Leather Tanning-
Generic Scenario for Estimating Occupational Exposures and Environmental Releases
-Draft-

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Page

ABSTRACT AND RELEASE AND EXPOSURE CALCULATION SUMMARY TABLES

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 tanning chemicals. These estimation techniques may be used by CEB to evaluate future leather tanning premanufacture notices (PMNs) and existing leather tanning PMNs. 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). Note that chemicals involved with leather dyeing are addressed in CEB's Generic Scenario for Leather Dyeing.

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 Table 1.

Table 1

Release and Exposure Calculations for the Use of Leather Tanning Chemicals

General Facility Estimates	
Number of Sites:	NS = up to 315 sites
Number of Workers (workers/site):	$NW = 0.75 \times NW_{total}$
Operation Days:	OD = up to 350 days/year

Release Calculations	
Medium	**Calculations**
Water (kg/site-day)	$WR = \frac{100\% \times PV}{NS \times OD}$
Air (kg/site-day)	AR = negligible
Landfill (kg/yr)	LR = 1 ? 3% × PV LR = 1 to 3% × PV
Incineration (kg/yr)	IR = expected

ABSTRACT AND RELEASE AND EXPOSURE CALCULATION SUMMARY TABLES

Table 1 (Continued)

Occupational Exposure
Inhalation (mg/day):

Vapor inhalation is negligible due to low vapor pressure. If PMN chemical is in solid form, the inhalation exposure due to particulates can be calculated by the following equation:

$$I = C_{PMN} \times 1.25\ mg/m^3 \times 8\ hr/day\ exposure$$

1) If the PMN is a solid compound containing Cr:

$$C_{PMN} = 1\ mg/m^3 \times \frac{1}{\left(\frac{\text{Cr weight} \times \text{\# Cr Molecules PMN compound}}{\text{PMN weight}}\right)}$$

2) If the tanning compound is a mixture of the PMN chemical, chromium compound and other compounds:

$$C_{PMN} = 1\ mg/m3 \times \frac{\text{PMN\%}}{\left(\frac{\text{Cr weight} \times \text{\# Cr Molecules compound}}{\text{Cr Compound Weight}}\right) \times \text{Cr Compound \%}}$$

3) If the concentration is greater than 15 mg/m^3 (based on the calculations above), the OSHA PEL for particulates not otherwise regulated is 15 mg/m^3 (8-hr. time weighted average).

Error!

re-calculate the C_{PMN}:

$$C_{PMN} = 15\ mg/m^3 \times PMN\%$$

ABSTRACT AND RELEASE AND EXPOSURE CALCULATION SUMMARY TABLES

Table 1 (Continued)

4) If the quantity of solid tanning agent handled is less than 54 kg/site-day:

Worst case: $I = 0.161$ mg/kg × quantity of tanning agent × PMN%

Typical case: $I = 0.0477$ mg/kg × quantity of tanning agent × PMN%

Dermal (mg/day):

$$D_{exp} = 900 \text{ mg/day} \times PMN_c$$

Where:

AR	=	Amount of PMN chemical released to air (kg/site-yr)
C_{PMN}	=	Concentration of PMN particles in air
Cr Compound %	=	Wt% of chromium compound in the tanning solution
Cr Compound Weight	=	Molecular weight of Compound containing chromium (g/mole)
Cr Molecules in PMN Compound	=	Number of chromium atoms present in the PMN molecular formula
Cr weight	=	Molecular weight of chromium (51.97 g/mole)
D_{exp}	=	Potential dermal exposure (mg/day)
I	=	Inhalation exposure (mg/day)
IR	=	Amount of PMN chemical incinerated (kg/yr)
LR	=	Amount of PMN chemical released to Land (kg/yr)
NS	=	Number of Sites
NW_{prod}	=	Number of production workers
NW_{total}	=	Number of employees (Default = 42 workers/site)
OD	=	Days of operation
PMN_c	=	Concentration of PMN chemical in original formulation (wt%)
PMN%	=	Wt% of PMN chemical in the tanning-agent
PMN Weight	=	Molecular weight of PMN chemical (g/mole)
PV	=	Production volume of PMN chemical
WR	=	Amount of PMN chemical released to water (kg/site-day)

GENERIC SCENARIO: LEATHER TANNING

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 prescribe a standardized methodology to estimate occupational exposures and releases to the environment for new chemical substances that will be incorporated into products used by industrial and commercial laundries. EPA/OPPT frequently receives PMN's for chemicals used in industrial and commercial laundry products and wishes to create a generic scenario for use of these chemicals predicated on information readily available to the Agency.

1.3 Methodology for Developing Estimation Techniques

The original generic scenario for leather tanning was used as a guideline for the new generic scenario. Updated data for the leather tanning industry has been included in this new generic scenario. References listed in the generic scenario were updated with the latest information available. The 1998 Census information on the number of workers and sites for the leather tanning 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 tanning 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 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.

GENERIC SCENARIO: LEATHER TANNING

2.0 INDUSTRY SUMMARY AND BACKGROUND

Tanning is the process of converting the cellular structure of skin into a network of collagen fibers. The tanning process preserves the hide, makes it softer, more pliable and durable. The three types of hides and skins most often used in leather manufacture are from cattle, sheep, and pigs.[1]

Tanning is the reaction of collagen fibers in the hide with tannins, chromium, alum, or other chemical agents. The most common tanning agents used in the US are trivalent chromium and vegetable tannins extracted from specific tree barks.[1]

There are approximately 315 tanneries in the leather industry.[6] According to the Census Bureau 1998 County Business patterns, 80% of the tanneries employ less than 50 employees.[6] Chrome tanning comprises greater than 95% of the market, only a few leather tanneries use the vegetable tanning process.[7]

GENERIC SCENARIO: LEATHER TANNING

3.0 PROCESS DESCRIPTION[1,12]

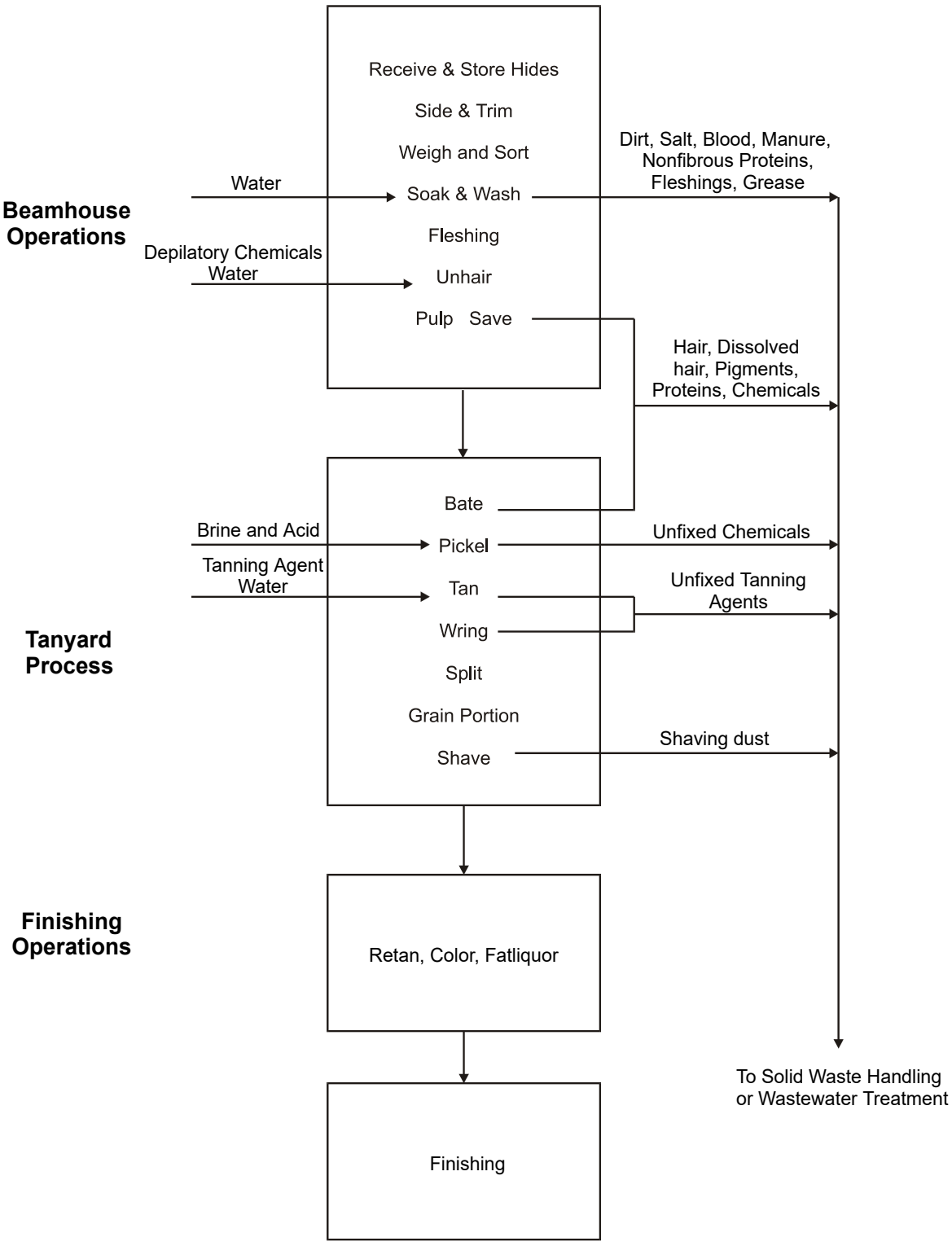
The following process descriptions of chrome and vegetable tanning, highlight the major processing steps of leather making and what types of chemicals are used during the processes. Figure 3-1 presents a general flow diagram for the leather tanning process. The first steps of the process are referred to as beamhouse operations, which include trimming, soaking, fleshing, and unhairing. These operations take place for both chrome and vegetable tanning. Table 2 lists chemicals that are typically used in beamhouse operations. Next, tanyard processes take place, which include bating, pickling, tanning, wringing, and splitting. Lastly, finishing processes include conditioning, staking, dry milling, buffing, spray finishing, and plating. This generic scenario will focus on tanyard operations.

Table 2

Chemicals Typically Used in Beamhouse Operations[11]

Chemical	Use
o Phenylphenol 2-(Thiocyanomethylthio) benzothiazole Diiodomethyl-p-tolysolfone 1,2-Benzisothrazolin-3-one	Bactericides
Nonyl phenol ethoxylate Polyglycol ether Alkyl benzene sulphonates Sodium dioctylsulphosuccinate Alcohol ethoxylates Alkyl ether phosphates Ethoxylated caster oil Ethoxylated vegetable oil Fatty alcohol ethoxylate Ethoxylated tridecanol Alkyl polyglycol ether Sodium alkyl sulphonates Isotridecanol ethoxylate Fatty alcohol polyglycol ether Phosphate esters Sulfur succinate	Wetting agents/ Detergents

Figure 3-1. Leather Tanning Process Flow Diagram



GENERIC SCENARIO: LEATHER TANNING

3.1 Chrome Tanning

95% of leather tanning facilities in the U.S. use chrome tanning processes.[7] Chrome tanning creates soft, pliable leather that is usually made from lighter-weight cattle hides and from the skin of sheep, lambs, goats, and pigs. In chrome tanning, additional processes of retanning, dyeing, and fatliquouring are usually performed to produce usable leathers and a preliminary degreasing step may be necessary when using animal skins, such as sheepskin.

Chrome tanning is performed using a one-bath process. The tanning process usually takes place in large rotating vessels for approximately 24 hours. The hides are in a pickled state at a pH of 3 or lower, the chrome tanning materials are introduced and the pH is raised. Following tanning, the chrome tanned leather is piled down, wrung, and graded for the thickness and quality, split into flesh and grain layers, and shaved to the desired thickness. The grain leathers from the shaving machine are then separated for retanning, dyeing, and fatliquoring.

The tanning agents used in this industry are chromium compounds, cresols, formaldehyde, and phenol. Other primary chemicals used are sulfuric acid, paranitrophenol, and 2-phenylphenol.[12]

3.2 Vegetable Tanning

The vegetable tanning process is used to produce heavy leathers and sole leathers. The vegetable tanning process usually takes 3 weeks to complete. Vegetable tanning uses tannin, a natural product found in the bark, leaves and fruits of chestnut, oak and hemlock trees. The concentration of the tannin starts out low and is gradually increased as the tannage proceeds. Vegetable tanning consists of stringing hides on large frames, located inside large vats. The hides are transferred to many different bins, each containing a stronger solution of tannin.

GENERIC SCENARIO: LEATHER TANNING

4.0 SCREENING LEVEL ESTIMATION TECHNIQUES/METHODS

Water is essential to leathermaking and is used in virtually all manufacturing processes. Discharge flow rates range from 3 up to 5,380 m^3/day, depending on the leather tanning process used. The weighted average flow rate of 74 tanneries is 1,480 m^3/day. The weighted average of median water use ratio is 46 L of water to kg of leather.[1] The flow data from these 74 tanneries are presented in Appendix A. Effluent Guidelines for Leather Tanning and Finishing divide this industry into nine categories. Also, in Appendix A is water use data for each category.

Since a majority of tanning agents contain chromium, occupational exposure to any new chemicals will be minimal because chromium compounds have an OSHA PEL of 1 mg/m^3 as chromium.[13] Given that the tanning process involves the use of water, it is expected that a solid PMN chemical used in the tanning process will be distributed in a solution. Particulate exposure will only take place when a solid PMN is added to the manufacturing solutions.

The following subsections present estimation techniques and methods for environmental releases and occupational exposures.

4.1 General Facility Estimates

The number of leather tanneries in the U.S. is 315 facilities. Engineering judgment should be used to determine the number of sites the PMN will be used at if other information is not available.

Number of Sites [NS]: Up to 315 sites[6]

GENERIC SCENARIO: LEATHER TANNING

Number of Workers [NW_{prod}]:

The total number of employees in the leather tanning and finishing industry is approximately 13,400 for 315 facilities.[6] Eighty percent of these facilities employ less than 50 workers.[6] Based on several NIOSH surveys it can be assumed that 75% of tannery employees are production workers. Therefore, if the total number of employees at the facility is known, the number of production workers (those with potential occupational exposure to the PMN chemical) can be calculated.[9,10]

$$NW_{prod} = 0.75 \times NW_{total}$$

If the number of employees at the facility is unknown, assume the average number of employees.

Error!

The default number of workers per facility is estimated to be 75% of the average total number of employees.

Default: $NW_{prod} = 0.75 \times 42 = 32$ workers/facility

Days of Operation [OD]: Assume up to 350 days/yr[7]

4.2 Environmental Releases

The following paragraphs and equations provide estimations for environmental release to water, air, land, and incineration.

GENERIC SCENARIO: LEATHER TANNING

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

Water releases can be assumed to include up to 100% of the production volume of the PMN chemical because most PMN chemicals are expected to be removed from the leather during various piling, wringing, and grading steps. The waste is typically sent to on-site wastewater treatment, a POTW, or solid waste handling. If a PMN is expected to remain on the hide, this quantity should be subtracted from the amount released to water. Based on production volume, number of sites, and days of operation involving the PMN chemical, the daily water release can be calculated as follows:

$$WR = \frac{\text{up 100\%} \times PV}{NS \times OD}$$

Where: WR = Release of PMN chemical to water (kg/site-day)
PV = Production volume of PMN chemical (kg/yr)
NS = Number of sites (tanneries) (calculated in Section 4.1)
OD = Days of operation

Basis: All process water containing tanning agent(s) is treated and sent to POTW and/or released to the environment. Note: Many leather tanning facilities operate their own on-site wastewater treatment plants. In many cases the chromium and other heavy metals are removed by pre-treatment using high pH liquors from beamhouse operations to precipitate the metals.[12]

GENERIC SCENARIO: LEATHER TANNING

Air [AR (kg/site-day)]:

Air releases are expected to be negligible. CEB does not have a method to estimate an air release due to particulates and the vapor pressures of typical tanning agents are below 0.01 torr. However, if the vapor pressure is above 0.01 torr, Standard CEB estimation models should be used to estimate the potential release to air.

AR = Negligible (solid PMN; or Liquid PMN, VP < 0.01 torr)

Where: AR = Release of PMN chemical to air

Land [LR (kg/yr)]:

Land releases are due to PMN chemical residue that remains in the shipping containers. CEB's standard estimate for residue in the container is 1% (solid) or 3% (liquid) of the production volume.

LR = 1 to 3% × PV

Where: LR = Release of PMN chemical to land
PV = Production volume

Basis: Container Residue[7]. CEB's estimate for container residue is 1% (solid) or 3% (liquid).

Incineration [IR (kg/yr)]:

Incineration releases are not expected. All PMN chemical waste is expected to be released to water or land.[7]

IR = Not expected

Where: IR = Release of PMN chemical to incinerator

Basis: All waste is released to land or water[7]

4.3 Occupational Exposure

Inhalation [I (mg/day)]:

Chrome leather tanning processes comprise greater than 95% of the market. The OSHA PEL for chromium is 1 mg/m^3.[13] Also, a majority of the solid PMN chemicals are distributed in solutions which would minimize particulate exposure. Therefore, inhalation exposure is expected to be minimal. Vapor inhalation exposure is not expected because PMN chemicals are typically solids distributed in solution with a low vapor pressure. The following equation(s) calculates the potential inhalation exposure to the PMN chemical in a solid form.

The inhalation exposure is:

$$I = C_{PMN} \times 1.25 \text{ mg/m}^3 \times 8 \text{ hr/day}$$

GENERIC SCENARIO: LEATHER TANNING

The concentration of PMN particles in the air ($C_{m,unk}$) can be calculated using the following ratio:

$$C_{m,\ unk} = C_{m,\ known} \times \frac{Y_{unk}}{Y_{known}}$$

Where:
- $C_{m,unk}$ = concentration of particles in air of unknown compound
- $C_{m,known}$ = concentration of particles in air of the known compound
- Y_{unk} = weight fraction of PMN in mixture
- Y_{known} = weight fraction of known compound in mixture

1) If the PMN compound contains chromium, and the PEL for chromium is 1 mg/m^3, then the maximum allowable concentration of PMN particles in the air can be calculated from the maximum allowable concentration of chromium (OSHA PEL).

$$C_{PMN} = 1\ \frac{mg}{m^3} \times \frac{1}{\left(\frac{\text{Cr weight} \times \text{Number Cr molecules PMN compound}}{\text{PMN weight}}\right)}$$

2) If the PMN compound is in a mixture with a chromium compound, then the maximum concentration of PMN particles in air can be calculated in the same manner.

$$C_{PMN} = C_{Cr} \times \frac{\text{Wt \% PMN (mixture)}}{\text{Wt \% Cr (mixture)}}$$

Therefore:

$$C_{PMN} = C_{Cr} \times \frac{\text{PMN \%}}{\left(\frac{\text{Cr weight} \times \text{Number Cr Molecules Cr compound}}{\text{Cr Compound Weight}}\right) \times \text{Cr Compound \%}}$$

3) In some cases, the concentration of PMN in air (C_{PMN}) calculated above may be higher than the OSHA PEL for total particulates, 15 mg/m^3. A more realistic worst-case estimate is to assume the OSHA PEL is the maximum concentration for potential exposure. In these cases, C_{PMN} should be recalculated.

Error!

re-calculate the C_{PMN}:

$C_{PMN} = 15 \text{ mg/m}^3 \times \text{PMN\%}$

4) If the use rate of the solid PMN is less than 54 kg/site-day; then CEB small quantity weighing scenario should be followed.

Error!

Error!

GENERIC SCENARIO: LEATHER TANNING

Where: I = Inhalation exposure (m/day)
C_{PMN} = Concentration of particles in air of PMN (mg/m^3)
Cr Weight = Molecular weight of Chromium (51.97 g/mole)
Cr Molecules in PMN Compound = Number of Chromium atoms present in the PMN molecular formula
PMN weight = Molecular weight of PMN chemical (g/mole)
C_{cr} = Concentration of particles in air of the chromium compound (mg/m^3) (default value = 1 mg/m^3)
PMN% = Weight percent of PMN in the tanning agent
Cr Molecules in Cr Compound = Number of chromium atoms present in the chromium compound molecular formula
Cr Compound Weight = Molecular weight of Compound containing Chromium (g/mole)
Cr Compound % = Wt% of Chromium compound in the tanning solution

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

Chromium and formaldehyde are suspected human carcinogens (workers are expected to wear appropriate personal protective equipment and facilities are expected to install appropriate engineering controls). Also, the tanning solution typically is maintained at a pH of less than 2.8 in order for the chromium to penetrate the leather. Therefore, the potential dermal exposure to tanning agents is expected to be intermittent and up to 900 mg/day if gloves are not worn.[8] The following dermal estimate is the potential exposure to the PMN if gloves are not worn.

$$D_{exp} = 900 \text{ mg/day} \times PMN_C$$

Where: D_{exp} = Potential dermal exposure (mg/day)
900 = Exposure to tanning agent based on incidental contact, one hand, liquid. If pH <2, corrosive; no dermal exposure expected.
PMN_c = Concentration of PMN chemical

5.0 ADDITIONAL INFORMATION[1]

The office of water program has developed an effluent guidelines for the leather tanning industry. The TDD was reviewed for information that may help in release and exposure estimates. Potentially useful data include:

- BOD_s - 40 mg/L
- TSS - 60 mg/L
- Oil and Grease - 20 mg/L
- Total chromium - 1 mg/L
- pH - range of 6.0 to 9.0

GENERIC SCENARIO: LEATHER TANNING

6.0 OTHER SOURCES

All sources have been used to complete this generic scenario.

7.0 DATA GAPS AND UNCERTAINTIES

The typical use rate of the PMN chemical in a tannery is needed. The amount could be estimated based on the amount of trivalent chromium sulfate typically used. This information is needed in order to estimate the number of sites that will use the PMN chemical.

Additional information on the actual number of operating days per year at a tannery is needed.

Information on the "exhaustion" rate of a typical tanning agent containing the PMN.

8.0 REFERENCES

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9. NIOSH Survey Abstracts, NIOSH - 00189587

10. NIOSH Survey Abstracts, NIOSH - 00195594

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12. Emergency Planning and Community Right-to-Know Act Section 313 Reporting Guidance for the Leather Tanning and Finishing Industry. EPA 745-B-00-012. U.S. EPA OPPT. April 2000.

13. Code of Federal Regulation. 29 part 1910. Occupational Safety and Health Standards. U.S. Department of Labor/OSHA. July 2000.

APPENDIX A

Table 3

Leather Tanning - Water Usage[1]

Subcategory	Number of Tanneries	Median Water Use Ratio (L/kg)	Water Use, Low range (m^3/day)	Water Use, High range (m^3/day)	Average Water Use (m^3/day)
Hair Pulp/ Chrome Tan/Retan-Finish	28	54.2	151	5380	2765.5
Hair Save/ Chrome Tan/ Retan-Wet Finish	4	48.4	26	1380	703
Hair Save on Pulp/ Non-Chrome Tan/ Retan-Wet Finish	12	40.9	114	1890	1002
Retan/ Wet Finish (Sides)	8	40.1	53	2380	1216.5
No Beamhouse	13	48.4	3	530	266.5
Through-the-Blue	3	17.5	182	662	422
Shearling	1	78.5	1020	1360	1190
Pigskin	1	41.7	227	1850	1038.5
Retan/ Wet Finish (splits)	4	25	102	269	185.5
Total	74				
Average (weighted)		46.3	113	2851.9	1482.5