text{chem_mass}}$) by the following equation:

$$C_{\text{chem_mass}} = \frac{C_{\text{chem_volumetric}} \times MW_{\text{chem}}}{V_{\text{molar}}} \quad [\text{Eqn. B-9}]$$

$$C_{\text{chem_mass}} = 0.4 \text{ mg/m}^3 \text{ for typical and } C_{\text{chem_mass}} = 25.8 \text{ mg/m}^3 \text{ for worst case}$$

Finally, the mass concentration of the chemical and the standard default values presented in Table 5-2 for the container unloading activity are used to estimate the amount of inhalation exposure per worker using the following calculation:

$$\text{EXP}_{\text{inhalation}} = C_{\text{chem_mass}} \times \text{RATE}_{\text{breathing}} \times \text{TIME}_{\text{exposure}} \quad [\text{Eqn. B-10}]$$

$$\text{EXP}_{\text{inhalation}} = (0.41 \text{ to } 25) \text{ mg/m}^3 \times 1.25 \text{ m}^3/\text{hr} \times \left(\frac{4,803 \text{ containers/site - yr}}{333 \text{ days/yr} \times 20 \text{ containers/hr}} \right)$$

$$\text{EXP}_{\text{inhalation}} = 0.37 - 23 \text{ mg chem./worker - day}$$

...over 250 days/year.

Dermal Exposure to Liquids:

The potential worker exposure to the chemical within the liquid adhesive component is calculated using the *EPA/OPPT 2-Hand Dermal Contact with Liquid Model*:

$$\text{EXP}_{\text{dermal}} = Q_{\text{liquid_skin}} \times \text{AREA}_{\text{surface}} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \quad [\text{Eqn. 5-3a}]$$

$$= \left[\frac{0.7 \text{ to } 2.1 \text{ mg adhes.}}{\text{cm}^2 - \text{incident}} \right] \times 840 \text{ cm}^2 \times \frac{1 \text{ incident}}{\text{day}} \times \frac{1 \text{ mg chem.}}{\text{mg comp.}}$$

$$\text{EXP}_{\text{dermal}} = \frac{588 - 1,764 \text{ mg chem.}}{\text{day}}$$

...over 250 days/year

6.3.3 Exposure to Liquids During Container Cleaning (Exposure B)

Inhalation Exposure to Liquids:

Using the vapor generation rate calculated in Release 2 and the CEB standard model for estimating inhalation exposure due to evaporation of volatile chemicals (*EPA/OPPT Mass Balance Model*), ChemSTEER calculates the worker exposure using the following equations:

Table 6-8. Summary of ChemSTEER Inputs for Exposure B

| Parameter | Units | ChemSTEER Input |
|--------------------------------|----------------------|------------------------------------|
| $F_{\text{mixing_factor}}$ | dimensionless | Typical = 0.5 Worst Case = 0.1 |
| $TEMP_{\text{ambient}}$ | K | 298 |
| MW_{chem} | g/mol | 100 |
| $RATE_{\text{ventilation}}$ | ft ³ /min | Typical = 3000 Worst Case = 500 |
| $Q_{\text{vapor_generation}}$ | g/s | Typical = 1.2×10^{-5} |
| $RATE_{\text{breathing}}$ | m ³ /hour | 1.25 |
| V_{molar} | L/mol | 24.45 |
| $RATE_{\text{fill}}$ | containers/hr | 20 |
| $TIME_{\text{exposure}}$ | hours/day | 0.72 |

$$C_{\text{chem_volumetric}} = \frac{(1.7 \times 10^5) \times TEMP_{\text{ambient}} \times Q_{\text{vapor_generation}}}{MW_{\text{chem}} \times RATE_{\text{ventilation}} \times F_{\text{mixing_factor}}} \quad [\text{Eqn. B-7}]$$

$$C_{\text{chem_volumetric}} = 4.0 \times 10^{-3} \text{ ppm for typical and } C_{\text{chem_volumetric}} = 0.12 \text{ ppm for worst case}$$

Next, the volumetric concentration is converted to a mass concentration ($C_{\text{chem_mass}}$) by the following equation:

$$C_{\text{chem_mass}} = \frac{C_{\text{chem_volumetric}} \times MW_{\text{chem}}}{V_{\text{molar}}} \quad [\text{Eqn. B-9}]$$

$$C_{\text{chem_mass}} = 1.7 \times 10^{-2} \text{ mg/m}^3 \text{ for typical and } C_{\text{chem_mass}} = 0.5 \text{ mg/m}^3 \text{ for worst case}$$

Finally, the mass concentration of the chemical and the standard default values presented in Table 5-3 for the container cleaning activity are used to estimate the amount of inhalation exposure per worker using the following calculation:

$$EXP_{\text{inhalation}} = C_{\text{chem_mass}} \times RATE_{\text{breathing}} \times TIME_{\text{exposure}} \quad [\text{Eqn. B-10}]$$

$$EXP_{\text{inhalation}} = (0.017 \text{ to } 0.49) \text{ mg/m}^3 \times 1.25 \text{ m}^3/\text{hr} \times \left(\frac{4,803 \text{ containers/site - yr}}{333 \text{ days/yr} \times 20 \text{ containers/hr}} \right)$$

$$EXP_{\text{inhalation}} = 0.015 - 0.44 \text{ mg chem./worker - day}$$

...over 250 days/year.

Dermal Exposure to Liquids:

The potential worker exposure to the chemical within the liquid adhesive component is calculated using the *EPA/OPPT 2-Hand Dermal Contact with Liquid Model*:

$$\begin{aligned} \text{EXP}_{\text{dermal}} &= Q_{\text{liquid_skin}} \times \text{AREA}_{\text{surface}} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} && \text{[Eqn. 5-6a]} \\ &= \left[\frac{0.7 \text{ to } 2.1 \text{ mg adhes.}}{\text{cm}^2 \text{ - incident}} \right] \times 840 \text{ cm}^2 \times \frac{1 \text{ incident}}{\text{day}} \times \frac{1 \text{ mg chem.}}{\text{mg comp.}} \\ \text{EXP}_{\text{dermal}} &= \frac{588 - 1,764 \text{ mg chem.}}{\text{day}} \\ &\dots \text{over 250 days/year} \end{aligned}$$

6.3.4 Inhalation Exposure During Operation of Open Mixing Vessels (Exposure C)

Since the chemical is volatile, the adhesive product is assumed to be formulated within a closed vessel; therefore, no inhalation exposures are expected during the mixing operation.

6.3.5 Exposure from Sampling Liquid Adhesive Product (Exposure D)

Inhalation Exposure:

Using the vapor generation rate calculated in Release 7 and the CEB standard model for estimating inhalation exposure due to evaporation of volatile chemicals (*EPA/OPPT Mass Balance Model*), ChemSTEER calculates the worker exposure using the following equations:

Table 6-9. Summary of ChemSTEER Inputs for Exposure D

| Parameter | Units | ChemSTEER Input |
|-------------------------------|----------------------|---|
| F _{mixing_factor} | dimensionless | Typical = 0.5 Worst Case = 0.1 |
| TEMP _{ambient} | K | 298 |
| MW _{chem} | g/mol | 100 |
| RATE _{ventilation} | ft ³ /min | Typical = 3000 Worst Case = 500 |
| Q _{vapor_generation} | g/s | Typical = 4.1 × 10 ⁻⁶ Worst Case = 3.3 × 10 ⁻⁵ |
| RATE _{breathing} | m ³ /hour | 1.25 |
| V _{molar} | L/mol | 24.45 |
| TIME _{exposure} | hours/day | 1 |

$$C_{\text{chem_volumetric}} = \frac{(1.7 \times 10^5) \times \text{TEMP}_{\text{ambient}} \times Q_{\text{vapor_generation}}}{\text{MW}_{\text{chem}} \times \text{RATE}_{\text{ventilation}} \times F_{\text{mixing_factor}}} \quad \text{[Eqn. B-7]}$$

$C_{\text{chem_volumetric}} = 1.4 \times 10^{-3}$ ppm for typical and $C_{\text{chem_volumetric}} = 0.3$ ppm for worst case

Next, the volumetric concentration is converted to a mass concentration ($C_{\text{chem_mass}}$) by the following equation:

$$C_{\text{chem_mass}} = \frac{C_{\text{chem_volumetric}} \times MW_{\text{chem}}}{V_{\text{molar}}} \quad [\text{Eqn. B-9}]$$

$C_{\text{chem_mass}} = 5.7 \times 10^{-3} \text{ mg/m}^3$ for typical and $C_{\text{chem_mass}} = 1.4 \text{ mg/m}^3$ for worst case

Finally, the mass concentration of the chemical and the standard default values presented in Table 5-5 for the product sampling activity are used to estimate the amount of inhalation exposure per worker using the following calculation:

$$\text{EXP}_{\text{inhalation}} = C_{\text{chem_mass}} \times \text{RATE}_{\text{breathing}} \times \text{TIME}_{\text{exposure}} \quad [\text{Eqn. B-10}]$$

$$\begin{aligned} \text{EXP}_{\text{inhalation}} &= (5.7 \times 10^{-3} \text{ to } 1.4) \text{ mg/m}^3 \times 1.25 \text{ m}^3/\text{hr} \times 1 \text{ hr/site} - \text{day} \\ \text{EXP}_{\text{inhalation}} &= 7.1 \times 10^{-3} - 1.7 \text{ mg chem./worker} - \text{day} \\ &\dots \text{over } 250 \text{ days/year.} \end{aligned}$$

Dermal Exposure:

The potential worker exposure to the chemical within the liquid adhesive product is calculated using the *EPA/OPPT 2-Hand Dermal Contact with Liquid Model*:

$$\text{EXP}_{\text{dermal}} = Q_{\text{liquid_skin}} \times \text{AREA}_{\text{surface}} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}} \quad [\text{Eqn. 5-7}]$$

$$\begin{aligned} &= \left[\frac{0.7 \text{ to } 2.1 \text{ mg adhes.}}{\text{cm}^2 - \text{incident}} \right] \times 420 \text{ cm}^2 \times \frac{1 \text{ incident}}{\text{day}} \times \frac{1 \text{ mg chem.}}{\text{mg comp.}} \times \frac{0.75 \text{ mg comp.}}{\text{mg adhes.}} \\ \text{EXP}_{\text{dermal}} &= \frac{220 - 662 \text{ mg chem.}}{\text{day}} \\ &\dots \text{over } 250 \text{ days/year} \end{aligned}$$

6.3.6 Exposure to Liquids During the Equipment Cleaning of Mixers and Other Process Equipment (Exposure E)

Inhalation Exposure:

Using the vapor generation rate calculated in Release 9 and the CEB standard model for estimating inhalation exposure due to evaporation of volatile chemicals (*EPA/OPPT Mass Balance Model*), ChemSTEER calculates the worker exposure using the following equations:

Table 6-10. Summary of ChemSTEER Inputs for Exposure E

| Parameter | Units | ChemSTEER Input |
|--------------------------------|----------------------|------------------------------------|
| $F_{\text{mixing_factor}}$ | dimensionless | Typical = 0.5 Worst Case = 0.1 |
| $TEMP_{\text{ambient}}$ | K | 298 |
| MW_{chem} | g/mol | 100 |
| $RATE_{\text{ventilation}}$ | ft ³ /min | Typical = 3000 Worst Case = 500 |
| $Q_{\text{vapor_generation}}$ | g/s | 9.2×10^{-4} |
| $RATE_{\text{breathing}}$ | m ³ /hour | 1.25 |
| V_{molar} | L/mol | 24.45 |
| $TIME_{\text{exposure}}$ | hours/day | 4 |

$$C_{\text{chem_volumetric}} = \frac{(1.7 \times 10^5) \times TEMP_{\text{ambient}} \times Q_{\text{vapor_generation}}}{MW_{\text{chem}} \times RATE_{\text{ventilation}} \times F_{\text{mixing_factor}}} \quad [\text{Eqn. B-7}]$$

$$C_{\text{chem_volumetric}} = 0.31 - 9.3 \text{ ppm}$$

Next, the volumetric concentration is converted to a mass concentration ($C_{\text{chem_mass}}$) by the following equation:

$$C_{\text{chem_mass}} = \frac{C_{\text{chem_volumetric}} \times MW_{\text{chem}}}{V_{\text{molar}}} \quad [\text{Eqn. B-9}]$$

$$C_{\text{chem_mass}} = \frac{(0.68 \text{ to } 20) \text{ ppm} \times 100 \text{ g/mol}}{24.45 \text{ L/mol}}$$

$$C_{\text{chem_mass}} = 1.3 - 38 \text{ mg/m}^3$$

Finally, the mass concentration of the chemical and the standard default values presented in Table 5-6 for the process equipment cleaning activity are used to estimate the amount of inhalation exposure per worker using the following calculation:

$$EXP_{\text{inhalation}} = C_{\text{chem_mass}} \times RATE_{\text{breathing}} \times TIME_{\text{exposure}} \quad [\text{Eqn. B-10}]$$

$$EXP_{\text{inhalation}} = (2.8 \text{ to } 82) \text{ mg/m}^3 \times 1.25 \text{ m}^3/\text{hr} \times 4 \text{ hrs/site} - \text{day}$$

$$EXP_{\text{inhalation}} = 6.4 - 190 \text{ mg chem./worker} - \text{day}$$

...over 250 days/year.

Dermal Exposure:

$$\begin{aligned}
 \text{EXP}_{\text{dermal}} &= Q_{\text{liquid_skin}} \times \text{AREA}_{\text{surface}} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}} \quad [\text{Eqn. 5-8}] \\
 &= \left[\frac{0.7 \text{ to } 2.1 \text{ mg adhes.}}{\text{cm}^2 \text{ - incident}} \right] \times 840 \text{ cm}^2 \times \frac{1 \text{ incident}}{\text{day}} \times \frac{1 \text{ mg chem.}}{\text{mg comp.}} \times \frac{0.75 \text{ mg comp.}}{\text{mg adhes.}} \\
 \text{EXP}_{\text{dermal}} &= \frac{441 - 1,323 \text{ mg chem.}}{\text{day}} \\
 &\dots \text{over 250 days/year}
 \end{aligned}$$

6.3.7 Exposure from Packaging Adhesive Product (Exposure F)

Inhalation Exposure to Liquid Adhesive:

Using the vapor generation rate calculated in Release 10 and the CEB standard model for estimating inhalation exposure due to evaporation of volatile chemicals (*EPA/OPPT Mass Balance Model*), ChemSTEER calculates the worker exposure using the following equations:

Table 6-11. Summary of ChemSTEER Inputs for Exposure E

| Parameter | Units | ChemSTEER Input |
|-------------------------------|----------------------|---|
| F _{mixing_factor} | dimensionless | Typical = 0.5 Worst Case = 0.1 |
| TEMP _{ambient} | K | 298 |
| MW _{chem} | g/mol | 100 |
| RATE _{ventilation} | ft ³ /min | Typical = 3000 Worst Case = 500 |
| Q _{vapor_generation} | g/s | Typical = 3.1 × 10 ⁻⁴ Worst Case = 6.2 × 10 ⁻⁴ |
| RATE _{breathing} | m ³ /hour | 1.25 |
| V _{molar} | L/mol | 24.45 |
| TIME _{exposure} | hours/day | 8 |

$$C_{\text{chem_volumetric}} = \frac{(1.7 \times 10^5) \times \text{TEMP}_{\text{ambient}} \times Q_{\text{vapor_generation}}}{\text{MW}_{\text{chem}} \times \text{RATE}_{\text{ventilation}} \times F_{\text{mixing_factor}}} \quad [\text{Eqn. B-7}]$$

$C_{\text{chem_volumetric}} = 0.10$ ppm for typical and $C_{\text{chem_volumetric}} = 6.3$ ppm for worst case

Next, the volumetric concentration is converted to a mass concentration ($C_{\text{chem_mass}}$) by the following equation:

$$C_{\text{chem_mass}} = \frac{C_{\text{chem_volumetric}} \times \text{MW}_{\text{chem}}}{V_{\text{molar}}} \quad [\text{Eqn. B-9}]$$

$C_{\text{chem_mass}} = 0.41$ mg/m³ for typical and $C_{\text{chem_mass}} = 26$ mg/m³ for worst case

Finally, the mass concentration of the chemical and the standard default values presented in Table 5-7 for the adhesive product packaging activity are used to estimate the amount of inhalation exposure per worker using the following calculation:

$$EXP_{\text{inhalation}} = C_{\text{chem_mass}} \times RATE_{\text{breathing}} \times TIME_{\text{exposure}} \quad [\text{Eqn. B-10}]$$

$$EXP_{\text{inhalation}} = (0.41 \text{ to } 26) \text{ mg/m}^3 \times 1.25 \text{ m}^3/\text{hr} \times \left(\frac{6,404 \text{ containers/site - yr}}{333 \text{ days/yr} \times 20 \text{ containers/hr}} \right)$$

$$EXP_{\text{inhalation}} = 0.51 - 31 \text{ mg chem./worker - day}$$

...over 250 days/year.

Dermal Exposure to Liquid Adhesive:

$$EXP_{\text{dermal}} = Q_{\text{liquid_skin}} \times AREA_{\text{surface}} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}} \quad [\text{Eqn. 5-9}]$$

$$= \left[\frac{0.7 \text{ to } 2.1 \text{ mg adhes.}}{\text{cm}^2 - \text{incident}} \right] \times 840 \text{ cm}^2 \times \frac{1 \text{ incident}}{\text{day}} \times \frac{1 \text{ mg chem.}}{\text{mg comp.}} \times \frac{0.75 \text{ mg comp.}}{\text{mg adhes.}}$$

$$EXP_{\text{dermal}} = \frac{441 - 1,323 \text{ mg chem.}}{\text{day}}$$

...over 250 days/year

7 DATA GAPS/UNCERTAINTIES AND FUTURE WORK

This ESD relies on anecdotal data and information gathered from various sources to generate general facility estimates, release estimates, and exposure estimates. EPA wishes to make this ESD as detailed and up-to-date as possible, such that the risk-screening assessments reflect current industrial practices. This ESD could be improved by collecting measured data and associated information to verify or supersede the anecdotal data and information.

EPA is most interested in obtaining information about the adhesives formulation industry that is characterized as “typical” or “conservative” (i.e., worse case), and is applicable to a generic formulation site. While EPA welcomes site-specific information as valuable to this ESD, additional qualifiers of how reflective it is to the industry are needed to ensure its transparency if used in the ESD. Reviewers should also feel free to recommend additional resources that may be useful to the development of this ESD.

The key data gaps are summarized below. Note that the data gaps are listed in order of importance (the first being most important):

1. The ESD incorporates average facility production rates that are estimated using several different sources of adhesive production amounts and numbers of U.S. formulation sites. The quality of these production rates could be improved with additional data on typical formulation site component use rates or adhesive production rates for the various types (e.g., kg/batch, kg/site-day).
2. The ESD assumes that formulators use a single component product (containing the chemical of interest) for all adhesive formulations of the same type. Additional information on the validity of this assumption would improve the quality of the estimates. In other words, might adhesive formulators alternately use one of several available types of tackifiers when formulating a water-based adhesive?
3. No industry-specific information was found that could be used to quantify the amount of adhesive product that may be released/disposed as a result of QA/QC sampling activities (Release 6). The ESD uses standard EPA models to estimate the amount of volatile chemical that may be released during sampling (Release 7), and to estimate the associated worker exposures during this activity (Exposure D). No data specific to the adhesives formulation industry were found. Additional loss fraction or monitoring data for operations involving product sampling would improve these estimates.

4. No specific information was found on the typical release control technologies employed in adhesive formulation processes (e.g., wastewater treatment, air release controls). The releases calculated in this ESD reflect the amount of chemical released directly from the process. Information on control technologies and the prevalence of their use would further improve this ESD.
5. No specific information was found on the typical PPE employed in adhesive formulation processes (e.g., gloves, face shields, respirators). The exposures calculated in this ESD reflect the potential amount of direct exposure with no mitigating PPE worn by the workers, as a worst case. Information on PPE and the prevalence of their use would further improve this ESD.
6. Many of the defaults used in the calculations are based on available data found to date for each of the adhesive types discussed in this ESD. In some cases, data for one adhesive type are used in estimates for another adhesive type (e.g., available data for a water-based PSA is used as a default for all water-based adhesives). Additional information on the appropriateness of transferring data from one adhesive type to another, in the absence of type-specific data would further improve the quality of the calculations.
7. This ESD presents the available concentration data for the various adhesive types found to date. Additional formulation data that could be used to generally demonstrate typical concentrations of the components used in the various adhesives would further enhance the calculations.
8. Specific data on the numbers of workers performing the various exposure activities in the adhesive formulation process were not found; therefore, it is assumed that all 22 workers per site perform each of the exposure activities. Additional information on the numbers workers performing each exposure activity would further enhance the calculations.
9. The ESD utilizes available information from two adhesive formulators to estimate the amount of off-spec product that may be disposed in a year. Additional information for estimating the amount of component loss via disposal of adhesive off-spec products would enhance these estimates.
10. No information was found on the specific adhesive component and product shipping/packaging methods, or particular container types used within the various adhesive formulation processes. The ESD assumes that 55-gallon drums are used for both the components and the adhesive products.
11. No information was found to describe the typical empty container waste handling practices for each adhesive type. This information would further improve the quality of the estimates.

12. Specific input on the reasonableness of the default values used in the general facility estimates (e.g., batch duration, number of operating days per year) would enhance the quality of the calculations.
13. The ESD uses standard EPA estimates to determine the amount of residue remaining in the formulation process equipment. Industry-specific loss fraction for adhesive residues removed from the equipment would further improve the estimates.
14. Industry-specific monitoring data for operations involving volatile liquids would enhance the estimates for vented or fugitive releases and associated worker inhalation exposures.
15. Industry-specific dermal monitoring data for all operations involving workers manually handling the adhesive components or formulated products would enhance the estimates.

8 REFERENCES

The specific information researched in the development of this document include process description, operating information, chemicals used, wastes generated, worker activities, and exposure information. Specific sources investigated in the development of this ESD include documents and data from the following sources:

- U.S. Environmental Protection Agency (EPA);
- U.S. Occupational Safety and Health Administration (OSHA);
- U.S. National Institute for Occupational Safety and Health (NIOSH);
- U.S. Census Bureau;
- Organisation for Economic Co-operation and Development (OECD);
- Environment Canada;
- North Carolina Division of Pollution Prevention and Environmental Assistance;
- Kirk-Othmer Encyclopedia of Technology;
- Various trade association websites (e.g., Adhesives and Sealants Council - www.ascouncil.org); and,
- Industry specific journals and technical literature (e.g., Adhesives and Sealants Industry - www.adhesivesmag.com, SpecialChem Innovations and Solutions in Adhesives and Sealants - www.specialchem4adhesives.com).

While each of these sources was reviewed for information, not all provided information specific to adhesives formulation. The references specifically cited in this ESD are provided below.

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**APPENDIX A:
ESTIMATION EQUATION SUMMARY AND DEFAULT PARAMETER VALUES**

Summary of Release and Exposure Estimation Equations

Table A-1 summarizes the equations introduced in Section 3 of this document. These equations may be used in evaluating releases of and exposures to chemicals used in the formulation of adhesive products. A description of each input variable and associated default is provided in Table A-2.

Table A-1. Adhesive Formulation Release and Exposure Calculation Summary

| General Facility Estimates | |
|--|--|
| Annual Facility Production Rate ($Q_{\text{adhes_site_yr}}$): | |
| | $Q_{\text{adhes_site_yr}} = Q_{\text{adhes_site_prod_rate}} \times F_{\text{adhes}}$ (Eqn. 3-1) |
| Number of Sites (N_{sites}): | |
| | $N_{\text{sites}} = \frac{Q_{\text{chem_yr}}}{Q_{\text{adhes_site_yr}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}}}$ (Eqn. 3-2) |
| The value for N_{sites} , calculated using Equation 3-2 should be rounded up to the nearest integer value. $Q_{\text{adhes_site_yr}}$ should then be adjusted for the N_{sites} integer value (to avoid errors due to rounding): | |
| | $Q_{\text{adhes_site_yr}} = \frac{Q_{\text{chem_yr}}}{N_{\text{sites}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}}}$ |
| *Note: If the number of formulation sites is known, the previous equation may also be used to estimate the resulting average annual production rate for use in subsequent calculations. | |
| Annual Number of Batches (batch/site-year) ($N_{\text{bt_site_yr}}$): | |
| | $N_{\text{bt_site_yr}} = \frac{Q_{\text{adhes_site_yr}}}{Q_{\text{adhes_bt}}}$ (Eqn. 3-3) |
| Days of Operation (days/year) ($\text{TIME}_{\text{working_days}}$): | |
| | $\text{TIME}_{\text{working_days}} = \frac{N_{\text{bt_site_yr}}}{N_{\text{bt_site_day}}}$ (Eqn.3-4) |
| Daily Use Rate of the Chemical of Interest (kg chemical/site-day) ($Q_{\text{chem_site_day}}$): | |
| | $Q_{\text{chem_site_day}} = Q_{\text{adhes_bt}} \times N_{\text{bt_site_day}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}}$ (Eqn. 3-5) |
| Annual Number of Adhesive Component Containers Emptied per Facility (containers/site-year) ($N_{\text{cont_semtpry_ite_yr}}$): | |
| | $N_{\text{cont_empty_site_yr}} = \frac{Q_{\text{chem_site_day}} \times \text{TIME}_{\text{working_days}}}{F_{\text{chem_comp}} \times Q_{\text{cont_empty}}}$ (Eqn. 3-6) |
| Annual Number of Adhesive Product Containers Filled per Facility (containers/site-year) ($N_{\text{cont_fill_site_yr}}$): | |
| | $N_{\text{cont_fill_yr}} = \frac{Q_{\text{chem_site_day}} \times \text{TIME}_{\text{working_days}}}{F_{\text{chem_comp}} \times F_{\text{comp_adhes}} \times Q_{\text{cont_fill}}}$ (Eqn. 3-7) |

| Release Calculations | | |
|---|--|--|
| Source | Possible Medium | Daily Release Rates (kg/site-day), Elocal (for Given Sources) |
| Container Residue | Water Landfill Incineration | <p>If $N_{\text{cont_empty_site_yr}}$ is fewer than $\text{TIME}_{\text{working_days}}$:</p> $\text{Elocal}_{\text{container_residue_disp}} = Q_{\text{cont_empty}} \times F_{\text{chem_comp}} \times F_{\text{container_residue}} \times N_{\text{cont_empty_site_day}}$ <p>... released over $[N_{\text{cont_empty_site_yr}}]$ days/year from $[N_{\text{sites}}]$ sites (Eqn. 4-1a)</p> <p>If $N_{\text{cont_empty_site_yr}}$ is greater than $\text{TIME}_{\text{working_days}}$:</p> $\text{Elocal}_{\text{container_residue_disp}} = Q_{\text{chem_site_day}} \times F_{\text{container_residue}}$ <p>... released over $[\text{TIME}_{\text{working_days}}]$ days/year from $[N_{\text{sites}}]$ sites (Eqn. 4-1b)</p> |
| Container Cleaning (Volatile Releases) | Air | EPA/OPPT Penetration Model (See Section 4.3) |
| Transfer Operations (Volatile Releases) | Air | EPA/OAQPS AP-42 Loading Model (See Section 4.4) |
| Transfer Operations (Dust Releases) | Air Water Landfill Incineration | <p>The portion of release that may be captured by the control technology</p> $\text{Elocal}_{\text{dust_captured}} = Q_{\text{form_chem_site_day}} \times F_{\text{dust_generation}} \times F_{\text{dust_control}} \quad (\text{Eqn. 4-2})$ <p>The portion of release that will not be captured by the control technology</p> $\text{Elocal}_{\text{dust_fugitive}} = Q_{\text{form_chem_site_day}} \times F_{\text{dust_generation}} \times (1 - F_{\text{dust_control}}) \quad (\text{Eqn. 4-3})$ |
| Process Vents (Volatile Releases) | Air | EPA/OPPT Penetration Model (See Section 4.6) |
| Product Sampling Wastes | Water Landfill Incineration | EPA does not currently have a model for quantifying this release. |
| Product Sampling (Volatile Releases) | Air | EPA/OPPT Penetration Model (See Section 4.8) |
| Process Equipment Residue | Water Landfill Incineration | <p>If $N_{\text{bt_site_yr}}$ or known number of cleanings is fewer than $\text{TIME}_{\text{working_days}}$:</p> $\text{Elocal}_{\text{equipment_cleaning}} = Q_{\text{adhes_bt}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}} \times N_{\text{bt_site_day}} \times F_{\text{equipment_cleaning}}$ <p>... released over $[N_{\text{bt_site_yr}}]$ days/year from $[N_{\text{sites}}]$ sites (Eqn. 4-5a)</p> <p>If $N_{\text{bt_site_yr}}$ is greater than $\text{TIME}_{\text{working_days}}$:</p> $\text{Elocal}_{\text{equipment_cleaning}} = Q_{\text{chem_site_day}} \times F_{\text{equipment_cleaning}}$ <p>... released over $[\text{TIME}_{\text{working_days}}]$ days/year from $[N_{\text{sites}}]$ sites (Eqn. 4-5b)</p> |
| Equipment Cleaning (Volatile Releases) | Air | EPA/OPPT Penetration Model (See Section 4.10) |

| Release Calculations | | |
|--|-----------------------------|---|
| Source | Possible Medium | Daily Release Rates (kg/site-day), Elocal (for Given Sources) |
| Packaging Operations (Volatile Releases) | Air | EPA/OAQPS AP-42 Loading Model (See Section 4.11) |
| Off-Spec Product Wastes | Water Landfill Incineration | $N_{\text{off-spec_days_site_yr}} = \frac{N_{\text{bt_site_yr}} \times F_{\text{off-spec_bt}}}{N_{\text{off-spec_bt_day}}} \quad (\text{Eqn. 4-6})$ $E_{\text{local_off-spec}} = Q_{\text{adhes_bt}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}}$ <p>...released over [N_{off-spec_days_site_yr}] days/year from [N_{sites}] sites (Eqn. 4-7)</p> |

| Occupational Exposure Calculations | |
|--|--|
| Number of Workers Exposed Per Site: | |
| Up to 22 workers per site (USCB, 2002). | |
| Inhalation Exposure from Unloading Solid or Liquid Chemicals: | |
| <i>Liquid Chemicals:</i> | |
| EPA/OPPT Mass Balance Inhalation Model (See Section 5.3) | |
| <i>Solid Chemicals:</i> | |
| $Q_{\text{comp_site_day}} = \frac{Q_{\text{chem_site_day}}}{F_{\text{chem_comp}}} \quad (\text{Eqn. 5-1})$ | |
| If $Q_{\text{comp_site_day}}$ is <i>greater than</i> 54 kg/site-day: | |
| $\text{EXP}_{\text{inhalation}} = C_{\text{particulate}} \times \text{RATE}_{\text{breathing}} \times \text{TIME}_{\text{exposure}} \times F_{\text{chem_comp}} \quad (\text{Eqn. 5-2a})$ | |
| ...over [the lesser of $N_{\text{cont_empty_site_yr}}$ or $\text{TIME}_{\text{working_days}}$, up to 250] days/year | |
| If $Q_{\text{comp_site_day}}$ is <i>less than or equal to</i> 54 kg/site-day: | |
| $\text{EXP}_{\text{inhalation}} = Q_{\text{comp_site_day}} \times F_{\text{chem_comp}} \times F_{\text{exposure}} \quad (\text{Eqn. 5-2b})$ | |
| ...over [the lesser of $N_{\text{cont_empty_site_yr}}$ or $\text{TIME}_{\text{working_days}}$, up to 250] days/year | |
| Dermal Exposure from Unloading Solid or Liquid Chemicals: | |
| <i>Liquid Chemicals:</i> | |
| $\text{EXP}_{\text{dermal}} = Q_{\text{liquid_skin}} \times \text{AREA}_{\text{surface}} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \quad (\text{Eqn. 5-3a})$ | |
| ... over [the lesser of $N_{\text{cont_empty_site_yr}}$ or $\text{TIME}_{\text{working_days}}$ (consistent with Section 4.4), up to 250] days per year | |
| <i>Solid Chemicals:</i> | |
| $\text{EXP}_{\text{dermal}} = \text{up to } 3,100 \text{ mg/incident} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \quad (\text{Eqn. 5-3b})$ | |
| ... over [the lesser of $N_{\text{cont_empty_site_yr}}$ or $\text{TIME}_{\text{working_days}}$, up to 250] days per year | |
| Inhalation Exposure to Solids or Liquids During Container Cleaning: | |
| <i>Liquid Chemicals:</i> | |
| EPA/OPPT Mass Balance Inhalation Model (See Section 5.4) | |
| <i>Solid Chemicals:</i> | |
| $Q_{\text{comp_residue_site_day}} = \frac{E_{\text{local}}_{\text{container_residue_disp}}}{F_{\text{chem_comp}}} \quad (\text{Eqn. 5-4})$ | |
| If $Q_{\text{comp_residue_site_day}}$ is <i>greater than</i> 54 kg/site-day: | |
| $\text{EXP}_{\text{inhalation}} = C_{\text{particulate}} \times \text{RATE}_{\text{breathing}} \times \text{TIME}_{\text{exposure}} \times F_{\text{chem_comp}} \quad (\text{Eqn. 5-5a})$ | |
| ... over [the lesser of $N_{\text{cont_empty_site_yr}}$ or $\text{TIME}_{\text{working_days}}$ (consistent with Section 4.2), up to 250] days per year | |
| If $Q_{\text{comp_residue_site_day}}$ is <i>less than or equal to</i> 54 kg/site-day: | |
| $\text{EXP}_{\text{inhalation}} = Q_{\text{comp_residue_site_day}} \times F_{\text{chem_comp}} \times F_{\text{exposure}} \quad (\text{Eqn. 5-5b})$ | |
| ... over [the lesser of $N_{\text{cont_empty_site_yr}}$ or $\text{TIME}_{\text{working_days}}$ (consistent with Section 4.2), up to 250] days per year | |

| Occupational Exposure Calculations |
|---|
| <p>Dermal Exposure to Solids or Liquids During Container Cleaning:</p> <p><i>Liquid Chemicals:</i></p> $EXP_{\text{dermal}} = Q_{\text{liquid_skin}} \times AREA_{\text{surface}} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \quad (\text{Eqn. 5-6a})$ <p>... over [the lesser of $N_{\text{cont_empty_site_yr}}$ or $TIME_{\text{working_days}}$ (consistent with Section 4.2), up to 250] days per year</p> <p><i>Solid Chemicals:</i></p> $EXP_{\text{dermal}} = \text{up to } 3,100 \text{ mg/incident} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \quad (\text{Eqn. 5-6b})$ <p>... over [the lesser of $N_{\text{cont_empty_site_yr}}$ or $TIME_{\text{working_days}}$ (consistent with Section 4.2), up to 250] days per year</p> |
| <p>Inhalation Exposure During Operation of Open Mixing Vessels:</p> <p>EPA/OPPT Mass Balance Inhalation Model (See Section 5.5)</p> |
| <p>Exposure from Sampling Liquid Adhesive Product:</p> <p><i>Inhalation Exposure:</i></p> <p>EPA/OPPT Mass Balance Inhalation Model (See Section 5.6)</p> <p><i>Dermal Exposure:</i></p> $EXP_{\text{dermal}} = Q_{\text{liquid_skin}} \times AREA_{\text{surface}} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}} \quad (\text{Eqn. 5-7})$ <p>... over [the lesser of $N_{\text{cont_empty_site_yr}}$ or $TIME_{\text{working_days}}$ (consistent with Section 4.8), up to 250] days per year.</p> |
| <p>Exposure to Liquids During the Equipment Cleaning of Mixers and Other Process Equipment:</p> <p><i>Inhalation Exposure:</i></p> <p>EPA/OPPT Mass Balance Inhalation Model (See Section 5.8)</p> <p><i>Dermal Exposure:</i></p> $EXP_{\text{dermal}} = Q_{\text{liquid_skin}} \times AREA_{\text{surface}} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}} \quad (\text{Eqn. 5-8})$ <p>... over [the number of cleanings per year (consistent with Section 4.9), up to 250] days per year.</p> |
| <p>Exposure from Packaging Liquid Adhesive Product:</p> <p><i>Inhalation Exposure:</i></p> <p>EPA/OPPT Mass Balance Inhalation Model (See Section 5.8)</p> <p><i>Dermal Exposure:</i></p> $EXP_{\text{dermal}} = Q_{\text{liquid_skin}} \times AREA_{\text{surface}} \times N_{\text{exp_incident}} \times F_{\text{chem_comp}} \times F_{\text{comp_adhes}} \quad (\text{Eqn. 5-9})$ <p>... over [the lesser of $N_{\text{cont_fill_site_yr}}$ or $TIME_{\text{working_days}}$ (consistent with Section 4.11), up to 250] days per year.</p> |

Table A-2. Summary of Equation Parameter Default Values Used in the ESD

| Variable | Variable Description | Default Value | Data Source |
|---------------------------------|---|--|------------------|
| AREA _{surface} | Surface area of contact (cm ²) | 840 cm ² (2 hands) 420 cm ² (1 hand) | CEB, 2000 |
| C _{particulate} | Concentration of particulate in workers breathing zone (OSHA Total PNOR PEL (8-hr TWA) (mg/m ³)) | 15 | 29 CFR 1910.1000 |
| F _{adhes} | Fraction of the total adhesive type produced that incorporates the chemical of interest (kg adhesive with chemical/kg total adhesive produced) | 1 | EPA assumption |
| F _{chem_comp} | Mass fraction of the chemical of interest in the adhesive component (kg chemical/kg component) | 1 | EPA assumption |
| F _{comp_adhes} | Mass fraction of the component in the formulated adhesive product (kg component/kg adhesive) | 0.85 For elastomer/polymer used in an unknown adhesive type | See Table 3-3 |
| F _{container_residue} | Fraction of adhesive component remaining in the container as residue (kg component remaining/kg component in full container) | 0.03 | CEB, 2002a |
| F _{dust_control} | Control technology capture efficiency | 0 (no control technology) | EPA assumption |
| F _{equipment_cleaning} | Fraction of adhesive product released as residual in process equipment (kg adhesive released/kg batch capacity) | 0.02 | CEB, 1992a |
| F _{exposure} | Weight fraction of total particulate adhesive component or product in the workers' breathing zone (mg chemical/kg handled) | 0.0477 (typical) 0.161 (worst case) | CEB, 1992b |
| F _{dust_generation} | Loss fraction of chemical during transfer/unloading of solid powders | 0.005 | CEB, 2006b |
| F _{off-spec_bt} | Fraction of the annual number of batches that are disposed as off-spec product waste (number of off-spec batches/annual number of batches per year) | 0.01 | SRRP, no date |
| N _{bt_site_day} | Daily number of adhesive batches formulated at each site (batches/site-day) | 1 | EPA assumption |
| N _{exp_incident} | Number of exposure incidents per day (incidents/day) | 1 | CEB, 2000 |
| N _{off-spec_bt_day} | Number of off-spec batches per day | 1 | EPA assumption |
| Q _{adhes_bt} | Mass of adhesive formulated per batch (kg adhesive/batch) | 4,000 | CEB, no date |
| Q _{adhes_site_yr} | Annual facility adhesive production rate (kg adhesive/site-yr) | 1,600,000 For unknown adhesive type formulated at "other" sites | See Table 3-2 |
| Q _{liquid_skin} | Quantity of liquid adhesive component or product remaining on skin (mg/cm ² -incident) | 0.7 (low end) 2.1 (high end) | CEB, 2000 |

| Variable | Variable Description | Default Value | Data Source |
|---|---|-------------------------|----------------|
| $Q_{\text{liquid_skin}} \times \text{AREA}_{\text{surface}}$ (for solids) | Quantity of dermal exposure to solids | 3,100 mg/incident | CEB, 2000 |
| $\text{RATE}_{\text{breathing}}$ | Typical worker breathing rate (m ³ /hr) | 1.25 | CEB, 1991 |
| $\text{RHO}_{\text{adhes}}$ | Density of the adhesive product (kg/L) | 1 | EPA assumption |
| $\text{RHO}_{\text{component}}$ | Density of the adhesive component (kg/L) | 1 | EPA assumption |
| $V_{\text{cont_fill}}$ | Volume of adhesive product per filled container (L/container) | 208 (55-gallon drum) | EPA assumption |
| $V_{\text{cont_empty}}$ | Volume of adhesive component per container (L/container) | 208 (55-gallon drum) | EPA assumption |

**APPENDIX B:
BACKGROUND INFORMATION AND EQUATIONS/DEFAULTS FOR THE
STANDARD EPA ENVIRONMENTAL RELEASE AND WORKER EXPOSURE
MODELS**

B.1. INTRODUCTION

This appendix provides background information and a discussion of the equations, variables, and default assumptions for each of the standard release and exposure models used by EPA in estimating environmental releases and worker exposures. The models described in this appendix are organized into the following five sections:

- Section B.2: Chemical Vapor Releases & Associated Inhalation Exposures;
- Section B.3: Container Residue Release Models (non-air);
- Section B.4: Process Equipment Residue Release Models (non-air);
- Section B.5: Dust Emissions from Transferring Solids Model;
- Section B.6: Chemical Particle Inhalation Exposure Models; and
- Section B.7: Dermal Exposure Models.

Please refer to the guidance provided in the ESD for estimating environmental releases and worker exposures using these standard models, as it may suggest the use of certain overriding default assumptions to be used in place of those described for each model within this appendix.

This appendix includes a list of the key reference documents that provide the background and rationale for each of the models discussed. These references may be viewed in their entirety through the ChemSTEER Help System. To download and install the latest version of the ChemSTEER software and Help System, please visit the following EPA web site:

<http://www.epa.gov/opptintr/exposure/docs/chemsteer.htm>

B.2. CHEMICAL VAPOR RELEASES & ASSOCIATED INHALATION EXPOSURES

This section discusses the models used by EPA to estimate chemical vapor generation rates and the resulting volatile releases to air and worker inhalation exposures to that chemical vapor. The volatile air release models (discussed in B.2.1) calculate both a vapor generation rate ($Q_{\text{vapor_generation}}$; g/sec) and the resulting daily release rate of the chemical vapors to air. The *EPA/OPPT Mass Balance Inhalation Model* (discussed in Section B.2.2) uses the value of $Q_{\text{vapor_generation}}$, calculated by the appropriate release model, to estimate the resulting inhalation exposure to that released vapor.

B.2.1 Vapor Generation Rate and Volatile Air Release Models

The following models utilize a series of equations and default values to calculate a chemical vapor generation rate ($Q_{\text{vapor_generation}}$; g/sec) and the resulting daily volatile air release rate ($E_{\text{local_air}}$; kg/site-day):

- *EPA/OPPT Penetration Model* – evaporative releases from an exposed liquid surface located indoors;
- *EPA/OPPT Mass Transfer Coefficient Model* – evaporative releases from an exposed liquid surface located outdoors; and
- *EPA/OAQPS AP-42 Loading Model* – releases of volatile chemical contained in air that is displaced from a container being filled.

Each of these models is described in greater detail in the following sections:

B.2.1.1 EPA/OPPT Penetration Model

Model Description and Rationale:

The *EPA/OPPT Penetration Model* estimates releases to air from evaporation of a chemical from an open, exposed liquid surface. This model is appropriate for determining volatile releases from activities that are performed *indoors*¹ or when air velocities are expected to be *less than or equal to 100 feet per minute*.

A draft paper (Arnold and Engel, 1999) evaluating the relative performance of this model and the *Mass Transfer Coefficient Model* against experimentally measured evaporation rates described laminar airflow conditions existing up to 100 feet per minute. The paper compared the *Penetration Model* to experimental evaporation rate data measured under laminar (less than 100 feet per minute) and turbulent (above 100 feet per minute) airflow conditions. While the *Penetration Model* did not provide accurate estimates of evaporation rates under turbulent air flow conditions (relative to the *Mass Transfer Coefficient Model*), the results modeled under laminar flow conditions were found to more closely approximate the experimental data (usually within 20 percent). It is assumed that the conditions of an indoor work area most closely approximate laminar airflow conditions.

The model was originally developed using Fick's second law of diffusion. Model results were tested against experimental results of a study on evaporation rates for 15 compounds studied at different air velocities and temperatures in a test chamber. The experimental data confirmed the utility and accuracy of the model equation. Sample activities in which the *Penetration Model* may be used to estimate volatile releases to air are sampling liquids and cleaning liquid residuals from smaller transport containers (e.g., drums, bottles, pails).

¹Similar air releases from surfaces located at *outdoor* locations (air speeds > 100 ft/min) are calculated using the *Mass Transfer Coefficient Model* (see the description provided in this section of Appendix B).

Model Equations:

The model first calculates the average vapor generation rate of the chemical from the exposed liquid surface using the following equation:

[B-1]

$$Q_{\text{vapor_generation}} = \frac{(8.24 \times 10^{-8}) \times MW_{\text{chem}}^{0.835} \times F_{\text{correction_factor}} \times VP_{\text{chem}} \times \left(\frac{1}{29} + \frac{1}{MW_{\text{chem}}} \right)^{0.25} \times RATE_{\text{air_speed}}^{0.5} \times AREA_{\text{opening}}}{TEMP_{\text{ambient}}^{0.05} \times D_{\text{opening}}^{0.5} \times P_{\text{ambient}}^{0.5}}$$

Where:

| | | |
|---------------------------------|---|--|
| $Q_{\text{vapor_generation}}$ | = | Average vapor generation rate (g of chemical/sec) |
| MW_{chem} | = | Molecular weight of the chemical of interest (g/mol) |
| $F_{\text{correction_factor}}$ | = | Vapor pressure correction factor (EPA default = 1) ¹ |
| VP_{chem} | = | Vapor pressure of the chemical of interest (torr) |
| $RATE_{\text{air_speed}}$ | = | Air speed (EPA default = 100 feet/min; value must be \leq 100 feet/min for this model) |
| $AREA_{\text{opening}}$ | = | Surface area of the static pool or opening (cm^2 ; $B \times D_{\text{opening}}^2 / 4$) |
| $TEMP_{\text{ambient}}$ | = | Ambient temperature (EPA default = 298 K) |
| D_{opening} | = | Diameter of the static pool or opening (cm; See Table B-1 for appropriate EPA default values) |
| P_{ambient} | = | Ambient pressure (EPA default = 1 atm) |

Note: The factor 8.24×10^{-8} in Equation B-1 accounts for various unit conversions. See Arnold and Engel, 1999, for the derivation of this constant.

Using the vapor generation rate ($Q_{\text{vapor_generation}}$) calculated in Equation B-1, the model then estimates the daily release to air for the activity using the following equation:

$$E_{\text{local_air}} = Q_{\text{vapor_generation}} \times TIME_{\text{activity_hours}} \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}} \quad [\text{B-2}]$$

Where:

| | | |
|---------------------------------|---|---|
| $E_{\text{local_air}}$ | = | Daily release of the chemical vapor to air from the activity (kg/site-day) |
| $Q_{\text{vapor_generation}}$ | = | Average vapor generation rate (g of chemical/sec; see Equation B-1) |
| $TIME_{\text{activity_hours}}$ | = | Operating hours for the release activity per day (hours/site-day; See Table B-1 for appropriate EPA default values) |

¹The default vapor pressure correction factor, $F_{\text{correction_factor}}$, assumes that the chemical-containing material in the evaporating pool exhibits the vapor pressure of the chemical of interest, as a worst case (i.e., effective VP of the evaporating material = $F_{\text{correction_factor}} \times VP_{\text{chem}}$). Alternatively, Raoult's Law may be assumed (i.e., effective VP = mole fraction of the chemical in the material $\times VP_{\text{chem}}$), thus the $F_{\text{correction_factor}}$ may be set equivalent to the chemical's mole fraction in the material, if known. Note: in the absence of more detailed data, the chemical's weight fraction within the material formulation may be used to approximate its mole fraction.

References:

- Arnold, F.C. and Engel, A.J. Pre-publication draft article entitled, *Evaporation of Pure Liquids from Open Surfaces*. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. October 1999.
- U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1 (Equation 4-24 and Appendix K). U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

B.2.1.2 EPA/OPPT Mass Transfer Coefficient Model*Model Description and Rationale:*

The *EPA/OPPT Mass Transfer Model* estimates releases to air from the evaporation of a chemical from an open, exposed liquid surface. This model is appropriate for determining this type of volatile release from activities that are performed *outdoors*¹ or when air velocities are expected to be *greater than 100 feet per minute*. A draft paper (Arnold and Engel, 1999) evaluating the relative performance of this and the *Penetration Model* against experimentally measured evaporation rates, described laminar airflow conditions existing up to 100 feet per minute. It is assumed that the conditions of an indoor process area most closely approximate laminar air flow conditions, while outdoor conditions approximate turbulent airflow conditions above 100 feet per minute.

As discussed in the draft paper, the model is predicated on the solution of the classical mass transfer coefficient model with the gas-phase mass transfer coefficient estimated by the correlation of Mackay and Matsugu. Results were tested against experimental results on 19 compounds generated by four different experimenters over a wide range of experimental conditions. While the *Mass Transfer Coefficient Model* matched the data well (usually within 20 percent), it was found that the *Penetration Model* (see description in previous section) outperformed the *Mass Transfer Coefficient Model* under laminar flow (i.e., “indoor”) conditions. Therefore, the *Penetration Model* is used as a default for estimating indoor evaporation rates, while the *Mass Transfer Coefficient Model* is used for outdoor rates. Sample activities in which the *Mass Transfer Coefficient Model* may be used to estimate volatile releases to air are cleaning liquid residuals from process equipment and bulk transport containers (e.g., tank trucks, rail cars).

¹Similar air releases from surfaces located at *indoor* locations (air speeds ≤ 100 ft/min) are calculated using the *Penetration Model* (see the description provided in this section of Appendix B).

Model Equations:

The model first calculates the average vapor generation rate of the chemical from the shallow pool using the following equation:

[B-3]

$$Q_{\text{vapor_generation}} = \frac{(1.93 \times 10^{-7}) \times MW_{\text{chem}}^{0.78} \times F_{\text{correction_factor}} \times VP_{\text{chem}} \times \left(\frac{1}{29} + \frac{1}{MW_{\text{chem}}} \right)^{0.33} \times RATE_{\text{air_speed}}^{0.78} \times AREA_{\text{opening}}}{TEMP_{\text{ambient}}^{0.4} \times D_{\text{opening}}^{0.11} \times (TEMP_{\text{ambient}}^{0.5} - 5.87)^{\frac{2}{3}}}$$

Where:

| | | |
|---------------------------------|---|---|
| $Q_{\text{vapor_generation}}$ | = | Average vapor generation rate (g of chemical of interest/sec) |
| MW_{chem} | = | Molecular weight of the chemical of interest (g/mol) |
| $F_{\text{correction_factor}}$ | = | Vapor pressure correction factor (EPA default = 1) ¹ |
| VP_{chem} | = | Vapor pressure of the chemical of interest (torr) |
| $RATE_{\text{air_speed}}$ | = | Air speed (EPA default = 440 feet/min; value must be > 100 feet/min for this model) |
| $AREA_{\text{opening}}$ | = | Surface area of the static pool or opening (cm ² ; $B \times D_{\text{opening}}^2 / 4$) |
| $TEMP_{\text{ambient}}$ | = | Ambient temperature (EPA default = 298 K) |
| D_{opening} | = | Diameter of the static pool or opening (cm; See Table B-1 for appropriate EPA default values) |

Note: The factor 1.93×10^{-7} in Equation B-3 accounts for various unit conversions. See Arnold and Engel, 1999, for the derivation of this constant.

Using the vapor generation rate ($Q_{\text{vapor_generation}}$) calculated in Equation B-3, the model then estimates the daily release to air for the activity using the following equation:

$$E_{\text{local_air}} = Q_{\text{vapor_generation}} \times TIME_{\text{activity_hours}} \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}} \quad [\text{B-4}]$$

Where:

| | | |
|---------------------------------|---|---|
| $E_{\text{local_air}}$ | = | Daily release of the chemical vapor to air from the activity (kg/site-day) |
| $Q_{\text{vapor_generation}}$ | = | Average vapor generation rate (g of chemical/sec; see Equation B-3) |
| $TIME_{\text{activity_hours}}$ | = | Operating hours for the release activity per day (hours/site-day; See Table B-1 for appropriate EPA default values) |

¹The default vapor pressure correction factor, $F_{\text{correction_factor}}$, assumes that the chemical-containing material in the evaporating pool exhibits the vapor pressure of the chemical of interest, as a worst case (i.e., effective VP of the evaporating material = $F_{\text{correction_factor}} \times VP_{\text{chem}}$). Alternatively, Raoult's Law may be assumed (i.e., effective VP = mole fraction of the chemical in the material $\times VP_{\text{chem}}$), thus the $F_{\text{correction_factor}}$ may be set equivalent to the chemical's mole fraction in the material, if known. Note: in the absence of more detailed data, the chemical's weight fraction within the material formulation may be used to approximate its mole fraction.

References:

- Arnold, F.C. and Engel, A.J. Pre-publication draft article entitled, *Evaporation of Pure Liquids from Open Surfaces*. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. October 1999.
- U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

B.2.1.3 EPA/OAQPS AP-42 Loading Model*Model Description and Rationale:*

The EPA's Office of Air Quality Planning and Standards (OAQPS) *AP-42 Loading Model* estimates releases to air from the displacement of air containing chemical vapor as a container/vessel is filled with a liquid. This model assumes that the rate of evaporation is negligible compared to the vapor loss from the displacement.

This model is used as the default for estimating volatile air releases during both loading activities and unloading activities. This model is used for unloading activities because it is assumed while one vessel is being unloaded another is assumed to be loaded. The *EPA/OAQPS AP-42 Loading Model* is used because it provides a more conservative estimate than either the *EPA/OPPT Penetration Model* or the *Mass Transfer Coefficient Model* for unloading activities.

Model Equations:

The model first calculates the average vapor generation rate of the chemical from the displacement during loading/filling operation using the following equation:

[B-5]

$$Q_{\text{vapor_generation}} = \frac{F_{\text{saturation_factor}} \times MW_{\text{chem}} \times \left(V_{\text{cont_empty}} \times \frac{3785.4 \text{ cm}^3}{\text{gal}} \right) \times \left(\frac{\text{RATE}_{\text{fill}}}{3600 \text{ sec/hour}} \right) \times F_{\text{correction_factor}} \times \left(\frac{VP_{\text{chem}}}{760 \text{ torr/atm}} \right)}{R \times \text{TEMP}_{\text{ambient}}}$$

Where:

| | | |
|---------------------------------|---|---|
| $Q_{\text{vapor_generation}}$ | = | Average vapor generation rate (g of chemical/sec) |
| $F_{\text{saturation_factor}}$ | = | Saturation factor (See Table B-1 for appropriate EPA default values) |
| MW_{chem} | = | Molecular weight of the chemical of interest (g/mol) |
| $V_{\text{cont_empty}}$ | = | Volume of the container (gallons; see Table B-1 for appropriate EPA default values) |
| $\text{RATE}_{\text{fill}}$ | = | Fill rate (containers/hour; see Table B-1 for appropriate EPA default values) |

| | | |
|---------------------------------|---|--|
| $F_{\text{correction_factor}}$ | = | Vapor pressure correction factor (EPA default =1) ¹ |
| VP_{chem} | = | Vapor pressure of the chemical of interest (torr) |
| R | = | Universal Gas Constant (82.05 atm-cm ³ /mol-K) |
| $TEMP_{\text{ambient}}$ | = | Ambient temperature (EPA default = 298 K) |

Using the vapor generation rate ($Q_{\text{vapor_generation}}$) calculated in Equation B-5, the model then estimates the daily release to air for the activity using the following equation:

$$E_{\text{local_air}} = Q_{\text{vapor_generation}} \times \text{TIME}_{\text{activity_hours}} \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}} \quad [\text{B-6}]$$

Where:

| | | |
|--|---|---|
| $E_{\text{local_air}}$ | = | Daily release of the chemical vapor to air from the activity (kg/site-day) |
| $Q_{\text{vapor_generation}}$ | = | Average vapor generation rate (g of chemical/sec; see Equation B-5) |
| $\text{TIME}_{\text{activity_hours}}$ | = | Operating hours for the release activity per day (hours/site-day; see Table B-1 for appropriate EPA default values) |

Reference:

U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1 (Equation 4-21). U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

¹The default vapor pressure correction factor, $F_{\text{correction_factor}}$, assumes that the chemical-containing material in the evaporating pool exhibits the vapor pressure of the chemical of interest, as a worst case (i.e., effective VP of the evaporating material = $F_{\text{correction_factor}} \times VP_{\text{chem}}$). Alternatively, Raoult's Law may be assumed (i.e., effective VP = mole fraction of the chemical in the material $\times VP_{\text{chem}}$), thus the $F_{\text{correction_factor}}$ may be set equivalent to the chemical's mole fraction in the material, if known. Note: in the absence of more detailed data, the chemical's weight fraction within the material formulation may be used to approximate its mole fraction.

Table B-1. Standard EPA Default Values Used in Vapor Generation Rate/Volatile Air Release Models

| Activity Type (Location) | $V_{\text{cont empty}}$ (gallons) | D_{opening} (cm) | $\text{RATE}_{\text{fill}}$ (containers/hour) | $F_{\text{saturation factor}}$ | $\text{TIME}_{\text{activity hours}}$ (hours/site-day) |
|--|---------------------------------------|------------------------------|--|--------------------------------|---|
| Container-Related Activities (e.g., filling, unloading, cleaning, open surface/evaporative losses): | | | | | |
| Bottles (Indoors) | 1 (Range: <5) | 5.08 (<5,000 gals) | 60 | Typical: 0.5 Worst Case: 1 | Number of containers handled per site-day_ $\text{RATE}_{\text{fill}}$ |
| Small Containers (Indoors) | 5 (Range: 5 to <20) | | 20 | | |
| Drums (Indoors) | 55 (Range: 20 to <100) | | | | |
| Totes (Indoors) | 550 (Range: 100 to <1,000) | | | | |
| Tank Trucks (Outdoors) | 5,000 (Range: 1,000 to <10,000) | 7.6 (≥5,000 gals) | 2 | 1 | |
| Rail Car (Outdoors) | 20,000 (Range: 10,000 and up) | | 1 | | |
| Equipment Cleaning Activities: | | | | | |
| Multiple Vessels (Outdoors) | Not applicable | 92 | Not applicable | 1 | 4 |
| Single, Large Vessel (Outdoors) | | | | | 1 |
| Single, Small Vessel (Outdoors) | | | | | 0.5 |
| Sampling Activities: | | | | | |

| Activity Type (Location) | V _{cont empty} (gallons) | D _{opening} (cm) | RATE _{fill} (containers/hour) | F _{saturation factor} | TIME _{activity hours} (hours/site-day) |
|-------------------------------|---|--|---|--------------------------------|---|
| Sampling Liquids (Indoors) | Not applicable | Typical: 2.5 ^a Worst Case: 10 | Not applicable | 1 | 1 |
| Other Activities: | | | | | |
| Continuous Operation | If other scenario-specific activities are identified that use one of the vapor generation rate/air release models described in this section, the ESD will describe the model and provide appropriate default values for the model parameters. | | | 1 | 24 |
| Batch Operation | | | | | Lesser of: (Hours/batch × Batches/site-day) or 24 |

a - The "typical" diameter default value of 2.5 cm was adopted as a policy decision in 2002, which supersedes the previous default value of 7 cm shown in the 1991 U.S. EPA reference document.

B.2.2 Chemical Vapor Inhalation Model

The following sections describe the EPA standard model for estimating worker inhalation exposures to a chemical vapor, utilizing a vapor generation rate ($Q_{\text{vapor_generation}}$).

B.2.2.1 EPA/OPPT Mass Balance Model

Model Description and Rationale:

The *EPA/OPPT Mass Balance Model* estimates a worker inhalation exposure to an estimated concentration of chemical vapors within the worker's breathing zone. The model estimates the amount of chemical inhaled by a worker during an activity in which the chemical has volatilized and the airborne concentration of the chemical vapor is estimated as a function of the source vapor generation rate ($Q_{\text{vapor_generation}}$). This generation rate may be calculated using an appropriate standard EPA vapor generation model (see Equation B-1, Equation B-3, or Equation B-5) or may be an otherwise known value.

The *EPA/OPPT Mass Balance Model* also utilizes the volumetric ventilation rate within a given space and includes simplifying assumptions of steady state (i.e., a constant vapor generation rate and a constant ventilation rate) and an assumed mixing factor for non-ideal mixing of air. The default ventilation rates and mixing factors provide a typical and worst case estimate for each exposure. The airborne concentration of the chemical cannot exceed the level of saturation for the chemical.

An evaluation of the model was performed against collected monitoring data for various activities (see the 1996 AIHA article). This evaluation confirmed that the Mass Balance Model is able to conservatively predict worker inhalation exposures within one order of magnitude of actual monitoring data and is an appropriate model for screening-level estimates.

Model Equations:

The model first calculates the volumetric concentration of the chemical vapor in air using the following equation:

$$C_{\text{chem_volumetric}} = \frac{(1.7 \times 10^5) \times \text{TEMP}_{\text{ambient}} \times Q_{\text{vapor_generation}}}{\text{MW}_{\text{chem}} \times \text{RATE}_{\text{ventilation}} \times F_{\text{mixing_factor}}} \quad [\text{B-7}]$$

Where:

| | | |
|------------------------------------|---|--|
| $C_{\text{chem_volumetric}}$ | = | Volumetric concentration of the chemical vapor in air (ppm) |
| $Q_{\text{vapor_generation}}$ | = | Average vapor generation rate (g of chemical/sec; see Equation B-1, Equation B-3, or Equation B-5, as appropriate) |
| $\text{TEMP}_{\text{ambient}}$ | = | Ambient temperature (EPA default = 298 K) |
| MW_{chem} | = | Molecular weight of the chemical of interest (g/mol) |
| $\text{RATE}_{\text{ventilation}}$ | = | Ventilation rate (ft ³ /min; see Table B-2 for appropriate EPA default values) |

$F_{\text{mixing_factor}}$ = Mixing factor (dimensionless; see Table B-2 for appropriate EPA default values)

Note: The factor 1.7×10^5 in Equation B-7 accounts for various unit conversions. See Fehrenbacher and Hummel, 1996, for the derivation of this constant.

Note that the airborne concentration of the chemical vapor cannot exceed the saturation level of the chemical in air. Equation B-8 calculates the volumetric concentration at the saturation level based on Raoult's Law. Use the lesser value for the volumetric concentration of the chemical vapor ($C_{\text{chem_volumetric}}$) calculated in either Equation B-7 or Equation B-8 in calculating the mass concentration of the chemical of interest in the air (see Equation B-9).

$$C_{\text{chem_volumetric}} = F_{\text{correction_factor}} \times VP_{\text{chem}} \times \frac{10^6 \text{ ppm}}{P_{\text{ambient}}} \quad [\text{B-8}]$$

Where:

$C_{\text{chem_volumetric}}$ = Volumetric concentration of the chemical of interest in air (ppm)

$F_{\text{correction_factor}}$ = Vapor pressure correction factor (EPA default = 1)¹

VP_{chem} = Vapor pressure of the chemical of interest (torr)

P_{ambient} = Ambient pressure (Default = 760 torr)

Note: Raoult's law calculates the airborne concentration as a mole fraction. The factor 10^6 in Equation B-8 accounts for the unit conversion from mole fraction to ppm.

The volumetric concentration of the chemical of interest in air (calculated in either Equation B-7 or Equation B-8) is converted to a mass concentration by the following equation:

$$C_{\text{chem_mass}} = \frac{C_{\text{chem_volumetric}} \times MW_{\text{chem}}}{V_{\text{molar}}} \quad [\text{B-9}]$$

Where:

$C_{\text{chem_mass}}$ = Mass concentration of the chemical vapor in air (mg/m^3)

$C_{\text{chem_volumetric}}$ = Volumetric concentration of the chemical vapor in air (ppm, see Equation B-7 or B-8, as appropriate)

MW_{chem} = Molecular weight of the chemical of interest (g/mol)

V_{molar} = Molar volume (Default = 24.45 L/mol at 25°C and 1 atm)

Assuming a constant breathing rate for each worker and an exposure duration for the activity, the inhalation exposure to the chemical vapor during that activity can be estimated using the following equation:

¹The default vapor pressure correction factor, $F_{\text{correction_factor}}$, assumes that the chemical-containing material in the evaporating pool exhibits the vapor pressure of the chemical of interest, as a worst case (i.e., effective VP of the evaporating material = $F_{\text{correction_factor}} \times VP_{\text{chem}}$). Alternatively, Raoult's Law may be assumed (i.e., effective VP = mole fraction of the chemical in the material $\times VP_{\text{chem}}$), thus the $F_{\text{correction_factor}}$ may be set equivalent to the chemical's mole fraction in the material, if known. Note: in the absence of more detailed data, the chemical's weight fraction within the material formulation may be used to approximate its mole fraction.

$$EXP_{\text{inhalation}} = C_{\text{chem_mass}} \times RATE_{\text{breathing}} \times TIME_{\text{exposure}} \quad [\text{B-10}]$$

Where:

| | | |
|---------------------------|---|---|
| $EXP_{\text{inhalation}}$ | = | Inhalation exposure to the chemical vapor per day (mg chemical/worker-day) |
| $C_{\text{chem_mass}}$ | = | Mass concentration of the chemical vapor in air (mg/m^3 ; see Equation B-9] |
| $RATE_{\text{breathing}}$ | = | Typical worker breathing rate (EPA default = $1.25 \text{ m}^3/\text{hr}$) |
| $TIME_{\text{exposure}}$ | = | Duration of exposure for the activity (hours/worker-day; see Table B-2 for appropriate EPA default values (≤ 8 hours/worker-day)) |

References:

- Fehrenbacher, M.C. and Hummel, A.A.¹. "Evaluation of the Mass Balance Model Used by the EPA for Estimating Inhalation Exposure to New Chemical Substances". *American Industrial Hygiene Association Journal*. June 1996. 57: 526-536.
- U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1 (Equation 4-21). U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

¹Note: This reference is currently not available for viewing in the ChemSTEER Help System.

Table B-2. Standard EPA Default Values Used in the *EPA/OPPT Mass Balance Inhalation Model*

| Activity Type (Location) | V _{cont empty} (gallons) | RATE _{fill} (containers/hour) | RATE _{air speed} (feet/min) | RATE _{ventilation} ^a | F _{mixing factor} | TIME _{exposure} (hours/day) |
|--|--------------------------------------|---|---|---|---------------------------------|--|
| Container-Related Activities (e.g., filling, unloading, cleaning, open surface/evaporative losses): | | | | | | |
| Bottles (Indoors) | 1 Range: <5 | 60 | 100 (Indoors) | Typical: 3,000 Worst Case: 500 (Indoors) | Typical: 0.5 Worst Case: 0.1 | Lesser of: (Number of containers handled per site-day)) RATE _{fill} or 8 |
| Small Containers (Indoors) | 5 Range: 5 to <20 | | | | | |
| Drums (Indoors) | 55 Range: 20 to <100 | 20 | 440 (Outdoors) | Average: 237,600 Worst Case: 26,400 × (60 × RATE _{air_speed}) 5,280 ³ (Outdoors) | | |
| Totes (Indoors) | 550 Range: 100 to <1,000 | | | | | |
| Tank Trucks (Outdoors) | 5,000 Range: 1,000 to <10,000 | 2 | | | | |
| Rail Car (Outdoors) | 20,000 Range: 10,000 and up | 1 | | | | |
| Equipment Cleaning Activities: | | | | | | |
| Multiple Vessels (Outdoors) | Not applicable | | 440 (Outdoors) | Average: 237,600 Worst Case: 26,400 × (60 × RATE _{air_speed}) 5,280 ³ (Outdoors) | Typical: 0.5 Worst Case: 0.1 | 4 |
| Single, Large Vessel (Outdoors) | | | | | | 1 |
| Single, Small Vessel (Outdoors) | | | | | | 0.5 |

| Activity Type (Location) | V _{cont empty} (gallons) | RATE _{fill} (containers/hour) | RATE _{air speed} (feet/min) | RATE _{ventilation} ^a | F _{mixing factor} | TIME _{exposure} (hours/day) |
|-------------------------------|--|---|---|--|---------------------------------|---|
| Sampling Activities: | | | | | | |
| Sampling Liquids (Indoors) | Not applicable | | 100 (Indoors) | Typical: 3,000 Worst Case: 500 (Indoors) | Typical: 0.5 Worst Case: 0.1 | 1 |
| Other Activities: | | | | | | |
| Continuous Operation | If other scenario-specific activities are identified that use one of the vapor generation rate models with the <i>Mass Balance Inhalation Model</i> described in this section, the ESD will describe the models and provide appropriate default values for the model parameters. | | | | Typical: 0.5 Worst Case: 0.1 | ≤8 |
| Batch Operation | | | | | | |

a - If the appropriate vapor generation rate model is the *EPA/OAQPS AP-42 Loading Model* (see Equation B-5) for an outdoor activity, the RATE_{air_speed} should be set to 440 feet/min, as a default in determining the worst case RATE_{ventilation}.

B.3. CONTAINER RESIDUE RELEASE MODELS (NON-AIR)*Model Description and Rationale:*

EPA has developed a series of standard models for estimating the quantity of residual chemical remaining in emptied shipping containers that is released to non-air media (e.g., water, incineration, or landfill) when the container is either rinsed or disposed. All of the residue models assume a certain portion or fraction of the chemical remains in the emptied container to be later rinsed or discarded with the empty container.

The default parameters of model are defined based upon the particular size/type of container (e.g., small containers, drums, or large bulk), as well as the physical form of the chemical residue (e.g., liquid or solid). These defaults are based upon data collected during a 1988 EPA-sponsored study of residuals in containers from which materials have been poured or pumped.

Model Equation:

All of the models discussed in this section utilize the following common equation for calculating the amount of chemical residue:

$$E_{\text{local_container_residue_disp}} = F_{\text{container_residue}} \times Q_{\text{total_daily_container}} \quad [\text{B-11}]$$

Where:

| | | |
|--|---|---|
| $E_{\text{local_container_residue_disp}}$ | = | Daily release of the chemical residue to water, incineration, or landfill from the cleaning or disposal of empty shipping containers (kg/site-day) |
| $F_{\text{container_residue}}$ | = | Fraction of the amount of the total chemical in the shipping container remaining in the emptied container (dimensionless; see Table B-3 for appropriate EPA default values) |
| $Q_{\text{total_daily_container}}$ | = | Total (daily) quantity of the chemical contained in the shipping containers prior to emptying (kg of chemical/site-day; see Table B-4 for appropriate EPA default values) |

Each model, however, utilizes unique default values within that equation based upon the relative size of the container and the physical form of the chemical residue. These default values are summarized in Table B-3 and Table B-4. The following models are the standard EPA models for estimating container residues:

- *EPA/OPPT Small Container Residual Model;*
- *EPA/OPPT Drum Residual Model;*
- *EPA/OPPT Bulk Transport Residual Model;* and
- *EPA/OPPT Solid Residuals in Transport Containers Model.*

The default frequency with which the container residues are released ($\text{TIME}_{\text{days_container_residue}}$, days/site-year) must be appropriately “paired” with the total daily quantity

of chemical contained in the containers ($Q_{\text{total_daily_container}}$) used in calculating the daily release. Thus, Table B-4 also contains the appropriate EPA default values for $\text{TIME}_{\text{days_container_residue}}$.

References:

- U.S. EPA. Chemical Engineering Branch. Memorandum: *Standard Assumptions for PMN Assessments*. From the CEB Quality Panel to CEB Staff and Management. October 1992.
- U.S. EPA. Office of Pesticides and Toxic Substances. *Releases During Cleaning of Equipment*. July 1988.

Table B-3. Standard EPA Default Values for Use in the Container Residual Release Models

| Chemical Form | Container Type | V _{cont empty} (gallons) | Model Title | F _{container residue} ^a |
|---------------|-----------------|--------------------------------------|---|--|
| Liquid | Bottle | 1 Range: <5 | <i>EPA/OPPT Small Container Residual Model</i> | Central Tendency: 0.003 High End: 0.006 |
| | Small Container | 5 Range: 5 to <20 | | |
| | Drum | 55 Range: 20 to <100 | <i>EPA/OPPT Drum Residual Model</i> | Central Tendency: 0.025 High End ^b : 0.03 (for <u>pumping</u> liquid out of the drum) Alternative defaults: Central Tendency: 0.003 High End: 0.006 (for <u>pouring</u> liquid out of the drum) |
| | Tote | 550 Range: 100 to <1,000 | <i>EPA/OPPT Bulk Transport Residual Model</i> | Central Tendency: 0.0007 High End: 0.002 |
| | Tank Truck | 5,000 Range: 1,000 to <10,000 | | |
| | Rail Car | 20,000 Range: 10,000 and up | | |
| Solid | Any | Any | <i>EPA/OPPT Solid Residuals in Transport Containers Model</i> | 0.01 |

a - These defaults are based on the 1988 EPA study investigating container residue and summarized in the 1992 internal EPA memorandum (see *References* in this section for the citations of these sources).

b - The 1992 EPA memorandum reference document contains the previous default of 0.04 for the high-end loss fraction (F_{container residue}) for the *Drum Residual Model*; however, this value was superseded by an internal policy decision in 2002. Per 40 CFR 261.7(b)(1) of the Resource Conservation and Recovery Act (RCRA), “a container or an inner liner removed from a container that has held any hazardous wastes, except waste that is a compressed gas or that is identified as an acute hazardous waste...is empty if...(ii) no more than 2.5 centimeters (1 inch) remain on the bottom of the container or liner or (iii)(A) no more than 3 percent by weight of the total capacity of the

container remains in the container or inner liner if the container is equal to or less than 110 gallons in size...”. The 3 percent high-end default is consistent with the range of experimental results documented in the 1988 EPA study (see *References* in this section for a citation of this study).

Table B-4. Standard EPA Methodology for Calculating Default $Q_{\text{total_daily_container}}$ and $\text{TIME}_{\text{days_container_residue}}$ Values for Use in the Container Residual Models

| Number of Containers Emptied per Day | $Q_{\text{total daily container}}$ (kg/site-day) | $\text{TIME}_{\text{days container residue}}$ (days/year) |
|--------------------------------------|--|---|
| 1 or more | (Mass quantity of chemical in each container (kg/container)) × (Number of containers emptied per day) | Total number of operating days for the facility/operation |
| Less than 1 | Mass quantity of chemical in each container (kg/container) | Total number of containers emptied per site-year |

B.4. PROCESS EQUIPMENT RESIDUE RELEASE MODELS (NON-AIR)*Model Description and Rationale:*

EPA has developed two standard models for estimating the quantity of residual chemical remaining in emptied process equipment that is released to non-air media (e.g., water, incineration, or landfill) when the equipment is periodically cleaned and rinsed. The residue models assume a certain portion or fraction of the chemical remains in the emptied vessels, transfer lines, and/or other equipment and is later rinsed from the equipment during cleaning operations and discharged with the waste cleaning materials to an environmental medium.

The default parameters of the model are defined based upon whether the residues are being cleaned from a *single* vessel or from *multiple* pieces of equipment. These defaults are based upon data collected during an EPA-sponsored study of residuals in process equipment from which materials have pumped or gravity-drained.

Model Equation:

The models discussed in this section utilize the following common equation for calculating the amount of chemical residue:

$$E_{\text{local}_{\text{equip_cleaning}}} = F_{\text{equip_residue}} \times Q_{\text{total_chem_capacity}} \quad [\text{B-12}]$$

Where:

| | | |
|---|---|---|
| $E_{\text{local}_{\text{equip_cleaning}}}$ | = | Daily release of the chemical residue to water, incineration, or landfill from cleaning of empty process equipment (kg/site-day) |
| $F_{\text{equip_residue}}$ | = | Fraction of the amount of the total chemical in the process equipment remaining in the emptied vessels, transfer lines, and/or other pieces (dimensionless; see Table B-5 for appropriate EPA default values) |
| $Q_{\text{equip_chem_capacity}}$ | = | Total capacity of the process equipment to contain the chemical in question, prior to emptying (kg of chemical/site-day; see Table B-6 for appropriate EPA default values) |

Each model, however, utilizes unique default values within that equation based upon whether the residues are cleaned from a single vessel or from multiple equipment pieces. These default values are summarized in Table B-5 and Table B-6. The following models are the standard EPA models for estimating process equipment residues:

- *EPA/OPPT Single Process Vessel Residual Model; and*
- *EPA/OPPT Multiple Process Vessel Residual Model.*

The default frequency with which the equipment residues are released ($\text{TIME}_{\text{days_equip_residue}}$, days/site-year) must be appropriately “paired” with the total capacity of the equipment to contain the chemical of interest ($Q_{\text{equip_chem_capacity}}$) used in calculating the daily release. Thus, Table B-6 also contains the appropriate EPA default values for $\text{TIME}_{\text{days_equip_residue}}$.

References:

- U.S. EPA. Chemical Engineering Branch. Memorandum: *Standard Assumptions for PMN Assessments*. From the CEB Quality Panel to CEB Staff and Management. October 1992.
- U.S. EPA. Office of Pesticides and Toxic Substances. *Releases During Cleaning of Equipment*. July 1988.

Table B-5. Standard EPA Default Values for Use in the Process Equipment Residual Release Models

| Model Title | $F_{\text{equip residue}}^a$ |
|--|---|
| <i>EPA/OPPT Single Process Vessel Residual Model</i> | Conservative: 0.01 (for <u>pumping</u> process materials from the vessel) *Alternative defaults: Central Tendency: 0.0007 High End to Bounding: 0.002 (alternative defaults for <u>gravity-draining</u> materials from the vessel) |
| <i>EPA/OPPT Multiple Process Vessel Residual Model</i> | Conservative: 0.02 |

a - These defaults are based on the 1988 EPA study investigating container residue and summarized in the 1992 internal EPA memorandum (see *References* in this section for the citations of these sources).

Table B-6. Standard EPA Methodology for Calculating Default $Q_{\text{equip chem capacity}}$ and $\text{TIME}_{\text{days equip residue}}$ Values for Use in the Process Equipment Residual Models

| Process Type | Number of Batches per Day | $Q_{\text{equip chem capacity}}$ (kg/site-day) | $\text{TIME}_{\text{days equip residue}}$ (days/year) |
|--------------|---------------------------|--|---|
| Batch | 1 or more | (Mass quantity of chemical in each batch (kg/batch)) × (Number of batches run per day) | Total number of operating days for the facility/operation |
| | Less than 1 | Mass quantity of chemical in each batch (kg/batch) | Total number of batches run per site-year |
| Continuous | Not applicable | Daily quantity of the chemical processed in the equipment (kg/site-day) | Total number of operating days for the facility/operation |

Note: Please refer to the ESD for any overriding default assumptions to those summarized above. Equipment cleaning may be performed periodically throughout the year, as opposed to the default daily or batch-wise cleaning frequencies shown above. For example, facilities may run dedicated equipment for several weeks, months, etc within a single campaign before performing equipment-cleaning activities, such that residuals remaining in the emptied are released less frequently than the standard default $\text{TIME}_{\text{days equip residue}}$ summarized above in Table B-6. Care should be given in defining the appropriate $Q_{\text{total daily container}}$ and $\text{TIME}_{\text{days container residue}}$ to be used in either of the standard EPA process equipment residue models.

B.5. DUST EMISSIONS FROM TRANSFERRING SOLIDS MODEL

EPA has developed the *EPA/OPPT Dust Emissions from Transferring Solids Model* to estimate the releases from dust generation during the unloading/transferring of solid powders. While there are multiple potential industrial sources of dust (e.g., grinding, crushing), the scope of this model is limited to transferring/unloading of solids. Specifically, this can be defined as activities where packaging/transport materials are opened and contents are emptied either into a feed system and conveyed or directly added into a process tank (e.g., reactor, mixing tank).

Model Description and Rationale:

The EPA/OPPT Dust Emissions from Transferring Solids Model estimates that 0.5% of the solid powder transferred may be released from dust generation. This model is based on 13 sources, including site visit reports, Organisation for Economic Co-operation and Development (OECD) Emission Scenario Documents (ESD), EPA's AP-42 Emission Factors, and Premanufacture Notice submissions (EPA's new chemicals review program). Each source contained estimates of the quantity of solid powder that may be lost during transfers for a specific industry. The different sources contained dust loss data or loss fraction estimates from a variety of industries including paint and varnish formulation, plastic manufacturing, printing ink formulation, rubber manufacturing, and chemical manufacturing. These estimates ranged from negligible to 3% of the transferred volume. The mean of the upper bound from each data set was 0.5%.

Additionally, dust generation test data were reviewed. A study by Plinke, et al. investigated key parameters for developing a theoretical approach for estimating dust losses based on moisture content, particle size, drop height, and material flow (Plinke, 1995). Dust generation rates during unloading and transfers were measured for four materials. The highest measured dust generation rate was 0.5%. These data further justified the adoption of a 0.5% loss fraction as a conservative estimate.

For the media of release of the dust generated, most facilities utilize some type of control device(s) to collect fugitive emissions. Many facilities collect fugitive dust emissions from these operations in filters and dispose of the filters in landfills or by incineration. Wet scrubbers may also be utilized by industry. However, in some cases, uncontrolled/uncollected particulates may be small enough to travel several miles from the facility, resulting in environmental and human exposures to the chemical of interest beyond the boundaries of the site. Fugitive dust emissions may also settle to facility floors and are disposed of when floors are cleaned (water if the floors are rinsed or land or incineration if the floors are swept). Therefore, as a conservative assumption the model assumes an uncontrolled release to air, water, incineration, or landfill.

If facility-specific information states a control technology is employed, the release may be partitioned to the appropriate media. If the control technology efficiency information is not available, the *CEB Engineering Manual* may be utilized for control technology efficiencies. Table B-7 provides estimated efficiencies for common control technologies.

Table B-7. Default Control Technology Efficiencies

| Control Technology | Default Control Technology Capture Efficiency (%) | Notes/Source | Default Media of Release for Controlled Release |
|-------------------------------|--|--|--|
| None (default) | 0 | No control technology should be assumed as conservative. | N/A |
| Filter (such as a baghouse) | 99 | For particles > 1 μ m. CEB Engineering Manual. | Incineration or Land |
| Cyclone/Mechanical Collectors | 80 | For particles > 15 μ m CEB Engineering Manual. | Incineration or Land |
| Scrubber | Varies 95 may be assumed | Consult Table 7-1 of the CEB Engineering Manual. | Water |

Model Equation:

Based on these data, the model estimates the portion of the release that is not captured or the uncontrolled release using the following equation. As a default this material is assumed released to air, water, incineration, or land.

$$E_{\text{local}_{\text{dust_fugitive}}} = Q_{\text{transferred}} \times F_{\text{dust_generation}} \times (1 - F_{\text{dust_control}}) \quad [\text{B-13}]$$

Where:

| | | |
|--|---|--|
| $E_{\text{local}_{\text{dust_fugitive}}}$ | = | Daily amount not captured by control technology from transfers or unloading (kg/site-day) |
| $Q_{\text{transferred}}$ | = | Quantity of chemical transferred per day (kg chemical/site-day) |
| $F_{\text{dust_generation}}$ | = | Loss fraction of chemical during transfer/unloading of solid powders (Default: 0.005 kg released/kg handled) |
| $F_{\text{dust_control}}$ | = | Control technology capture efficiency (kg captured/kg processed) (Default: If the control technology is unknown, assume capture efficiency = 0 kg captured/kg processed, see Table B-7). |

The following equation estimates the portion of dust release captured by the control technology. The default media of release for this material should be selected based on the information presented in Table B-7.

$$E_{\text{local}_{\text{dust_captured}}} = Q_{\text{transferred}} \times F_{\text{dust_generation}} \times F_{\text{dust_control}} \quad [\text{B-14}]$$

Where:

| | | |
|--|---|---|
| $E_{\text{local}_{\text{dust_captured}}}$ | = | Daily amount captured by control technology from transfers or unloading (kg/site-day) |
| $Q_{\text{transferred}}$ | = | Quantity of chemical transferred per day (kg chemical/site-day) |

| | | |
|-------------------------------|---|--|
| $F_{\text{dust_generation}}$ | = | Loss fraction of chemical during transfer/unloading of solid powders (Default: 0.005 kg released/kg handled) |
| $F_{\text{dust_control}}$ | = | Control technology capture efficiency (kg captured/kg processed) (Default: If the control technology is unknown, assume capture efficiency = 0 kg captured/kg processed, see Table B-7). |

References:

- U.S. EPA. Chemical Engineering Branch. "Generic Model to Estimate Dust Releases from Transfer/Unloading Operations of Solid Powders". November 2006.
- U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1 (page 4-11). U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.
- Plinke, Marc A.E., et al. "Dust Generation from Handling Powders in Industry." *American Industrial Hygiene Association Journal*. Vol. 56: 251-257, March 1995.

B.6. CHEMICAL PARTICLE INHALATION EXPOSURE MODELS

The following EPA standard models may be used to estimate worker inhalation exposures to particles containing the chemical of interest:

- *EPA/OPPT Small Volume Solids Handling Inhalation Model*; and
- *OSHA Total Particulates Not Otherwise Regulated (PNOR) Permissible Exposure Limit (PEL)-Limiting Model*.

Each of these models is an alternative default for calculating worker inhalation exposures during the following particulate-handling activities, based upon the relative daily amount of particulate material being handled:

- Unloading and cleaning solid residuals from transport containers/vessels;
- Loading solids into transport containers/vessels; and
- Cleaning solid residuals from process equipment.

For amounts up to (and including) 54 kg/worker-shift, the *EPA/OPPT Small Volume Solids Handling Inhalation Model* is used, as it more accurately predicts worker exposures to particulates within this range than the *OSHA Total PNOR PEL-Limiting Model*. The *Small Volume Solids Handling Inhalation Model* is based on exposure monitoring data obtained for workers handling up to 54 kg of powdered material. Beyond this data-supported limit, EPA assumes that exposures within occupational work areas are maintained below the regulation-based exposure limit for "particulates, not otherwise regulated".

The *EPA/OPPT Small Volume Solids Handling Model* is also the exclusive model used for any solids sampling activity. Each of these models is described in detail in the following sections.

B.6.1 EPA/OPPT Small Volume Solids Handling Inhalation Model

Model Description and Rationale:

The *EPA/OPPT Small Volume Solids Handling Inhalation Model* utilizes worst case and typical exposure factors to estimate the amount of chemical inhaled by a worker during handling of *small volumes*¹ (i.e., ≤ 54 kg/worker-shift) of solid/powdered materials containing the chemical of interest. The handling of these small volumes is presumed to include scooping, weighing, and pouring of the solid materials.

The worst case and typical exposure factor data were derived from a study of dye weighing and adapted for use in situations where workers are presumed to handle small volumes of solids in a manner similar to the handling in the study. The maximum amount of dye handled in the study was 54 kg/worker-shift, so the *Small Volume Solids Handling Inhalation Model* is presumed to be valid for quantities up to and including this amount. In the absence of more specific exposure data for the particular activity, EPA uses these data to estimate inhalation exposures to solids transferred at a rate up to and including 54 kg/worker-shift. This model assumes that the exposure concentration is the same as the concentration of the chemical of interest in the airborne particulate mixture.

Note that the amount handled per worker per shift is typically unknown, because while the throughput may be known, the number of workers and the breakdown of their activities are typically unknown. For example, while two workers may together handle 100 kg of material/day, one worker may handle 90 kg of material/day and the other may only handle 10 kg of material/day. Therefore, as a conservative estimate EPA assumes that the total throughput ($Q_{\text{facility_day}}$; kg/site-day) is equal to the amount handled per worker ($Q_{\text{shift_handled}}$; kg/worker-shift), if site-specific information is not available.

Model Equation:

The model calculates the inhalation exposure to the airborne particulate chemical using the following equation:

$$\text{EXP}_{\text{inhalation}} = (Q_{\text{shift_handled}} \times N_{\text{shifts}}) \times F_{\text{chem}} \times F_{\text{exposure}} \quad [\text{B-15}]$$

Where:

| | | |
|----------------------------------|---|---|
| $\text{EXP}_{\text{inhalation}}$ | = | Inhalation exposure to the particulate chemical per day (mg chemical/worker-day) |
| $Q_{\text{shift_handled}}$ | = | Quantity of the solid/particulate material containing the chemical of interest that is handled by workers each shift (kg/worker-shift; see Table B-8 for appropriate EPA default) |

¹Worker inhalation exposures to particulates handled in amounts *greater than 54 kg/worker-shift* are calculated using the *OSHA Total PNOR PEL-Limiting Model* (see the description provided in this section of Appendix B).

| | | |
|-----------------------|---|--|
| | | values; must be ≤ 54 kg/worker-shift for this model to be valid) |
| N_{shifts}^1 | = | Number of shifts worked by each worker per day (EPA default = 1 shift/day) |
| F_{chem} | = | Weight fraction of the chemical of interest in the particulate material being handled in the activity (dimensionless; refer to the ESD discussion for guidance on appropriate default value) |
| F_{exposure} | = | Exposure factor; amount of total particulate handled that is expected to be inhaled (EPA defaults: 0.0477 mg/kg (typical) and 0.161 mg/kg (worst case)) |

Table B-8. Standard EPA Default Values for $Q_{\text{daily_handled}}$ in the EPA/OPPT Small Volume Solids Handling Inhalation Model

| Activity Type | Default $Q_{\text{shift_handled}}^2$ (kg/worker-day) |
|---|---|
| Loading and Unloading Containers | Quantity of material in each container (kg/container) × Number of containers/worker-shift |
| Container Cleaning | Quantity of residue in each container (kg/container) × Number of container/worker-shift |
| Process-Related Activity (equipment cleaning, sampling): | |
| Continuous process: | Daily throughput of material / Number of shifts per day |
| Batch process (<1 batch per day): | Quantity of material per batch |
| Batch process (>1 batch per day): | Quantity of material per batch × Number of batches per shift |

References:

U.S. EPA. Chemical Engineering Branch. Generic Scenario: *Textile Dyeing*. October 15, 1992.

U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1 (page 4-11). U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

U.S. EPA Economics, Exposure and Technology Division³. *Textile Dye Weighing Monitoring Study*. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington D.C., EPA 560/5-90-009. April 1990.

¹Note that this value is the number of shifts worked by *each worker* per day. This value would only be greater than one if a worker worked for over eight hours in a given day.

²The appropriate quantity of material handled by each worker on each day may vary from these standard CEB defaults, per the particular scenario. Be sure to consult the discussion presented in the ESD activity description in determining the most appropriate default value for $Q_{\text{daily_handled}}$.

³Note: This reference is currently available for viewing in the ChemSTEER Help System.

B.6.2 OSHA Total PNOR PEL-Limiting Model

Model Description and Rationale:

The *OSHA Total Particulates Not Otherwise Regulated (PNOR) Permissible Exposure Limit (PEL)-Limiting Model* estimates the amount of chemical inhaled by a worker during handling of solid/powdered materials containing the chemical of interest. The estimate assumes that the worker is exposed at a level no greater than the OSHA PEL for *Particulate, Not Otherwise Regulated*, total particulate. Operations are generally expected to comply with OSHA's federal regulation regarding total particulate exposures. This model assumes that the exposure concentration is the same as the concentration of the chemical of interest in the airborne particulate mixture.

The *OSHA Total PNOR PEL-Limiting Model* is used in cases where workers are handling quantities of solid/powdered materials *in excess of 54 kg/worker-shift*¹. As stated in Section B.6.1, the *Small Volume Solids Handling Model*, based on monitoring data, provides a more realistic estimate of worker inhalation exposures to smaller quantities particulate material. The data used by the *Small Volume Solids Handling Model* are supported up to and including 54 kg solid material handled per worker-shift. Beyond this amount, EPA assumes the occupational exposures are maintained below the regulatory exposure limit contained in the *OSHA Total PNOR PEL-Limiting Model*, although the exposures provided by this model are considered to be worst-case, upper-bounding estimates.

Refer to Table B-8 for the standard EPA assumptions used in determining the appropriate quantity of particulate material handled to determine the applicability of this model to a given activity.

NOTE: The OSHA Total PNOR PEL (used as the basis for the model calculations) is an 8-hour time-weighted average (TWA); therefore, *worker exposures must be assumed to occur over an 8-hour period* for the *OSHA Total PNOR PEL-Limiting Model* estimate to be valid basis for the calculated inhalation exposure estimate.

Model Equations:

The model first calculates the mass concentration of the airborne particulate chemical using the following equation:

$$C_{\text{chem_mass}} = C_{\text{total_mass}} \times F_{\text{chem}} \quad [\text{B-16}]$$

Where:

$$C_{\text{chem_mass}} = \text{Mass concentration of the chemical in air (mg/m}^3\text{)}$$

¹Worker inhalation exposures to particulates handled in amounts *up to and including 54 kg/worker-shift* are calculated using the *EPA/OPPT Small Volume Handling Inhalation Model* (see the description provided in this section of Appendix B).

| | | |
|--------------------------|---|--|
| $C_{\text{total_mass}}$ | = | Mass concentration of total particulate (containing the chemical) in air (EPA default = 15 mg/m ³ , based on the OSHA Total PNOR PEL, 8-hr TWA) |
| F_{chem} | = | Weight fraction of the chemical of interest in the particulate material being handled in the activity (dimensionless; refer to the ESD discussion for guidance on appropriate default value) |

Similar to Equation B-10 in the *EPA/OPPT Mass Balance Inhalation Model*, the *OSHA Total PNOR PEL-Limiting Model* then uses the mass airborne concentration of the chemical ($C_{\text{mass_chem}}$) in Equation B-16, to calculate the inhalation exposure to the particulate chemical using the following equation:

$$\text{EXP}_{\text{inhalation}} = C_{\text{chem_mass}} \times \text{RATE}_{\text{breathing}} \times \text{TIME}_{\text{exposure}} \quad [\text{B-17}]$$

Where:

| | | |
|----------------------------------|---|---|
| $\text{EXP}_{\text{inhalation}}$ | = | Inhalation exposure to the airborne particulate chemical per day (mg chemical/worker-day) |
| $C_{\text{chem_mass}}$ | = | Mass concentration of the particulate chemical in air (mg/m ³ ; see Equation B-17) |
| $\text{RATE}_{\text{breathing}}$ | = | Typical worker breathing rate (EPA default = 1.25 m ³ /hr) |
| $\text{TIME}_{\text{exposure}}$ | = | Duration of exposure for the activity (EPA default = 8 hours/worker-day ¹) |

References:

U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1 (Equations 4-1 and 4-11). U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

B.7. DERMAL EXPOSURE MODELS

Model Description and Rationale:

EPA has developed a series of standard models for estimating worker dermal exposures to liquid and solid chemicals during various types of activities. All of these dermal exposure models assume a specific surface area of the skin that is contacted by a material containing the chemical of interest, as well as a specific surface density of that material in estimating the dermal exposure. The models also assume *no use of controls or gloves* to reduce the exposure. These assumptions and default parameters are defined based on the nature of the exposure (e.g., one hand or two hand, immersion in material, contact with surfaces) and are documented in the references listed in this section.

¹Since the OSHA Total PNOR PEL is an 8-hr TWA, the exposure duration must be assumed as 8 hours/worker-day for the model defaults to apply.

In the absence of data, the EPA/OPPT standard models for estimating dermal exposures from industrial activities described in this section can be used. The models for exposures to liquid materials are based on experimental data with liquids of varying viscosity and the amount of exposure to hands was measured for various types of contact. Similar assessments were made based on experimental data from exposure to solids.

Model Equation:

All of the standard EPA models utilize the following common equation for calculating worker dermal exposures:

$$EXP_{\text{dermal}} = AREA_{\text{surface}} \times Q_{\text{remain_skin}} \times F_{\text{chem}} \times N_{\text{event}} \quad [\text{B-18}]$$

Where:

| | | |
|---------------------------|---|---|
| EXP_{dermal} | = | Dermal exposure to the liquid or solid chemical per day (mg chemical/worker-day) |
| $AREA_{\text{surface}}$ | = | Surface area of the skin that is in contact with liquid or solid material containing the chemical (cm ² ; see Table B-9 for appropriate EPA default values) |
| $Q_{\text{remain_skin}}$ | = | Quantity of the liquid or solid material containing the chemical that remains on the skin after contact (mg/cm ² -event; see Table B-9 for appropriate EPA default values) |
| F_{chem} | = | Weight fraction of the chemical of interest in the material being handled in the activity (dimensionless; refer to the ESD discussion for guidance on appropriate default value) |
| N_{event}^1 | = | Frequency of events for the activity (EPA default = 1 event/worker-day) |

Each model, however, utilizes unique default values within that equation based upon the nature of the contact and the physical form of the chemical material. These default values are summarized in Table B-9. The following models are the standard EPA models for estimating worker dermal exposures:

- *EPA/OPPT 1-Hand Dermal Contact with Liquid Model;*
- *EPA/OPPT 2-Hand Dermal Contact with Liquid Model;*
- *EPA/OPPT 2-Hand Dermal Immersion in Liquid Model;*
- *EPA/OPPT 2-Hand Dermal Contact with Container Surfaces Model; and*
- *EPA/OPPT 2-Hand Dermal Contact with Solids Model.*

¹Only one contact per day ($N_{\text{event}} = 1$ event/worker-day) is assumed because $Q_{\text{remain_skin}}$, with few exceptions, is not expected to be significantly affected either by wiping excess chemical material from skin or by repeated contacts with additional chemical material (i.e., wiping excess from the skin does not remove a significant fraction of the small layer of chemical material adhering to the skin and additional contacts with the chemical material do not add a significant fraction to the layer). Exceptions to this assumption may be considered for chemicals with high volatility and/or with very high rates of absorption into the skin.

For several categories of exposure, EPA uses qualitative assessments to estimate dermal exposure. Table B-10 summarizes these categories and the resulting qualitative dermal exposure assessments.

References:

U.S. EPA. Chemical Engineering Branch. *Options for Revising CEB's Method for Screening-Level Estimates of Dermal Exposure – Final Report*. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. June 2000.

U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

Table B-9. Standard EPA Default Values for Use in the Worker Dermal Exposure Models

| Default Model | Example Activities | AREA _{surface} ^a (cm ²) | Q _{remain skin} ^b (mg/cm ² - event) | Resulting Contact AREA _{surface} × Q _{remain skin} (mg/event) |
|---|---|--|--|---|
| Physical Form: Liquids | | | | |
| <i>EPA/OPPT 1-Hand Dermal Contact with Liquid Model</i> | <ul style="list-style-type: none"> Liquid sampling activities Ladling liquid/bench-scale liquid transfer | 420 (1 hand mean) | Low: 0.7 High: 2.1 | Low: 290 High: 880 |
| <i>EPA/OPPT 2-Hand Dermal Contact with Liquid Model</i> | <ul style="list-style-type: none"> Maintenance Manual cleaning of equipment and containers Filling drum with liquid Connecting transfer line | 840 (2 hand mean) | Low: 0.7 High: 2.1 | Low: 590 High: 1,800 |
| <i>EPA/OPPT 2-Hand Dermal Immersion in Liquid Model</i> | <ul style="list-style-type: none"> Handling wet surfaces Spray painting | 840 (2 hand mean) | Low: 1.3 High: 10.3 | Low: 1,100 High: 8,650 |
| Physical Form: Solids | | | | |
| <i>EPA/OPPT 2-Hand Dermal Contact with Container Surfaces Model</i> | <ul style="list-style-type: none"> Handling bags of solid materials (closed or empty) | No defaults | No defaults | < 1,100 ^c |
| <i>EPA/OPPT 2-Hand Dermal Contact with Solids Model</i> | <ul style="list-style-type: none"> Solid sampling activities Filling/dumping containers of powders, flakes, granules Weighing powder/scooping/mixing (i.e., dye weighing) Cleaning solid residues from process equipment Handling wet or dried material in a filtration and drying process | No defaults | No defaults | < 3,100 ²³ |

a - These default values were adopted in the 2000 EPA report on screening-level dermal exposure estimates (see *References* in this section for the citations of this sources) and are the mean values for men taken from the EPA Exposure Factors Handbook, 1997.

b - These default values were adopted in the 2000 EPA report on screening-level dermal exposure estimates (see *References* in this section for the citation of this source). The report derived the selected ranges of values for liquid handling activities from: U.S. EPA. A Laboratory Method to Determine the Retention of Liquids on the Surface of Hands. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Exposure Evaluation Division. EPA 747-R-92-003. September 1992.

c - These default values were adopted in the 2000 EPA report on screening-level dermal exposure estimates (see *References* in this section for the citation of this source). The report derived values for dermal contact for solids handling activities from: Lansink, C.J.M., M.S.C. Breelen, J. Marquart, and J.J. van Hemmen: Skin Exposure to Calcium Carbonate in the Paint Industry. Preliminary Modeling of Skin Exposure Levels to Powders Based on Field Data (TNO Report V 96.064). Rijswijk, The Netherlands: TNO Nutrition and Food Research Institute, 1996.

Table B-10. EPA Default Qualitative Assessments for Screening-Level Estimates of Dermal Exposure

| Category | Dermal Assessment |
|---|---|
| Corrosive substances (pH>12, pH<2) | Negligible |
| Materials at temperatures >140°F (60°C) | Negligible |
| Cast Solids (e.g., molded plastic parts, extruded pellets) | Non-Quantifiable (Some surface contact may occur if manually transferred) |
| “Dry” surface coatings (e.g., fiber spin finishes, dried paint) | Non-Quantifiable (If manual handling is necessary and there is an indication that the material may abrade from the surface, quantify contact with fingers/palms as appropriate) |
| Gases/Vapors | Non-Quantifiable (Some contact may occur in the absence of protective clothing) |

Source: U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

**APPENDIX C:
DATA RECEIVED FROM ENVIRONMENT CANADA**

On January 18, 2006, Environment Canada forwarded to EPA comments on an early version of the Adhesives Formulation ESD. Data that are relevant to this industry were also submitted for EPA's consideration. Where appropriate, references to the Canadian data are made in the main body of the ESD. These data, provided by the Existing Substances and New Substances Divisions of Environment Canada are presented below.

Canadian Adhesive Formulation Industry Wastewater Pollutants:

Pollutants that are discharged from this industry include ammonia, formaldehyde, phenolics, phosphorus, sulfate, BOD and COD. Additional information may be obtained from:

Canadian Water and Wastewater Association, *Directory of Sources of Contaminants Entering Municipal Sewer Systems*, 1st ed., March 2002.
\$15 CD-ROM available from: http://www.cwwa.ca/publicationorder_e.asp

Canadian Industry Census Data:

Canadian Census data from 1995-2004 were provided for EPA's consideration (please refer to Figure C-1). These data show that, although the total number of adhesive formulation sites and workers is less than those located in the United States, the number of employees per site is approximately equal to that of U.S. formulators.

In addition, Canadian industry summary data were also provided for adhesives formulators (please refer to Figure C-2). It is noted that six of the "major" adhesive formulation companies operating in Canada have their corporate offices in the United States (two of these were identified as among the seven dominant U.S. companies in Section 3.2).

U.S. Polyurethane Consumption Rate:

It was noted that in 2000, 242 million pounds of polyurethane adhesives were consumed (i.e., used) in the U.S., per a source entitled, *End Use Market Survey of the Polyurethanes Industry*, 2002.

NAICS 32552 - Adhesives and sealants

These statistics are for the Adhesives and sealants industry, based on the North American Industry Classification System (NAICS) code 32552.

| Principal statistics** | | | | | |
|-------------------------------|-----------------------|-----------------------|-------------------|---------------------|---------------------|
| | Establishments | Shipments, \$M | Employment | Imports, \$M | Exports, \$M |
| 1995 | 45 | 415 | 1 967 | 278 | 85 |
| 1996 | 48 | 494 | 2 286 | 295 | 111 |
| 1997 | 50 | 485 | 2 150 | 331 | 119 |
| 1998 | 50 | 460 | 2 296 | 418 | 136 |
| 1999 | 46 | 473 | 2 362 | 483 | 162 |
| 2000 | 71 | 616 | 2 078 | 485 | 167 |
| 2001 | 71 | 612 | 2 055 | 492 | 168 |
| 2002 | 70 | 627 | 2 129 | 520 | 185 |
| 2003 | 69 | 759 | 2 458 | 477 | 190 |
| 2004 | 70* | 813* | 2 460* | 485 | 216 |

Source: Statistics Canada

* Industry Canada estimates

** Beginning in 2000, data includes very small establishments. This accounts for the large jump in establishments, and for part of the increase in shipments and employment.

This industry comprises establishments primarily engaged in manufacturing glue, adhesives and related products.

Exclusion(s): Establishments primarily engaged in:

- manufacturing roofing cement (32412, Asphalt Paving, Roofing and Saturated Materials Manufacturing)
- manufacturing gypsum-based caulking compounds, joint compounds and patching plaster (32742, Gypsum Product Manufacturing)

Examples:

- Adhesives
- Caulking compounds (except gypsum-based)
- Epoxy adhesives
- Glue (except dental)
- Joint compounds (except gypsum-based)
- Mucilage adhesives
- Pastes
- Pipe sealing compounds
- Putty, plumbers'
- Rubber cement
- Sealants
- Sealing compounds for pipe threads and joints
- Starch glues

Source: Statistics Canada; <http://strategis.gc.ca/epic/internet/inchemicals-chimiques.nsf/en/bt01217e.html>.

Figure C-1. Canadian Census Data for the Adhesives and Sealants Industry

For further information, please contact:

John Margeson
 Industry Canada
 Manufacturing Industries Branch
 235 Queen Street
 Ottawa, Ontario K1A 0H5
 Tel.: (613) 954-3016
 Fax: (613) 952-8988
 E-mail: margeson.john@ic.gc.ca

Table 1. Major Firms

| Company | Head office location | Location of plants |
|--------------------------------|----------------------|--|
| Chembond | Canada | Brampton, Ontario Brantford, Ontario |
| Dural div. of Multibond | Canada | Dorval, Quebec Etobicoke, Ontario |
| Forbo Adhesives | USA | Pointe Claire, Québec |
| H.B. Fuller | USA | Boucherville, Québec |
| GE Silicones | USA | Pickering, Ontario |
| Halltech | Japan | West Hill, Ontario |
| Helmitin | Canada | Montréal, Québec Toronto, Ontario |
| Mapei | Italy | Laval, Québec Woodbridge, Ontario Delta, British Columbia |
| Mulco | Canada | Longueuil, Québec |
| Nacan Products | United Kingdom | Toronto, Ontario Boucherville, Québec Surrey, British Columbia |
| Roberts Company Canada | USA | Brampton, Ontario |
| Technical Adhesives | Canada | Mississauga, Ontario |
| 3M Canada | USA | London, Ontario |
| Tremco | USA | Toronto, Ontario Boucherville, Québec |

Industry Association

Adhesives and Sealants Manufacturers Association of Canada (ASMAC)
 P.O. Box 296, Station A
 Etobicoke, Ontario M9C 4V3
 Tel.: (416) 410-6116
 Fax: (416) 410-6116
 E-mail: asmac@sympatico.ca

Source: Excerpt from the Industry Profile for the Adhesives and Sealants Industry;
<http://strategis.gc.ca/epic/internet/inchemicals-chimiques.nsf/en/bt01251e.html>

Figure C-2. Canadian Adhesives and Sealants Industry Summary