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Emission Scenario Document (ESD) on the Use of Textile Dyes

Series No. 36

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EMISSION SCENARIO DOCUMENT (ESD) ON THE USE OF TEXTILE DYES



A cooperative agreement among FAO, ILO, UNDP, UNEP, UNIDO, UNITAR, WHO, World Bank 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 non-volatile chemicals used in textile dyes. The document focuses primarily on the application of dyes to fibers, yarns and fabrics by batch or continuous processes. The document presents standard approaches for estimating the environmental releases of and occupational exposures to non-volatile chemicals used in dye formulations.

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). The comments received will be forwarded to the OECD Task Force on Exposure Assessment (TFEA), 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 (http://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 non-volatile chemical components contained in dye formulations. 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

The U.S. Environmental Protection Agency (EPA) developed this ESD using relevant data¹ and information on the use of textile dyes in the textile industry, including process descriptions, operating information, types of dyes 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. Non-occupational exposures and environmental releases during consumer use are outside the scope of this document.

The primary sources of information cited in this ESD include information published by the U.S. Census Bureau's Economic Census and various EPA and other government sources (e.g. OECD and regional or state pollution prevention organizations). Additionally, industry experts such as Dr. Warren Jasper (North Carolina State University College of Textiles) and the Ecological and Toxicological

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 the ESD.

Association of Dyes and Organic Pigments (ETAD) provided input for this ESD. Additional information on the sources investigated and the references cited in this document are presented in Section 8.

The information in this document is based on U.S. data. Certain aspects of the application process of dye products 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 non-volatile chemical components used during the use of dye products in batch and continuous processes. The scope of the ESD will only cover the industrial end use of textile dyes. The manufacturing of the dyes, the formulation of dyestuffs, the use of the product manufactured with the dye (e.g. use of textiles, fabrics), and end of life considerations are outside the scope of the ESD. Note that for the purposes of the ESD, the use of dye in the textiles dyeing process is considered to be the dye application to yarn, textile or fabric, and does not assess releases from subsequent finishing steps, which may involve washing steps. Figure 1 provides an illustration of the scope of the ESD within the lifecycle of a chemical of interest.

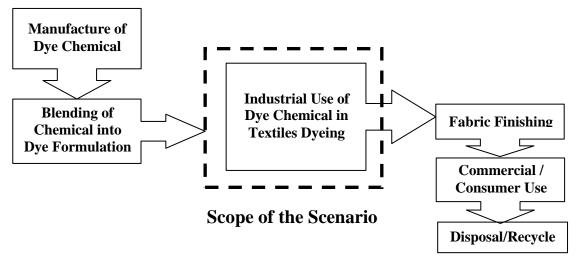


Figure 1. Textile Dye Chemical Life-Cycle Diagram

To estimate environmental releases for the dyeing process, this ESD assumes that chemicals used in textile dyes are nonvolatile. EPA often assumes chemicals are nonvolatile if the vapor pressure is less than 0.001 torr (0.133 Pa). Nonvolatile chemicals result in negligible releases to air from volatilization and negligible associated inhalation exposures (CEB, 1991). However, other air releases (e.g. dust generation) from process operations may occur.

The methods for estimating the following facility operating parameters and the releases and exposures to chemicals used during the application of dye products onto fibers, yarns, or fabrics are discussed in this ESD, including:

• Number of sites in the United States applying dyes containing the chemical of interest onto various substrates;

- Releases of chemicals during transfer from the container into the process (storage or mixing vessel);
- Releases from transport container residue (via container cleaning or direct disposal of empty containers);
- Releases from disposal of spent dye bath;
- Releases from equipment cleaning operations;
- Number of workers that may come into contact with the dye product during the textile dyeing process;
- Inhalation and dermal exposures during container unloading;
- Inhalation and dermal exposures during container cleaning and disposal;
- Dermal exposures during dye machine operation;
- Dermal exposures during disposal of spent dyebath.

The estimation methods in this ESD apply to any dye component, regardless of its function within the dye formulation.

How this document was developed

EPA, with support from Eastern Research Group, Inc. (ERG), has developed this ESD on the use of textile dyes. The scope of the ESD is designed to serve the needs of both OECD programs as well as EPA. In the United States, the Risk Assessment Division (RAD) 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 chemicals used in the use of textile dyes. The occupational exposure methods are included so that the ESD may be used to fully support EPA's chemical review programs.

This ESD supersedes EPA's 1992 Use of Textile Dyes Generic Scenario. This ESD is considered an additional ESD that covers a portion of the textile finishing industry and is not meant to supersede the 2004 OECD ESD on the Textile Finishing Industry. This ESD has been revised and expanded to meet EPA's revised quality standards for generic scenarios (EPA, 2014). Differences between the previous and updated scenario include:

- General facility estimates (e.g. daily use rate, number of sites, operating days);
- Degree of fixation or exhaustion for each dye;
- Occupational exposure and environmental release estimates.

A Draft ESD was developed in June 2011 and has been revised multiple times based on internal CEB comments. The July 2011 revision applied the mass fraction of main dyestuff used per day to the daily dye formulation use rate, based on information in OECD's 2004 Emission Scenario Document on Textile Finishing Industry (OECD, 2004). The July 2012 revision updated the number of exposure days from 250 to 148, based on information reported in PMN submissions from 2006 through 2011, specified default fixation/exhaustion rates for unknown dye types, and added exposure estimates from container cleaning. The March 2013 version characterized the U.S. textile production of 9,100 kg/site-day as a typical value (range of 3,520-50,000 kg/site-day). The June 2013 version was a minor update that provided a summary of updates from EPA's 1992 scenario. This update includes further information from O'Neill *et al.* (1999) for dye fixation ranges (Table 1-2). The April 2015 revision updated the number of exposure days from 148 to 157, and also provided a range of operating days based on information reported in PMN submissions from 2006 through 2016 revision updated the number of exposure days from 148 to 157, and also provided a range of operating days based on information reported in PMN submissions from 2006 through 2014.

This document is published under 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

1. The textile industry is comprised of a diverse, fragmented group of establishments that produce or process textile-related products (fiber, yarn, fabric) for further processing into apparel, home furnishings, and industrial goods. Textile establishments receive and prepare fibers; transform fibers into yarn, thread, or webbing; convert the yarn into fabric or related products; and dye and finish these materials at various stages of production. The process of converting raw fibers into finished apparel and nonapparel textile products is complex; thus, most textile mills specialize in specific products. Little overlap occurs between knitting and weaving, or among production of manmade, cotton, and wool fabrics (OECA, 1997).

2. Textiles are manufactured beginning with raw fibers. Textile fibers can be harvested from natural sources (*e.g.* wool, cotton) or manufactured from regenerative cellulose materials (*e.g.* rayon, acetate), or it can be entirely synthetic (*e.g.* polyester, nylon). After the raw natural or manufactured fibers are shipped from the farm or the chemical plant, they pass through four main stages of processing (OECA, 1997):

- Yarn production;
- Fabric production;
- Wet processing; and
- Garment Manufacturing.

3. Dyeing may occur in several of these stages, but is primarily completed during the Wet Processing (also called Finishing) stage. This is described in more detail in Section 2.

1.1 Textiles Dyeing Process within the Textile Industry

4. The textiles dyeing process falls under two North American Industrial Classification System (NAICS) industries: Broadwoven Fabric Finishing Mills (NAICS Code 313311) and Textile and Fabric Finishing (except Broadwoven Fabric Mills) (NAICS Code 313312). Table 1-1 presents the number of establishments and production workers reported in the 2011 Economic Census for each of these industries. The majority of these establishments are geographically concentrated in the state of California, followed by New York and North Carolina. The sales of all textiles generated 5.2 billion dollars revenue in 2011, which represents a market decline of 21% domestically since 2007 (USCB, 2007).

NAICS Code	Description	Number of Establishments	Number of Employees
313311	Broadwoven Fabric Finishing Facilities	480	11,289
313312	Textile and Fabric Finishing (except Broadwoven Fabric) Mills	438	12,264

Table 1-1. Number of Sites and Production Workers in the Textile Finishing Industry

Source: USCB, 2011

1.2 Types of Dyes

5. Dyes may be classified in several ways (e.g. according to chemical constitution, application class, or end-use). The primary classification of dyes is based on the fibers to which they can be applied and the chemical nature of each dye (OECA 1997).

6. Reactive and direct dyes are most commonly used for cotton dyeing; disperse dyes are used typically for polyester dyeing. Reactive dyes react with fiber molecules to form chemical bonds. Direct dyes can color fabric directly without the aid of an affixing agent. Direct dyes are the simplest dyes to apply and the cheapest in their initial and application costs, although there are tradeoffs in the dyes' shade range and wetfastness. A variety of auxiliary chemicals may be used during dyeing to assist in dye absorption and fixation into the fibers. Disperse dyes require additional factors, such as dye carriers, pressure, and heat, to penetrate synthetic fibers. Disperse dyes are dispersed in water where the dyes are dissolved into fibers. Vat dyes, such as indigo, are also commonly used for cotton and other cellulosic fibers (OECA, 1997). Each dye has a certain fixation rate which determines the percentage of dye that adheres to the substrate. Fixation rates for various dyes are summarized in Table 1-2 at the end of this section.

7. In the United States, it is estimated that reactive dyes account for 20-25% of all dyes consumed in the textile industry, followed by disperse at 20%, acid dyes at 15-20%, and fluorescent whitening agents at 10-15%. Cotton/rayon accounts for 60% of all dye consumption, followed by polyester at 15-20% and nylon at 15-20% (IHS, 2014).

8. The following subsections discuss the different types of dyes in more detail. Table 1-2 at the end of this section lists the major dye classes, fixation rates, and the types of fibers for which they have an affinity. Factors that companies consider when selecting a dye include: the type of fibers being dyed, desired shade, dyeing uniformity, and fastness (desired stability or resistance of stock or colorants to influences such as light, alkali, etc.) (OECA, 1997).

1.2.1 Acid Dyes

9. Acid dyes are water-soluble anionic compounds applied to nylon, wool, silk, and some modified acrylic textiles in an acidic medium. Some acid dyes are also used for coloring food and paper. However, they exhibit little affinity for cellulosic or polyester fiber. Colors generally are bright, and the material exhibits good to excellent fastness properties. Acid dyes have one or more sulfonic or carboxylic acid groups in their molecular structure. The dye-fiber affinity is the result of ionic bonds between the sulfonic acid part of the dye and the basic amino groups in wool, silk, and nylon fibers (ORD, 1996).

10. Mordants can be used to improve wetfastness and perspiration fastness of acid dyes, although shades tend to be duller. Mordants include Cr, Sn, Cu, and Al. Because of environmental concerns surrounding mordants, their use in acid dyeing in the United States has essentially ceased (ORD, 1996).

1.2.2 Azoic Dyes (Napthol Dyes)

11. Azoic dyes, also known as naphthol dyes, are used on cellulosic fibers (particularly cotton) but may also be applied to rayon, cellulose acetate, linen, jute, hemp, and sometimes polyester. Azoic dyes are made up of two chemically reactive compounds, which are applied to the fabric in a two-stage process. The reaction of the two compounds in the fiber produces the colored azo chromophore. During dyeing, the azoic dye forms inside the fibers (ORD, 1996).

12. The Colour Index (CI) refers to the components used in azoic dyeing as CI Azoic Coupling Components and CI Azoic Diazo Components. The coupling components are mostly derived from beta-naphthol and are available in powder or liquid form, while the diazo components are available as free bases (fast color bases) and diazonium salts (fast color salts). The depth of shade is determined by the extent to which the coupling component is absorbed when the diazo component is applied to the fiber (ORD, 1996).

13. Azoic dyes produce bright and dark shades of yellow, orange, red, maroon, navy blue, brown, and black. The dyes exhibit good lightfastness and fastness to peroxide and other bleaches. They can be applied in a variety of ways (e.g. continuously or using yarn, jet, beck, or jig dyeing processes). Use of azoic dyes has declined over the years, however, because of application costs and concerns about the possible presence of carcinogenic naphthylamines in wastewater effluents (ORD, 1996).

1.2.3 Basic (Cationic) Dyes

14. Basic dyes were the first synthetically manufactured dye class. They were initially used to dye silk and wool (using a mordant), but they exhibited poor fastness properties. Modified basic dyes were developed and are now used exclusively to color synthetic fibers such as acrylic, modacrylic, and modified nylons and polyesters, in which their fastness is acceptable. Basic dyes are rarely used on natural fibers, both because of their poor light-and washfastness and because of the need for mordants (ORD, 1996).

15. Basic dyes have limited water solubility and are applied in weakly acidic dyebaths. Ionic bonds are formed between the action in the dye and the anionic site on the fiber. As a class, basic dyes are among the brightest dyes available. In addition, they have unlimited color range and good fastness properties (except in natural fibers, as noted above). Good preparation (scouring) is necessary to remove the surface additives applied for knitting and weaving. Basic dyes are strongly bound and do not migrate easily; therefore, temperature must be used to carefully control exhaustion to ensure level dyeing (ORD, 1996).

1.2.4 Direct Dyes

16. Direct dyes are water-soluble, anionic compounds used extensively for coloring paper but also for dyeing cotton, rayon, linen, jute, hemp, silk, and nylon fibers, as well as mixtures of fibers and leather. The term "direct dye" refers to the fact that these dyes can be applied directly to cellulosics without mordants. The dyes are absorbed into hydrophilic fibers as the fibers expand in the water solution. Sodium chloride or sodium sulfate salts are added to the dyebath to counteract the slightly negative charge cellulosics have in aqueous solution. The molecular structure of direct dyes is narrow and flat, permitting these molecules to align with flat cellulose fibrils, where the dye molecules are held in place through Van der Waals forces and hydrogen bonds (ORD, 1996).

17. Although direct dyes yield bright, deep colors, they vary greatly in light fastness. They are widely used to color cellulosic materials including those that need high fastness (e.g. upholstery and drapery

fabrics). Also, they are limited in washfastness and their ability to withstand exposure to moisture (e.g. perspiration) unless the fabric is after treated with a chemical fixative in a common procedure called after fixing. These fixatives react with the dye, holding the dye molecules in place. Direct dyes are more economical than reactive or vat dyes, but their use has declined in recent years as reactives with superior end use properties have gained popularity (ORD, 1996).

1.2.5 Disperse Dyes

18. Because of the growing world dominance of polyester fibers in textile use, disperse dyes are the largest volume dye class used today (IHS, 2014). Disperse dyes have a very low water solubility, and are applied as a dispersion of finely ground powders in the dyebath. The particles dissolve at low concentrations in the aqueous dyeing medium but transfer into the synthetic fiber polymer because of their higher solubility in the substrate. High temperatures and superatmospheric pressures are sometimes used for application. This reduces the need for chemical accelerants (e.g. dye carriers), which are required at lower temperatures (ORD, 1996).

19. Disperse dyes are used for oleophilic fibers (polyester and other synthetics) that do not accept water-soluble dyes. They are used largely for synthetic fibers, mainly polyester but also cellulose acetate rayon (also called regenerated cellulose fibers), nylon, and acrylic fibers. For polyesters, disperse dyes offer a full shade range. Because of the limited buildup properties and poor washfastness in dark shades, however, disperse dyes are used mostly to obtain pastel shades in nylons and acrylics. Disperse dyes tend to have good fastness to light, perspiration, laundering, and dry cleaning. They also have good resistance to color transfer by contact or rubbing (crocking) (ORD, 1996).

1.2.6 Reactive or Fiber-Reactive Dyes

20. Fiber reactive dyes are water-soluble, anionic dyes that provide high wetfastness and require relatively simple dyeing methods. In terms of volume, they are currently the second-largest dye class in the world just behind disperse dyes (IHS, 2014). They are mainly used for dyeing cellulosic fibers such as cotton and rayon but are also sometimes used for wool, silk, nylon, and leather. Fiber reactive dyes have largely replaced direct, azoic, and vat dyes and are the largest dye class (in commercial value) in the United States. Because of the bright shades available, particularly orange, scarlet, and turquoise, they are popular choices for color fashion apparel (ORD, 1996).

21. Fiber reactive dyes form covalent chemical bonds with the fiber and become part of the fiber, giving excellent fastness properties. Because of their solubility, leveling takes place rapidly before fixation, which provides flexibility in dye application methods. To exhaust the dyes, however, large amounts of salt are generally necessary, and substantial amounts of dye can remain unfixed at the end of the process. After dyeing, the fabric is afterwashed with an anionic surfactant to remove unreacted dye (ORD, 1996).

22. Some improvements in fixation of fiber reactive dyes have been made, particularly with the introduction of bifunctional reactive dyes. Bifunctional dyes have two reactive groups, which increases the efficiency of dye fixation. Low-bath-ratio equipment can also be used to reduce salt requirements, and padbatch dyeing using cold reactive dyes that require no salt is a viable alternative (ORD, 1996).

1.2.7 Mordant Dyes (Chrome Dyes)

23. Mordant dyes are used mainly in wool dyeing, although they also are used to dye silk and nylon and to print wool, silk, and cellulosic fibers. In general, mordant dyes have fair to good fastness properties. These dyes usually contain a ligand functionality capable of reacting strongly with salts of aluminum, chromium, cobalt, copper, nickel, or iron to give differently colored metal complexes. Mordants are now

used infrequently in the United States because of concern about toxic metal salts in the wastewater effluent (ORD, 1996).

1.2.8 Sulfur Dyes

24. Sulfur dyes are mainly used for dyeing cotton and rayon substrates. They may also be used for dyeing blends of cellulosic and synthetic fibers, including nylons and polyesters, and are occasionally used for dyeing silk (ORD, 1996).

25. The synthesis of sulfur dyes is based on the reaction at high temperature of organic compounds containing nitro and amino groups with sulfur or sodium sulfide. The dyes contain sulfur both as an integral part of the chromophore and in polysulfide pendant chains (ORD, 1996).

26. Sulfur dyes are reduced with sodium sulfide to a water soluble form before application to the fiber. In their reduced form, sulfur dyes are soluble and have an affinity for cellulose. Sulfur dyes color by absorption, like direct dyes, but with exposure to air they oxidize to re-form the original insoluble dye inside the fiber. This makes them very resistant to oxidizing bleaches (e.g., peroxide) and resistant to removal by washing (ORD, 1996).

27. Sulfur dyes have good to excellent washfastness and moderate to good light fastness. They are relatively inexpensive compared with other dyes. Although they encompass a broad shade range, sulfur dyes are mostly used for dark shades because lighter shades have poorer resistance to light and laundering. The shade range for sulfur dyes includes brick reds, browns, burnt oranges, and blacks. Sulfur dyes tend to be dull compared with other dye classes. Deep indigo denim colors are often obtained by applying indigo dyes over a sulfur "bottom" (ORD, 1996).

28. Sulfur dyes have decreased popularity in the United States, Western Europe and Japan because of environmental concerns associated with the dye manufacturing process; however, sulfur dyes are still popular in other parts of the world where environmental regulations are less stringent (IHS, 2014).

1.2.9 Vat Dyes

29. Vat dyes are the oldest and among the more chemically complex dyestuffs. They are used most often for dyeing and printing cotton and cellulosic fibers, and for end uses that require good fastness properties, such as toweling, industrial uniforms, military uniforms, and tenting. Although most commonly used for cottons and cellulosics, they can also be applied to nylon and polyester/cellulosic blends and are sometimes used for dyeing wool and acetate (ORD, 1996).

30. Vat dyes have excellent fastness properties when properly selected, and are often used on cotton and cellulosic fabrics that will be subjected to severe conditions of washing and bleaching (e.g. sewing threads). Vat dyes can be used on all fibers except those sensitive to alkalis (ORD, 1996).

31. Vat dyes are applied by exhaust or continuous methods. They are either supplied in water soluble reduced "leuco" form or reduced with a reducing agent such as sodium hydrosulfite. Then they are allowed to migrate into the fiber by an exhaustion process (for batch dying) or by steaming (for continuous dyeing). When this migration into the fiber is complete, the substrate is rinsed to remove surface dye, then the dye is oxidized back to its water insoluble form within the fiber. The result is a dyeing of very high fastness to washing (ORD, 1996).

32. Vat dyes offer a good range of colors, but shade ranges are generally dull. Because of this, preparation, including bleaching and mercerizing, is important. Mercerizing helps the dyer achieve deeper shades and produce adequate cover on raw cotton. Vat dyes are insoluble in water but are readily soluble in

alkaline solution. Vat dyes can be applied by continuous methods or by exhaust dyeing procedures (ORD, 1996).

1.2.10 Pigments

33. Pigments differ from dyes in that they:

- Remain insoluble during application;
- Have no affinity for the fibers;
- Require binders; and
- Do not react with the fibers.

34. Little penetration of the color into the substrate occurs with pigments. Instead, pigments are usually mixed with a vehicle that hardens upon drying, forming an opaque coating. Pigments are used extensively in textile printing (ORD, 1996).

Dye Class	Description ^a	Method ^a	Fibers Typically Applied to ^a	Range of Fixation (%)	Average Fixation (%) = default value ^c
Acid	water- soluble anionic compounds	Exhaust/ Beck/Continu ous (carpet)	wool nylon	85-98 ^{a,c}	90 (1 SO ₃ group) 95 (> 1 SO ₃ group)
Azoic	naphthol, reactive dyes	Exhaust/Pack age	cellulose	76-95 ^{a,c}	84 (continuous)
Basic	water-soluble, applied in weakly acidic dyebaths; very bright dyes	Exhaust/ Beck	acrylic some polyesters	a 95- 100 ^{a,c,d}	99 (batch)
Direct	water- soluble, anionic compounds; can be applied directly to cellulosics without mordants (or metals like chromium and copper)	Exhaust/ Beck/ Continuous	cotton rayon other cellulosics	64-96 ^{a,b,c}	88 (batch)
Disperse	not water- soluble	High temperature exhaust Continuous	polyester acetate other synthetics	80- 100 ^{a,c,d}	95 (continuous) 97 (batch)
Premetalliz ed or Metal- Containing	description not available	Exhaust/ Beck	Wool, nylon	82-98 ^{a,c}	94 (batch)
Reactive	water- soluble, anionic compounds; largest dye class	Exhaust/ Beck Cold pad batch/ Continuous	cotton other cellulosics wool	50-97 ^{a,b,d}	95 (batch, wool) 75 (batch, cotton) 80 (continuous, cotton)
Sulfur	organic compounds containing sulfur or sodium sulfide	Continuous	cotton other cellulosics	60-95 ^{a,c}	70 (continuous)
Vat	oldest dyes; more chemically complex; water- insoluble	Exhaust/ Package/ Continuous	cotton other cellulosics	70-95 ^{a,b,c}	85 (continuous)

Sources: a – OECA, 1997, b – Jasper, 2011, c – OECD, 2004. These default values are to be associated with release model for disposal of spent dye bath (Section 4.4). d – O'Neill et al., 1999

2 PROCESS DESCRIPTION

35. Woven and knit fabrics cannot be processed into apparel and other finished goods until the fabrics have passed through several water-intensive wet processing stages. Wet processing enhances the appearance, durability, and serviceability of fabrics by converting undyed and unfinished goods, known as "gray" or "greige" goods, into finished consumers' goods. Also known as finishing, wet processing has been broken down into four stages in this section for simplification: fabric preparation, dyeing, printing, and finishing. These stages, shown in Figure 2-1, involve treating gray goods with chemical baths and often require additional washing, rinsing, and drying steps. Note that some of these steps may be optional depending on the style of fabric being manufactured (OECA, 1997).

36. Most manufactured textiles are shipped from textile mills to commission dyeing and finishing shops (for further processing in integrated mills) for final coloring or finishing. Alternatively, dyers and finishers may purchase gray goods from mills for conversion to finished textiles. The finisher then sells the finished piece to apparel, furnishing, and industrial textile product manufacturers. A wide range of equipment is used for textile dyeing and finishing (OECA, 1997).

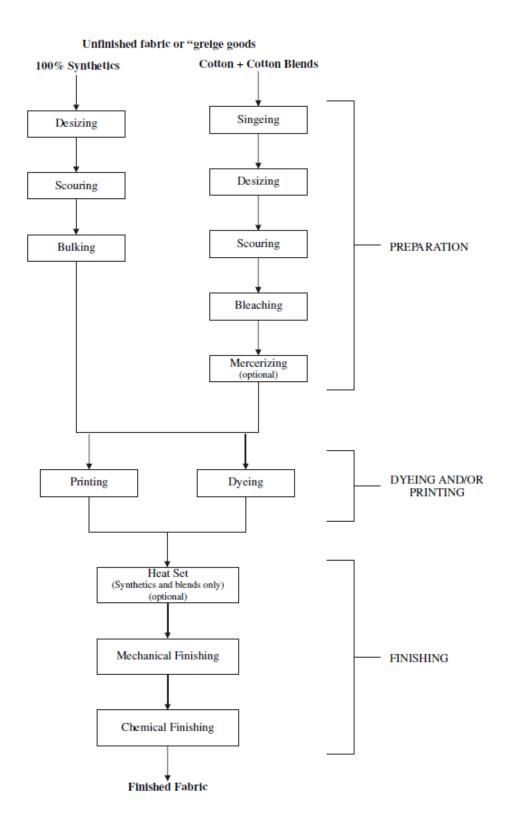
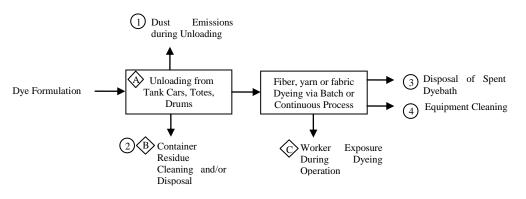


Figure 2-1. Typical Wet Processing Steps for Fabrics (OECA, 1997)

37. Textiles are dyed using both continuous and batch processes, and dyeing may take place at any of several stages of the manufacturing process. Figure 2-2 illustrates the general use of textile dyes and the associated release sources and worker exposure activities.

38. Liquid and solid dye formulations are typically unloaded from transport containers (e.g. drums) directly into the dyeing machine. Although dye products may be supplied using feed lines, this ESD assumes they are poured or weighed manually (Release 2, Exposure B) to present more conservative exposure estimates. Unloading is considered to be the main exposure point, because exposure occurs at the highest chemical concentration and because of potential inhalation of powder dyes.

39. ETAD states that the receiving application facility typically rinses container residuals into the dyeing process, or the empty container is landfilled or incinerated (Release 1, Exposure A) (ETAD, 2011). Release of spent dye bath to wastewater is expected to be the main release source, depending on the dye exhaustion rate.



 \bigcirc = <u>Environmental Releases</u>:

- 1. Transfer operation losses of dust emissions (release to POTW, air, incineration, or landfill).
- 2. Container residues from dye transport container (release to POTW, incineration or landfill).
- 3. Disposal of spent dyebath (release to POTW).
- 4. Equipment cleaning (release to POTW)

- A. Inhalation (solid particulate dyes only) and dermal exposure during equipment loading/container unloading.
- B. Inhalation (solid particulate dyes only) and dermal exposure during container cleaning.
- C. Dermal exposure during dyeing operation.

Figure 2-2. General Textile Dyeing Process

2.1 Batch Processing

40. For the most part, dyeing is accomplished in batch processes. While the details of each type batch process may be different, the basic batch dyeing follows this process: a textile substrate is immersed in a bath of (usually) water in which dye is dispersed or dissolved. With agitation and heat, the dyestuff diffuses through the solution (b), is sorbed at the fiber surface (c), and then diffuses into the fiber (d). This process can be done for fibers, yarns or fabrics (Kirk-Othmer, 2004).

2.1.1 Fiber Dyeing

41. Fibers may be dyed before they are spun into yarns or woven or knit into textile fabrics. Fiber dyeing is usually accomplished by pumping dye liquor through a stationary mass of fibers. Fiber is prepacked into some form of perforated basket, which is then loaded into the kettle or kier containing the dyebath. Packing must be even to avoid the creation of channels and tight spots and consequently unlevel dyeing. Although since the fiber is later to be thoroughly mixed in yarn formation, unlevelness is more tolerable in fiber dyeing than in yarn or fabric dyeing. During dyeing the kettle is usually enclosed (Kirk-Othmer, 2004).

2.1.2 Yarn Dyeing

42. Less than 10% of the textile dyeing is done in the yarn stage (IHS, 2014). Textiles may be dyed in yarn form before they are used to weave or knit a pattern or design into the cloth. Yarn is dyed in one of two forms: skein or package. While obsolete methods of skein dyeing involved moving skeins through a stationary bath, in both cases today the dyebath is moved through yarn that is held in place (Kirk-Othmer, 2004). Figure 2-3 shows an example of a skein dyeing apparatus and a package dyeing apparatus.

43. Skeins (or hanks) are hung from poles: The use of two poles per skein keeps the skein extended during dyeing. A frame with many poles is suspended in the dyebath, and the liquor is circulated (usually upward to float the skeins off the poles and avoid "stick marks") through the mass of yarn. Since the yarn is only partly constrained, the method allows the yarn to achieve bulkiness, and the method is useful for knitting and carpet yarns. Skein dyeing involves winding the skeins from cones, and backwinding onto cones after dyeing. Together with the loading and unloading onto the poles, the overall process tends to be labor intensive (Kirk-Othmer, 2004).

44. In package dyeing, yarn is wound onto perforated metal or plastic formers the form of conical or parallel sided cylinders, called cones or cheeses, respectively. Several packages are placed on perforated spindles of a carrier: depending on the diameter of the packages, different carriers might be used in a given kettle. Horizontal spindle machines including those consisting of multiple single-spindle kettles have been developed, but usually multiple spindle carriers arranged vertically are used. The whole carrier, with many spindles carrying packages, is placed in the kettle where dye liquor is pumped through the spindles and through the yarn. Generally, the flow is from inside to outside of the package, but periodic reversal increases levelness (Kirk-Othmer, 2004).

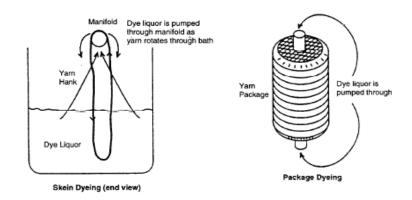


Figure 2-3. Yarn Dyeing Methods (ORD, 1996)

2.1.3 Fabric Dyeing

45. The majority of textile material is dyed in the form of fabric; in the United States, approximately 80% of textile dyeing is done in the fabric stage (IHS, 2014).³ There are four different machine types for such processes: Beam Dyeing; Jig Dyeing; Winch or Beck Dyeing; and Jet Dyeing (Kirk-Othmer, 2004).

2.1.3.1 Beam Dyeing

46. This method is similar to package dyeing of yarn: flat fabric is wound onto a perforated steel cylinder and placed in a kettle through which dye liquor is pumped, as shown in Figure 2-4. The method is good for lightweight synthetic-fiber fabrics through which liquid flows easily. Since the fabric is constrained and flat, it is also useful for materials that might crease (Kirk-Othmer, 2004).

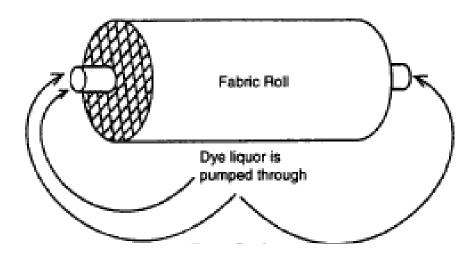


Figure 2-4. Beam Dyeing Method (ORD, 1996)

³ Includes apparel fabrics, carpeting, draperies, furniture covering, bedding, and other fabrics.

2.1.3.2 Jig Dyeing

47. Fabric is also dyed in flat form in a jig dyeing machine (or jigger). However, in this machine the liquor is stationary while the fabric is run through it. Several hundred meters of cloth are wound around a roller on one side of a jig. The goods are run off the beam through a small-volume, V-shaped dyebath and wound on to a second beam. Figure 2-5 illustrates an older jig dyeing machine, with a larger dyebath. When the entire cloth has been wound on the opposite beam, the clutch is reversed and the cloth travels back in the opposite direction. The fabric is in contact with the dyebath for the very short time as it passes through the bath, therefore diffusion processes occur as the fabric is turning on the beam. Because of low temperature and liquor ratios, the jig is especially suitable for cotton fabrics: The flat form is also helpful in avoiding creases in filament acetate and nylon fabrics (Kirk-Othmer, 2004).

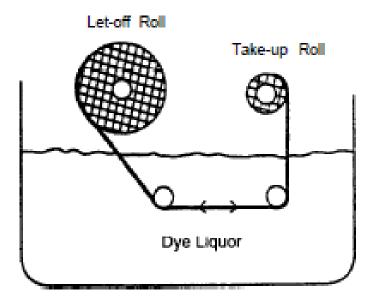


Figure 2-5. Jig Dyeing Method (end view) (ORD, 1996)

2.1.3.3 Winch or Beck Dyeing

48. Winch or beck dyeing is one of the oldest mechanized forms of dyeing fabric. Like the jig, the bath is stationary while the fabric moves to provide the relative motion. Machines can run fabrics in either open-width or rope forms. The beck is usually considered a rope-form machine. The machine in its basic form consists of a shallow box (the beck) which has a gradual low curvature in the back and a rather high vertical rise in the front, as seen in Figure 2-6. One end is passed over the top of this reel and sewn to the back end to form an endless loop. The tub is filled with the dye liquor and the fabric is immersed in it. A driven elliptical reel (the winch) lifts fabric from the front of the dyebath, over the top of the reel, and redeposits it at the back of the bath. The fabric then slowly moves forward through the dye liquor from the back of the winch, where it is again lifted by the reel. Becks and winches are generally enclosed machines. The gentle action makes it suitable for delicate fabrics (Kirk-Othmer, 2004).

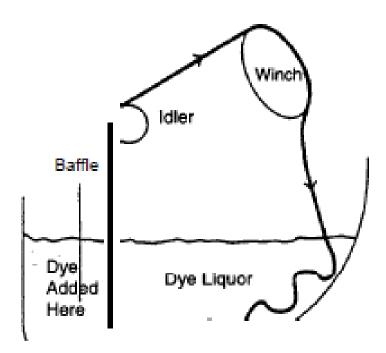


Figure 2-6. Beck Dyeing Method (end view) (ORD, 1996)

2.1.3.4 Jet dyeing

49. Jet dyeing machines have become the most popular batch dyeing machine: most new machines installed are of this type. Like the beck machine, fabrics are processed as end-joined loops in rope form. The jet machine replaces the winch as the means of moving the fabric with a narrow orifice into which dye liquor is pumped. This forms a venturi, and drives the fabric at speeds of 200 m/min or more (Kirk-Othmer, 2004).

50. While becks and jigs each tend to have a fairly uniform layout, jet dyeing machines come in a variety of styles. Two main types exist: the long horizontal cylindrical machines ideally suited for synthetic fabrics where the fabric travels along the length of the cylinder; or cylindrical, upright pear, bell-shaped, or J-box autoclaves where the fabric moves around the circumference of the apparatus, as seen in Figure 2-7. These autoclave types can have more than one fabric rope per autoclave and are suitable for most fabrics (Kirk-Othmer, 2004).

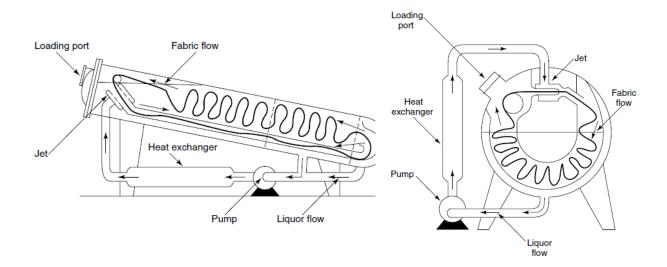
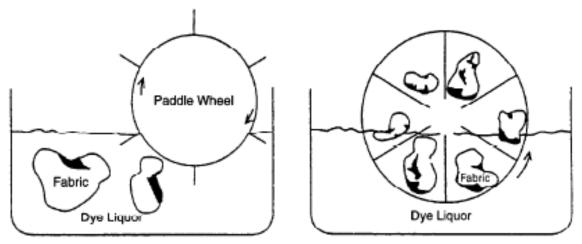


Figure 2-7. Long cylindrical jet drying machine (left); Upright cylindrical jet drying machine (right) (Kirk-Othmer, 2004)

2.1.4 Garment Dyeing

51. Garment dyeing involves the dyeing of woven or knit cloth and may be accomplished by batch or continuous processes. The choice between batch and continuous dyeing usually depends on such factors as fabric construction, cost considerations, the dye classes chosen (and their applicability to batch or continuous equipment), the minimum lot size required for economical running, and the availability of equipment. Generally, except for dye jobs involving less than 1,000 meters of cloth, most woven material is dyed by continuous processes. Most knit cloth, on the other hand, is dyed by batch methods because it cannot withstand the tension of the continuous range (Kirk-Othmer, 2004).

52. Among the older machines are paddle machines in which a bath is circulated by a paddle. The bath may be an annular oval, with the axle holding the paddle blades just above the liquor surface. As the paddle rotates it moves liquor and goods around the annulus. Alternatively a V-shaped bath is used in which the paddle forces liquor and goods downward. For hosiery dyeing, a widely used machine used a perforated drum, divided into compartments, rotating in the dyebath. These machines are shown in Figure 2-8. Newer machines tend to be based on front-loading commercial washers/dry cleaning machines. Again, a rotating perforated compartmentalized drum revolves in the dyebath, although the garments are not continuously submerged (Kirk-Othmer, 2004).



Paddle Dyeing

Rotary Garment Dyeing

Figure 2-8. Garment Dyeing Methods (ORD, 1996)

2.2 Continuous Dyeing

53. When large amounts of a single color are required, continuous processing is more efficient. Uncolored material is fed into the system and colored material is withdrawn continuously. Continuous dyeing is most suited to fabric, and most woven goods. Continuous yarn dyeing is most commonly used in the application of indigo to warp yarns to be woven into denim (Kirk-Othmer, 2004).

54. Dye application may be via a spray or by foam, but is most often done by padding, in which the material is immersed in dye solution, then squeezed between rollers to reduce and control the uptake to a consistent level (dip and nip). The feed of dye solution must be controlled to maintain a constant volume in the trough. The dwell time in the solution is very short, and fabric must be prepared to allow for rapid wetting. In addition, padding solutions typically include a wetting agent. Some systems use two dips and two nips to achieve more thorough wetting (Kirk-Othmer, 2004).

55. The expression of excess dye is accomplished by squeeze rollers, referred to as bowls. Most bowls consist of a medium density rubber roller across the width of which pressure can be applied. This roller presses against a stainless steel or a hard rubber roller. These rollers may be mounted either vertically or horizontally between the squeeze rollers, as seen in Figure 2-9 (Kirk-Othmer, 2004).

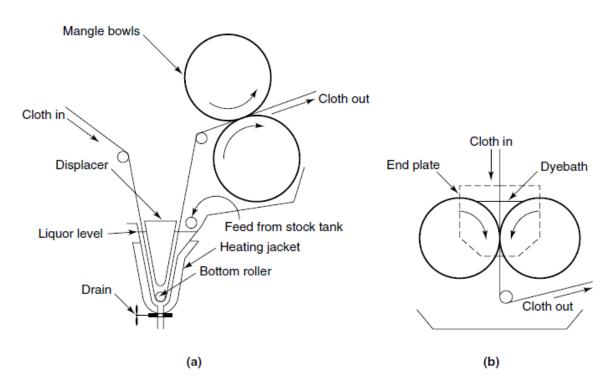


Figure 2-9. Typical Pad Mangle Configuration: (a) inclined vertical pad mangle with V-shaped trough; (b) horizontal wedge-nip pad mangle. (Kirk-Othmer, 2004)

3 OVERALL APPROACH AND GENERAL FACILITY ESTIMATES

56. This ESD presents EPA's standard approach for estimating environmental releases of and worker exposures to chemicals of interest during the industrial textile dyeing process.

57. 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 textile 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 sitespecific 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.

58. This section of the ESD presents general facility calculations for application sites, which estimate daily use rates of dyes, the number of textile dyeing sites, and the number of days that the dye is expected to be used in the textile dyeing process.

59. Section 4 of the ESD presents the environmental release assessments for the general textile dyeing process, which use the general facility estimates to estimate the quantity of chemical released from various points in the application process and the most likely media of release for each release source.

60. Section 5 of the ESD presents the occupational exposure assessments for the textile dyeing process, which use 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

61. Through the remainder of this section, a method utilizing available dye products industry data is described to determine daily use rate of the chemical of interest for a textile dyeing site. The chemical daily use rate ($Q_{chem_site_day}$) can be estimated using the daily dye formulation use rates ($Q_{dye_formulation_day}$) and the concentration of the chemical of interest in the dye formulation. The number of textile dyeing (N_{sites}) may then be determined from the daily use rate, days of operation (TIME_{operating_days}) and the annual production of the chemical for this use (Q_{chem_yr}).

62. 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.

Parameter	Description	ESD Section		
$TIME_{operating_days}$	Annual number of days the formulation product is applied at each facility (days/yr).	3.2		
F_{chem_dye}	Mass fraction of the chemical of interest in the dye formulation (kg chemical/kg dye formulation).	3.3		
Qdye_formulation_day	^{ation_day} Daily use rate for the dye formulation at each facility (kg of dye formulation/site-day).			
$Q_{chem_site_day}$	^{m_site_day} Daily use rate for the chemical of interest at each facility (kg of chemical/site-day).			
N _{sites}	Number of facilities using the chemical of interest in textile dyeing processes (sites).	3.6		
N _{container_unload_site_yr}	^{container_unload_site_yr} Number of transport containers unloaded at each site per year (containers/site-yr)			
F _{chem_dyebath}	Mass fraction of the chemical of interest in the dyebath	3.8		

Table 3-1. Summary of General Facility Parameters for Textile Dyeing Sites

63. 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 Days of Operation (TIME_{operating_days})

64. Textile dyeing facilities typically operate between 5 to 7 days per week (Jasper, 2011a) over 50 weeks per year (ETAD, 2011), resulting between 250 to 350 operating days per year. However, the facility would likely not use the same dye formulation for the entire operating time. If the number of operating days using the chemical of interest is known, that value should be used. A search of 31 past PMN submissions from 2006 through 2014 revealed an approximate average of 157 operating days per year, over a range of 31 (5th percentile) to 295 (95th percentile) days per year (EPA, 2015). If site-specific information about the number of operating days using the chemical of interest is not known, EPA recommends assuming 157 days per site-year. Alternative values can also be selected depending on the assessment needs. For example, if environmental releases are a concern, 31 days per site-year may be assumed to maximize daily release estimates. Alternatively, if occupational exposures are a concern, the number of days may be increased.

TIME_{operating_days} = Number of operating days per site-year (Default: 157 days/year)

3.3 Mass Fraction of the Chemical of Interest in the Dye Formulation (F_{chem_dye})

65. The chemical of interest may only be a fraction of the dye formulation. Powder dyes typically contain 50 to 75% active chemical of interest and liquids contain 10 to 25% active chemical of interest (ETAD, 2011). If specific information about the chemical-containing dye is not known, EPA recommends assuming the high end of the chemical of interest when performing the calculations in this assessment, in order to provide more conservative exposure assessments:

 F_{chem_dye} = Mass fraction of the chemical of interest in the dye formulation (Defaults: *solid*: 0.75 kg chemical/kg dye formulation; *liquid*: 0.25 kg chemical/kg dye formulation)

3.4 Daily Use Rate of Dye Formulation (Q_{dye_formulation_day})

66. EPA's 1994 Fabric Finishing Generic Scenario (EPA, 1994) estimates a typical U.S. production of 9,100 kg/site-day of finished textiles (range of 3,520-50,000 kg/site-day), based on data provided in fabric finishing PMNs during 1993 and 1994. If no submission-specific information is available EPA recommends assuming a textile production rate of 9,100 kg/site-day; however, the user may choose the high- or low-end of the range depending on specific assessment needs. OECD indicates that a facility typically uses multiple dyestuffs per day, but suggests that a primary dyestuff may be used more frequently than others. OECD estimates that the median share of textiles processed per day using the primary dyestuff is 30%. EPA suggests that this percentage be used to estimate the daily use rate for the dyestuff containing the chemical of interest. Additionally, OECD estimates that as a "realistic worst case," powder dye formulations are used in an amount of 5% of the textile (0.05 kg dye formulation/kg textile), and liquid dye formulations in an amount of 10% (0.10 kg dye formulation/kg textile) (OECD, 2004).

$$Q_{dye_{formultion_{day}}} = V_{fabric} \times F_{fabric} \times F_{dye_{fabric}}$$
(3-1)

$Q_{dye_formulation_day}$	=	Daily use rate of the dye formulations (kg dye formulation /site- day)
V_{fabric}	=	Amount of textile dyed per site-day (default = 9,100 kg textile processed/site-day)
F_{fabric}	=	Mass fraction of textile treated with the dyestuff (default = 0.3 kg textiles dyed/kg textile processed)
F_{dye_fabric}	=	Mass fraction of dye used per textile dyed (defaults: powder dyes $= 0.05$ kg dye formulation/kg textile dyed; liquid dyes $= 0.10$ kg dye formulation/kg textile dyed)

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

67. The daily use rate of the chemical of interest during textile dyeing is estimated using Equation 3-2, based on the daily dye formulation use rate and the concentration of the chemical of interest. As a default, it is assumed that only the dye formulation containing the chemical of interest is used ($F_{dye} = 1$), Section 3.4 above assumed as a default that 30% of the textiles at a facility are dyed with the primary dyestuff, resulting in an overall estimated usage rate of 30%. F_{fabric} (Section 3.4) and F_{dye} (Section 3.5) can both be adjusted based on submission information to account for the use of multiple dyes and fabrics at a facility.

$$Q_{\text{chem_site_day}} = Q_{\text{dye_formultion_day}} \times F_{\text{chem_dye}} \times F_{\text{dye}}$$
(3-2)

Where:

$Q_{chem_site_day}$	=	Daily use rate of the chemical of interest contained in the dye formulation (kg chemical used/site-day)
$Q_{dye_formulation_day}$	=	Daily use rate of the dye formulation (kg dye formulation /site- day) (see Section 3.4)
F_{dye}	=	Mass fraction of the chemical of interest in the dye formulation (kg chemical of interest/kg dye formulation; see Section 3.3) Mass fraction of the dye formulation containing the chemical interest used per the total amount of dye formulation used (kg dye formulation with chemical of interest/kg dye formulation used; default = 1).

3.6 Number of Sites (N_{sites})

68. The number of facilities using the chemical of interest (N_{sites}) depends on the total annual production of the chemical of interest for this use (Q_{chem_yr}), the daily use rate of the chemical of interest ($Q_{chem_site_day}$), and the annual operating days (TIME_{operating_days}). Equation 3-3 demonstrates how the number of textile dyeing facilities using a chemical of interest could be determined:

$$N_{sites} = \frac{Q_{chem_yr}}{Q_{chem_site_day} \times TIME_{operating_days}}$$
(3-3)
Where:

$$N_{sites}^{4} = Number of textiles dyeing sites using the dye formulation (sites)$$

$$Q_{chem_yr} = Annual production volume of the chemical of interest for this use (kg chemical/yr)$$

$$Q_{chem_site_day} = Daily use rate of the chemical of interest contained in dye formulations (kg chemical used/site-day; see Section 3.5)$$

$$TIME_{operating_days} = Number of operating days at textile dyeing sites (days/yr)$$

(Default: 157 days/yr; see Section 3.2)

69. Note that the calculated value of N_{sites} should not exceed the total number of textile finishing facilities known to operate in the United States. According to the U.S. Census Bureau's 2011 *County Business Patterns* (CBP), there are 918 textile finishing facilities in the United States, employing a total of 23,553 people (USCB, 2011).

$$TIME_{operating_days} = \frac{Q_{chem_yr}}{N_{sites} \times Q_{chem_site_day}}$$

 $TIME_{operating_days}$ is rounded to the nearest non-zero integer.

⁴The value for N_{sites} , calculated using Equation 3-3 should be rounded to the nearest non-zero integer value. TIME_{operating_days} should then be adjusted for the N_{sites} integer value (to avoid errors due to rounding) while maintaining the same value of $Q_{chem_site_day}$ calculated in Section 3.5.

Summary of the Relationship of General Facility Parameters

The values for days of operation (TIME_{operating_days}), daily use rate of the chemical of interest ($Q_{chem_site_day}$), and number of manufacturing sites (N_{sites}) are related. This ESD presents one method for estimating N_{sites} using estimated default values for: 1) the annual production quantity of the chemical of interest for this use; 2) the total number of operating days per year at the end use site(s); and 3) the daily use rate of the chemical at a single site.

If N_{sites} and $TIME_{operating_days}$ are known, $Q_{chem_site_day}$ can be calculated directly without using Equation 3-2. This alternative calculation is:

$$Q_{chem_site_day} = \frac{Q_{chem_yr}}{N_{sites} \times TIME_{operating_days}}$$

If N_{sites} is known and TIME_{operating_days} is unknown, EPA recommends that using the default assumption that textile dyeing operations occur 157 days per year and $Q_{chem_site_day}$ be calculated using the above equation.

EPA recommends calculating the chemical of interest throughput based on the methodology presented in Section 3.5, and compare it to the throughput based on number of sites and operating days, as calculated above.

3.7 Number of Dye Formulation Containers Emptied per Facility (N_{container_unload_site_yr})

70. The number of dye product 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 formulation. Dyes can be transported in containers ranging from 25 kg through 1,000 kg (ETAD, 2011) but according correspondence with Dr. Warren Jasper (NC State University College of Textiles), most are shipped in 35-gallon drums (Jasper, 2011). EPA suggests that a default transportation container size of a 35-gallon drum could be used in the absence of site-specific information. Engineering judgment should be used to determine if another container type or size is more appropriate. If the density of the formulation is not known, the density for water can be used as a default (1 kg/L).

$$N_{\text{container_unload_site_yr}} = \frac{Q_{\text{chem_site_day}} \times \text{TIME}_{\text{operating_days}}}{F_{\text{chem}} \times V_{\text{container}} \times \text{RHO}_{\text{form}}}$$
(3-4)

Where:

$N_{container_unload_site_yr}$	=	Number of transport containers unloaded at each site per year (containers/site-yr)
$Q_{chem_site_day}$	=	Daily use rate of the chemical of interest per site (kg chemical used/site-yr) (see Section 3.5)
TIME _{operating_days}	=	Number of operating days (Default: 157 days/yr; See Section 3.2)
F _{chem_dye}	=	Mass fraction of the chemical of interest in the dye formulation
		(kg chemical/kg dye formulation) (See Section 3.3)
V _{container}	=	Volume of transport container (Default: 132.5 L
		formulation/container (35-gallon drum); See Table B-1 in
		Appendix B for alternative default container volumes)
RHO _{form}	=	Density of dye formulation (kg/L formulation; Default: 1 kg/L)

3.8 Mass Fraction of Chemical of Interest in the Dye Bath (F_{chem_dyebath})

71. ETAD states that the bath concentrations may vary depending on the desired shade of the fiber, yarn, or fabric. Typical dye concentrations may range from 1.5-2.5%. Lighter shades may be as low as 0.2-0.3% and heavier shades may be between 4-6% (ETAD, 2011). In the absence of site specific data, EPA recommends assuming the high end of the range to generate more conservative worker exposures.

$$F_{chem_{dyebath}} = F_{chem_{dye}} \times F_{dye_{dyebath}}$$
(3-5)

$$= Mass fraction of the chemical of interest in the dyebath (kg chemical/kg dyebath)$$

5.		
$F_{chem_dyebath}$	=	Mass fraction of the chemical of interest in the dyebath (kg
		chemical/kg dyebath)
F _{chem_dye}	=	Mass fraction of the chemical of interest in the dye formulation
		(kg chemical/kg dye formulation) (See Section 3.3)
$F_{dye_dyebath}$	=	Mass fraction of the dye formulation in the dyebath (default: 0.06
		kg dye formulation/kg dyebath)

4 ENVIRONMENTAL RELEASE ASSESSMENTS

72. This section presents approaches for estimating the amount of the chemical of interest released during the textile dyeing process. The release sources are presented in the order discussed in Section 2 (see Figure 2-2) and include the most likely receiving media (e.g. air, water, landfill, or incineration). The primary sources of release include dust releases from solid powder transfer, container residue, disposal of spent dyebath and process equipment cleaning. Key default values used for the release estimates, accompanied by their respective references, are provided in Table A-1 of Appendix A.

73. It is generally assumed that during the use of dye products, losses of the chemical of interest are minimized in actual practice; however, some pre-process or other upstream releases will occur. Because losses are assumed to be minimized, the methodology presented in this section for estimating releases of the chemical of interest from the dyeing 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 (e.g. the total amount of chemical released from the process should not exceed the amount that enters the process).

74. 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 sites using the chemical of interest (N_{sites}) (See Equation 3-3).

75. Some of the 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.

76. 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 4.4 for estimating the amount of the chemical of interest released from the spent dyebath, which assumes that the dye not affixed to the substrate is released to water. Table 4-1 summarizes the release estimation methods used in this ESD.

77. 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.

78. EPA has developed a software package (ChemSTEER) containing the standard EPA models (except the EPA/OPPT Dust Emissions from Solid Transfers Model) as well as all current EPA defaults. 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.

Release Source #	Description	Model Name or Description ^a	Standard EPA Model (✓)
1	Transfer operation dust emissions of solid powder chemical to air, landfill, POTW, or incineration during unloading	5	~
2	Container residue losses to POTW, incineration or landfill	 Specific model used is based on the type and size of the containers, and on the physical state of the formulation: EPA/OPPT Bulk Transport Residual Model EPA/OPPT Drum Residual Model EPA/OPPT Small Container Residual Model 	~
3	Disposal of spent dye batch to POTW.	Loss rate is based on available industry- specific data.	
4	Equipment cleaning residue losses to POTW	EPA/OPPT Single Process Vessel Residual Model	\checkmark

Table 4-1. Summary of Use of Textile Dyes Scenario Release Models

OPPT – Office of Pollution Prevention and Toxics.

79. All release equations below estimate daily release rates for a given site. To estimate annual releases for all sites for a given source, the daily release rates must be multiplied by the number of days of release and by the total number of sites using the textile dye (N_{sites}).

4.1 Control Technologies

80. Water is used extensively for the textile dyeing process. Pollution may be controlled via sludge ponds, water treatment and recovery (Jasper, 2011). EPA recommends that as a default, it should be assumed all aqueous wastes are discharged to a publicly owned treatment works (POTW) for pretreatment prior to discharge to surface waters.

4.2 Transfer Operations Losses to POTW, Air, Incineration or Landfill from Unloading the Dye Formulation (Release 1)

81. For nonvolatile liquid dye formulations, this release is negligible. When solid powders are unloaded, dust may be generated from transfer operations. The *EPA/OPPT Dust Emissions from Transferring Solids Model* may be used to estimate dust releases generated during the transfer of solid dye formulations. This model assumes that up to 0.5 percent of the transferred quantity may be released to the environment. The rationale, defaults, and limitations of these models are further explained in Appendix B.

82. 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 may also be utilized by 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, this release is conservatively assumed released to air, water, incineration, or land.

83. The daily release of fugitive dust emissions can be estimated using the daily use rate (Qchem_site_day).

84. If the facility-specific information states a control technology is employed, the release may be partitioned to the appropriate media. Table 4-2 provides estimated efficiencies for more common control technologies that may be used in the radiation curable products industry.

Table 4-2. Estimated Control Technology Efficience	ies
--	-----

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

85. 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:

$$Elocal_{dust_captured} = Q_{chem_site_day} \times F_{dust_generation} \times F_{dust_control}$$
(4-1)

Where:

Elocal_{dust_captured} Daily amount captured by control technology from = transfers or unloading (kg/site-day) Daily use rate of chemical per site-day (kg/site-day; see Q_{chem_site_day} = Section 3.5) = Loss fraction of chemical lost during transfer/unloading of F_{dust_generation} solid powders (Default = 0.005 kg of released/kg handled; EPA, 2007) Control technology capture efficiency (kg captured/kg = F_{dust_control} processed) (Default: If the control technology is unknown, assume capture efficiency = 0 kg captured/kg processed, see Table 4-2 for alternative efficiencies).

86. 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:

Elocal _{dust_fugitive} = Q_{chem_site_day} × F_{dust_generation} ×
$$(1 - F_{dust_control})$$
 (4-2)

Where:

 $Elocal_{dust_{fugitive}} = Daily amount not captured by control technology from transfers or unloading (kg/site-day)$ $Q_{chem_site_day} = Daily use rate of chemical per site-day (kg/site-day; see$

Secti	ion 3.5)
$F_{dust_generation}$	= Loss fraction of chemical lost during transfer/unloading of solid powders
	(Default = 0.005 kg of released/kg handled; EPA, 2007)
$F_{dust_control}$	= 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 4-2 for alternative efficiencies).

87. 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.

4.3 Container Residue Losses to POTW, Incineration, or Landfill (Release 2)

88. Containers that are used to transport dye formulations contain residuals that may be released into the environment. ETAD indicates that the residuals may be handled in several different ways. The container residual may be rinsed out and used in the dyeing process, containers may be returned to the manufacturer or formulator for reuse, or transport boxes may be landfilled or incinerated (ETAD, 2011). Because these media of release are facility-dependent, EPA recommends assessing releases to POTW, incineration or landfill if site-specific information is not known. Note that while containers may be shipped back to the manufacturer or formulator, EPA assumes that containers are cleaned or disposed at the use site in order to generate conservative release estimates.

89. Container sizes range from 25 kg through 1,000 kg (ETAD, 2011; Jasper, 2011). EPA suggests that a default transportation container size of a 35-gallon drum should be used if no information is provided. 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).

90. The amount of dye remaining in transport containers will likely depend on the size of the transport container and the physical form of the component product. Therefore, 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;
- *EPA/OPPT Solid Residuals in Transport Containers Model* may be used for containers of all sizes containing solids.

91. Note that these models estimate between 0.2 (bulk containers) and 3 percent (drums) of the received material may be released to the environment. 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. Standard EPA/OPPT models are subject to change; therefore, the current version of the standard EPA/OPPT model should be used.

92. Dyes may be received as liquids or solids. If the physical state of the component is not known, EPA suggests using engineering judgment to determine if the chemical of interest should be assumed a solid or liquid for the purposes of the assessment.

93. The annual number of containers used per year ($N_{container_unload_site_yr}$) is estimated based on the daily use rate of the component and the container size (see Section 3.7). EPA recommends assuming 35-gallon (132.5 L) drums as default. If the fraction of the chemical in the dye formulation is unknown, assume 75 percent concentration for solid dye formulations or 25 percent concentration for liquid dye formulations (see Section 3.3).

94. If the $N_{container_unload_site_yr}$ value is fewer than the days of operation (TIME_{operating_days}), the days of release equal $N_{container_unload_site_yr}$ and the daily release is calculated based on the following equation:

Elocal _{container_residue_dkp} =
$$V_{container} \times RHO_{formulation} \times F_{chem_dye} \times F_{container_residue} \times N_{container_unload_site_day}$$
 (4-3a)

This release will occur over [N_{container unload site yr}] days/year from [N_{sites}] sites

Where:

$Elocal_{container_residue_disp}$	=	Daily release of chemical of interest from container residue (kg chemical/site-day)
V _{container}	=	Volume of transport container (Default: 132.5 L
		formulation/container (35-gallon drum; see Table B-1 in
		Appendix B for alternative default container volumes)
RHO _{formulation}	=	Density of dye formulation (kg/L formulation; Default: 1 kg/L for
		the density of water)
F_{chem_dye}	=	Mass fraction of the chemical of interest in the dye formulation
		(kg chemical/kg dye formulation) (See Section 3.3)
F _{container_residue}	=	Fraction of dye component remaining in the container as residue
		(Default: liquid - 0.03 kg dye formulation remaining/kg shipped
		for drums (EPA, 2002); see Appendix B for defaults used for
		other container types)
$N_{container_unload_site_day}^{5}$	=	Number of containers unloaded per site, per day (Default: 1 container/site-day)

95. If $N_{container_unload_site_yr}$ is greater than TIME_{operating_days} (See Section 3.2), more than one container is unloaded per day (e.g., $N_{container_unload_site_day} > 1$). The days of release should equal the days of operation, and the average daily release can be estimated based on Equation 4-3b:

$$N_{container_unload_site_day} = \frac{N_{container_empty_site_yr}}{TIME_{operating_day\,s}}$$
(N_{container_unload_site_day} should be rounded up to the nearest integer.)
Where:
$$N_{container_unload_site_yr} = Annual number of containers emptied containing chemical of interest per site (containers/site-yr) (See Section 3.7)$$

 $TIME_{operating_days}$ = Annual number of days the dye product is formulated (days/yr) (See Section 3.2)

⁵ The daily number of containers unloaded per site may be estimated as (consistent with Section 3.7):

$$Elocal_{container_{residue_{disp}}} = Q_{chem_{site_{day}}} \times F_{container_{residue}}$$
(4-3b)

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

Where:

$Elocal_{container_residue_disp}$	=	Daily release of chemical of interest from container residue (kg chemical/site-day)
$Q_{chem_site_day}$	=	Daily use rate of the chemical of interest (kg chemical/site-day)
		(See Section 3.5)
F _{container_residue}	=	Fraction of dye formulation remaining in the container as residue
		(Default: 0.03 kg dye formulation remaining/kg shipped for drums
		(EPA, 2002); see Appendix B for defaults used for other container
		types)

4.4 Disposal of Spent Dyebath to POTW (Release 3)

96. Because of the large amounts of water used in textile dyeing processes, aqueous wastes are often treated or recovered (Jasper, 2011). As stated in Section 4.1, EPA recommends that as a default, it should be assumed all aqueous wastes are discharged directly POTW prior to discharge to surface waters. Disposal of spent dyebath is assumed to occur at the end of each dyeing operation to POTW. The daily release of spent dyebath is assumed to be the amount of chemical that is not affixed to the textile. Table 1-2 lists typical fixation rates for various types of dyes and process types. If the type of dye is listed in the table, use the fixation rate available. If the type of dye and process are unknown, EPA recommends choosing the lowest average fixation rate of 70% (sulfur dye, continuous process), to generate more conservative release estimates. For an unknown dye type in a batch process, EPA recommends 75% fixation (reactive dye, cotton, batch process). Daily releases are calculated using the following equation:

Elocal _{spent_dyebath} =
$$Q_{chem_site_day} \times (1 - F_{fixation})$$
 (4-4)

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

Where:

Elocal _{spent_dyebath}	=	Daily release of chemical of interest from disposal of spent
		dyebath (kg chemical/site-day)
$Q_{chem_site_day}$	=	Daily use rate of the chemical of interest (kg chemical/site-day)
-		(See Section 3.5)
F _{fixation}	=	Fraction of dye product affixed on to textile during dyeing process
		substrate (Default: see Table 1-2; 70% for unknown dye and
		process type)

4.5 Equipment Cleaning to POTW (Release 4)

97. Equipment used to dye textiles may contain residues that need to be rinsed before starting a new textile batch. The amount of residual dye formulation chemical remaining in the process equipment may be estimated using the *EPA/OPPT Single Process Vessel Residual Model*. The model assumes that no more than one percent of the batch size or capacity of the process remains in the equipment as residue that is released as equipment cleaning waste. As a conservative estimate, EPA assumes that cleaning residuals are disposed with the spent dyebath to POTW after each batch.

98. The daily release of chemical residue in the process equipment is calculated using the following equation:

 $Elocal_{equipment_cleaning} = Q_{chem_site_day} \times F_{equipment_cleaning}$ (4-5)

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

Elocal _{equipment_cleaning}	=	Daily release of chemical of interest from equipment cleaning (kg chemical/site-day)
$Q_{chem_site_day}$	=	Daily use rate of the chemical of interest in the dye formulation
		(kg chemical/site-day) (See Section 3.5)
$F_{equipment_cleaning}$	=	Fraction of dye product released as residual in process equipment (Default: 0.01 kg product released/kg batch holding capacity (EPA, 1992))

5 OCCUPATIONAL EXPOSURE ASSESSMENTS

99. The following section presents estimation methods for worker exposures to the chemical of interest during the application process. Figure 2-2 illustrates the occupational activities performed within the application process that have the greatest potential for worker exposure to the chemical. Table 5-1 summarizes the exposure estimation methods used in this ESD.

100. 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.

101. EPA has developed a software package (ChemSTEER) containing these models as well as all current EPA defaults. Inhalation and dermal exposures are presented in terms of quantity per day; absorption and toxicity are outside the scope of the ESD. Appendix B provides additional information on ChemSTEER, including EPA models.

Exposure Activity	Description	Route of Exposure / Physical Form	Model Name or Description ^a	Standard EPA Model (✓)
A	A Exposure to liquid or solid dye product during unloading or transferring	powder dust	 Specific model is based on the volume of total material handled: <i>EPA Small Volume Handling Model (Based on data from dye weighing operations)</i> <i>OSHA PNOR PEL-Limiting Model</i> 	~
		-	 Specific model is based on the physical form of the material: EPA/OPPT 2-Hand Dermal Contact with Liquids Model EPA/OPPT Direct 2-Hand Dermal Contact with Solids Model 	~
В	solid dye product		 Specific model is based on the volume of total material handled: EPA Small Volume Handling Model OSHA PNOR PEL-Limiting Model 	~
		Dermal exposure to liquid chemical or solid chemical	Specific model is based on the	~
С	Exposure to liquid dye product during machine operation	Dermal exposure to liquid chemical	EPA/OPPT 2-Hand Dermal Contact with Liquids Model	✓

Table 5-1. Summary of Dye Application Scenario Exposure Models

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

5.1 Personal Protective Equipment

102. Textile dye workers typically wear safety glasses, goggles, aprons, respirators, and/or masks (ETAD, 2001; Jasper, 2011). However, exposure mitigation by PPE is affected by many factors including: availability, cost, worker compliance, impact on job performance, chemical and physical properties of the substance and protective clothing, and the use, decontamination, maintenance, storage, and disposal practices applicable to the industrial operation (EPA, 1997). The effectiveness of PPE are analyzed separately from this ESD. Therefore, the conservative, screening-level occupational exposure estimates presented do not account for PPE. Actual occupational exposure may be significantly less than the estimates presented in this ESD.

5.2 Number of Workers Exposed Per Site and Days per Year of Exposure

103. ETAD estimated that there would be one worker exposed during weighing and one worker during dyeing and disposal (ETAD, 2011). The Textile Dye Weighing Monitoring Study (TDWMS) revealed that on average 1 to 2 workers are exposed per shift, over typically 3 shifts per day (EPA, 1990). A search of recent PMN submissions revealed company estimates of between 1 to 6 workers. EPA recommends estimating between 3 to 6 workers exposed per day, with 1 to 2 workers exposed during dye weighing, 1 to 2 workers exposed during container cleaning, and 1 to 2 exposed during dyeing and disposal. As discussed in Section 3.2, EPA recommends assuming 157 operating days per year. The reader should note that 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 fulltime employment and considers an individual worker's vacation, sick, and weekend time (i.e., a 40-hour work week over 50 weeks per year).

5.3 Exposure from Unloading and Transferring Dye Product (Exposure A)

104. Workers may connect transfer lines or manually unload chemicals from transport containers into dyeing equipment or storage. If the concentration of the chemical in the dye formulation (F_{chem_dye}) is unknown, default concentrations may be assumed as a conservative default, as previously discussed in Section 3.3. As stated in Section 5.2, EPA recommends assuming between 1 to 2 workers exposed per site-day for this activity.

5.3.1 Inhalation Exposure

5.3.1.1 Liquids

105. Inhalation exposure is expected to be negligible for non-volatile chemicals (VP < 0.001 torr).

5.3.1.2 Solids:

106. The transfer of solid dye product from containers to storage or the dyeing equipment generates particulates. The degree of inhalation exposure to particulates depends on the concentration of the chemical of interest in the dye (F_{chem_dye}), the potential concentration of the dye in the worker's breathing zone ($C_{particulate}$), and the total amount of dye formulation the worker is exposed to per day in performing this activity ($Q_{dye_formulation_day}$).

107. Two equations can be used to determine worker exposure. Selection of the appropriate equation should be based on the amount of dye formulation the worker is exposed to per day ($Q_{dye_formulation_day}$), not the amount of chemical of interest the worker is exposed to ($Q_{chem_site_day}$). Additional explanation of the two standard EPA models used to estimate inhalation exposure to solid powder is presented in Appendix B.

108. If the transfer rate of the solid dye formulation containing the chemical of interest $(Q_{dye_{formulation_{day}}})$ is *greater than* 54 kg/site-day, EPA recommends using the OSHA Total Particulates Not Otherwise Regulated (PNOR) PEL-Limiting Model:

$$EXP_{inhalation} = C_{particulate} \times RATE_{breathing} \times TIME_{exposure} \times F_{chem}$$
(5-1a)

109. This exposure will occur over TIME_{operating_days}, up to 250 days/year.

Where:

EXP _{inhalation}	=	Inhalation exposure to the chemical of interest per day (mg chemical of interest/day)
C _{particulate}	=	Concentration of particulate dye product 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 _{breathing}	=	Typical worker breathing rate (Default: 1.25 m ³ /hr (EPA, 1991))
TIME _{exposure}	=	Duration of exposure (Default: 8 hrs/day; Note: because the default value for $C_{particulate}$ is an 8-hr TWA*, the 8 hrs/day value must be used)
F_{chem_dye}	=	Mass fraction of the chemical of interest in the dye product (mg chemical/mg dye product) (See Section 3.3)

*TWA = Time-weighted average

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

111. If the transfer rate of the solid powder dye containing the chemical of interest ($Q_{dye_formulation_day}$) is *less than or equal to* 54 kg/site-day, EPA recommends using the EPA/OPPT Small Volume Solids Handling Inhalation Model. This model was derived from the 1990 study of textile dye weighing operations (TDWMS), which conducted exposure monitoring for dye weighing rooms at 24 textiles wet processing plants. The study was intended to estimate the distribution of dye concentrations in the dye weigher's breathing zone. The typical weight fraction of the total particulate in the dye product component in the worker's breathing zone was calculated based on the arithmetic mean of the data collected (0.0477 mg exposure/kg dye). The worst case scenario was based on the point where there was 95% confidence that no more than 10% of the data were greater than the value (EPA, 1990). These values are used in the following equation:

$$EXP_{inhalation} = Q_{dye_{formultion_{day}}} \times F_{chem_{dye}} \times F_{exposure}$$
(5-1b)

112. This exposure will occur over TIME_{operating_days}, up to 250 days/year.

EXP _{inhalation}	=	Inhalation exposure to the chemical of interest per day (mg chemical of interest/day)
$Q_{dye_formulation_day}$	=	Daily amount of dye formulation transferred into the process (kg dye/site-day) (See Section 3.4)
F_{chem_dye}	=	Mass fraction of the chemical of interest in the dye formulation (mg chemical/mg dye formulation) (See Section 3.3)

 $F_{exposure}$ = Weight fraction of the total particulate dye product component in the workers breathing zone (Default: 0.0477 (typical) to 0.161 (worst) mg component exposure/kg of dye handled (EPA, 1992))

5.3.2 Dermal Exposure:

113. 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 liquid chemicals from transport containers to mixing vessels. Workers may manually scoop or pour solid or liquid dye product chemicals into the process equipment.

114. For a liquid dye formulation the EPA recommends the *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* to estimate dermal exposure to the chemical of interest. For solid dye formulation, EPA recommends the *EPA/OPPT Direct 2-Hand Dermal Contact with Solids Model* 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. Both models are discussed below.

5.3.2.1 Liquid

115. To estimate the potential worker exposure to the chemical of interest in a liquid dye product for this activity, EPA recommends the *EPA/OPPT 2-Hand Dermal Contact with Liquid Model*:

$$EXP_{dermal} = Q_{liquid skin} \times AREA_{surface} \times N_{exp incident} \times F_{chem dye}$$
(5-2a)

116. This exposure will occur over TIME_{operating_days} up to 250 days per year.

EXP _{dermal}	=	Potential dermal exposure to the chemical of interest per day (mg
		chemical/day)
$Q_{liquid_{skin}}$	=	Quantity of liquid dye product 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 (EPA, 2000))
AREA _{surface}	=	Surface area of contact (Default: 1070 cm ² for 2 hands (EPA,
		2013))
$N_{exp_{incident}}^{6}$	=	Number of exposure incidents per day (Default: 1 incident/day)
F _{chem_dye}	=	Mass fraction of the chemical of interest in the dye formulation
- •		(mg chemical/mg dye formulation) (See Section 3.3)

⁶Only one contact per day (N_{exp_incident} = 1 event/worker-day) is assumed because Q_{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 (e.g., 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.

5.3.2.2 Solids

117. To estimate the potential worker exposure to the chemical of interest in a solid dye product for this activity, EPA recommends *the EPA/OPPT Direct 2-Hand Dermal Contact with Solids Model*:

$$EXP_{dermal} = up \text{ to } 3,100 \text{ mg component/incident} \times N_{exp \text{ incident}} \times F_{chem dtye}$$
(5-2b)

118. This exposure will occur over TIME_{operating_days} up to 250 days per year.

Where:

EXP _{dermal}	=	Potential dermal exposure to the chemical of interest per day (mg chemical/day)
$N_{exp_incident}$	=	Number of exposure incidents per day (Default: 1 incident/day) (see Equation 5-2a)
F_{chem_dye}	=	Mass fraction of the chemical of interest in the dye product (mg chemical/mg dye product) (See Section 3.3)

5.4 Exposure During Transport Container Cleaning (Exposure B)

119. Workers may be exposed while rinsing containers used to transport textile dyes. If the concentration of the chemical in the component (F_{chem}) is unknown, 75% percent concentration for powder dyes and 25% for liquid dyes may be assumed as a conservative default, as previously discussed in Section 3.3. As stated in Section 5.2, EPA recommends assuming between 1 to 2 workers exposed per site-day for this activity.

5.4.1 Inhalation Exposure:

5.4.1.1 Liquids

120. Inhalation exposure is expected to be negligible for non-volatile chemicals (VP < 0.001 torr).

5.4.1.2 Solids

Where:

121. The cleaning of solid powders from transport containers may generate dust particulates. The degree of inhalation exposure to particulates depends on the concentration of the chemical of interest in the dye (F_{chem_dye}), the potential concentration of the dye in the worker's breathing zone ($C_{particulate}$), and the total amount of dye formulation residual removed from the containers ($Q_{dye_formulation_residue}$). The following equation may be used to estimate the amount of dye formulation residual handled by a worker during container cleaning:

$$Q_{dye_formulation_residue} = \frac{Elocal_{container_residue_disp}}{F_{chem_dye}}$$
(5-3)

$$Q_{dye_formulation_residue} = Quantity of dye formulation handled during container cleaning (kg dye formulation/site-day)$$
Elocal_{container_residue_disp} = Daily release of chemical of interest from container residue (kg chemical of interest/site-day; see Section 4.3)

 F_{chem_dye} = Weight fraction of the chemical of interest in the dye formulation (Defaults: *solid*: 0.75 kg chemical/kg dye formulation; *liquid*: 0.25 kg chemical/kg dye formulation; See Section 3.3)

122. Two equations can be used to determine worker exposure. Selection of the appropriate equation (Equation 5-4a or Equation 5-4b) should be based on the amount of dye formulation residue the worker is exposed to per day ($Q_{dye_formulation_residue}$), not the amount of chemical of interest disposed from container cleaning per day (Elocal_{container_residue_disp}). A further explanation, including the background and model defaults, of the two standard EPA/OPPT models used to estimate inhalation exposure to solid powder is presented in Appendix B.

123. If the quantity of solid dye formulation residue containing the chemical of interest handled per day ($Q_{dye_formulation_residue}$) is *greater than* 54 kg/site-day, EPA recommends using the OSHA Total Particulates Not Otherwise Regulated (PNOR) PEL-Limiting Model:

$$EXP_{inhalation} = C_{particulat} \times RATE_{breathing} \times TIME_{exposure} \times F_{chem}$$
(5-4a)

124. This exposure will occur over [the lesser of $N_{container_unload_site_yr}$ or TIME_{operating_days} (consistent with Section 4.3), up to 250] days/year.

Where:

$\mathrm{EXP}_{\mathrm{inhalation}}$	=	Inhalation exposure to the chemical of interest per day (mg chemical of interest/day)
Cparticulate	=	Concentration of particulate dye product 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 _{breathing}	=	Typical worker breathing rate (Default: 1.25 m ³ /hr (EPA, 1991))
TIME _{exposure}	=	Duration of exposure (Default: 8 hrs/day; Note: because the default value for $C_{particulate}$ is an 8-hr TWA*, the 8 hrs/day value <u>must</u> be used)
F_{chem_dye}	=	Mass fraction of the chemical of interest in the dye product (mg chemical/mg dye product) (See Section 3.3)

*TWA = Time-weighted average

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

126. If the quantity of the solid powder dye formulation residue containing the chemical of interest $(Q_{dye_formulation_residue})$ is *less than or equal to* 54 kg/site-day, EPA recommends using the EPA/OPPT Small Volume Solids Handling Inhalation Model:

$$EXP_{inhalation} = Q_{dye_{formultion_{residue}}} \times F_{chem_{dye}} \times F_{exposure}$$
(5-4b)

127. This exposure will occur over [the lesser of $N_{container_unload_site_yr}$ or TIME_{operating_days} (consistent with Section 4.3), up to 250] days/year.

Where:

EXP _{inhalation}	=	Inhalation exposure to the chemical of interest per day (mg
0		chemical of interest/day)
$Q_{dye_formulation_residue}$	=	Daily amount of dye formulation transferred into the process (kg dya(aita day) (Saa Saation 3.4)
F _{chem dye}	_	dye/site-day) (See Section 3.4) Mass fraction of the chemical of interest in the dye formulation
Chem_dye	_	(kg chemical/kg dye formulation) (See Section 3.3)
F _{exposure}	=	Weight fraction of the total particulate dye product component in
		the workers breathing zone (Default: 0.0477 (typical) to 0.161
		(worst) mg component exposure/kg of dye handled (EPA, 1992))

5.4.2 Dermal Exposure:

128. 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 liquid chemicals from transport containers to mixing vessels. Workers may manually scoop or pour solid or liquid dye product chemicals into the process equipment.

129. For a liquid dye formulation the EPA recommends the *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* to estimate dermal exposure to the chemical of interest. For solid dye formulation, EPA recommends the *EPA/OPPT Direct 2-Hand Dermal Contact with Solids Model* 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. Both models are discussed below.

5.4.2.1 Liquids

130. To estimate the potential worker exposure to the chemical of interest in a liquid dye product for this activity, EPA recommends using the following equation:

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

131. This exposure will occur over [the lesser of $N_{container_unload_site_yr}$ or TIME_{operating_days} (consistent with Section 4.3), up to 250] days/year.

Where:

EXP _{dermal}	=	Potential dermal exposure to the chemical of interest per day (mg chemical/day)
Q_{liquid_skin}	=	Quantity of liquid dye product 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 (EPA, 2000))
AREA _{surface}	=	Surface area of contact (Default: 1070 cm ² for 2 hands (EPA, 2013))
$N_{exp_incident}^{7}$	=	Number of exposure incidents per day (Default: 1 incident/day)

⁷Only one contact per day ($N_{exp_incident} = 1$ event/worker-day) is assumed because Q_{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

F _{chem_dye}	=	Mass fraction of the chemical of interest in the dye formulation
		(mg chemical/mg dye formulation) (See Section 3.3)

5.4.2.2 Solids:

132. To estimate the potential worker exposure to the chemical of interest in a solid dye product for this activity, EPA recommends using the following equation (EPA, 2000):

$$EXP_{dermal} = up \text{ to } 3,100 \text{ mg component/incident} \times N_{exp_{incident}} \times F_{chem_{dtye}}$$
(5-5b)

133. This exposure will occur over [the lesser of $N_{container_unload_site_yr}$ or TIME_{operating_days} (consistent with Section 4.3), up to 250] days/year.

Where:

EXP _{dermal}	=	Potential dermal exposure to the chemical of interest per day (mg
		chemical/day)
$N_{exp_incident}$	=	Number of exposure incidents per day (Default: 1 incident/day)
		(see Equation 5-5a)
F _{chem_dye}	=	Mass fraction of the chemical of interest in the dye product (mg
		chemical/mg dye product) (See Section 3.3)

5.5 Exposure from Machine Operation (Exposure C)

134. Workers may be exposed to the chemical of interest in the liquid dyebath during removal of dyed goods after batch processes or during handling of dyed rolls of material. The concentration of the chemical in the dyebath was discussed previously in Section 3.8. As stated in Section 5.2, EPA recommends assuming between 1 to 2 workers exposed per site-day for this activity.

5.5.1 Inhalation Exposure:

135. Inhalation exposure is expected to be negligible for non-volatile chemicals (VP < 0.001 torr).

5.5.2 Dermal Exposure:

136. 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 is further explained in Appendix B.

137. To estimate the potential worker exposure to the chemical of interest in a liquid dye product for this activity, EPA recommends using the following equation:

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

This exposure will occur over TIME_{operating_days} up to 250 days per year.

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.

EXP _{dermal}	=	Potential dermal exposure to the chemical of interest per day (mg chemical/day)
Q_{liquid_skin}	=	Quantity of liquid dye product component remaining on skin (Default: 0.7 mg component/cm ² -incident (low-end) for routine or incidental contact (EPA, 2000))
AREA _{surface}	=	Surface area of contact (Default: 1070 cm^2 for 2 hands (EPA, 2013))
$N_{exp_incident}^{8}$	=	Number of exposure incidents per day (Default: 1 incident/day)
$F_{chem_dyebath}$	=	Mass fraction of the chemical of interest in the dyebath (mg chemical/mg dye formulation) (See Section 3.8)

⁸Only one contact per day ($N_{exp_incident} = 1$ event/worker-day) is assumed because Q_{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.

6 SAMPLE CALCULATIONS

138. 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 present in a liquid component of an dye product that is spray applied onto a substrate. The default values used in these calculations are presented in Sections 3 through 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_{chem_yr}) is 10,000 kg chemical/yr.
- 2. Chemical of interest is part of a solid dye formulation at an unknown percentage.
- 3. Chemical of interest is a reactive dye with an unknown fixation rate.
- 4. Dyeing application process and textile type is unknown.

6.1 General Facility Information for Application of Dye Products

6.1.1 Days of Operation (TIME_{operating_days})

139. If specific information is not available to estimate the days of operation using the chemical of interest (TIME_{operating_days}) at a textile dyeing manufacturing site, a default value of 157 days per year should be assumed.

6.1.2 Mass Fraction of the Chemical of Interest in the Dye Formulation (F_{chem_dye})

140. The mass fraction (F_{chem_dye}) of the solid chemical in the dye formulation is unknown; therefore a default value of 0.75 is assumed.

 F_{chem_dye} = Mass fraction of the chemical of interest in the dye formulation (Defaults: *solid*: 0.75 kg chemical/kg dye formulation; *liquid*: 0.25 kg chemical/kg dye formulation)

6.1.3 Daily Use Rate of Dye Formulation (Q_{dye_formulation_day})

141. The daily dye formulation use rate is not specified; therefore the default fabric use rate and mass fractions result in a dye use rate of 136.5 kg/day for powder dye formulations.

$$Q_{dye_{formultion_{day}}} = V_{fabric} \times F_{fabric} \times F_{dye_{fabric}}$$
(3-1)

_ 9,100	kg textile pr	1000000000000000000000000000000000000
_	site – day	kg textile processed kg textile dyed
_ 136.5	kg dy e form	lation
_	site – day	
$Q_{dye_formulation_day}$	=	Daily use rate of the dye formulations (kg dye formulation /site-
		day)
V_{fabric}	=	Amount of textile dyed per site-day (default = 9,100 kg fabric processed /site-day)
F_{fabric}	=	Mass fraction of textile treated with the dyestuff (default = 0.3 kg
		textile dyed/kg textile processed)
F_{dye_fabric}	=	Mass fraction of dye used per textile dyed (defaults: powder dyes $= 0.05$ kg dye formulation/kg textile dyed; liquid dyes $= 0.10$ kg dye formulation/kg textile dyed)

Daily Use Rate of Chemical of Interest ($Q_{chem_site_day}$) 6.1.4

The daily use rate of the chemical of interest during textile dyeing can be estimated using 142. Equation 3-1:

$$Q_{\text{chem}_{\text{site}_{\text{day}}}} = Q_{\text{dye}_{\text{formultion}_{\text{day}}}} \times F_{\text{chem}_{\text{dye}}} \times F_{\text{dye}}$$
(3-2)

$$Q_{\text{chem}_{\text{site}_{\text{day}}}} = \frac{136.5 \text{ kg dye formulation}}{\text{site} - \text{day}} \times 0.75 \times 1 = \frac{102.4 \text{ kg chemical}}{\text{site} - \text{day}}$$

Where:

$Q_{chem_site_day}$	=	Daily use rate of the chemical of interest contained in the dye
		formulation (kg chemical used/site-day)
$Q_{dye_formulation_day}$	=	Daily use rate of the dye formulation (kg dye formulation /site-
		day) (see Section 6.1.3)
F _{chem_dye}	=	Mass fraction of the chemical of interest in the dye formulation
		(see Section 6.1.2)
F _{dye}		Mass fraction of the dye formulation containing the chemical interest per the amount of dye formulation used (Default = 1).

6.1.5 Number of Sites (N_{sites})

The number of textile dyeing facilities using the chemical of interest (N_{sites}) can be estimated 143. using Equation 3-2:

$$N_{sites} = \frac{Q_{chem_yr}}{Q_{chem_site_day} \times TIME_{operating_days}}$$
(3-3)

$$N_{\text{sites}} = \frac{10,000 \text{ kg chemical}}{\text{yr}} \times \frac{\text{site - day}}{102.4 \text{ kg chemical}} \times \frac{\text{yr}}{148 \text{ days}} = 0.62 \text{ site} = 1 \text{ site}$$
$$= \qquad \text{Number of sites using the precursor chemical (sites)}$$
$$= \qquad \text{Annual production volume of chemical of interest (kg)}$$

144. Because the number of sites is rounded to 1, Equation 3-3 is rearranged and the number of use days is back-calculated using the number of sites:

$$TIME_{operating_days} = \frac{Q_{chem_yr}}{N_{sites} \times Q_{chem_site_day}}$$
$$TIME_{operating_days} = \frac{10,000 \text{ kg chemical/yr}}{1 \text{ site} \times 102.4 \text{ kg}} = 97.7 \text{ days} = 98 \text{ days}$$

6.1.6 Number of Transport Containers Unloaded per Site (N_{container_unload_site_yr})

145. The number of transport containers unloaded annually per site can be estimated based on the daily chemical use rate, container size, operating days, container volume, and the concentration of the dye formulation. Because the transport container size is unknown, 35-gallon drums were chosen as default:

$N_{container_unload_site_yr}$		$\underline{A}_{day} \times TIME_{operating}$ $V_{container} \times RHO_{form}$						
$=\frac{102.4 \text{ kg chemical}}{\text{site - day}}$	$\times \frac{98 \mathrm{day}\mathrm{s}}{\mathrm{yr}} \times$	$\frac{1 \text{ kg formulatio n}}{0.75 \text{ kg chemical}}$	$\times \frac{\text{container}}{132.5 \text{ L}}$	$\times \frac{L}{1 \text{ kg form}}$	ulation		(3-4	4)
$=101 \frac{\text{container}}{\text{site - yr}}$								
ntainer_unload_site_yr	= Nun	nber of transport	containers	unloaded	at each	site	per :	yea

Where:

$N_{container_unload_site_yr}$	=	Number of transport containers unloaded at each site per year
		(containers/site-yr)
$Q_{chem_site_day}$	=	Daily use rate of chemical per site (kg chemical/site-yr)
TIME _{operating_days}	=	Number of operating days (days/yr)
F _{chem_dye}	=	Mass fraction of the chemical of interest in the dye formulation
		(kg chemical/kg dye formulation) (See Section 6.1.2)
V _{container}	=	Volume of transport container (Default: 35 gallon drum = 132.5
		L)
RHO _{formulation}	=	Density of chemical formulation (assumed 1 kg/L for liquids)

6.1.7 Mass Fraction of Chemical of Interest in the Dye Bath (F_{chem_dyebath})

146. Because the concentration of dye formulation in the dyebath is unknown, the default values are used:

$$F_{\text{chem}_{dyebth}} = F_{\text{chem}_{dye}} \times F_{dye_{dyebth}}$$

$$= 0.75 \times 0.06 = 0.045$$
(3-5)

$F_{chem_dyebath}$	=	Mass fraction of the chemical of interest in the dyebath (%) (kg
F_{chem_dye}	=	chemical/kg dyebath) Mass fraction of the chemical of interest in the dye formulation (kg chemical/kg dye formulation) (See Section 6.1.2)

 $F_{dye_dyebath}$ = Mass fraction of the dye formulation in the dyebath (default: 0.06 kg dye formulation/kg dyebath)

6.2 Environmental Releases

6.2.1 Release to POTW, Air, Incineration or Landfill from Unloading Solid Dye Formulation (Release 1)

147. Release from transfer operations is shown in Equation 4-2, assuming no control technology:

Elocal _{dust_fugitive} = Q_{chem_site_day} × F_{dust_generation} × (1 - F_{dust_control})
=
$$\frac{102.4 \text{ kg chemical}}{\text{site - day}} \times \frac{0.005 \text{ kg released}}{\text{kg handled}} \times (1 - 0)$$

= 0.5 kg/site - day
(4-2)

This release will occur over 98 days/yr at 1 use site.

6.2.2 Release to POTW, Incineration, or Landfill from Container Residue (Release 2)

148. Since the number of containers used per site per year ($N_{container_unload_site_yr}$, Section 6.1.6 is greater than the days of operation (TIME_{operating_days}; Section 6.1.1), the days of release equals the number of days or operation and the daily release is calculated based on the following equation:

$$Elocal_{container_residue_disp} = Q_{chem_site_day} \times F_{container_residue}$$
(4-3b)

$$Elocal_{container_residue_disp} = \frac{102.4kg \ chemical}{site-day} \times 0.03 = \frac{3 \ kg \ chemical}{site-day}$$

This release will occur over 98 days/year from 1 site.

Where:

Elocal _{container_residue_disp}	=	Daily release of chemical of interest from container residue (kg
		chemical/site-day)
$Q_{chem_site_day}$	=	Daily use rate of the chemical of interest (kg chemical/site-day)
		(See Section 6.1.4)
F _{container_residue}	=	Fraction of dye formulation remaining in the container as residue
		(Default: 0.03 kg dye formulation remaining/kg shipped for drums
		(EPA, 2002); see Appendix B for defaults used for other container
		types)

6.2.3 Release to POTW from Disposal of Spent Dyebath (Release 3)

149. Because the chemical of interest is a reactive dye with unknown fabric and type of process, the fixation rate was conservatively assumed to be 75%, based on the values provided in Table 1-2.

Elocal _{spent_dy elath} = Q_{chem_site_day} ×
$$(1 - F_{fixation})$$
 (4-4)

$$=\frac{102.4 \text{ kg chemical}}{\text{site - day}} \times (1 - 0.75) = \frac{25.6 \text{ kg chemical}}{\text{site - day}}$$

This release will occur over 98 days/year from 1 site. Where:

Elocal _{spent_dyebath}	=	Daily release of chemical of interest from disposal of spent
. – .		dyebath (kg chemical/site-day)
Q _{chem_site-day}	=	Daily use rate of the chemical of interest (kg chemical/site-day)
		(See Section 6.1.4)
F _{fixation}	=	Fraction of dye product affixed on to textile during dyeing process
		substrate (Default: 0.75; Table 1-2 - lowest typical reactive dye
		fixation rate)

This release will occur over 98 days/year from 1 site.

6.2.4 Equipment Cleaning

150. The daily release of chemical residue in the process equipment is calculated using the following equation:

Elocal _{equipment_cleaning} = Q_{chem_site_day} × F_{equipment_cleaning} (4-5)
=
$$\frac{102.4 \text{ kg chem}}{\text{site} - \text{day}} \times 0.01 = \frac{1 \text{ kg chem}}{\text{site} - \text{day}}$$

This release will occur over 98 days/year from 1 site.

Where:

Elocal _{equipment_cleaning}	=	Daily release of chemical of interest from equipment cleaning (kg		
		chemical/site-day)		
Qchem_site_day	=	Daily use rate of the chemical of interest in the dye product (kg		
		chemical/site-day) (See Section 6.1.4)		
Fequipment_cleaning	=	Fraction of dye product released as residual in process equipment		
		(Default: 0.01 kg product released/kg batch holding capacity		
		(EPA, 1992))		

6.3 Occupational Exposures

6.3.1 Exposure from Unloading and Transferring Dye Product (Exposure A)

6.3.1.1 Inhalation

151. Transfer rate of the solid dye formulation containing the chemical of interest ($Q_{dye_{formulation_{day}}}$) is *greater than* 54 kg/site-day (136.5 kg dye formulation/site-day). EPA recommends using the OSHA Total Particulates Not Otherwise Regulated (PNOR) PEL-Limiting Model:

$$EXP_{inhalation} = C_{particulat} \times RATE_{breathing} \times TIME_{exposure} \times F_{chem_dye}$$
(5-1a)
= $15 \frac{component}{m^3} \times 1.25 \frac{m^3}{hr} \times 8 \frac{hr}{day} \times 0.75 = 112.5 \text{ mg chemical/day}$

This exposure will occur over 98 days/year.

Where:

EXP _{inhalation}	=	Inhalation exposure to the chemical of interest per day (mg chemical of interest/day)
C _{particulate}	=	Concentration of particulate dye product 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 _{breathing}	=	Typical worker breathing rate (Default: 1.25 m ³ /hr (EPA, 1991))
TIME _{exposure}	=	Duration of exposure (Default: 8 hrs/day; Note: because the default value for $C_{particulate}$ is an 8-hr TWA*, the 8 hrs/day value <u>must</u> be used)
F_{chem_dye}	=	Mass fraction of the chemical of interest in the dye product (mg chemical/mg dye product) (See Section 6.1.2)

*TWA = Time-weighted average

6.3.1.2 Dermal

$$\begin{split} & EXP_{dermal} = up \text{ to } 3,100 \text{ mg componenti/hcident} \times N_{exp_incident} \times F_{chem_dy\varepsilon} \end{split} \tag{5-2b} \\ & = <3,100 \text{ mg component / incident } \times 1 \times 0.75 = <2,325 \text{ mg/day} \end{split}$$

Where:

EXP _{dermal}	=	Potential dermal exposure to the chemical of interest per day (mg chemical/day)
$N_{exp_incident}$	=	Number of exposure incidents per day (Default: 1 incident/day) (see Equation 5-2a)
F_{chem_dye}	=	Mass fraction of the chemical of interest in the dye product (mg chemical/mg dye product) (See Section 6.1.2)

6.3.2 Exposure During Transport Container Cleaning (Exposure B)

6.3.2.1 Inhalation:

$Q_{dye_formultion_residue} = -$	Elocal _{container_residue_dsp} F _{chem_dye}	(5-3)
$=\frac{3\frac{\text{kg chemical}}{\text{site-day}}}{0.75\frac{\text{kg chemical}}{\text{kg dye formulat}}}$		

$Q_{dye_formulation_residue}$	=	Quantity of dye formulation handled during container cleaning
		(kg dye formulation/site-day)
$Elocal_{container_residue_disp}$	=	Daily release of chemical of interest from container residue (kg
		chemical of interest/site-day; see Section 4.3)

$$F_{chem_dye}$$
 = Weight fraction of the chemical of interest in the dye formulation
(Defaults: *solid*: 0.75 kg chemical/kg dye formulation; *liquid*: 0.25 kg chemical/kg dye formulation: See Section 3.3)

152. Transfer rate of the solid dye formulation containing the chemical of interest $(Q_{dye_formulation_day})$ is *less than* 54 kg/site-day. EPA recommends using the EPA/OPPT Small Volume Solids Handling Inhalation Model:

$$EXP_{inhalation} = Q_{dye_{formultion_{residue}}} \times F_{chem_{dye}} \times F_{exposure}$$
(5-4b)

$$=4\frac{\text{kg dye formulation}}{\text{site-day}} \times 0.75\frac{\text{kg chemical}}{\text{kg dye formulation}} \times 0.0477 - 0.161\frac{\text{mg exposure}}{\text{kg dye handled}} = 0.11 - 0.49 \,\text{mg chemical/day}$$

This exposure will occur over 98 days/year.

Where:

EXP _{inhalation}	=	Inhalation exposure to the chemical of interest per day (mg
		chemical of interest/day)
$Q_{dye_formulation_residue}$	=	Daily amount of dye formulation transferred into the process (kg
		dye/site-day) (See Section 3.4)
F _{chem_dye}	=	Mass fraction of the chemical of interest in the dye formulation
- •		(kg chemical/kg dye formulation) (See Section 3.3)
F _{exposure}	=	Weight fraction of the total particulate dye product component in
-		the workers breathing zone (Default: 0.0477 (typical) to 0.161
		(worst) mg component exposure/kg of dye handled (EPA, 1992))

6.3.2.2 Dermal:

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

= < 3,100 mg component/incident \times 1 \times 0.75 = < 2,325 mg/day

This exposure will occur over 98 days per year.

Where:

EXP _{dermal}	=	Potential dermal exposure to the chemical of interest per day (mg chemical/day)
$N_{exp_incident}$	=	Number of exposure incidents per day (Default: 1 incident/day) (see Equation 5-5a)
F_{chem_dye}	=	Mass fraction of the chemical of interest in the dye product (mg chemical/mg dye product) (See Section 6.1.2)

6.3.3 Exposure from Dye Machine Operation (Exposure C)

153. To estimate the potential worker exposure to the chemical of interest in a liquid dye product for this activity, EPA recommends using the following equation:

$$EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times N_{exp_incident} \times F_{chem_dyebth}$$
(5-6)
= 0.7 mg component¢m² - incident×1070cm² × 1 incident/day × 0.045 mg chem/mg dye
= 33.7 mg chemical/day

This exposure will occur over 98 days per year.

Where:

EXP _{dermal}	=	Potential dermal exposure to the chemical of interest per day (mg chemical/day)
Q_{liquid_skin}	=	Quantity of liquid dye product component remaining on skin (Default: 0.7 mg component/cm ² -incident (low-end) for routine or incidental contact (EPA, 2000))
AREA _{surface}	=	Surface area of contact (Default: 1070 cm ² for 2 hands (EPA, 2013))
$N_{exp_incident}$	=	Number of exposure incidents per day (Default: 1 incident/day)
F _{chem_dyebath}	=	Mass fraction of the chemical of interest in the dyebath
(Default: 0.04	5 mg che	emical/mg dye formulation; see Section 6.1.7)

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7 DATA GAPS/UNCERTAINTIES AND FUTURE WORK

154. This ESD relies on industry 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.

155. EPA is most interested in obtaining information about the dye products use industry that is characterized as "typical" or "conservative" (e.g. worse case), and is applicable to an industrial use 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.

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

- 1. No updated information was found on the annual or daily chemical dye rates. Industry contacts have indicated that the range of use rates is very wide and it would be very difficult to choose an average or typical use rate. An annual dye use rate for this ESD was estimated using a fabric use rate and dye use rates for the amount of fabric from the 2004 OECD ESD on Textile Finishing (OECD, 2004).
- 2. No specific information was found on the specific types of PPE used in the textiles dyeing process. Information on the specific PPE (materials, specification) and the prevalence of their use would further improve this ESD.
- 3. Industry-specific dermal monitoring data for all operations involving workers manually handling the dye formulations products would enhance the estimates.

8 REFERENCES

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¹ This material includes data or information derived from IHS Products provided to the US Environmental Protection Agency. IHS Products have been provided to the US Environmental Protection Agency for its internal use and in the context of a license agreement. By receiving and accessing this material you agree that IHS is not liable to you or any third party for your use of and/or reliance on the IHS data and information contained in this document, and any such use shall be at your own risk.

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APPENDIX A: ESTIMATION EQUATION SUMMARY AND DEFAULT PARAMETER VALUES

A.1 Summary of Release and Exposure Estimation Equations for Textile Dyeing Sites

Table A-1 summarizes the equations introduced in Sections 3, 4, and 5 of this document. These equations may be used in evaluating releases of and exposures to chemicals used in the textile dyeing process. A description of each input variable and associated default is provided in Table A-2.

Table A-1. Textile Dye Release and Exposure Calculation Summary

General Facility Estimates Daily Use Rate of Dye Formulation (Q_{dye_formulation_day}) $Q_{dye \text{ formultion } day} = V_{fabric} \times F_{fabric} \times F_{dye fabric}$ (Eqn. 3-1) Daily Use Rate of the Chemical of Interest (Q_{chem site day}): $Q_{chem site day} = Q_{dye formulation day} \times F_{chem dye} \times F_{dye}$ (Eqn. 3-2) Number of Sites (N_{sites}) $N_{sites} = \frac{Q_{chem_yr}}{Q_{chem_site_day} \times TIME_{operating_days}}$ (Eqn. 3-3) The value for N_{sites}, calculated using Equation 3-3, should be rounded up to the nearest integer value. TIME_{operating_days} should then be adjusted for the N_{sites} integer value (to avoid errors due to rounding): $\text{TIME}_{\text{operating_days}} = \frac{Q_{\text{chem}_y\text{r}}}{N_{\text{sites}} \times Q_{\text{chem}_s\text{ite}_d\text{ay}}}$ Number of Dye Formulation Containers Emptied per Facility (Ncontainer_unload_site_yr) $N_{container_unload_site_yr} = \frac{Q_{chem_site_day} \times TIME_{operating_days}}{F_{chem} \times V_{container} \times RHO_{form}}$ (Eqn. 3-4) Mass Fraction of Chemical of Interest in the Dye Bath (Fchem_dyebath)

$$F_{\text{chem}_{dyebth}} = F_{\text{chem}_{dye}} \times F_{dye_{dyebth}}$$
(Eqn. 3-5)

Source	Possi ble Medi um	Daily Release Rates (kg/site-day), Elocal (for Given Sources)	
Transfer of Dye Formulatio n (solid powder only)	POT W	Elocal _{dust_fugitive} = $Q_{chem_site_day} \times F_{dust_generation} \times (1 - F_{dust_control})$ (Eqn. 4-2)	
Container Residue	POT W Land Incine ration	If $N_{container_unload_site_yr}$ is fewer than $TIME_{operating_days}$: $Elocal_{container_residue_disp}$ $= V_{container} \times RHO_{formulation} \times F_{chem_dye} \times F_{container_residue} \times N_{container_unload_site}$ 3a) This release will occur over $[N_{container_unload_site_yr}]$ days/year from $[N_{sites}]$ If $N_{container_unload_site_yr}$ is greater than $TIME_{operating_days}$: $Elocal_{container_residue_disp} = Q_{chem_site_day} \times F_{container_residue}$ This release will occur over $[TIME_{operating_days}]$ days/year from $[N_{sites}]$ s	sites. (Eqn. 4-3b)
Disposal of Spent Dyebath	POT W	Elocal _{spent_dyebath} = $Q_{chem_site_day} \times (1 - F_{fixation})$ This release will occur over [TIME _{operating_days}] days/year from [N _{sites}] s	(Eqn. 4-4)
Equipment Cleaning	POT W	$Elocal_{equipment_cleaning} = Q_{chem_site_day} \times F_{equipment_cleaning}$ This release will occur over [TIME_operating_days] days/year from [N_sites] sites.	(Eqn. 4-5)

Table A-2. Environmental Release Calculation Summary

Table A-3. Occupational Exposure Calculation Summary

Occupational Exposure Calculations						
Number of Workers Exposed Per Site:						
1-2 workers per shift, 3 shifts per day = 3-6 total workers (EPA, 1990)						
Exposure During the Transfer of Dye Product:						
Inhalation (solid powders only):						
OSHA PNOR PEL-Limiting Model (greater than 54 kg/site-day)	OSHA PNOR PEL-Limiting Model (greater than 54 kg/site-day)					
$EXP_{inhalation} = C_{particulate} \times RATE_{breathing} \times TIME_{exposure} \times F_{chem}$	(Eqn. 5-1a)					
EPA Small Volume Handling Model (less than or equal to 54 kg/site-day)						
$EXP_{inhalation} = C_{particulae} \times RATE_{breathing} \times TIME_{exposure} \times F_{chem}$	(Eqn. 5-1b)					
This exposure will occur over $\text{TIME}_{\text{operating}_{\text{days}}}$ up to 250 days per	year.					
Dermal (liquid):						
$EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times N_{exp_incident} \times F_{chem_dye}$	(Eqn. 5-2a)					
This exposure will occur over TIME _{operating_days} up to 250 days per <i>Dermal (solid):</i>	year.					
$EXP_{dermal} = up \text{ to 3,100 mg component/incident } \times N_{exp_incident} \times F_{chem_dtye}$	(Eqn. 5-2b)					
This exposure will occur over TIME _{operating_days} up to 250 days per year.						

Occupational Exposure Calculations	
Exposure During Container Cleaning:	
Inhalation (solid powders only):	
Amount of Dye Residual Handled During Container Cleaning $Q_{dye_formultion_residue} = \frac{Elocal_{container_residue_disp}}{F_{chem_dye}}$ 5-3)	(Eqn.
OSHA PNOR PEL-Limiting Model (greater than 54 kg/site-day) $EXP_{inhalation} = C_{particulate} \times RATE_{breathing} \times TIME_{exposure} \times F_{chem}$	(Eqn. 5-4a)
EPA Small Volume Handling Model (less than or equal to 54 kg/site-day) $EXP_{inhalation} = C_{particulat} \times RATE_{breathing} \times TIME_{exposure} \times F_{chem}$ This exposure will occur over TIME _{operating_days} up to 250 days per	(Eqn. 5-4b) year.
Dermal (liquid):	
$EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times N_{exp_incident} \times F_{chem_dye}$	(Eqn. 5-5a)
This exposure will occur over TIME _{operating_days} up to 250 days per <i>Dermal (solid):</i>	year.
$EXP_{dermal} = up \text{ to 3,100 mg component/incident } \times N_{exp_{incident}} \times F_{chem_{dtye}}$	(Eqn. 5-5b)
This exposure will occur over $TIME_{operating_days}$ up to 250 days per	year.
Exposures During Machine Operation:	
Dermal:	
$EXP_{dermal} = Q_{liquid_skin} \times AREA_{surface} \times N_{exp_incident} \times F_{chem_dyebth}$	(Eqn. 5-6)
This exposure will occur over TIME _{operating_days} up to 250 days per	year.

Variable	Variable Description	Default Value	Data Source		
AREA _{surface}	Surface area of contact (cm ²)	1070 (2 hands)	EPA, 2013		
C _{particulate}	Concentration of particulate dye product component in the workers breathing zone (mg component/m3)15Appendix				
$Elocal_{container_residue_disp}$	Daily release of chemical from container residue (kg chemical/site-day)				
$Elocal_{dust_generation}$	Daily release of dust from transfers/unloading (kg/site-day)	Calculated	Section 4.2		
$Elocal_{equipment_cleaning}$	Daily release of chemical of interest from equipment cleaning (kg chemical/site- day)	Calculated	Section 4.5		
$Elocal_{process_disp}$	Daily release of the chemical to the environment, after control technology (kg chemical/site-day) Calculated Section				
$Elocal_{spent_dyebath}$	Daily release of chemical of interest from disposal of spent dyebath (kg chemical/site-day)	Section 4.4			
EXP _{inhalation}	Inhalation exposure to the chemical of interest per day (mg chemical of interest/day)	Calculated	Section 5.3		
EXP _{dermal}	Potential dermal exposure to the chemical of interest per day (mg chemical/day)	Calculated	Section 5.3 & 5.4		
F_{chem_dye}	Mass fraction of the chemical of interest in the dye formulation (kg chemical/kg dye formulation).	solid: 0.75; liquid 0.25	ETAD, 2011		
$F_{chem_dyebath}$	Mass fraction of the chemical of interest in the dyebath (kg chemical/kg dyebath)CalculatedSection 3.8		Section 3.8		
$F_{container_residue}$	Fraction of dye component remaining in the container as residue0.03EPA 2002				
$F_{dust_generation}$	Fraction of chemical lost during transfers/unloading of solid powders0.005EPA, 2007				
$F_{dye_dyebath}$	Mass fraction of the dye formulation in the dyebath (default: 0.06 kg dye formulation/kg dyebath)	0.06	ETAD, 2011		

Table A-4. Parameter Declaration and Documentation Summary

Variable	Variable Description	Default Value	Data Source		
$F_{equipment_cleaning}$	Fraction of dye chemical released as residual in process equipment 0.01		EPA, 1992		
F _{exposure}	Weight fraction of the total particulate dye product component in the workers breathing zone.	0.0477 (typical) 0.161 (worst case)	EPA, 1992		
F _{fixation}	Fraction of dye product affixed on to textile during dyeing process substrate (Default: see)	textile during dyeing process substrate See Table 1-2			
$N_{container_unload_site_yr}$	Number of transport containers unloaded at each site per year (containers/site-yr)	Calculated	Section 3.7		
$N_{exp_incident}$	Number of exposure incidents per day (incident/day)	1	EPA, 2000		
N _{sites}	Number of facilities using the chemical of interest in textile dyeing processes (sites).	Section 3.6			
$Q_{chem_site_day}$	Daily use rate for the chemical of interest at each facility (kg of chemical/site-day).Calculated		Section 3.5		
Q_{chem_yr}	Annual production volume of the chemical of interest for this use (kg chemical/yr) Chemical Specific		Manufacturer		
$Q_{dye_formulation_day}$	Daily use rate for the dye formulation at each facility (kg of dye formulation/site- day).		Section 3.4		
$Q_{dye_formulation_residue}$	Quantity of dye formulation handled during container cleaning (kg of dye formulation/site-day).		Section 5.4		
Q_{liquid_skin}	Quantity of liquid dye product component remaining on skin (mg/cm ² - incident) 0.7 (low end) 2.1 (high end)		EPA, 2000		
RATE _{breathing}	Typical worker breathing rate (m ³ /hr)	1.25	EPA, 1991		
RHO _{form}	Density of the dye formulation (kg/L)	1	EPA assumption		
TIME _{exposure}	Duration of exposure (hr/day)	8	Appendix B		
$TIME_{operating_days}$	Annual number of days the formulation product is applied at each facility (days/yr).	Calculated	Section 3.2		
V _{container}	Volume of transport container (L/container)	132.5	Jasper, 2011		

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: Container Residue Release Models (non-air);
- Section B.3: Process Equipment Residue Release Models (non-air);
- Section B.4: Dust Emissions from Transferring Solids Model;
- Section B.5: Chemical Particle Inhalation Exposure Models; and
- Section B.6: 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, except for the EPA/OPPT Dust Emissions from Solid Transfers Model. 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 Container Residue Release Models (non-air)

B.2.1 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:

	Elocal _{co}	ontainer_res	$_{ m idue_disp} = F_{ m container_residue} imes Q_{ m total_daily_container}$	[B-1]
Where:				
	Elocal _{container_residue_disp}	=	Daily release of the chemical residue to water, incinera	ation, or
			landfill from the cleaning or disposal of empty containers (kg/site-day)	shipping
	Fcontainer_residue	=	Fraction of the amount of the total chemical in the	11 0
			container remaining in the emptied container (dimension	less; see
			Table B-1 for appropriate EPA default values)	
	$Q_{total_daily_container}$	=	Total (daily) quantity of the chemical contained in the	
			containers prior to emptying (kg of chemical/site-day; see	ee Table
			B-2 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-1 and Table B-2. 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 (TIME_{days_container_residue}, days/siteyear) must be appropriately "paired" with the total daily quantity of chemical contained in the containers ($Q_{total_daily_container}$) used in calculating the daily release. Thus, Table B-2 also contains the appropriate EPA default values for TIME_{days_container_residue}.

References:

EPA (1992) "Memorandum: Standard Assumptions for PMN Assessments. From the CEB Quality Panel to CEB Staff and Management", October 1992.

EPA (1988), "Releases During Cleaning of Equipment", July 1988.

Table B-1. Standard EPA Default Values for Use in the Container Residual Release Model
--

Chemical Form	Container Type	V _{cont_empty} (gallons)	Model Title
Liquid	Bottle	1 Banga: <5	EPA/OPPT Small Container Residual Model
	Small	Range: <5	
	Container	Range: 5 to <20	

	Drum	55	EPA/OPPT Drum Residual Model
		Range: 20 to <100	
	Tote	550	EPA/OPPT Bulk Transport Residual Model
		Range: 100 to <1,000	
	Tank Truck	5,000	
		Range: 1,000 to	
		<10,000	
	Rail Car	20,000	
		Range: 10,000 and up	
Solid	Any	Any	EPA/OPPT Solid Residuals in Transport Containers
			Model

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).

Number of Containers Emptied per Day	Q _{total_daily_container} (kg/site-day)	TIME _{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

Table B-2. Standard EPA Methodology for Calculating Default Qtotal_daily_container and TIMEdays_container_residue Values for Use in the Container Residual Models

B.3 Process Equipment Residue Release Models (non-air)

B.3.1 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.

B.3.2 Model Equation

The models discussed in this section utilize the following common equation for calculating the amount of chemical residue:

$$Elocal_{equip_cleaning} = F_{equip_residue} \times Q_{total_chem_capacity}$$
[B-2]

Where:

Elocal _{equip_cleaning}	=	Daily release of the chemical residue to water, incineration, or
		landfill from cleaning of empty process equipment (kg/site-day)
$F_{equip_residue}$	=	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-3 for appropriate EPA
		default values)
Qequip_chem_capacity	=	Total capacity of the process equipment to contain the chemical in
1 1 - 1 5		question, 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 whether the residues are cleaned from a single vessel or from multiple equipment pieces. These default values are

summarized in Table B-3 and Table B-4. 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 (TIME_{days_equip_residue}, days/siteyear) must be appropriately "paired" with the total capacity of the equipment to contain the chemical of interest ($Q_{equip_chem_capacity}$) used in calculating the daily release. Thus, Table B-4 also contains the appropriate EPA default values for TIME_{days_equip_residue}.

References:

- EPA (1992), "Memorandum: Standard Assumptions for PMN Assessments. From the CEB Quality Panel to CEB Staff and Management.", October 1992.
- EPA (1998), "Releases During Cleaning of Equipment", July 1988.

Table B-3. Standard EPA Default Values for Use in the Process Equipment Residual Release Models

Model Title	$\mathbf{F}_{equip_residue}^{a}$
EPA/OPPT Single Process Vessel Residual Model	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)
EPA/OPPT Multiple Process Vessel Residual Model	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).

Process Type	Number of Batches per Day	Q _{equip_chemcapacity} (kg/site-day)	TIME _{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

Table B-4. Standard EPA Methodology for Calculating Default Qequip_chem_capacity and TIMEdays_equip_residue Values for Use in the Process Equipment Residual Models

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 TIME_{days_equip_residue} summarized above in Table B-4. Care should be given in defining the appropriate Q_{total_daily_container} and TIME_{days_container_residue} to be used in either of the standard EPA process equipment residue models.

B.4 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).

B.4.1 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 (PMN) 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-5 provides estimated efficiencies for common control technologies.

	Default Control Technology Capture		Default Media of Release for Controlled
Control Technology	Efficiency (%)	Notes/Source	Release
None (default)	0	No control technology	N/A
		should be assumed as	
		conservative.	
Filter (such as a	99	For particles > 1 um.	Incineration or Land
baghouse)		CEB Engineering	
		Manual.	
Cyclone/Mechanical	80	For particles > 15 um	Incineration or Land
Collectors		CEB Engineering	
		Manual.	
Scrubber	Varies	Consult Table 7-1 of the	Water
	95 may be assumed	CEB Engineering	
		Manual.	

Table B-5. Default Control Technology Efficiencies

B.4.2 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.

$$Elocal_{dust_{fugitive}} = Q_{transferred} \times F_{dust_{generation}} \times (1 - F_{dust_{control}})$$
[B-3]

Where:

Elocal _{dust_fugitive}	=	Daily amount not captured by control technology from transfers
		or unloading (kg/site-day)
Qtransferred	=	Quantity of chemical transferred per day (kg chemical/site-day)
F _{dust_generation}	=	Loss fraction of chemical during transfer/unloading of solid
-0		powders (Default: 0.005 kg released/kg handled)
F _{dust_control}	=	Control technology capture efficiency (kg captured/kg processed)
		(Default: If the control technology is unknown, assume capture
		efficiency = $0 \text{ kg captured/kg processed}$, see Table B-5).

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-5.

$$Elocal_{dust_captured} = Q_{transferred} \times F_{dust_generation} \times F_{dust_control}$$
[B-4]

Where:

Elocal _{dust_captured}	=	Daily amount captured by control technology from transfers or
		unloading (kg/site-day)
Q _{transferred}	=	Quantity of chemical transferred per day (kg chemical/site-day)

$F_{dust_generation}$	=	Loss fraction of chemical during transfer/unloading of solid
_0		powders (Default: 0.005 kg released/kg handled)
$F_{dust_control}$	=	Control technology capture efficiency (kg captured/kg processed)
		(Default: If the control technology is unknown, assume capture
		efficiency = $0 \text{ kg captured/kg processed}$, see Table B-5).

References:

- EPA (2007), "Generic Model to Estimate Dust Releases from Transfer/Unloading Operations of Solid Powders". July 2007.
- EPA (1991), "CEB Manual for the Preparation of Engineering Assessment", Volume 1 (page 4-11). Contract No. 68-D8-0112. February 1991.
- Plinke, Marc A.E., et al. (1995), "Dust Generation from Handling Powders in Industry", American Industrial Hygiene Association Journal. Vol. 56: 251-257, March 1995.

B.5 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 Handing 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.5.1 EPA/OPPT Small Volume Solids Handling Inhalation Model

B.5.1.1 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 (e.g., \leq 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_{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.

B.5.1.2 Model Equation:

The model calculates the inhalation exposure to the airborne particulate chemical using the following equation:

$$EXP_{inhalation} = (Q_{shift_handled} \times N_{shifts}) \times F_{chem} \times F_{exposure}$$
[B-5]

Where:

EXP _{inhalation}	=	Inhalation exposure to the particulate chemical per day (mg chemical/worker-day)
$Q_{\rm shift_handled}$	=	Quantity of the solid/particulate material containing the chemical of interest that is handled by workers each shift (kg/worker-shift; see Table B-6 for appropriate EPA default values; must be ≤ 54 kg/worker-shift for this model to be valid)
${\rm N_{shifts}}^2$	=	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)

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).

²Note 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.

 $F_{exposure}$ = 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-6. Standard EPA Default Values for Q_{daily_handled} in the EPA/OPPT Small Volume Solids Handling

 Inhalation Model

Activity Type	Default Q _{shift_handled} ¹ (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) \times Number of container/worker-shift
Process-Related Activity (equipment cleaning, sampling):	
Continuous process: Batch process (<1 batch per day): Batch process (>1 batch per day):	Daily throughput of material / Number of shifts per day Quantity of material per batch Quantity of material per batch × Number of batches per shift

References:

EPA (1992), "Generic Scenario: Textile Dyeing", October 15, 1992.

EPA (1991) "CEB Manual for the Preparation of Engineering Assessment", Volume 1 (page 4-11). Contract No. 68-D8-0112. February 1991.

EPA (1990) "Textile Dye Weighing Monitoring Study", EPA 560/5-90-009. April 1990.

B.5.2 OSHA Total PNOR PEL-Limiting Model

B.5.2.1 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-shift¹. As stated in Section B.5.1, the Small Volume

¹The 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_{daily_handled}.

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-6 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 timeweighted 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.

B.5.2.2 Model Equations:

The model first calculates the mass concentration of the airborne particulate chemical using the following equation:

$$C_{chem_mass} = C_{total_mass} \times F_{chem}$$
[B-6]

Where:

C _{chem_mass}	=	Mass concentration of the chemical in air (mg/m ³)
C_{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)

The OSHA Total PNOR PEL-Limiting Model then uses the mass airborne concentration of the chemical (C_{mass_chem}) in Equation B-6, to calculate the inhalation exposure to the particulate chemical using the following equation:

		$EXP_{inhalation} =$	$C_{chem_mass} \times RATE_{breathing} \times TIME_{exposure}$	[B-7]
Where:				
	$\mathrm{EXP}_{\mathrm{inhalation}}$	=	Inhalation exposure to the airborne particulate chemical	per day
	~		(mg chemical/worker-day)	. 3
	C _{chem_mass}	=	Mass concentration of the particulate chemical in air (mg	g/m ³ ; see
			Equation B-17)	
	RATE _{breathing}	=	Typical worker breathing rate (EPA default = $1.25 \text{ m}^3/\text{hr}$)	

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).

TIME _{exposure}	=	Duration	of	exposure	for	the	activity	(EPA	default	=	8
-		hours/work	ker-	day^1)							

References:

EPA (1991), "CEB Manual for the Preparation of Engineering Assessment", Volume 1 (Equations 4-1 and 4-11). Contract No. 68-D8-0112. February 1991.

B.6 Dermal Exposure Models

B.6.1 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.

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.

B.6.2 Model Equation:

All of the standard EPA models utilize the following common equation for calculating worker dermal exposures:

$$EXP_{dermal} = AREA_{surface} \times Q_{remain_skin} \times F_{chem} \times N_{event}$$
[B-8]

Where:

EXP _{dermal}	=	Dermal exposure to the liquid or solid chemical per day (mg chemical/worker-day)
AREA _{surface}	=	Surface area of the skin that is in contact with liquid or solid material containing the chemical (cm ² ; see Table B-7 for appropriate EPA default values)
Q_{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-
F _{chem}	=	7 for appropriate EPA default values) Weight fraction of the chemical of interest in the material being handled in the activity (dimensionless; refer to the ESD discussion
N_{event}^{2}	=	for guidance on appropriate default value) Frequency of events for the activity (EPA default = 1 event/worker-day)

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.

²Only one contact per day ($N_{event} = 1$ event/worker-day) is assumed because Q_{remain_skin} , with few exceptions, is not expected to be significantly affected either by wiping excess chemical material from skin or by repeated

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.

For several categories of exposure, EPA uses qualitative assessments to estimate dermal exposure. Table B-8 summarizes these categories and the resulting qualitative dermal exposure assessments.

References:

- EPA (2000), "Options for Revising CEB's Method for Screening-Level Estimates of Dermal Exposure Final Report". June 2000.
- EPA (1991), "CEB Manual for the Preparation of Engineering Assessment, Volume 1", Contract No. 68-D8-0112. February 1991.

contacts with additional chemical material (e.g., 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.

Default Model	Example Activities	AREA _{surface} ^a (cm ²)	Q _{remain_skin} (mg/cm ² - event)	Resulting Contact AREA _{surface} × Q _{remain_skin} (mg/event)
Physical Form: Liquids				
EPA/OPPT 1-Hand Dermal Contact with Liquid Model	Liquid sampling activitiesLadling liquid/bench-scale liquid transfer	420 (1 hand mean)	Low: 0.7 High: 2.1	Low: 290 High: 880
EPA/OPPT 2-Hand Dermal Contact with Liquid Model	 Maintenance Manual cleaning of equipment and containers Filling drum with liquid Connecting transfer line 	1070 (2 hand mean)	Low: 0.7 High: 2.1	Low: 590 High: 1,800
EPA/OPPT 2-Hand Dermal Immersion in Liquid Model	Handling wet surfacesSpray painting	1070 (2 hand mean)	Low: 1.3 High: 10.3	Low: 1,100 High: 8,650
Physical Form: Solids EPA/OPPT 2-Hand Dermal Contact with Container Surfaces Model	• Handling bags of solid materials (closed or empty)	No defaults	No defaults	< 1,100 ^c
EPA/OPPT 2-Hand Dermal Contact with Solids Model	 Solid sampling activities Filling/dumping containers of powders, flakes, granules Weighing powder/scooping/mixing (e.g., 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

Table B-7. Standard EPA Default Values for Use in the Worker Dermal Exposure Models

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: 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.

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Table B-8. 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: 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.