United States
Environmental Protection
Agency

Office of Pesticides
and Toxic Substances

EPA 560/4-88-004q
March 1988

EPA

Title III Section 313 Release Reporting Guidance

Estimating Chemical Releases From Rubber Production and Compounding

Emergency Planning and
Community Right-to-Know Act of 1986

Estimating Chemical Releases From Rubber Production and Compounding

Facilities engaged in rubber production and compounding 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 (rubber production and compounding facilities generally fall under SIC codes 2822 and 2830) 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 who produce rubber 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 rubber production, 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 rubber production 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.

Synthetic rubber manufacturing

Monomers: 1,3-butadiene, styrene, acrylonitrile, ethylene, ethylene glycol, propylene glycol, propylene, 1,3-toluene diisocyanate, ethylene dichloride, epichlorohydrin, acrylic acid, ethyl acrylate, butyl acrylate, chloroprene, ethylene oxide

Retarders: Phthalic anhydride, n-nitrosodiphenylamine

Catalysts: Cobalt compounds, nickel compounds, titanium tetrachloride

Antioxidants: Phenylene diamine

Short stops: Hydroquinone

Solvents: Toluene, methyl chloride (chloromethane), 1,1,2-trichloroethane

Cooling tower corrosion inhibitors: Chromium compounds, zinc compounds

Miscellaneous chemicals: Sodium hydroxide, sulfuric acid, various additives

Rubber compounding

Processing aids: Zinc compounds

Accelerators: Zinc compounds, ethylene thiourea, diethanolamine

Age restorers: Nickel compounds, hydroquinone, phenol, alpha-naphthylamine, p-phenylenediamine

Vulcanizing agents: Selenium compounds, zinc compounds, lead compounds

Initiator: Benzoyl peroxide

Accelerator activators: Zinc compounds, lead compounds, ammonia

Plasticizers: Dibutyl phthalate, dioctylphthalate, bis (2-ethylhexyl adipate)

Miscellaneous ingredients: Titanium dioxide, cadmium compounds, organic dyes, antimony compounds

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 as byproducts or impurities. Toxic compounds that are incorporated into your products (for example, monomers, plasticizers, and vulcanizing agents) would be considered "processed" because they become part of the marketed finished product. Acids, caustics, solvent carriers, degreasing solvents, cleaning agents, and other chemicals that do not become part of the finished product would be considered "otherwise used."

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: Calculating annual use of sodium hydroxide at a synthetic rubber manufacturing facility.

In 1987, a synthetic rubber plant purchased 70,000 gallons of a 50 percent sodium hydroxide solution for use in its caustic washing process. At the beginning of the year, 10,000 gallons of this solution was in storage, and 5,000 gallons remained in storage at the end of the year. According to Section 313 definitions, sodium hydroxide is considered "otherwise used" in this process. The quantity of sodium hydroxide otherwise used during the year can be estimated by the following calculation:

Annual usage of solution =

10,000 gallons (beginning inventory) +

70,000 gallons (purchased) –

5,000 gallons (ending inventory)

= 75,000 gallons

Amount of NaOH used =

75,000 gallons of NaOH solution x

1.5253 (specific gravity of 50% NaOH) ÷

8.33 lb/gal (density of water) x

0.5 lb NaOH/1 lb solution

= 476,866 lb

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.

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 figures presented in this pamphlet are example flow diagrams for synthetic rubber production by the emulsion production process. 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.

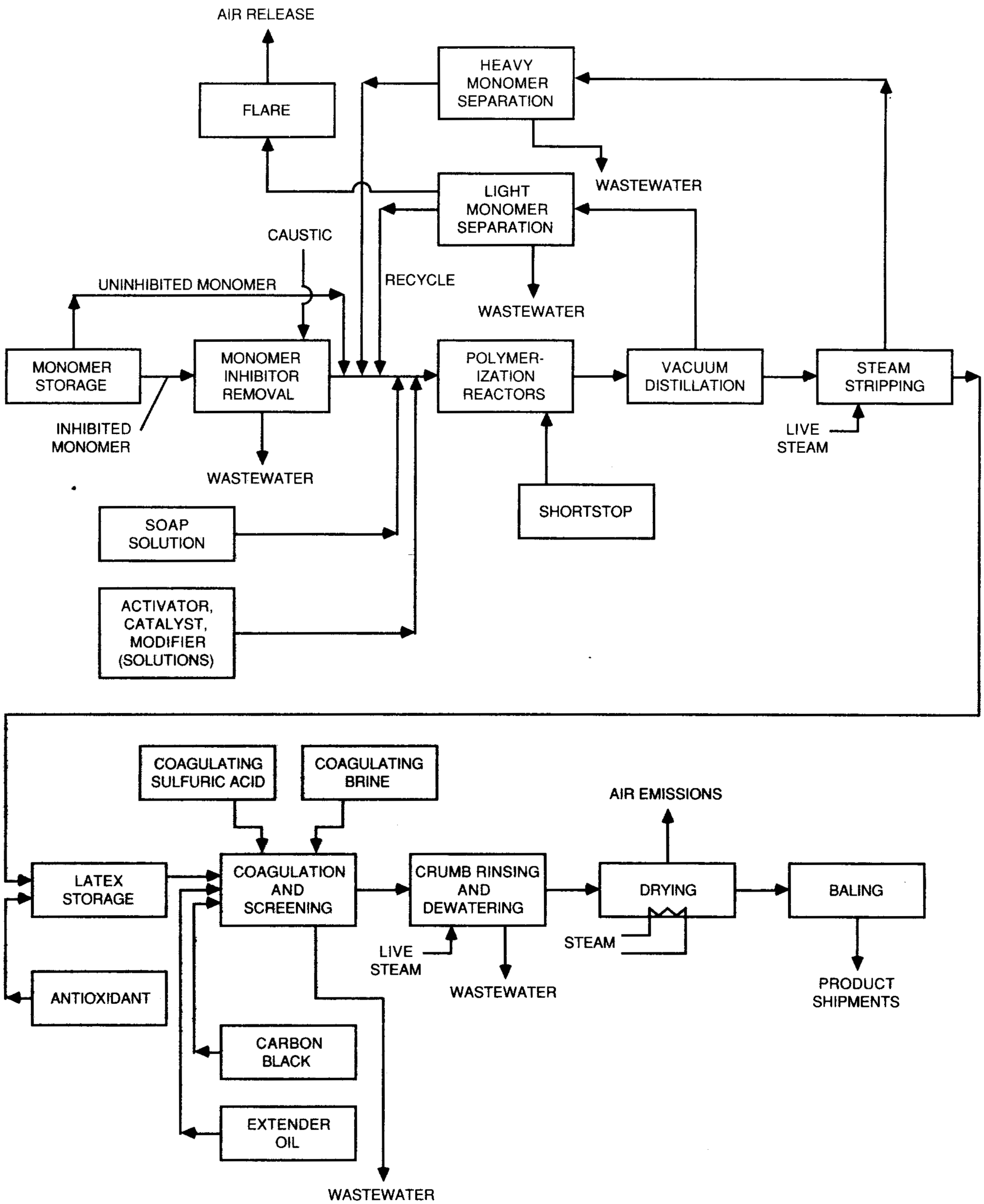
Releases from synthetic rubber production are primarily in the form of wastewater. Wastewater from these facilities comes from one of three sources: 1) utility wastewater, such as cooling tower blowdown; 2) process wastewater, such as the decant water from solvent separators; and 3) wastewater from equipment and area washdowns. Process wastewater and equipment cleanup wastewater are usually combined in a single plant effluent stream.

Solid wastes in this production process are present primarily as suspended solids in plant wastewater. The rubber solids that collect on much of the process equipment are either removed by hand or washed off with water and discarded in the general plant wastewater. These solids are subsequently removed from the wastewater treatment plant as sludge.

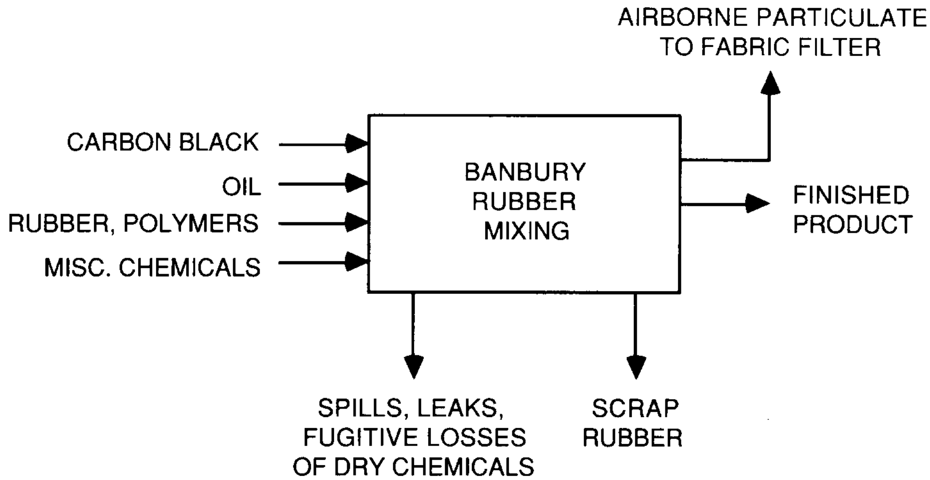
Atmospheric releases (primarily monomers) generally emanate from the monomer recovery process, absorber vents, and drying operations. Fugitive emissions of gaseous organic compounds are possible from virtually all of the processes associated with synthetic rubber manufacturing. These fugitive emissions include minor leaks to the atmosphere from pumps, relief valves and fittings, and from loading, unloading, and storage operations.

Releases from rubber compounding facilities are primarily in the form of fugitive air emissions and solid wastes. Fugitive air emissions occur primarily from mixing operations. Solid wastes generally occur in the form of scrap and scorched rubber; dusts and powders from fabric filters in the mixing and compounding areas and from unloading, storage, and equipment cleanup operations; and contaminated lubricating oil "oozings" from process mixers.

Your reporting must account for all releases.



Example Flow Diagram for Crumb Rubber Production by Emulsion Polymerization (adapted from Source Assessment: Rubber Processing State-of-the-Art)



Example Flow Diagram of Rubber Compounding Process

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.

The complexity of the rubber manufacturing and compounding processes, the many separate steps involved, and the irregular batch-type operation make release estimation a difficult task. When direct measurement data are not available, emission factors and mass balances, supplemented by engineering assumptions, must be used. Mass balance estimates are most effective for chemicals that are "otherwise used," such as catalysts, solvents, acids, and bases. Because these chemicals do not become part of the product, the quantity used is equal to the quantity released as waste before treatment. Engineering assumptions can then be used to determine into which media the chemical is released (air, wastewater, or solid waste). Caution should be exercised when using the mass balance technique to estimate chemical releases when the raw material input and product output streams are large, as small errors in purchasing and production data can lead to large errors in release estimates.

The mass balance estimation technique is quite applicable to rubber compounding operations because of the precision required when weighing out additives for the rubber recipe. Given detailed information on chemical inputs and knowledge of the quantity of chemical retained in the product and chemically transformed during processing, one can calculate chemical releases by determining the difference.

Toxic Releases Via Wastewater

Ideally, the wastewater streams will be combined into a single effluent stream for which measurements of flow and concentrations are available. Some monitoring information may be available from wastewater discharge permits and in-house sampling studies. Wastewater flows and release parameters such as biochemical oxygen demand, chemical oxygen demand, suspended solids, etc., will be summarized on your discharge permit; however, concentrations for specific listed compounds may not be available.

When direct measurement information is unavailable, an alternative estimation technique must be used. For "otherwise used" compounds with extremely low vapor pressures (for example, metal catalysts), you may assume that all of the chemical used is released in wastewater. If wastewater treatment is used, a portion of these compounds will be transferred to the wastewater sludge or biodegraded, whereas the remainder will be discharged with the wastewater.

Example: Using a mass balance to estimate releases of cobalt compounds from a cobalt-based catalyst.

In 1987, a synthetic rubber production facility produced 80,000 pounds of polybutadiene. A homogeneous cobalt-based catalyst was used in the reaction process. Samples of the rubber product contained 170 ppm of cobalt. Purchasing and inventory records indicate that 64,000 pounds of $CoCl_2$ catalyst was processed.

Assuming that the catalyst is the only source of cobalt in the process and that all equipment-cleaning wastes are washed into the facility's sewers, the quantity of cobalt released can be estimated by mass balance. The quantity of cobalt lost as waste is calculated as follows:

Amount of cobalt entering process =

64,000 lb $CoCl_2$ x

59 lb Co/130 lb $CoCl_2$

= 29,046 lb

Amount of cobalt in product =

80,000 tons polybutadiene x

2,000 lb/ton x

170 lb cobalt/1,000,000 lb polybutadiene

= 27,200 lb

Amount of cobalt lost as waste =

29,046 lb (entering process) –

27,200 lb (in product)

= 1,846 lb

It can be assumed that the 1,846 pounds of cobalt was lost through equipment washdowns. If untreated wastewater from the facility was discharged to a publicly owned treatment *works (POTW), the facility could report that 1,900 pounds of cobalt was "transferred to POTW." If pretreatment was provided on site and a wastewater sludge was generated, estimates of the quantity of cobalt released as solid waste would also have to be considered.*

The problems inherent with the use of mass balances for large processes are evident if you assume that the quantity of cobalt found in the polybutadiene product was 200 ppm rather than 170 ppm. At 200 ppm, the quantity of cobalt leaving as product would be 32,000 pounds, which exceeds the quantity of cobalt entering the process. Thus, a small analytical error in the product stream could cause a large error in the release estimation.

Toxic Releases to Air

Atmospheric emissions data may be available from process monitoring information (vent flows and concentrations), air operating permits, or the technical literature. Most of the information available on air emissions will be in the form of total VOC and particulate emissions. Engineering calculations and assumptions can often be used to convert this type of information into releases of specific toxic compounds. If mass balance calculations are used, you can assume that any releases of extremely volatile compounds (such as butadiene) will be to the atmosphere.

Example: Using an emission factor to estimate atmospheric releases from a monomer recovery process.

A monomer plant produces 40,000 tons of crumb emulsion latex per year. Emission measurement data are not available, and an accurate mass balance calculation is difficult to perform because of the large input and output streams. According to EPA's Compilation of Air Pollutant Emission Factors, total volatile organic emissions are approximately 5.2 pounds per ton of latex produced. An occupational monitoring program at this plant indicated that butadiene concentrations in the ambient air were typically 9 times greater than styrene concentrations. Because butadiene and styrene will make up the vast majority of the VOC emissions, it can be assumed that total butadiene and styrene air releases are 5.2 pounds per ton of latex. Based on the 9-to-1 ratio of butadiene to styrene, process releases can be calculated as follows:

Amount of 1,3-butadiene released =

40,000 tons latex x

5.2 lb volatiles/1 ton latex x 90%

= 187,200 lb

Amount of styrene released =

40,000 tons latex x

(5.2 lb volatiles/1 ton latex) x 10%

= 20,800 lb

These releases are sent to a flare before being discharged to the atmosphere. Based on the manufacturer's experience and test data, the flare destruction efficiency is assumed to be 90 percent. Thus, the plant in this example could report annual releases of 19,000 pounds of 1,3-butadiene and 2,100 pounds of styrene.

Air releases from rubber compounding operations, which are typically in the form of particulates, are often controlled by fabric filters. If the fabric filter efficiency and quantity of particulate captured are known or can be estimated, air releases can be calculated. The specific chemical composition of the fabric filter dusts can then be used to estimate air releases of toxic chemicals.

Toxic Releases Via Solid Waste

In general, only direct measurement and mass balance techniques are useful for estimating toxic chemical releases in wastewater treatment sludge. Direct measurement data for wastewater sludge are often required before disposal will be approved. If direct measurement data are used to estimate wastewater releases, you may find a mass balance estimation technique useful for estimating releases via wastewater sludge.

Estimating solid wastes generated from rubber compounding operations usually requires mass balances and/or engineering calculations. For example, if the quantity of scrap rubber discarded and the concentration of a toxic constituent in the rubber product are known, multiplying these values will yield an estimate of the release of the constituent in the scrap (solid waste). The key to this approach is knowing the concentrations of toxic chemicals in the rubber product.

Example: Estimating zinc releases in solid wastes from a rubber compounding operation.

Based on the recipes used, a rubber compounder knows the concentration of zinc oxide in a particular rubber mixture is 2.5 percent by weight. Production records indicate that 2,000 tons of this rubber mixture was manufactured in 1987. Purchasing and inventory records indicate that 105,000 pounds of zinc oxide was processed during the year. The quantity of zinc oxide (and thus zinc) lost as solid waste can be calculated by mass balance as follows:

Amount of ZnO in product =

2,000 tons rubber product x

2,000 lb/ton x

0.025 lb ZnO/1 lb product

= 100,000 lb

Amount of ZnO in solid waste =

105,000 lb ZnO (processed) -

100,000 lb ZnO (in product)

= 5,000 lb

Amount of zinc in waste =

5,000 lb ZnO x

0.8 lb Zn/1 lb ZnO

= 4,000 lb

It may be assumed that all of the zinc lost through cleanups, scrap rubber, and fabric filter particulate (assuming the fabric filter capture efficiency is high) is released as solid waste.

Other Toxic Releases

Other wastes in the rubber production and compounding industry from which toxic chemicals may be released 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 your development of a 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, Title III Section 313 Release Reporting Requirements (EPA 560/4-87-001) 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 Rubber Production and Compounding

U.S. Environmental Protection Agency. Source Assessment: Rubber Processing State-of-the-Art. EPA-600/2-78-004. PB 281423/4. Cincinnati, Ohio. March 1978.

U.S. Environmental Protection Agency. The Rubber Processing Chemicals Data Base. EPA-600/2-84-030. January 1984.

U.S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors, Fourth Edition. AP-42. Research Triangle Park, North Carolina. September 1985.

U.S. Environmental Protection Agency. Industrial Process Profile for Environmental Use. Chapter 9: The Synthetic Rubber Industry. EPA-600/2-77-023. Cincinnati, Ohio. February 1977.

EPA

United States
Environmental Protection
Agency

Office of Pesticides and
Toxic Substances, WH-562A
Washington, D.C. 20460