Manufacture and Use of Paper Dyes-
Generic Scenario for Estimating Occupational Exposures and Environmental Releases
-Draft-

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TABLE OF CONTENTS

Page

LIST OF TABLES

Page

LIST OF FIGURES

Page

The purpose of this report is to develop a standardized approach that EPA's chemical engineering branch (CEB) can use to estimate potential occupational exposures and environmental releases from the manufacture, processing, and use of paper dyes. These estimation techniques may be used by CEB to evaluate future paper dye premanufacture notices (PMNs) and existing paper dyes. The document also presents an industry profile, a discussion of typical processes in the industry, including release and exposure points, control technologies, and worker personal protective equipment that is typically used (when applicable); and source reduction, pollution prevention, and material substitution alternatives (when applicable).

Information and data used to develop the estimation procedures were obtained from a review of the reference materials listed in Section 8.0. Based on this review, reasonable worst-case release and exposure estimations can be made using the methodology and calculations that are described in detail in Section 4.0. These calculations are summarized in the following tables:

Table 1

Release and Exposure Calculations for Processing of Chemical Substances Into Paper Dyes

General Facility Estimates

Number of Sites (NS):

$$NS = \frac{PV}{AU}$$

where,

Annual Use Rate (AU) (kg/site-yr):

$$AU = APR_d \times Y_{dye}$$

and,

$$APR_d = \frac{AP_d}{NS_d}$$

Daily Use Rate (DU) (kg/site-day):

$$DU = \frac{AU}{OD}$$

Operating Days per Site-Year (OD) (days/site-yr): 350

Number of Batches per Site-Year (NB_y) (btc/site-yr):

$$NB_y = \frac{PV}{NS \times CB}$$

Table 1 (Continued)

Occupational Exposure Calculations

Days Exposed per Year (ED) (days/yr): 250

Number of Workers Exposed (NW): NW = (30-45 workers/site) × NS

Inhalation Potential Dose Rate (I) (mg/day):

Unloading:

Solid Chemical Substance:

Assume Daily Use Rate > 54 kg/site-day, use OSHA PEL for nuisance dust:

$$I = C_m \times b \times h$$

where,

$$C_m = C_k \times Y_{cs}$$

Liquid Chemical Substance:

Negligible (VP <0.001 torr)

Packaging:

Solid Dye:

Assume Daily Production Rate of Dye > 54 kg/site-day and use the OSHA PEL for nuisance dust:

$$I = C_m \times b \times h$$

where,

$$C_m = C_k \times Y_{dye}$$

Table 1 (Continued)

Liquid Dye: Negligible (VP < 0.001 torr)

Dermal Exposure Dose Rate (D_{exp}) (mg/day):

Unloading:

Solid Chemical Substance: $D_{exp} = Y_{cs} \times 3{,}100$ mg/day over ED days/yr

Liquid Chemical Substance: $D_{exp} = Y_{cs} \times 1{,}800$ mg/day over ED days/yr

Packaging and Equipment Cleaning:

Powder Dye: $D_{exp} = Y_{dye} \times 3{,}100$ mg/day over ED days/yr

Liquid Dye: $D_{exp} = Y_{dye} \times 1{,}800$ mg/day over ED days/yr

Release Calculations	
Medium	
Water	Daily Release Rate (DR_w) (kg/site-day): $$DR_w = \frac{PV \times LF_w}{NS \times OD}$$
Air	Daily Air Releases (DR_a) (kg/site-day) : Negligible (VP < 0.01 torr)
Incineration	Annual Release to Incineration (AR_i) (kg/yr): Not expected
Landfill	Annual Landfill Release (AR_l) (kg/yr): $AR_l = PV \times LF_l$

Where:

AP_d = Total Annual Production of Dye (default = 125×10^6 kg/yr)
APR_d = Annual Production Rate of Dye (default = 12.5×10^6 kg/site-yr)
AR_i = Annual Release to Incineration (kg/site-yr)

Table 1 (Continued)

AR_l	=	Annual Release to Land (kg/site-yr)
AU	=	Annual Use Rate of Chemical Substance (kg/site-yr)
b	=	Inhalation Rate (default = 1.25 m^3/hour)
CB	=	Amount of Chemical per Batch (default = 1,891 to 37,830 kg/btc)
C_m	=	Concentration of chemical in air (mg/m^3)
C_k	=	Concentration of Particles (e.g. total dust or mist) in the air (default = 15 mg/m^3)
D_{exp}	=	Dermal Exposure Dose Rate (mg/day)
DR_a	=	Daily Release Rate to Air (kg/site-day)
DR_w	=	Daily Release Rate to Water (kg/site-day)
DU	=	Daily Use Rate of Chemical Substance (kg/site-day)
ED	=	Days Exposed per Year (days/yr)
h	=	Exposure Duration (default = 8 hrs/day)
I	=	Inhalation Potential Dose Rate (mg/day)
LF_l	=	Loss Fraction to Land (default = 2.0%)
LF_w	=	Loss Fraction to Water (default = 2.7%)
NB_y	=	Number of Batches per Site-Year (btc/site-yr)
NS	=	Number of Sites
NS_d	=	Total Number of Dye Manufacturing Sites (default = 10 sites)
NW	=	Total number of workers exposed to the chemical substance
OD	=	Operation Days per Site-Year (default = 350 days/site-yr)
PV	=	Production Volume of Chemical Substance (kg/yr)
Y_{dye}	=	Weight Fraction of the Chemical Substance in the Dye (default = 5-25%)
Y_{cs}	=	Weight Fraction of the Chemical Substance (assume = 100%, unless specified)

Table 2

Release and Exposure Calculations for End Use of Chemical Substances in Paper Dyes

General Facility Estimates

Number of Paper Dyeing Sites (NS_{dye}):

$$NS_{dye} = \frac{PV_{dye}}{AU_{dye}}$$

Production Volume of Dye (PV_{dye}):

$$PV_{dye} = \frac{PV}{Y_{dye}}$$

Annual Use Rate (AU) (kg/site-yr):

$$AU_{dye} = \frac{PV_p \times U_d \times 0.454 \text{ kg/lb}}{NS_p}$$

Daily Use Rate of Dye (kg/site-day) (DU_{dye}):

$$DU_{dye} = \frac{AU_{dye}}{OD}$$

Operating Days per Site-Year (OD) (days/site-yr): 350

Daily Use Rate of Chemical Substance (DU): $DU = DU_{dye} \times Y_{dye}$

Table 2 (Continued)

Occupational Exposure Calculations

Days Exposed per year (ED): 250

Number of Workers Exposed (NW): NW = 12 workers/site × NS

Inhalation Exposure (I) (mg/day):

Powder Dye:

Assume Daily Use Rate of Dye > 54 kg/site-day and use the OSHA PEL for nuisance dust:

$$I = C_m \times b \times h$$

where,

$$C_m = C_k \times Y_{dye}$$

Liquid Dye: Negligible (VP < 0.001 torr)

Dermal Exposure (D_{exp}) (mg/day):

Powder Dye: $D_{exp} = Y_{dye} \times 3{,}100$ mg/day over ED days/yr

Liquid Dye: $D_{exp} = Y_{dye} \times 1{,}800$ mg/day over ED days/yr

Table 2 (Continued)

Release Calculations	
Medium	
Water	Daily Release Rate (DR_w) (kg/site-day): $$DR_w = DU \times (1\text{-}EXH) \times LF_w$$
Air	Total Air Releases (DR_a) (kg/site-day): $$DR_a = DU \times (1\text{-}EXH) \times LF_a$$
Incineration	Total Release to Incineration (AR_i) (kg/yr): Not expected
Landfill	Total Landfill Release (AR_l) (kg/yr): $$AR_l = AU \times (1\text{-}EXH) \times LF_l$$

Where:

AR_i	=	Annual Release Rate to Incineration (kg/yr)
AR_l	=	Annual Release Rate to Land (kg/yr)
AU	=	Annual Use Rate of Chemical Substance (kg/site-yr)
AU_{dye}	=	Annual Use Rate of Dye (kg/site-yr)
b	=	Inhalation Rate (default = 1.25 m^3/hour)
C_m	=	Concentration of Chemical in Air (mg/m3)
C_k	=	Concentration of Particles (e.g. total dust or mist) in the air (default = 15 mg/m3)
D_{exp}	=	Dermal Exposure Dose Rate (mg/day)
DU	=	Daily Use Rate of Chemical Substance (kg/site-day)
DR_w	=	Daily Release Rate to Water (kg/site-day)
DR_a	=	Daily Release Rate to Air (kg/site-day)
ED	=	Days Exposed per Year (days/yr)
EXH	=	Percent Exhaustion onto Paper (default = 90%)
h	=	Exposure Duration (default = 8 hrs/day)
I	=	Inhalation Potential Dose Rate (mg/day)
LF_a	=	Loss Fraction to Air (default = 0.1%)

Table 2 (Continued)

LF_l	=	Loss Fraction to Land (default = 99.8%)
LF_w	=	Loss Fraction to Water (default = 0.1%)
NS_{dye}	=	Number of Paper Dyeing Sites
NS_p	=	Total Number of Paper Manufacturing Sites (default = 555)
NW	=	Total Number of Workers Exposed to the Chemical Substance
OD	=	Operation Days per Site-Year (default = 350 days/site-yr)
PV	=	Production Volume of Chemical Substance (kg/yr)
PV_{dye}	=	Production Volume of Dye (kg/yr)
PV_p	=	Production Volume of Paper (default = 44,679,000 short tons/yr)
U_d	=	Dye Use Rate per Ton of Paper (average = 2 lbs dye/ton paper)
Y_{dye}	=	Weight Fraction of the Chemical Substance in the Dye (default = 5-25%)

GENERIC SCENARIO: PAPER DYES

September, 2000

1.0 INTRODUCTION

1.1 Background

Under section 5 of the Toxic Substances Control Act (TSCA), the U.S. Environmental Protection Agency's (EPA's) Office of Pollution Prevention and Toxics (OPPT) evaluates new chemicals (i.e., those chemicals not listed on the TSCA inventory), for potential risks associated with their stated and potential uses. Existing chemicals may also be evaluated under sections 4 and 6 of TSCA for potential risks associated with their various uses. In these cases, EPA may develop regulatory controls and/or nonregulatory actions to protect human health and the environment from harm resulting from manufacturing, processing, transport, disposal, and current and potential new uses of existing and new chemical substances.

A new chemical, with certain exceptions, is any chemical that is not currently on the TSCA Inventory of Chemicals in commerce. The new chemical review under section 5 of TSCA requires an identification and mitigation of potential risks with the stated and potential uses of the new chemicals. Under section 5 of TSCA, companies are required to submit a Premanufacture Notification (PMN) at least 90 days prior to commercial production (including importation). The Chemical Engineering Branch (CEB) is responsible for preparing the occupational exposure and release assessments of the new chemicals. These assessments are based on information provided by the PMN submitter, information from readily available databases and literature sources, and standard estimating techniques used by CEB.

CEB has developed a number of "generic scenarios" and modeling approaches for quantifying sources and control efficiencies to use in assessing exposures and releases for various industries and unit operations. These generic scenarios contain a compilation of information from readily available sources and from past CEB assessments. They have helped CEB to standardize its assessments.

1.2 Purpose

The purpose of this document is to develop a generic scenario for the manufacturing, processing, and end use of paper dyes. EPA/OPPT frequently receives paper dye PMNs and is seeking to improve its capabilities to assess the risks to human health and the environment for this particular type of application. This generic scenario is a compilation of information related to the assessment of occupational exposures and releases it will serve as an aid to CEB in developing an standardized methodology for evaluating PMNs and existing paper dyes.

1.3 Methodology for Developing Estimation Techniques

The 1994 Manufacture and Use of Paper Dyes Generic Scenario was used as a guideline for this document. Updated data for the paper dyes industry has been included in this version. References listed in the generic scenario were updated with the latest information available.

1.4 Hierarchy for Developing Release and Occupational Exposure Estimates

The goal of this generic scenario is to standardize CEB's approach and methodology to develop accurate release and occupational exposure estimates for paper dyes. Actual data that are available and the need to make assumptions that are required for individual estimations may vary significantly between PMN reviews. Therefore, the following hierarchy in evaluating PMNs has been developed to provide consistent and accurate assessments.

1. Empirical data: Data obtained from the PMN submission or from contacts with the submitter should be considered first. It is assumed that data from testing will result in the most accurate release estimates. However, these data and the release and exposure estimates that result from their use should be compared to typical and historical release estimates.

2. Analogous data: It is possible that a facility may not have conducted testing on the PMN chemical, but did conduct tests on other similar chemicals. It may be appropriate to use results of these tests to estimate releases and exposures. These data and corresponding estimates should also be compared to typical and historical estimates.

3. Generic scenario: In lieu of site-specific testing or analogous data, it may be appropriate to use the methodology described in this generic scenario to develop reasonable worst-case estimates for releases and occupational exposures. The CEB engineer should compare the site-specific information with the assumptions used in the generic scenario and make reasonable adjustments to the methodology based on engineering judgement. The resulting estimates should be compared to historical estimates for consistency.

4. Regulatory limits: If neither site-specific data nor the information needed to develop reasonable estimates using the generic scenario are available, regulatory limits should be considered. It is possible that local, state, or federal agencies may have imposed (or will impose in the future) restrictions on production volumes or PMN concentrations in facility air, or releases. If such limits exist, they may be used as reasonable worst-case estimates.

5. Modeling: Other than the methodologies presented in this generic scenario, CEB has not developed modeling procedures to estimate releases or occupational exposures. If models are developed and verified through testing, CEB may consider adopting the modeling approach.

2.0 INDUSTRY SUMMARY AND BACKGROUND

2.1 Manufacture of Paper Dyes

Dyes are defined as substances that impart color to other materials or mixtures (i.e. substrates) by penetrating into the surface of the substrate (IUR, 1996). Dyes and other chemicals may be added during the paper-making process to give the paper product its desired color and preferred properties. Paper products are usually dyed with acid, basic, or direct dyes. The following is the U.S. consumption of dyes by the paper industry for 1971 (SRI, 1984):

Acid Dye	18.3
Direct Dye	12.5
Basic Dye	3.0
Total	33.8 million pounds

Approximately 3,000 different colorants are available commercially (over 7,000 after combination) and they can take the forms of liquid, powders, press cake, pastes, or dispersions (given all industry uses), (Hobbs, 1988). All paper dyes were in powder form until the 1960's, when liquid dyes began to replace dry dyes (Pulp and Paper, 1981). Liquids are more expensive to ship, but easier to handle, and reduce exposure potential. Twenty companies (33 locations) engage in the manufacture of organic dyes (RCRA, 1992).

2.2 Paper Dyeing

This section will be completed in future versions of the generic scenario.

3.0 PROCESS DESCRIPTION

3.1 Paper Dye Manufacturing

The basic steps involved in the manufacture of dyes for paper applications consist of charging raw materials to the reactor, a subsequent reaction step, product isolation, and drying, grinding, and finishing. Dye manufacture vessels range in size from 500 - 10,000 gal (2 - 40 m^3). Drying can be performed using air or vacuum ovens, rotary driers, spray driers, or drum flakers. Spray driers are the most frequently used (Kirk Othmer, Vol 8).

Organic dyes are manufactured from raw materials of aromatic organic compounds using batch processes. The following steps outline the process for azo dyes which comprise the largest chemical class of organic dyes:

1. Creation of a slurry of raw materials
2. Pre-reaction of raw materials
3. Diazotization reaction
4. Clarification *(not shown on flow diagram)*
5. Coupling reaction
6. Isolation (salt addition)
7. Plate and frame filter press (concentrating) and packaging if sold in wet form
8. Drying (tray or spray)
9. Standardizing
10. Packaging

Figure 3-1 provides a generalized process flow diagram for the manufacture of azo dyes. The production lines may or may not be dedicated to the manufacture of one color.

The first three steps, namely raw material slurrying, pre-reaction of raw materials, and the diazotization reaction, are often carried out in the same reaction vessel. The raw materials, water, ice (for temperature control) and other reaction components are added and the solution is agitated. Filter aids such as diatomaceous earth may be added to the diazotization reactor to remove particulate impurities from the diazonium ion intermediate. The spent filter aids are then collected in a plate and frame filter press and the press cake, called a clarification sludge, is discharged as waste (not shown on diagram). In some cases, additional reaction and clarification steps may be required to achieve the desired substitutions of functional groups.

The diazonium ion is then pumped into the coupling reactor, and the premixed, dissolved coupler is added under pH control. The coupled azo product is then isolated via the addition of a salt solution which decreases the solubility of the product. The isolated product is pumped to a large plate and frame filter press where the dye is concentrated into a presscake (if solid) or filtered (if a liquid). The presscake is transferred to containers and may be either sold in this wet

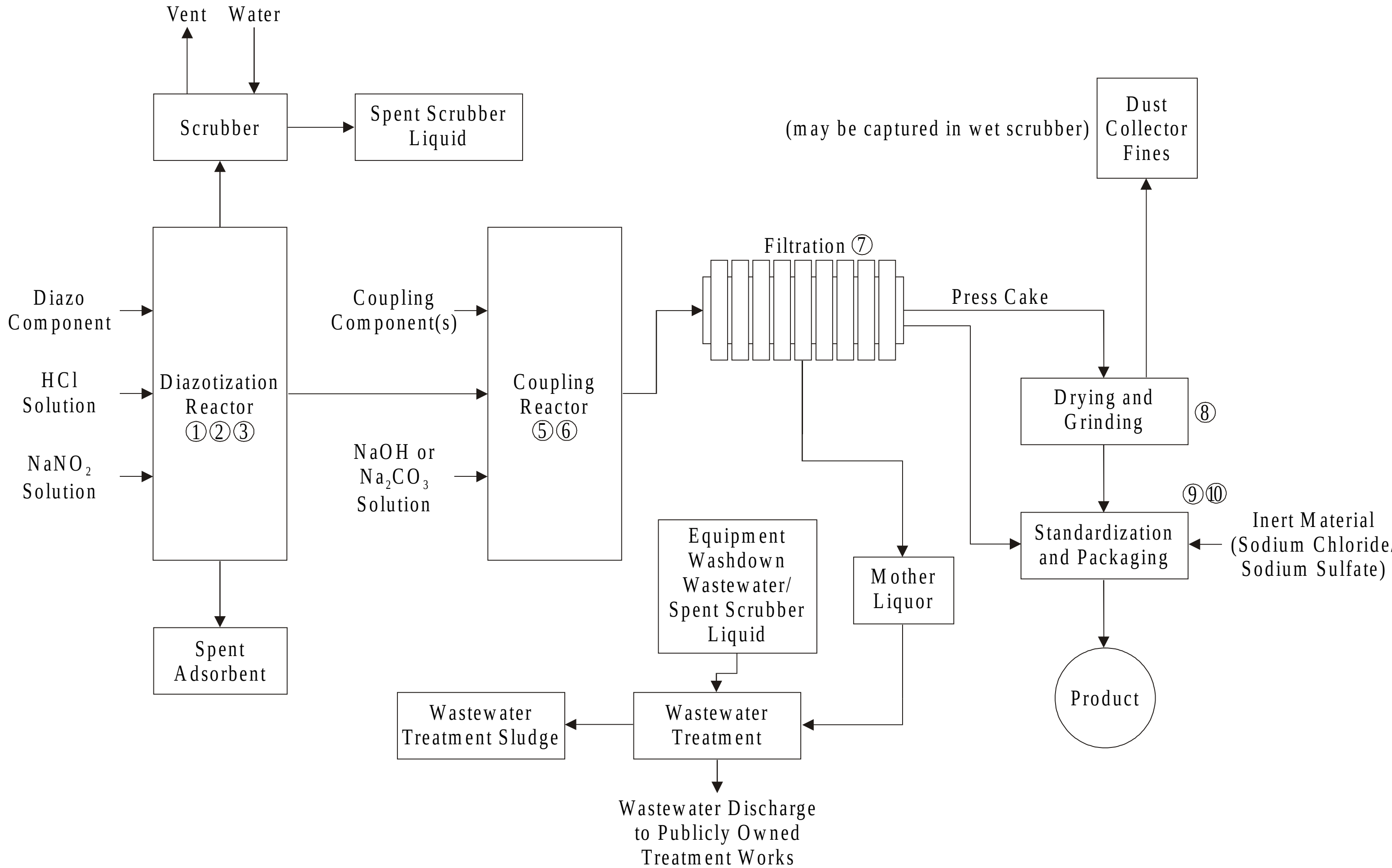

Figure 3-1. Process Flow Diagram for the Manufacture of Azo Dyes

form or further processed. Further processing (for solid dyes) includes drying and grinding into a fine powder. Drying may be performed via tray, conveyor belt, spray, or other drying techniques.

Following these steps, the solid or liquid product is standardized to obtain the desired dye formulation. Following standardization, the new chemical substance or dye chemical becomes less than 100 percent of the salable product. Typical values of a single new chemical substance in the salable product are 5 to 25 percent (CEB, 1991; ETAD, 1993).

The process for chemical classes other than azo dyes are similar to that described above, except that one reaction may take the place of the diazotization and coupling reactions. Isolation using a filter press and/or salt addition is generally used for all dye classes.

3.2 Paper Dye End Use

The basic steps in paper manufacturing include stock (pulp) preparation, sheet forming, pressing, and drying. The first step in the pulp preparation creates an aqueous slurry by beating and refining through mechanical agitation. Next, materials are added to improve brightness, opacity, smoothness, and softness. Additional materials are then added to increase the paper's resistance to penetration by liquids. Two types of continuous sheet forming and drying machines are used: the cylinder machine and the Fourdrinier machine.

Paper fibers are dyed in a batch or continuous process using a water suspension. In batch operations, the dye is added to the beater, pulper or stockchest. Continuous dyeing operations usually occur in modern mills (Kirk Othmer, 1988).

Dye can be added at almost any stage during the papermaking process. However, most paper is stock dyed. In stock dyeing, the paper fiber is dyed before the sheet is formed. Dry dye is added or liquid is metered into the pulper. Metering liquid can be done with automatic equipment.

Continuous dyeing constantly feeds dye solution at the fan pump or head box so the dye pulp goes immediately to the papermaking machine. Most manufacturers combine the two methods (Pulp and Paper, 1981).

4.0 SCREENING LEVEL ESTIMATION TECHNIQUES/METHODS

4.1 Manufacturing

In 1997, there were 37 synthetic organic dye manufacturers in the U.S. (BOC, 1999). In 1974, there were 10 dyestuff manufactures and the annual production volume of dye was 138,000 tons (125 million kg) (Kirk Othmer, Vol 8). By dividing the annual production by the number of dye manufacturers, it can be estimated that 12.5 million kg of dye are manufactured per site (APR_d).

In most cases, the chemical substance is likely to be the dye chemical rather than a raw material used to produce the dye. This assumption is based on the large number of commercial dyes available that are derivations of existing dyes or new combinations of the same raw materials. In some cases, new dyes may be imported for blending with other dyes to produce a new product.

4.1.1 General Facility Estimates

Because the chemical substance is likely to be the dye chemical instead of a raw material used to produce the dye chemical, it is possible that the number of paper dye manufacturing sites will be provided by the submitter. However, if the chemical substance is a raw material used to produce a dye, the following equation can be used to estimate the number of sites.

Number of Sites:

$$NS = \frac{PV}{AU}$$

where,

$$AU = APR_d \times Y_{dye}$$

and,

$$APR_d = \frac{AP_d}{NS_d}$$

Where:

AP_d	=	Total Annual Production of Dye (default = 125×10^6 kg/yr)
APR_d	=	Annual Production Rate of Dye (default = 12.5×10^6 kg/site-yr)
AU	=	Annual Use Rate of Chemical Substance (kg/site-yr)
NS_d	=	Total Number of Dye Manufacturing Sites (default = 10 sites)

PV = Production Volume of Chemical Substance (kg/yr)
Y_{dye} = Weight Fraction of New Chemical Substance in the Dye (5-25%); (CEB, 1991; ETAD, 1993)

Operating Days per Site-Year (OD): 350 days/site-year

Basis: standard CEB estimate for year-round operations

Daily Use Rate (DU) (kg/site-day):

$$DU = \frac{AU}{OD}$$

Where:

AU = Annual Use of Chemical Substance (kg/site-yr, equation provided in the Number of Sites section above)
OD = Operating Days per Site-Year (default = 350 days/yr)

Number of Batches (Nb_y) (batches/site-yr):

$$NB_y = \frac{PV}{NS \times CB}$$

Where:

PV = Production Volume of the Chemical Substance (kg/yr)
NS = Number of Sites
CB = Amount of Chemical per Batch (1,891 -37,830 kg/btc)

Basis: Dye manufacturing vessels range in size from 500 - 10,000 gal (Kirk Othmer, Vol 8); Convert to kg using 8.34 lbs/gal and 2.20462 lbs/kg.

4.1.2 Occupational Exposure Assessments

Potential worker inhalation and dermal exposure occurs mostly during equipment maintenance, drying/filtering and transfer activities. The inhalation and dermal exposure estimates vary based on the form of the dye. Because most paper dyes are expected to be handled in the form of a dry solid, inhalation exposure to particulates is a primary concern. Based on the minimum percent composition of chemical substance in the dye and the daily production rate of dye, it is assumed that the use rate of chemical substance and the production rate of dye are both greater than 54 kg/site-day. The following paragraph provides the basis for this assumption.

The total annual production of dye for the industry is 125 million kg. There are a total of 10 dye manufacturing sites. Therefore, the total annual production rate of dye per site is 12.5 million kg. Assuming that the dye manufacturing site operates 350 days/yr, it is estimated that the daily production rate of dye is 35,714 kg. For a minimum percent composition of chemical substance in the dye equal to 5%, no less than 1,785 kg of chemical substance will be consumed per day. The OSHA PEL for nuisance dust is used to estimate inhalation exposure to particulates for these daily use and production rates.

Most liquid dyes have low volatility. CEB's standard assumption is that the inhalation exposure to vaporization of new chemical substances is negligible if the pure vapor pressure is less than 0.001 torr. Dermal exposure estimates are provided for both the solid and liquid form.

Number of Workers (NW):

It is estimated that 10-15 workers are directly involved in dye manufacturing per shift per plant. Most plants operate on three 8-hr shifts per day (Rand, 1986). The Census of Manufacturers reports 1866 production workers at 37 synthetic organic dye manufacturing sites.

NW = (30-45 workers/site) × NS

Inhalation [I (mg/kg)]:

Unloading:

Solid Chemical Substance:

Assume Daily Use Rate > 54 kg/site-day and use the OSHA PEL for nuisance dust which is 15 mg dust/m^3 breathed (C_k) over a default exposure duration (h) of 8 hrs at a default inhalation rate (b) of 1.25 m^3/hr:

$$I = C_m \times b \times h$$

where,

$$C_m = C_k \times Y_{cs}$$

NOTE: The OSHA PEL is an 8 hr time weighted average; therefore, the exposure duration used is 8 hrs/day rather than the actual worker exposure duration.

Where:

b	=	Inhalation Rate (default = 1.25 m^3/hr)
h	=	Exposure Duration (default = 8 hrs/day)
C_m	=	Concentration of chemical in air (mg/m^3)
C_k	=	Concentration of Particles (e.g. total dust or mist) in the air (default = 15 mg/m3; OSHA PEL)
Y_{cs}	=	Weight Fraction of Chemical Substance (assume 100%, unless otherwise specified)

Liquid Chemical Substance: Negligible (VP <0.001 torr)

Packaging:

Solid Dye:

Assume Daily Production Rate > 54 kg/site-day and use the OSHA PEL for nuisance dust which is 15 mg dust/m^3 breathed (C_k) over a default exposure duration (h) of 8 hrs at a default inhalation rate (b) of 1.25 m^3/hr:

$$I = C_m \times b \times h$$

where,

$$C_m = C_k \times Y_{dye}$$

NOTE: The OSHA PEL is an 8 hr time weighted average; therefore, the exposure duration used is 8 hrs/day rather than the actual worker exposure duration.

Where:

b	=	Inhalation Rate (default = 1.25 m^3/hr)
h	=	Exposure Duration (default = 8 hrs/day)
C_m	=	Concentration of chemical in air (mg/m^3)
C_k	=	Concentration of Particles (e.g. total dust or mist) in the air (default = 15 mg/m3; OSHA PEL)
Y_{dye}	=	Weight Fraction of Chemical Substance in the Dye (5-25%); (CEB, 1991; ETAD, 1993)

Dermal:

Manufacturing of dyes from solid new chemical substances may require the following activities: Filling/dumping containers of powders, flakes or granules; handling wet or dried material in a filtration and drying process. Manufacturing of dyes from liquid new chemical substances may require the following activities: connecting transfer line, manual cleaning of equipment. Exposure estimates are based on the CEB Method for Screening - Level Assessments of Dermal Exposure (CEB, 2000).

Unloading:

Solid Chemical Substance: $D_{exp} = Y_{cs} \times 3{,}100$ mg/day over ED days/yr

Basis: Routine, direct handling of solids, 2 hands (CEB, 2000) (dumping containers of powders, flakes, granules)

Liquid Chemical Substance: $D_{exp} = Y_{cs} \times 1{,}800$ mg/day over ED days/yr

Basis: Incidental contact, two hands - liquid (CEB, 2000) (connecting transfer line)

Packaging and Equipment Cleaning:

Powder Dye: $D_{exp} = Y_{dye} \times 3{,}100$ mg/day over ED days/yr

Basis: Routine, direct handling of solids, 2 hands (CEB, 2000) (filling containers of powders, flakes, granules)

Liquid Dye: $D_{exp} = Y_{dye} \times 1{,}800$ mg/day over ED days/yr

Basis: Routine contact, two hands - liquid (CEB, 2000) (manual cleaning of equipment, filling drum with liquid)

Where:

Y_{dye} = Weight Fraction of Chemical Substance in the Dye (5-25%); (CEB, 1991; ETAD, 1993)

Y_{cs} = Weight Fraction of the Chemical Substance in the Raw Material (assume 100%, unless specified)

4.1.3 Release Assessments

Sources of environmental release during dye manufacturing include filtration liquors (called mother liquors), equipment wash down, and other process water, spent filter cloths and wastewater treatment solids. The latter two are not generated at all sites. Dye dust and fines are generated during drying, grinding, standardization, blending, and packaging operations. They may be captured in a baghouse and recycled to the process or disposed to a landfill, or they may be released to the atmosphere, allowed to settle on the floor, and washed into floor drains. TRI data on environmental release of dyes is scarce due to the low number of dyes on the TRI reporting list. Estimated releases, based on percentages of production volumes, were obtained from an SRI study (SRI, 1981).

Water [DR_w (kg/site-day)]:

$$DR_w = \frac{PV \times LF_w}{NS \times OD}$$

From: Filtration liquors, equipment wash down, and other process water
Basis: Assume 2.7% loss fraction to water (SRI, 1981)

Where:

LF_w = Loss Fraction to Water (default = 2.7%)
NS = Number of Sites
OD = Operating Days per Site-Year (default = 350 days/yr)
PV = Production Volume of Chemical Substance (kg/yr)

Air: Negligible (VP < 0.01 torr)

New chemical substances used as paper dyes are expected to be solid or non-volatile. CEB's standard assumption is that the release to air due to vaporization of PMN chemicals is negligible if the pure vapor pressure is < 0.01 torr.

Note: Submission estimates of solids released to air should be included.

Incineration: Not expected

Basis: Release of the chemical substance to incineration is not expected because all waste is expected to be released to water or land.

Land [Ar_l (kg/yr)]: $AR_l = PV \times LF_l$

From : Product Finishing
Basis: Assume 2.0% loss fraction to land (SRI, 1981)

Where:

LF_l = Loss Fraction to Land (default = 2.0%)
PV = Production Volume (kg/yr)

4.2 Use - Paper Dyes

In 1992, 555 paper mills were operating in the U.S. with 100,400 production employees that worked approximately 215,200,000 hours (BOC, 1992). In 1997, the total annual paper production volume was 44,679,000 short tons/yr (DOC, 1999).

4.2.1 General Facility Estimates

The calculation for the number of paper dyeing sites is based on a calculation for annual chemical use of dye. The annual use of dye (AU_{dye}) can be estimated as 73,096 kg dye/site-yr, as described by the equation below. If the shade of dye being used is known, the annual use of dye per site (AU_{dye}) can be more accurately estimated by substituting the appropriate dye use rate per ton of paper (U_d).

Number of Facilities [NS_{dye}]:

$$NS_{dye} = \frac{PV_{dye}}{AU_{dye}}$$

where,

$$PV_{dye} = \frac{PV}{Y_{dye}}$$

and,

$$AU_{dye} = \frac{PV_p \times U_d \times 0.454 \text{ kg/lb}}{NS_p}$$

Where:

AU_{dye} = Annual Use Rate of Dye (default = 73,096 kg/site-yr)
NS_p = Total Number of Domestic Paper Manufacturing Sites (default = 555 sites) (BOC, 1992)
PV = Production Volume of Chemical Substance (kg/yr)

PV_{dye} = Production Volume of Dye (kg/yr)
PV_p = Production Volume of Paper (default = 44,679,000 short tons/yr) (DOC, 1999)
U_d = Dye Use Rate (default = 2 lbs dye/ton paper) (EPA, 1981; Georgia Pacific, 1991)
$U_{d,l}$ = Dye Use Rate (light = 0.5 lbs dye/ton paper)
$U_{d,h}$ = Dye Use Rate (heavy = 7.0 lbs dye/ton paper)
Y_{dye} = Weight Fraction of the Chemical Substance in the Dye (default = 5-25%) (CEB 1991, and ETAD 1993)

Operating Days per Site-Year (OD): 350 days/yr

Basis: standard CEB estimate for year-round operations

Daily Use Rate [DU (kg/site - day)]:

$$DU = \frac{AU}{OD}$$

Where:

AU = Annual Use of Chemical Substance (kg/site-yr)
OD = Operating Days per Site-Year (default = 350 days/yr)

4.2.2 Occupational Exposure Assessments

Use of liquid dye and automated equipment greatly reduces the exposure potential. Up to four percent of the production workers at paper manufacturers hold positions associated with potential dye exposure (Soklow, 1984). Assuming a plant work force of 300 workers (DOL, 1991), up to 12 employees are potentially exposed to dye. Job categories in paper mills with potential dye exposures include: machine operators, engineering technicians, plumbers and pipe fitters, laborers and mixing operators (Soklow, 1984).

Number of Workers [NW]: NW = 12 workers/site × NS

Basis: It is estimated that there are 300 workers at a paper manufacturing plant. Four percent are potentially exposed to dye.

Days Exposed per Year (ED): 250 days/yr

Based on an annual use rate for dye (AU_{day}) of 73,096 kg/site-yr, the daily use rate can be calculated as 208 kg/site-day. For this daily use rate of dye, the OSHA PEL for nuisance dust is used to estimate inhalation exposure to particulates.

Inhalation Exposure [I (mg/day)]:

Powder Dye:

Assume Daily Use Rate > 54 kg/site-day and use the OSHA PEL for nuisance dust which is 15 mg dust/m^3 breathed (C_k) over a default exposure duration (h) of 8 hrs for a default inhalation rate (b) of 1.25 m^3/hr:

$$I = C_m \times b \times h$$

where,

$$C_m = C_k \times Y_{dye}$$

NOTE: The OSHA PEL is an 8 hr time weighted average; therefore, the exposure duration used is 8 hrs/day rather than the actual worker exposure

Where**:**

b	=	Inhalation Rate (default = 1.25 m^3/hr)
h	=	Exposure Duration (default = 8 hrs/day)
C_m	=	Concentration of chemical in air (mg/m^3)
C_k	=	Concentration of Particles (e.g. total dust or mist) in the air (15 mg/m3; OSHA PEL)
Y_{dye}	=	Weight Fraction of New Chemical Substance in the Dye (5-25%); (CEB, 1991; ETAD, 1993)

Liquid Dye: Negligible (VP <0.001 torr)

Basis: Liquid dyes are expected to be non-volatile. CEB assumes inhalation exposure to chemicals with VP < 0.001 torr to be negligible.

Dermal [D_{exp} (mg/day)]:

Dermal exposure during dyeing operations occurs when the worker is unloading the dye. Dermal estimates are based on CEB's Method for Screening - Level Assessments of Dermal Exposure (CEB, 2000).

Powder Dye: $D_{exp} = Y_{dye} \times 3{,}100$ mg/day over ED days/yr

Basis: Routine, direct handling of solids, 2 hands (CEB, 2000) (weighing powder/scooping/mixing)

Liquid Dye: $D_{exp} = Y_{dye} \times 1{,}800$ mg/day over ED

Basis: Incidental contact, two hands - liquid (CEB, 2000) (connecting transfer line)

Where:

ED	=	Days Exposed per Year (default = 250 days/yr)
Y_{dye}	=	Weight Fraction of the Chemical Substance in the Dye (default = 5-25%)

4.2.3 Release Assessments

Major sources of waste include trimmings, plant dust, wastewater treatment sludges, and other process residues. An estimated 99.8% of the waste is released as solid waste, 0.1% as air release, and 0.1% as water release. Assuming 90% exhaustion onto the paper, 10% is released to the environment (EPA,1981).

Water [DR_w (kg/site-day)]: $DR_w = DU \times (1\text{-}EXH) \times LF_w$

From: Process wastes
Basis: 90% exhaustion onto paper, 0.1% of waste to water

Where:

DU	=	Daily Use of Chemical Substance (kg/site-yr; equation provided under the General Facility Estimates section)
EXH	=	Percent Exhaustion onto Paper (default = 90%)
LF_w	=	Loss Fraction to Water (default = 0.1%)

Air[DR_a (kg/site-day)]: $DR_a = DU \times (1\text{-}EXH) \times LF_a$

From: Process wastes
Basis: 90% exhaustion onto paper, 0.1% of waste to air

Where:

DU	=	Daily Use of Chemical Substance (kg/site-yr; equation provided under the General Facility Estimates section)

EXH = Percent Exhaustion onto Paper (default = 90%)
LF_a = Loss Fraction to Air (default = 0.1%)

Incineration: Not expected

Basis: Release of the chemical substance to incineration is not expected because all waste is expected to be released to water, air, or land.

Land [Ar_l (kg/yr)]: $AR_l = AU \times (1\text{-}EXH) \times LF_l$

From: Process wastes
Basis: 90% exhaustion onto paper, 99.8% of waste to land

Where:

AU = Annual Use of Chemical Substance (kg/site-yr; equation provided under the General Facility Estimates section)
EXH = Percent Exhaustion onto Paper (90%)
LF_l = Loss Fraction to Land (99.8%)

5.0 ADDITIONAL INFORMATION

5.1 Pollution Prevention

Effluents from both dye works and dyehouses are treated before leaving the plant and in municipal treatment works. Acidic and alkaline liquors are neutralized and heavy metals are removed. The most common and widespread technique used in effluent treatment is biological treatment. It has been employed for over 140 years. Both aerobic (in the presence of oxygen) and anaerobic (without oxygen) systems are used. Activated sludge usually removes about 10-20% of the color.

Recently, manufacturers are trying to eliminate the generation of high volume mother liquors and salt wastes be developing processes that do not require salt addition and filtration.

6.0 OTHER SOURCES

This section will be completed in future versions of this generic scenario.

7.0 DATA GAPS AND UNCERTAINTIES

Release estimates for the use of dyes are based on data from a SRI International (SRI) study. Inventory Update rule (IUR) information contradicts this data. The SRI study indicates most of release is to land, while the IUR information indicates most of the release is to water. Research should be conducted to determine which of these is more accurate.

A more recent estimate for the amount of paper dye manufactured annually is needed. This is not available in the 1997 Census of Manufacturers report for Synthetic Organic Dyes. The Census of Manufacturers Report for Paper Mills was also reviewed, but dyes were not listed as materials consumed. Therefore, the calculations are still based on 1974 data.

The U.S consumption of annual paper dyes (from SRI) should be updated.

There was no citation for $U_{d,l}$ or $U_{d,h}$ in the original scenario.

The dermal exposure use estimates could be improved by adding an estimate for the actual dyeing operation. This would require the identification of activities resulting in exposure. The exposure estimates could be obtained from Dermal estimates are based on CEB's Method for Screening - Level Assessments of Dermal Exposure or facility data.

8.0 REFERENCES

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