Leather Dyeing-
Generic Scenario for Estimating Occupational Exposures and Environmental Releases

-Draft-

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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 use of leather dyeing chemicals. These estimation techniques may be used by CEB to future evaluate leather dyeing premanufacture notices (PMNs) and existing leather dyeing PMNs. The document also presents an industry profile, a discussion of typical processes in the industry, including release and exposure points, control technologies, 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 estimates can be made using the methodology and calculations that are described in detail in Section 4.0. These calculations are summarized in the following table.

Table 1

Release and Exposure Calculations for Leather Dyeing PMN Chemicals

General Facility Estimates	
Number of Sites:	$NS = \frac{PV}{1{,}000 \text{ kg/site-yr}}$
Chemical Use Rate per batch:	$DU = BS \times \% D \times PMN_c$
Days of Operation:	$OD = \frac{1{,}000 \text{ kg/site-yr}}{DU \times NB}$
Occupational Exposure	
Number of Workers Exposed:	$N_W = <7 \times NS$
Inhalation (mg/day):	
Weighing:	$I_W = 2.1 \text{ mg/m}^3 \times PMN_c \times 1.25 \text{ m}^3\text{/hr} \times 8 \text{ hr/day}$
Mixing:	$I_M = 0.009 \text{ mg/m}^3 \times PMN_c \times 1.25\text{m}^3\text{/hr} \times 8 \text{ hr/day}$
Dyeing and Drying:	Negligible
Buffing: Worst case	$I_B = 15 \text{ mg/m}^3 \times PMN_c \times 1.25 \text{ m}^3\text{/m} \times 8 \text{ hr/day}$
Typical case	$I_B = 1.1 \text{ mg/m}^3 \times PMN_c \times 1.25 \text{ m}^3\text{/m} \times 8 \text{ hr/day}$
Default PMNc:	50% for powder dyes 15% for liquid dyes
Dermal (mg/day):	
For solid PMN:	$D_{exp} = 3{,}100 \times PMN_c$
For liquid PMN:	$D_{exp} = 1{,}800 \times PMN_c$

Table 1 (Continued)

Release Calculations	
Medium	**Calculation**
Air	AR = negligible
Water	$WR = \frac{5 \text{ to } 40\% \times PV}{NS \times OD}$
Landfill	LR = 1.1% × PV
Incineration	IR = Not expected

Where:

%D	=	Percent weight of formulated dye on the leather (default 1.0% grain leather dyeing, 3.0% suede leather dyeing)[7]
AR	=	Amount of PMN chemical released to Air (kg/yr)
BS	=	Typical batch size, 450-900 kg (default = 680 kg)
D_{exp}	=	Potential dermal exposure
DU	=	Use rate per batch of PMN chemical
I_B	=	Inhalation exposure from buffing
I_M	=	Inhalation exposure from mixing
IR	=	Amount of PMN chemical incinerated
I_W	=	Inhalation exposure from weighing
LR	=	Amount of PMN chemical released to Land (kg/yr)
NB	=	Number of batches per day (default = 9)
NS	=	Number of Leather Dyeing Sites
N_W	=	Total number of workers
OD	=	Days of operation
PMN_c	=	Concentration of PMN (default 50% for powder dyes 15% for liquid dyes)[7]
PV	=	PMN chemical production volume
WR	=	Amount of PMN chemical released to Water (kg/day-site)

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 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 end use of leather dyeing chemicals. EPA/OPPT frequently receives leather dyeing 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 a standardized methodology for evaluating PMNs and leather dyeing chemicals.

1.3 Methodology for Developing Estimation Techniques

The current generic scenario for leather dyeing was used as a guideline for the new generic scenario. Updated data for the leather dyeing industry has been included in this generic scenario. References listed in the generic scenario were updated with the latest information available. The most recent Census information on the number of workers and sites for the leather dyeing industry was also obtained.

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 leather dyeing chemicals. 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 the 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. 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 PROFILE

There are approximately 315 tanneries[6] in the US and about 80% of the tanneries perform dyeing operations.[7] In the leather dyeing industry, the annual amount of PMN active colorant in the dyestuff solution used ranges from 200-2,500 kg/tannery, with an average use rate of 1,000 kg/tannery. The total number of hides dyed at each facility typically averages 1,000 sides/day. A batch consists of between 450 and 900 kg of leather with a typical value of 680 kg. This batch size corresponds to between 40 and 80 grain leather sides, and between 100 and 200 suede leather sides, based on a weight of 11kg/side of grain leather and 4.5 kg/side of suede leather.

Leather is not a homogenous product, but is derived from collagen and has been treated with one or more tanning agent(s). Almost all grain leather (i.e., glazed calf, glazed kid, and suede) have dye applied as the bottom color. The final shade is derived by application of a pigment finish. Pigments cover the imperfections in the leather.[5]

3.0 PROCESS DESCRIPTION

Leather is generally dyed in wooden drums or rotating vessels. A dye bath is prepared by adding a dye stuff to the dyeing equipment; surfactants and other auxiliaries may also be added. The bath temperature may range from 0° to 60°C. The leather is brought into the drum or rotating vessel, and the leather is dyed by gentle agitation for approximately 10 minutes. There are also semicontinuous processes ((multimac) dyeing machine) for leather dyeing.[5]

The amount of formulated dyestuff used per batch is 6.8 kg for the grain leather sides, and 20 kg for the suede leather sides. The amount of active PMN in the formulated dyestuff (% active PMN) is typically 50% for powdered dyes and 15% for liquid dyes (most dyes used in leather dyeing are acid dyes).

4.0 SCREENING LEVEL ESTIMATION TECHNIQUES/METHODS

4.1 General Facility Estimates

Generally, facility estimates that are calculated in the following subsections are the number of sites (tanneries) that use the PMN chemical, the use rate of the PMN chemical, and the number of days of operation for each site. This information is determined based on the production volume of the PMN chemical, the amount PMN chemical in each batch, and the number of batches per year.

Number of Sites:

The average yearly use rate of PMN active colorant in the dye stuff solution is 1,000 kg/tannery. The number of tanneries can be calculated by dividing the PMN chemical production volume by the average use rate of active colorant for each tannery. There are approximately 315 tanneries in the US.[6] About 80% of the tanneries perform dyeing operations. Therefore, the number of sites should not exceed 252 tanneries.[7]

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

Where:

NS	=	Number of sites (tanneries)
PV	=	Production volume of PMN chemical
UR	=	Average yearly use rate of PMN chemical per tannery (kg/site-yr) (default = 1,000 kg/site-yr)

Use Rate:

The average leather batch size is 680 kg. The amount of PMN chemical used for each batch depends on the amount of leather being dyed, the concentration of the PMN in the dyestuff, and the %D.

$$DU = BS \times \%D \times PMN_c$$

Where:

DU	=	Use rate per batch of the PMN chemical, kg/batch
PMN_c	=	Concentration of the PMN chemical (default = 50% for powdered dyes and 15% for liquid dyes)[7]

%D	=	Percent weight of formulated dye on the leather (default = 1.0% for grain leather dyeing and 3.0% for suede leather dyeing)[7]
BS	=	Average batch size (default = 680 kg leather

Days of Operation:

The number of days of operation for each tannery depends on the amount of PMN each tannery uses per year (default 1,000 kg), the amount of PMN used in each batch, and number of batches dyed each day. The following equation should be used to calculate the number of operating days.

$$OD = \frac{UR}{DU \times NB}$$

Where:

DU	=	Use rate per batch of PMN chemical
OD	=	Days of operation
NB	=	Number of batches per day at each site (default = 9)[7]
UR	=	Average yearly use rate of the PMN chemical per tanning (kg/site-yr) (default = 1,000 kg/site-yr)

4.2 Occupational Exposure

Number of workers and worker activities:[7]

Worker Activity	Number of Workers per Activity	Duration of Exposure (hrs/day)
Weighing	1	1.5
Mixing	1	8
Dyeing	1	8
Drying	2	8
Buffing	1-2	8
Total	<7	1.5 - 8

$$NW = < 7 \times NS$$

Where:

NW	=	Number of workers that may be exposed to the PMN chemical at each site
NS	=	Number of sites (calculated previously)

Dermal Exposure:

D_{exp} (mg/day) over OD days

For solid PMN, $D_{exp} = 3{,}100 \times PMN_c$
Basis: Routine, direct handling solids-2 hand[8] (weighing)

For liquid PMN, $D_{exp} = 1{,}800 \times PMN_c$
Basis: Routine, contact 2 hands-liquids[8] (mixing and filling)

Where:

D_{exp}	=	Potential dermal exposure due to weighing.
PMN_c	=	Concentration of PMN_c (solid, default = 50%; liquid, default = 15%)

Inhalation Exposure

Weighing: 0.001-3.2 mg/m^3 or an 8 hr geometric mean of 2.1 mg/m^3 total dust.[7]

$$I_W = 2.1 \text{ mg/m}^3 \times 1.25 \text{ m}^3\text{/hr} \times 8 \text{ hr/day} \times PMN_c$$

assume: PMN_c = 50% for powdered dyes and 15% for liquid dyes.

Mixing: 0.002-0.083 mg/m^3 or an 8 hr geometric mean of 0.009 mg/m^3 total dust.[7]

$$I_M = 0.009 \text{ mg/m}^3 \times 1.25 \text{ m}^3\text{/hr} \times 8 \text{ hr/day} \times PMN_c$$

assume: PMN_c = up to 50%

Dyeing and Drying: Inhalation is negligible

Buffing: 15 mg/m^3 total dust assuming worst case when ventilation equipment is not working. Otherwise use a range of 0.14-3.3 mg/m^3 or an 8 hr geometric mean of 1.1 mg/m^3 total dust.[7]

Typical $I_B = 1.1 \text{ mg/m}^3 \times 1.25 \text{ m}^3\text{/m} \times 8 \text{ hr/day} \times PMN_c$

Worst $I_B = 15 \text{ mg/m}^3 \times 1.25 \text{ m}^3\text{/m} \times 8 \text{ hr/day} \times PMN_c$

assume: PMN_c = up to 1%

Where:

I_W	=	Potential inhalation exposure due to weighing.
I_M	=	Potential inhalation exposure due to mixing.
I_B	=	Potential inhalation exposure due to sampling.

4.3 Environmental Releases

Air: Negligible

Basis: Solid PMN or Liquid PMN (VP < 0.01 torr)

Water: WR kg/site OD days

Source: Exhausted dyebath solution
To: POTW
Basis: Based on degree of exhaustion, ranges from 60-95%

Calculation:

$$WR = \frac{(1 - EXH) \times PV}{NS \times OD}$$

Where:

WR	=	Amount of PMN chemical released to water per site.
OD	=	Days of operation (calculated previously).
PV	=	Production volume of PMN chemical.
EXH	=	Degree of exhausting (default 60 - 95%)

Landfill: LR kg/yr

Source: Container residue, scrap and off spec material

Basis: 0.1% of PV from container residue and 1% of PV from scrap and off-spec material.[7]

Calculation: $LR = 1.1\% \times PV$

Where:

LR	=	Amount of PMN chemical released to land.
PV	=	Production volume of PMN chemical.

Incineration: Not expected

All releases of PMN go to wastewater or landfill.

5.0 ADDITIONAL INFORMATION

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

6.0 OTHER SOURCES

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

7.0 DATA GAPS AND UNCERTAINTIES

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

8.0 REFERENCES

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