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Title III Section 313 Release Reporting Guidance

Estimating Chemical Releases From Leather Tanning and Finishing

Estimating Chemical Releases From Leather Tanning and Finishing

Facilities engaged in leather tanning and finishing may be required to report annually any releases to the environment of certain chemicals regulated under Section 313, Title III, of the Superfund Amendments and Reauthorization Act (SARA) of 1986. If your facility is classified under SIC codes 20 through 39 (leather tanning and finishing plants generally fall under SIC code 3111) and has 10 or more full-time employees, for calendar year 1987 you must report all environmental releases of any Section 313-listed chemical or chemical category manufactured or processed by your facility in an amount exceeding 75,000 pounds per year or otherwise used in an amount exceeding 10,000 pounds per year. For calendar years 1988 and 1989 (and beyond), the threshold reporting quantity for manufactured or processed chemicals drops to 50,000 and 25,000 pounds per year, respectively.

This document has been developed to assist those in the leather tanning and finishing industry in the completion of Part III (Chemical Specific Information) of the Toxic Chemical Release Inventory Reporting Form. Included herein is general information on toxic chemicals used and process wastes generated, along with several examples to demonstrate the types of data needed and various methodologies available for estimating releases. If your facility performs other operations in addition to leather tanning and finishing, you must also include any releases of toxic chemicals from these operations.

Step One

Determine if your facility processes or uses any of the chemicals subject to reporting under Section 313.

A suggested approach for determination of the chemicals your facility uses that could be subject to reporting requirements is to make a detailed review of the chemicals and materials you have purchased. If you do not know the specific ingredients of a chemical formulation, consult your suppliers for this information. If they will not provide this information, you must follow the steps outlined to handle this eventuality in the instructions provided with the Toxic Chemical Release Inventory Reporting Form.

The list presented here includes chemicals typically used in leather tanning and finishing that are subject to reporting under Section 313. This list does not necessarily include all of the chemicals your facility uses that are subject to reporting, and it may include many chemicals that you do not use. You should also determine whether any of the listed chemicals are created during processing at your facility.

Biocides: Paranitrophenol (PNP), 2-phenylphenol (ortho-phenylphenol)

Pickling compounds: Sulfuric acid

Tanning agents: Chromium compounds, cresols, formaldehyde, phenol

Dyes, pigments, and coloring agents: Titanium dioxide, organo-metallic dyes/ pigments (barium, cadmium, chromium, cobalt, copper, lead, nickel, and zinc compounds), Acid Blue 9, Basic Green 4, Direct Black 38, cyanide-containing compounds

Miscellaneous solvents and chemicals: Acetone, ammonia, ammonium sulfate, chlorine, 1,2-dichlorobenzene, dichloromethane (methylene chloride), n-dioctyl phthalate (bis-[2-ethylhexyl] phthalate), ethyl benzene, glycol ethers, hexachloroethane, hydrochloric acid, methyl ethyl ketone, phosphoric acid, sodium hydroxide, tetrachloroethylene (perchloroethylene), 1,1,1-trichloroethane, trichloroethylene, toluene, xylene

Step Two

Determine if your facility surpassed the threshold quantities established for reporting of listed chemicals last year.

You must submit a separate Toxic Chemical Release Inventory Reporting Form for each listed chemical that is "manufactured," "processed," or "otherwise used" at your facility in excess of the threshold quantities presented earlier. Manufacture includes materials produced in byproduct or impurities. Toxic compounds that are incorporated into your products (for example, chromium in tanning formulations) would be considered "processed" because they become part of the marketed finished product. Degreasing solvents, cleaning agents, and other chemicals that do not become part of the finished product (for example, pickling agents and dye carriers) would be considered "otherwise used."

In leather tanning and finishing processes, the release of toxic chemicals to the environment usually results from the "processing" or "use" of these chemicals rather than their "manufacture." You must keep in mind, however, the toxic chemicals that may be "manufactured" indirectly during the process. For example, ammonia is generated during the biological decay of proteins in wastewater. Although ammonia is not a desired "product" of the tannery, it is nevertheless "manufactured" during the process, and if produced in sufficient quantities, it is subject to reporting requirements.

The amount of a chemical processed or otherwise used at your facility represents the amount purchased during the year, adjusted for beginning and ending inventories. To ascertain the amount of chemical in a mixed formulation, multiply the amount of the mixture (in pounds) by the concentration of the chemical (weight percent) to obtain the amount of chemical processed.

Example: Determining whether sulfuric acid was used in sufficient quantity to require reporting under Section 313.

A tanning facility used 95 percent pure sulfuric acid in the pickling process (and for other miscellaneous purposes). In 1987, 3,000 pounds of this material was in storage at the beginning of the year, 18,000 pounds was purchased, and 6,000 pounds was in storage at the end of the year. The quantity of H_2SO_4 used by this facility equals:

(3,000 lb x 0.95) (beginning inventory) +

(18,000 lb x 0.95) (purchased) –

(6,000 lb x 0.95) (ending inventory) x

= 14,250 lb

Because this amount exceeds the threshold quantity of 10,000 pounds for a chemical that is "otherwise used," the plant in this example would have to submit a Toxic Chemical Release Inventory Reporting Form for H_2SO_4.

A listed chemical may be a component of several formulations you purchase, so you may need to ask your supplier for information on the concentration (percentage) of the chemical in each. For chemical categories, your reporting obligations are determined by the total amounts of all chemicals in the category. For example, cyanide-containing compounds are found in sharpening agents, tanning agents, dyes, and pigments. The quantity of cyanide compounds used is the sum of the quantities used in these areas. For metal compounds, the amount of metal compound is used to determine whether threshold is exceeded, whereas the reported release represents the amount of parent metal only. For a substance such as lead chromate, the amount used must be considered in determining whether the threshold is met for both lead-containing and chromium-containing compounds.

You must complete a report for each chemical for which a threshold is exceeded. The thresholds apply separately; therefore, if you both process and use a chemical and either threshold is exceeded, you must report for both activities. If neither threshold is exceeded, no report is needed.

Step Three

Identify points of release for the chemical(s) subject to reporting.

An effective means of evaluating points of release for listed toxic chemicals is to draw a process flow diagram identifying the operations performed at your facility. The figure provided here (on pages 4 and 5) is an example flow diagram of a leather tanning process from beam house operations to finishing.

Because each facility is unique, you are strongly urged to develop a flow diagram for your particular operations that details the input of materials and chemicals and the waste sources resulting from the operation of each unit.

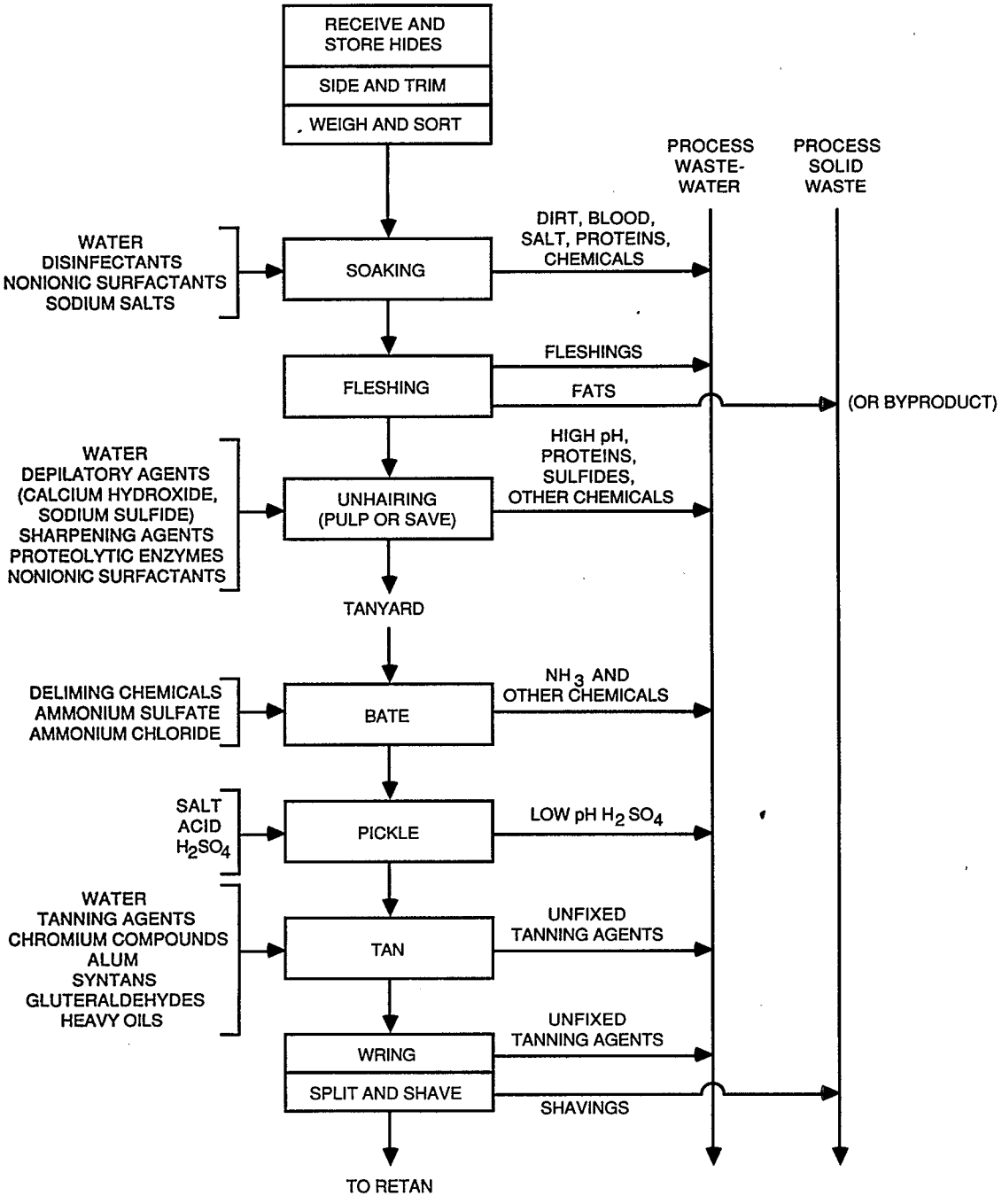
Wastewater is generated by almost every unit of operation in a leather tanning and finishing facility. Solid wastes containing toxic substances are generated from the following sources:

- **Shavings**
- **Buffing dust**
- **Wastewater screenings**
- **Wastewater treatment sludges**

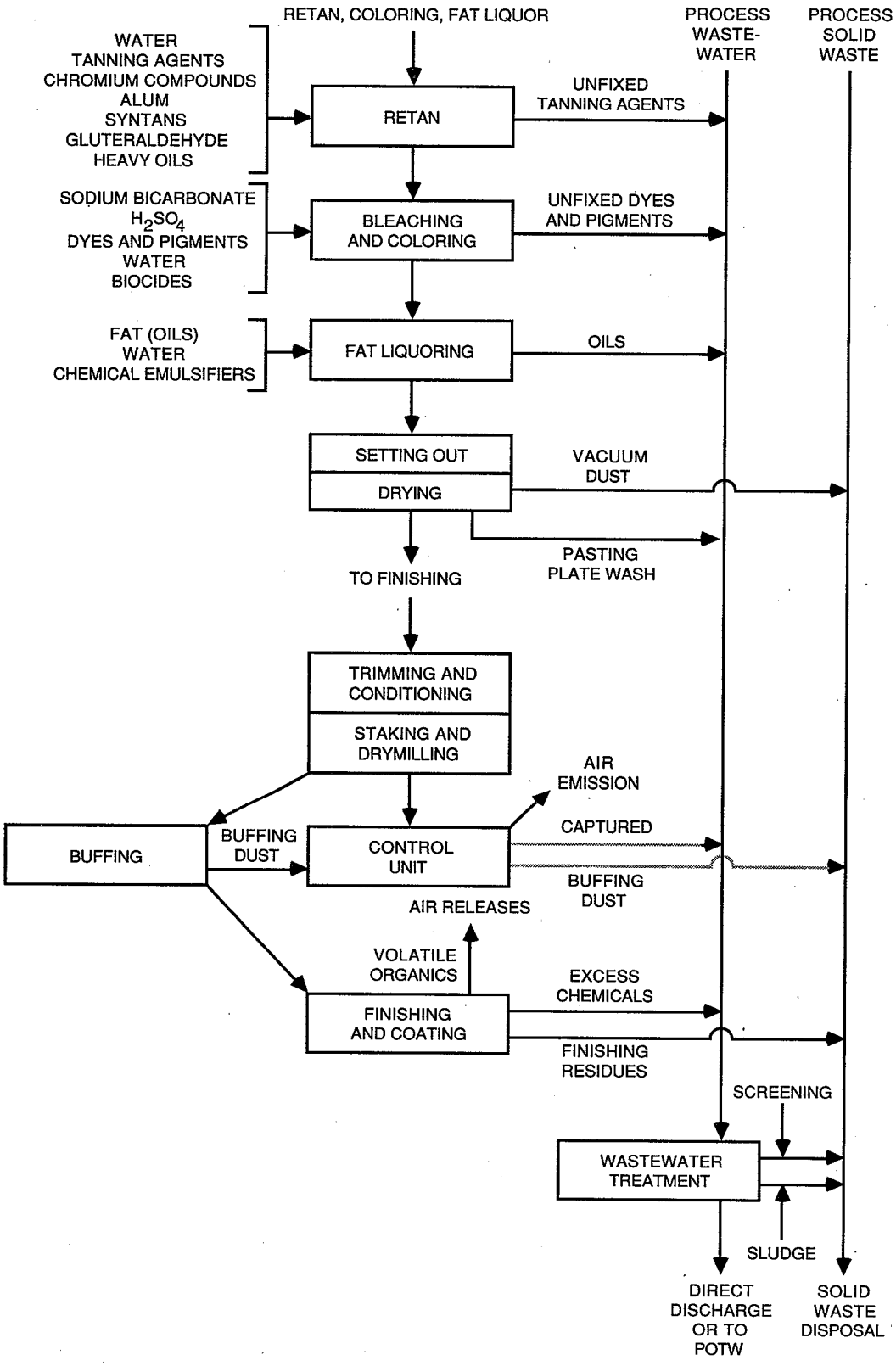
Some solid wastes are recycled into other products, such as leatherboard. If recycling/recovery is performed offsite, the amounts of toxic chemicals contained in the solid waste do not have to be reported; however, if these solid wastes are to be disposed of offsite, or if their fate is unknown, then they must be reported as an offsite transfer. If recycling is performed on site, the recycled wastes are not considered to be "disposed of" or "transferred"; they are simply considered an extension of the facility's processing operation. Any toxic chemicals released during recycling must be included in the facility's totals.

Buffing operations, coating operations in the finishing of leather (spray booths, dryers), and the degreasing of pigskin and sheepskin are all likely to generate air emissions that constitute toxic chemical releases. Typically, control devices are in place to limit emissions from these points, in which case, these sources are considered "stack or point emissions"; if not, they may be considered "fugitive or nonpoint air emissions," depending on the individual facility.

Your reporting must account for all releases.



Example Flow Diagram of Leather Tanning and Finishing



Example Flow Diagram of Leather Tanning and Finishing (continued)

Step Four

Estimate releases of toxic chemicals.

After all of the toxic chemicals and waste sources have been identified, you can estimate the releases of the individual chemicals. Section 313 requires that releases to air, water, and land and transfers to offsite facilities be reported for each toxic chemical meeting the threshold reporting values. The usual approach entails first estimating releases from waste sources at your facility (that is, wastewater, air release points, and solid waste) and then, based on the disposal method used, determining whether releases from a particular waste source are to air, water, land, or an offsite disposal facility.

In general, there are four types of release estimation techniques:

- **Direct measurement**
- **Mass balance**
- **Engineering calculations**
- **Emission factors**

Descriptions of these techniques are provided in the EPA general Section 313 guidance document, Estimating Releases and Waste-Treatment Efficiencies for the Toxic Chemical Release Inventory Form.

Provisions of the Clean Air Act, Clean Water Act, Resource Conservation and Recovery Act, and other regulations require monitoring of certain waste streams. If available, data gathered for these purposes can be used to estimate releases. When only a small amount of direct measurement data is available, you must decide if another estimation technique would give a more accurate estimate. Mass balance techniques and engineering assumptions and calculations can be used in a variety of situations to estimate toxic releases. These methods of estimation rely heavily on process operating parameters; thus, the techniques developed are very site-specific. Emission factors are available for some industries in publications referenced in the general Section 313 guidance document. Also, emission factors for your particular facility can be developed in-house by performing detailed measurements of wastes at different production levels.

If direct measurement data are not available, mass balances combined with engineering calculations provide the next most effective means of estimating releases at leather tanning and finishing facilities. Because most of the chemicals are "processed" or "otherwise used," the quantity of chemical input to the facility equals the quantity of the chemical leaving as product plus the quantity leaving as waste (before treatment). The quantity of chemical in the leather product should be known by the manufacturer (through engineering calculation of tanning and dyeing chemical uptake rates). If the chemical input quantity and the quantity leaving in the product are known, the quantity of chemical in the waste is also known. This is especially effective for estimating toxic metal releases, as they are not destroyed during treatment; rather, they are transferred from one medium to another. This method cannot be applied as easily to organic toxics because transformation during waste treatment must be accounted for. In general, the difficulty with this method is determining the quantity of chemical released in different media.

Toxic Releases Via Wastewater

Typically, wastewater is centrally collected, treated, and disposed of. For this reason, the release estimation often can be made by focusing on only one waste disposal stream.

Most facilities dispose of their wastewater to publicly owned treatment works (POTWs), whereas others discharge their wastewater directly to nearby bodies of water. Wastewater treatment standards set forth by EPA in 1983 require leather tanning and finishing facilities to meet effluent limitations for various wastewater parameters, including total chromium. Except for small facilities that dispose of their wastewater to POTWs, each facility, whether discharging to a POTW (under national pretreatment standards) or directly to a body of water (under the National Pollution Discharge Elimination System, NPDES) must monitor its wastewater output for total chromium. Some facilities are also required by their pretreatment or NPDES permits to monitor for other toxic chemicals, such as toxic metals (lead, copper, cadmium, nickel, and zinc) and ammonia. This monitoring information can be used directly in the calculation of toxic releases via wastewater, as shown in the following example.

Example: Using direct measurement to estimate toxic release via wastewater.

The NPDES permit of a leather tanning facility requires daily monitoring of wastewater flow volume and biweekly analysis of a daily composite sample of this discharge for total chromium. The amount of chromium in the wastewater can be calculated as follows:

Pounds of chromium released in wastewater per day =

gallons of wastewater/day x

micrograms of chromium/liter x

3.78 liters/gal x

1 lb/435,000,000 µg

The total chromium analytical results and the calculated releases calculated by this equation are presented below.

Discharge flow rate, million gal/day	*Total chromium, µg/liter*	*Releases, lb/day*
0.415	*918*	*3.2*
0.394	*700*	*2.3*
0.417	*815*	*2.8*
0.440	*683*	*2.5*
0.364	*787*	*2.4*
0.340	*840*	*2.4*
0.457	*865*	*3.3*
0.424	*643*	*2.3*
0.463	*958*	*3.7*
0.414	*681*	*2.4*
0.476	*680*	*2.7*
0.431	*627*	*2.3*
0.369	*807*	*2.5*
0.392	*729*	*2.4*
0.323	*964*	*2.6*
0.302	*722*	*1.8*
0.358	*566*	*1.7*
0.322	*510*	*1.4*
0.330	*630*	*1.7*
0.322	*630*	*1.7*
0.408	*652*	*2.2*
0.442	*649*	*2.4*
0.356	*695*	*2.1*
0.390	*758*	*2.5*
0.423	*658*	*2.3*
0.487	*970*	*3.9*

These data result in an average daily release of 2.44 pounds. If the plant discharges 250 days during the year, the total amount of chromium released to wastewater would thus be 610 pounds.

For toxic chemicals not monitored in the wastewater discharge, an alternative method of estimating releases is needed. One such method, discussed previously, is the use of a mass balance combined with engineering calculations. The following example shows how this method can be used to estimate releases of a toxic dye via wastewater.

Example: Using a mass balance and engineering calculations to estimate toxic release via wastewater:

In 1987, a tanning and finishing facility used a total of 89,000 pounds of Direct Black 38 in its coloring and bleaching process step. For the batches in which this dye was used, the pH level in the process drum was adjusted to 6.0. The percentage uptake of the dye in the leather is a function of a number of factors, including pH and the type of syntans present. The relationship between these factors can be found in standard references on leather processing. Based on such information, the facility operators estimated that the uptake rate for Direct Black 38 is 82 percent. This means 82 percent of the 89,000 pounds of Direct Black 38 was retained in the leather product and the remaining 15,020 pounds was drained to the wastewater collection system.

In the collection system at this facility, the dye flows through wastewater treatment before it is discharged, where it is biodegraded, volatilized to the air, or adsorbed onto sludge particles, or it passes through the process untreated. For dyes, the latter two fates are the most common. Data on wastewater treatment effectiveness are needed to finish the estimation of Direct Black 38 releases to water (percent passthrough) and to determine the quantity retained in the wastewater treatment sludge for ultimate disposal as solid waste (percent partitioned to sludge). Wastewater treatment effectiveness is very site- and operation-specific; therefore, estimates are not presented in this example.

It is suggested that any monitoring data for the chemical in question in the influent, effluent, and sludge of the treatment process be used to determine the chemical's fate. An elaborate set of monitoring data is not necessary; just enough to provide a rough estimate will do. Alternatively, you could look in the literature for wastewater treatment fates in systems similar to those at your facility that treat wastewater with similar characteristics. The EPA general Section 313 guidance document contains a number of citations on wastewater treatment effectiveness for some of the chemicals subject to reporting.

If your facility uses a listed mineral acid or base but this acid or base is effectively neutralized in use or during wastewater treatment (to pH of 6 to 9 as required by most effluent standards), no release quantities should be reported. If the acid or base is transformed into a reportable substance, however, you must estimate the quantity of this substance manufactured to determine if the threshold value has been reached. For example, sulfuric acid neutralized by sodium hydroxide yields sodium sulfate, which is a listed chemical.

Toxic Releases Via Solid Waste

Most solid wastes from tanning and finishing facilities are specifically excluded from hazardous waste regulations under RCRA. Releases of toxic chemicals in these wastes still must be estimated, however. The RCRA regulations exclude certain solid wastes from leather processing that contain chromium; the exclusion does not apply, however, if other materials are also present in the chromium-containing waste at levels deemed to be hazardous. Therefore, analytical monitoring of solid waste under RCRA generator requirements is site-specific for tanneries. If any solid wastes at your facility are subject to RCRA reporting requirements, this information can be used for direct estimating of toxic releases.

For solid wastes generated directly from the shaving and buffing of hides, the concentration of a toxic chemical in the solid waste is roughly equal to the concentration in the leather at that point in the process. Thus, if the amount of toxic chemical in the leather product and the quantity of shavings and buffing dust generated are known, the quantity of toxic chemical released in these particular solid wastes can be estimated. This estimating technique can be used in conjunction with a mass balance to estimate overall releases from the facility, as shown in the following example.

Example: Using a mass balance and engineering calculations to estimate solid waste releases of chromium.

In 1987, a leather tanning and finishing facility used 750,000 pounds of 15 percent (as Cr_2O_3) basic chromic sulfate solution in its tanning process. Wastewater monitoring data on the facility's effluent indicate that 3,600 pounds of Cr was discharged during the year. The 750,000 pounds of chromic sulfate solution used contained 77,000 pounds of Cr. In the tanning process at this facility, the overall chromium uptake rate in the leather is estimated to be 80 percent. Therefore, 61,600 pounds of Cr was left in the leather and 15,400 pounds was sent to wastewater treatment.

Based on estimates by facility operators, the quantity of shavings and buffing dust generated after tanning amounted to approximately 5 percent of the leather produced. Assuming that these solid wastes have the same concentration of Cr as the final product leather, they would contain the 5 percent (or 3,080 pounds) of the 61,600 pounds of Cr that remains fixed in the tanning process.

The quantity of Cr in the sludge generated during wastewater treatment would be the difference between the amount discharged to wastewater treatment (15,400 pounds) and the amount estimated to be in the wastewater effluent (3,600 pounds), or 11,800 pounds. The total Cr released via solid waste would be the sum of the sludge and shavings and buffing dust, or 14,880 pounds. Using this approach, the plant in this example could report a total release of 15,000 pounds of Cr via solid waste.

Emission factors can also be used in estimating toxic releases via solid waste. The EPA publication entitled "Assessment of Industrial Hazardous Waste Practices, Leather Tanning and Finishing Industry," contains factors based on quantities of various solid wastes generated by different types of facilities. It also includes typical concentrations of toxic metals found in these wastes. Emission factors should only be used when other methods of estimation cannot be applied, however.

Toxic Releases to Air

Typically, air emissions from leather tanning and finishing facilities will not have been measured. Therefore, mass balances and/or engineering calculations must be used. If the quantity of a toxic chemical has been directly measured in the solid waste and wastewater from a facility, the quantity released to air can be estimated by determining the difference between that amount and the total quantity of that chemical used. Usually, this much information will not be available on those compounds released to air; thus, engineering assumptions must be used.

Example: Using an engineering assumption to estimate air releases of 1,1,1-trichloroethane (1,1,1-TCE).

The chemical 1,1,1-TCE is used in the application of a coating in a leather-finishing facility. The coating is applied to the leather with a roll coating machine. The leather is then placed in a dryer, where the 1,1,1-TCE in the coating evaporates. It can be assumed that all of the

1,1,1-TCE is released to air. Assuming 50,000 pounds of this coating (containing 30 percent 1,1,1-TCE) is used in a year, 15,000 pounds of 1,1,1-TCE would be released to air. If the dryer vent is equipped with a control device, any transfer of 1,1,1-TCE to solid or liquid waste must be accounted for.

Other Toxic Releases

Leather tanning and finishing facilities produce other wastes from which toxic chemicals may be released. These include:

- **Residues from pollution control devices**
- **Wash water from equipment cleaning**
- **Product rejects**
- **Used equipment**
- **Empty chemical containers**

Releases from these sources may already have been accounted for, depending on the release estimation methods used. These items (and any other of a similar nature) should be included in the development of your process flow diagram.

The contribution of sources of wastes such as cleaning out vessels or discarding containers should be small compared with process losses. If you do not have data on such sources (or any monitoring data on overall water releases), assume up to 1 percent of vessel content may be lost during each cleaning occurrence. For example, if you discard (to landfill) "empty" drums that have not been cleaned, calculate the release as 1 percent of normal drum content. If the drums are washed before disposal, this may contribute 1 percent of the content to your wastewater loading.

Step Five

Complete the Toxic Chemical Release Inventory Reporting Form.

After estimating the quantity of each chemical released via wastewater, solid waste, and air emissions, you must determine the amount of each chemical released to water, land, or air or transferred to an offsite disposal facility. This determination will be based on the disposal method you use for each of your waste streams. Enter the release estimates for each chemical or chemical category in Part III of the Toxic Chemical Release Inventory Reporting Form. Also enter the code for each treatment method used, the weight percent by which the treatment reduces the chemical in the treated waste stream, and the concentration of the chemical in the influent to treatment (see instructions). Report treatment methods that do not affect the chemical by entering "0" for removal efficiency.

For More Information

Emergency Planning and Community Right-to-Know Hotline	(800) 535-0202 or (202) 479-2449 (in Washington, D.C. and Alaska)
Small Business Ombudsman Hotline	(800) 368-5888 or (703) 557-1938 (in Washington, D.C. and Virginia)

The EPA brochure, Emergency Planning and Community Right-to-Know Act, Section 313 Release Reporting Requirements (EPA 560/4-88-001) presents an overview of the new law. It identifies the types of facilities that come under the provisions of Section 313, the threshold chemical volumes that trigger reporting requirements, and what must be reported. It also contains a complete listing of the chemicals and chemical categories subject to Section 313 reporting. The EPA publication, Estimating Releases and Waste-Treatment Efficiencies for the Toxic Chemical Release Inventory Form (EPA 560/4-88-002), presents more detailed information on general release estimation techniques than is included in this document.

Additional Sources of Information on Releases From Leather Tanning and Finishing

U.S. Environmental Protection Agency. Development Document for Effluent Limitations Guidelines New Source Performance Standards and Pretreatment Standards for the Leather Tanning and Finishing Point Source Category. Washington, D.C. November 1982.

U.S. Environmental Protection Agency. Assessment of Potential Toxic Releases From Leather Industry Dyeing Operations. EPA-600/2-78-215. Cincinnati, Ohio. October 1978.

U.S. Environmental Protection Agency. Assessment of Industrial Hazardous Waste Practices, Leather Tanning and Finishing Industry. NTIS PB-261018. November 1976.

Thorstensen, T.C. Practical Leather Technology. R. E. Krieger Publishing Company, New York. 1976.

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