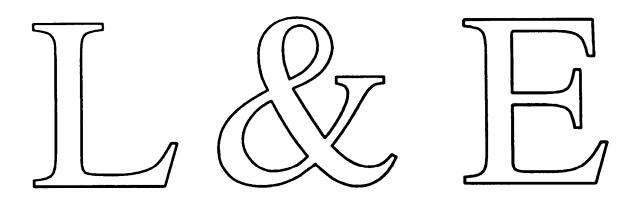
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LOCATING AND ESTIMATING AIR EMISSIONS FROM SOURCES OF 1,3-BUTADIENE





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LOCATING AND ESTIMATING AIR EMISSIONS FROM SOURCES OF 1,3-BUTADIENE

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EXECUTIVE SUMMARY

The 1990 Clean Air Act Amendments contain a list of 189 hazardous air pollutants (HAPs) which the U.S. Environmental Protection Agency must study, identify sources of, and determine if regulations are warranted. One of these HAPs, 1,3-butadiene (butadiene), is the subject of this document. This document describes the properties of butadiene as an air pollutant, defines its production and use patterns, identifies source categories of air emissions, and provides butadiene emissions data in terms of emission factors and national inventory estimates. The document is a part of an ongoing EPA series designed to assist the general public at large, but primarily State/local air agencies, in identifying sources of HAPs and determining emissions estimates.

Butadiene is primarily used in the manufacture of synthetic elastomers (rubbers, latexes) and for producing raw materials for nylon. Butadiene is emitted into the atmosphere from its production, its use as a chemical feedstock in the production of other chemicals, the use of these other chemicals, mobile sources, and from a wide variety of miscellaneous processes involving fossil fuel and biomass combustion, petroleum refining, secondary lead smelting, and wastewater treatment.

Including only sources for which estimates are available or can be calculated, total nationwide emissions are estimated at 121,002 tons per year (109,775 Mg/yr). The primary sources of butadiene emissions on a national level are on-road mobile (47%) and off-road mobile (35%). Table ES-1 illustrates the national emissions estimates developed for the more predominant butadiene categories. The main butadiene air emissions sources are on-road mobile, off-road mobile, biomass burning, butadiene users, and petroleum refining. Some of these estimates for the non-fuel combustion sources were obtained from the reports required under the Superfund Amendment and Reauthorization Act (SARA), Title III, Section 313. Other estimates are a function of national activity data combined with the best available emission factors.

Table ES-1. National Emission Estimates by Source Category^a

	Source	Applicable Year	Tons (Mg)	Percent
Mobile	On-road	1992	56,786 (51,517)	47.3
	Off-road	1990	41,883 (37,996)	34.9
	General aviation and air taxis	1994	107 (97)	0.1
Stationary	Biomass burning (forest fires & prescribed burning)	1989	19,931 (18,082)	16.0
	Major butadiene users ^b	1992	1,405 (1,275)	1.2
	Petroleum refining	1992	219 (199)	0.2
	Butadiene production	1992	191 (173)	0.2
	Secondary lead smelting	1990	134 (122)	0.1
	Miscellaneous other sources ^c	1992	106 (96)	0.1
Total			121,049 (109,004)	100.1

^a Only sources for which estimates were available or could be calculated are included. For example, emissions from open burning of tires have not been included.

b Includes following SIC Codes:

²⁸ Chemicals and allied products

²⁸¹² Alkalies and chlorine

²⁸¹⁹ Industrial inorganic chemicals, nec

²⁸²¹ Plastics materials synthetic resins and nonvulcanizable elastomers

²⁸²² Synthetic rubber (vulcanizable elastomers)

²⁸⁶⁵ Cyclic organic crudes and intermediates, and organic dyes and pigments

²⁸⁶⁹ Industrial organic chemicals, nec

²⁸⁷⁹ Pesticides and agricultural chemicals, nec

²⁸⁹¹ Adhesives and sealants

²⁸⁹⁹ Chemicals and chemical preparations, nec

Other sources reporting under SARA 313 include facilities identified with the following SIC Codes. Also included are two facilities without SIC Codes but which account for 15 tons per year (14 Mg/yr) combined, and one facility with an SIC Code that is not listed but which reported 0.04 tons per year (0.04 Mg/yr).

Wet corn milling

²³⁶⁹ Girl's, children's, and infant's outwear, nec

²⁶²¹ Paper mills

³³¹² Steel works, blast furnaces (including coke ovens), and rolling mills

³⁵⁷⁹ Office machines, nec

⁸⁷³¹ Commercial physical and biological research

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SECTION 1.0 PURPOSE OF DOCUMENT

The U.S. Environmental Protection Agency (EPA), State, and local air pollution control agencies are becoming increasingly aware of the presence of substances in the ambient air that may be toxic at certain concentrations. This awareness, in turn, has led to attempts to identify source/receptor relationships for these substances and to develop control programs to regulate emissions. Unfortunately, limited information is available on the ambient air concentrations of these substances or about the sources that may be discharging them to the atmosphere.

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of locating and estimating (L&E) documents such as this one that compiles available information on sources and emissions of these substances. Other documents in the series are listed below:

<u>Substance</u>	EPA Publication Number
Acrylonitrile	EPA-450/4-84-007a
Benzene (under revision)	EPA-450/4-84-007q
Cadmium	EPA-454/R-93-040
Carbon Tetrachloride	EPA-450/4-84-007b
Chlorobenzene (update)	EPA-454/R-93-044
Chloroform	EPA-450/4-84-007c
Chromium (supplement)	EPA-450/2-89-002
Chromium	EPA-450/4-84-007g
Coal and Oil Combustion Sources	EPA-450/2-89-001

<u>Substance</u>	EPA Publication Number
Cyanide Compounds	EPA-454/R-93-041
Epichlorohydrin	EPA-450/4-84-007j
Ethylene Dichloride	EPA-450/4-84-007d
Ethylene Oxide	EPA-450/4-84-0071
Formaldehyde	EPA-450/4-91-012
Manganese	EPA-450/4-84-007h
Medical Waste Incinerators	EPA-454/R-93-053
Mercury and Mercury Compounds	EPA-453/R-93-023
Methyl Chloroform	EPA-454/R-93-045
Methyl Ethyl Ketone	EPA-454/R-93-046
Methylene Chloride	EPA-454/R-93-006
Municipal Waste Combustors	EPA-450/2-89-006
Nickel	EPA-450/4-84-007f
Perchloroethylene and Trichloroethylene	EPA-450/2-89-013
Phosgene	EPA-450/4-84-007i
Polychlorinated Biphenyls (PCBs)	EPA-450/4-84-007n
Polycyclic Organic Matter (POM) (under revision)	EPA-450/4-84-007p
Sewage Sludge Incinerators	EPA-450/2-90-009
Styrene	EPA-454/R-93-011
Toluene	EPA-454/R-93-047
Vinylidene Chloride	EPA-450/4-84-007k
Xylenes	EPA-454/R-93-048

In addition, new documents currently under development will address lead, chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans, and arsenic and arsenic compounds.

This document deals specifically with 1,3-butadiene, commonly referred to as butadiene. Its intended audience includes Federal, State, and local air pollution personnel and others who are interested in locating potential emitters of 1,3-butadiene and estimating their air emissions.

Because of the limited availability of data on potential sources of 1,3-butadiene emissions and the variability in process configurations, control equipment, and operating procedure among facilities, this document is best used as a primer on (1) types of sources that may emit 1,3-butadiene, (2) process variations and release points that may be expected, and (3) available emissions information on the potential for 1,3-butadiene releases into the air. The reader is cautioned against using the emissions information in this document to develop an exact assessment of emissions from any particular facility. For facilities, most estimates are values reported by the facilities in 1984 in response to EPA requests for information and therefore may be out of date. Furthermore, not all facilities received requests, and those that received requests did not always provide complete responses. For more accurate estimates, the reader should seek more current and complete data.

It was thought at one point that the 1984 Chemical Manufacturers Association (CMA) facility data could be updated using the Toxic Release Inventory (TRI). However, because many of the chemical production facilities produce multiple chemicals, it was not possible to accurately apportion the TRI data to the specific CMA facilities.

An effort was made to obtain more up-to-date information than the 1984 data. A literature search was conducted and several databases were accessed. The most promising sources of potential data are the current Polymers/Resins National Emission Standard for Hazardous Air Pollutants (NESHAP) and Rubber Chemicals work. The polymers/resins NESHAP was to have been completed and published by fall, 1994, but because of the confidentiality of much of the data, it was not possible to obtain those data at the present time to include in this L&E document. The process descriptions in this L&E document should not differ greatly from those in the NESHAP. However, it is not certain at this time what data will be available from the NESHAP and how the data might differ from what is presently in the L&E.

The rubber chemicals work has been delayed, so that EPA can expand the definition of "rubber chemicals" to include a broader category of chemicals. It is not expected that information will be available in time to be included in this version of the Butadiene L&E.

It is possible, in some cases, that orders-of-magnitude differences may result between actual and estimated emissions, depending on differences in source configurations, control equipment, and operating practices. Thus, in all situations where an accurate assessment of 1,3-butadiene emissions is necessary, the source-specific information should be obtained to confirm the existence of particular emitting operations and the types and effectiveness of control measures, and to determine the impact of operating practices. A source test and/or material balance calculations should be considered as the best method of determining air emissions from an operation.

Most of the emission factors for the basic production and intermediate product sources presented in the text are based on the 1984 data. The supporting facility-specific data are provided in Appendix C. The emission rates for equipment leaks were developed by the CMA and are based on a 1989 study of equipment leak emissions at butadiene production facilities. These CMA rates are significantly different from the Synthetic Organic Chemical Manufacturing Industry (SOCMI) average emission rates, and, because they are specific to butadiene, are assumed to better represent equipment leak emissions at other butadiene user facilities; therefore, they were used to estimate annual emissions. Again, the reader should collect facility-specific data for the most accurate estimates.

The chemical industry as a whole has done a lot to reduce emissions since the early/mid 1980s as interest in air toxics has grown. A number of National Emission Standards for Hazardous Air Pollutants (NESHAP) have been promulgated that are expected to reduce butadiene emissions from facilities that are subject to the regulatory requirements. The recent NESHAP that will impact butadiene emissions the most include the Hazardous Organic NESHAP (HON) which has been promulgated April 22, 1994 and NESHAP for several of the Polymers and Resins categories that are under development. Others include the NESHAP for Publicly Owned Treatment Works, the Petroleum Refineries NESHAP and the NESHAP for

secondary lead production. Specific requirements and impacts are not included in this document. The reader should refer to the regulations to assess the reductions achieved.

The EPA also initiated a voluntary program in 1991 as a part of the Agency's pollution prevention strategy. Known as the 33/50 Program, companies committed to reducing facilities emissions for 17 high priority compounds. Although butadiene is not among the listed compounds, reductions would be achieved where butadiene was co-located with a listed compound or where shared equipment was modified to reduce emissions of the 17 high priority compounds.

In addition to the information presented in this document, another potential source of emissions data for 1,3-butadiene from facilities is the Toxic Chemical Release Inventory (TRI) form required by Title III, Section 313 of the 1986 Superfund Amendments and Reauthorization Act (SARA).² Section 313 requires owners and operators of facilities in certain Standard Industrial Classification Codes that manufacture, import, process, or otherwise use toxic chemicals (as listed in Section 313) to report annually their releases of these chemicals to all environmental media. As part of SARA 313, EPA provides public access to the annual emissions data.

The TRI data include general facility information, chemical information, and emissions data. Air emissions data are reported as total facility release estimates for fugitive emissions and point source emissions. No individual process or stack data are provided to EPA under the program. SARA Section 313 requires sources to use available stack monitoring data for reporting but does not require facilities to perform stack monitoring or other types of emissions measurement. If monitoring data are unavailable, emissions are to be quantified based on best estimates of releases to the environment.

The reader is cautioned that TRI will not likely provide facility, emissions, and chemical release data sufficient for conducting detailed exposure modeling and risk assessment.

In many cases, the TRI data are based on annual estimates of emissions (i.e., on emission factors, material balance calculations, and engineering judgment). We recommend the use of TRI data in conjunction with the information provided in this document to locate potential emitters of butadiene and to make preliminary estimates of air emissions from these facilities.

For mobile sources, more data are becoming available for on-road vehicles. Additionally, the EPA model that generates emission factors undergoes regular update. The on-road mobile sources section in this document should therefore be viewed as an example of how emissions can be determined and the reader should look for more detailed data for the most accurate estimates.

Limited data on off-road vehicles and other stationary sources are available. However, with EPA's increased emphasis on air toxics, more butadiene data are likely to be generated in the future.

As standard procedure, L&E documents are sent to government, industry, and environmental groups wherever EPA is aware of expertise. These groups are given the opportunity to review a document, comment, and provide additional data where applicable. Where necessary, the document is then revised to incorporate these comments. Although this document has undergone extensive review, there may still be shortcomings. Comments subsequent to publication are welcome and will be addressed based on available time and resources. In addition, any information on process descriptions, operating parameters, control measures, and emissions information that would enable EPA to improve on the contents of this document is welcome. Comments and information may be sent to the following address:

Leader, Emission Factor and Methodologies Team Emission Factor and Inventory Group (MD-14) U.S. Environmental Protection Agency Research Triangle Park, NC 27711

SECTION 2.0 OVERVIEW OF DOCUMENT CONTENTS

This section briefly outlines the nature, extent, and format of the material presented in the remaining sections of this report.

Section 3.0 provides a brief summary of the physical and chemical characteristics of butadiene and an overview of its production, uses, and emissions sources. This background section may be useful to someone who needs to develop a general perspective on the nature of butadiene, how it is manufactured and consumed, and potential production, use, and mobile sources of emissions.

Section 4.0 focuses on the production of butadiene and the associated air emissions. For each major production source category described in Section 4.0, an example process description and a flow diagram with potential emission points are given. Available emissions estimates were used to calculate emission factor ranges that show the potential for butadiene emissions before and after controls employed by industry. Also provided are estimates of annual emissions from equipment leaks. Individual companies that are reported in trade publications to produce butadiene are named.

Section 5.0 describes major source categories that use butadiene, primarily in the manufacture of synthetic elastomers. For each major production process, a description(s) of the process is given along with a process flow diagram(s). Potential emission points are identified on the diagrams and emission ranges are presented as estimates are available. Ranges of annual emissions due to equipment leaks are also given. Individual companies that use butadiene as a feedstock are reported.

Section 6.0 provides a brief summary on butadiene emissions from mobile sources. The section addresses both on-road and off-road sources.

Section 7.0 summarizes the source categories--termed miscellaneous sources--that use and potentially emit smaller quantities of butadiene. It also addresses emissions from indirect sources such as treatment of butadiene-containing wastewater and other potential sources that are not clearly users or indirect sources ("other" category). Limited information on these sources is available; therefore, varying levels of detail on the processes, emissions, and controls are presented. Locations of facilities for each source category as identified in the literature are provided.

The final section, Section 8.0, summarizes available procedures for source sampling and analysis of butadiene. This section provides an overview of applicable sampling procedures and cites references for those interested in conducting source tests.

Appendix A presents a summary table of the emission factors contained in this document. This table also presents the factor quality rating and the Source Classification Code (SCC) or Area/Mobile Source (AMS) code associated with each emission factor.

Appendix B provides a brief description of the basis for the national emission estimates appearing in Section 3.0. For each source, there is a description of the estimation approach and an example calculation.

Appendix C provides facility-specific data taken from Section 114 responses upon which the process vent and secondary source emission factors in Sections 4.0, 5.0, and 7.0 are based. Each facility has been assigned a letter code to prevent disclosure of its identity. In general, the equipment leak emissions shown were calculated by applying average CMA emission factors to the equipment component counts from the Section 114 responses. The exceptions are butadiene producers and miscellaneous users. For producers, equipment counts were summarized by CMA for 9 of the 11 facilities and the resulting emissions are presented as the most recent data. For the miscellaneous users, estimates based on SOCMI factors were

shown because equipment count data were not readily available to use with the average CMA emission factors. These were calculated in earlier work done by EPA.

Appendix D presents the procedure for the derivation of butadiene equipment leak emissions estimates associated with the production processes presented in Sections 4.0, 5.0, and 7.0. Calculations for pump seals and pressure relief valves appear as examples of these derivations.

Each emission factor listed in Sections 4.0 through 7.0 was assigned an emission factor rating (A, B, C, D, E, or U) based on the criteria for assigning data quality ratings and emission factor ratings as required in the document *Technical Procedures for Developing AP-42 Emission Factors and Preparing AP-42 Sections*.³ The criteria for assigning the data quality ratings to source tests are as follows:

- A Test(s) was performed by a sound methodology and reported in enough detail for adequate validation. These tests are not necessarily EPA reference test methods, although such reference methods are certainly to be used as a guide.
- B Test(s) was performed by a generally sound methodology but lacked enough detail for adequate validation.
- C Test(s) was based on a nonvalidated or draft methodology or lacked a significant amount of background data.
- D Test(s) was based on a generally unacceptable method but may provide an order-of-magnitude value for the source.

Once the data quality ratings for the source tests had been assigned, these ratings along with the number of source tests available for a given emission point were evaluated. Because of the almost impossible task of assigning a meaningful confidence limit to industry-specific variables (e.g., sample size vs. sample population, industry and facility variability, method of measurement), the use of a statistical confidence interval for establishing a representative emission factor for each source category was not practical. Therefore, some

subjective quality rating was necessary. The following factor quality ratings were used in the emission factor tables in this document:

<u>A - Excellent</u>. The emission factor was developed only from A-rated test data taken from many randomly chosen facilities in the industry population. The source category is specific enough to minimize variability within the source category population.

<u>B - Above average</u>. The emission factor was developed only from A-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As with the A rating, the source category is specific enough to minimize variability within the source category population.

<u>C - Average</u>. The emission factor was developed only from A- and B-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As with the A rating, the source category is specific enough to minimize variability within the source category population.

<u>D - Below average</u>. The emission factor was developed only from A- and B-rated test data from a small number of facilities, and there may be reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source category population.

 \underline{E} - \underline{Poor} . The emission factor was developed from C- and D-rated test data, and there may be reason to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population.

<u>U - Unrated or Unratable</u>. The emission factor was developed from suspect data with no supporting documentation to accurately apply an A through E rating. A "U" rating may be applied in the following circumstances:⁴

U1	=	Mass Balance (for example, estimating air emissions based
		on raw material input, product recovery efficiency, and
		percent control).

U2 = Source test deficiencies (such as inadequate quality assurance/quality control, questionable source test methods, only one source test).

U3 = Technology transfer. U4 = Engineering judgement.

U5 = Lack of supporting documentation.

This document does not contain any discussion of health or other environmental effects of butadiene, nor does it include any discussion of ambient air levels.

SECTION 3.0 BACKGROUND

3.1 NATURE OF THE POLLUTANT

Butadiene is a colorless, flammable gas with a pungent, aromatic odor. It has a boiling point between 24.8 and 23°F (-4 and -5°C). Table 3-1 summarizes butadiene's chemical and physical properties.^{5,6} Although butadiene is insoluble in water, it is slightly soluble in methanol and ethanol, and readily soluble at room temperature in common organic solvents such as benzene and ether.⁷ It forms azeotropes with ammonia, methylamine, acetaldehyde, n-butene, and 2-butene.⁵

Butadiene is a highly versatile raw material that is used commercially in a variety of reactions. These include:

- Diels-Alder reactions with dienophiles to form a six-membered ring compound with a 2,3 double bond,
- conversion to cyclic or open chain dimers and trimers,
- telomerization with active hydrogen compounds,
- addition reactions with electrophilic and free radical compounds,
- oxidation reactions,
- substitution reactions, and
- polymerization.

TABLE 3-1. PHYSICAL AND CHEMICAL PROPERTIES OF 1,3-BUTADIENE

Property	Value		
Structural Formula: C ₄ H ₆ , CH ₂ :CHCH:CH ₂			
Synonyms: biethylene, bivinyl, butadiene, butadiene monomer divinyl, erythrene, methylallene, pyrrolylene, vinyl ethylene			
CAS Registry Number: 106-99-0			
Molecular Weight	54.09		
Melting Point, °C	-108.91		
Boiling Point, °C	-4.41		
Partition Coefficient (log P, octanol/water)	1.99		
Density at 20°C, g/cm ³	0.6211		
Vapor Density	1.87		
Critical Density, g/cm ³	0.245		
Critical Temperature, °C	152		
Critical Pressure, MPa (psi)	4.32 (626)		
Critical Volume, mL/mol	221		
Vapor Pressure, atm:			
15.3°C	2.0		
47.0°C	5.0		
Flash Point, °C	-105		
Heat of Vaporization, J/g (cal/g):			
25°C	389 (93)		
bp	418 (100)		
Heat of Fusion, J/g (cal/g)	147.6 (35.28)		
Heat of Formation at 25°C, kJ/mol (kcal/mol):			
Gas	110.2 (26.33)		
Liquid	88.7 (21.21)		
Free Energy of Formation at 25 °C, kJ/mol (kcal/mol):			
Gas	150.7 (36.01)		
Explosive Limits, vol % butadiene in air:			
Lower	2.0		
Upper	11.5		
Solubility in Water at 20°C, mg/L	735		

Source: References 5 and 6.



Polymerization, with additions occurring at both the 1,2 and the 1,4 positions, are the basis for synthetic elastomer production, the major use of butadiene.⁸

Because of its reactivity, butadiene is estimated to have an atmospheric lifetime on the order of four hours, where atmospheric lifetime is defined as the time required for the concentration to decay to 1/e (37 percent) of its original value. Actual lifetime depends on the conditions at the time of release. The primary removal mechanisms are through chemical reactions with hydroxyl radicals and ozone. Therefore, factors influencing butadiene's atmospheric lifetime--time of day, sunlight intensity, temperature, etc.--also include those affecting the availability of hydroxyl radicals and ozone.

3.2 OVERVIEW OF PRODUCTION AND USE

Butadiene production in the United States is accomplished through either of two processes: recovery of butadiene from a mixed-C₄ hydrocarbon stream generated during ethylene production, or through oxidative dehydrogenation of n-butenes. Almost all, [1.47 millions tons (1.33 million megagrams) in 1993] results from recovery of butadiene as a byproduct of ethylene generation. Of the 10 U.S. producers, 8 are located in Texas and 2 in Louisiana.⁸ The majority of these producers generate the feedstock at the same location as butadiene production.⁸

Seventy-five percent of butadiene is used in synthetic elastomer production, 30 percent of which is dedicated to styrene-butadiene rubber; 20 percent to polybutadiene; 10 percent to styrene-butadiene latex; and 5 percent each to neoprene, acrylonitrile-butadiene-styrene resin, and nitrile rubber. A second major use of butadiene is in adiponitrile production (15 percent), the raw material for nylon 6,6 production. The remaining 10 percent is used for miscellaneous products; exports comprise less than 1 percent. Figure 3-1 illustrates these uses and the subsequent consumer end products. 8,11,12,13,14,15,16

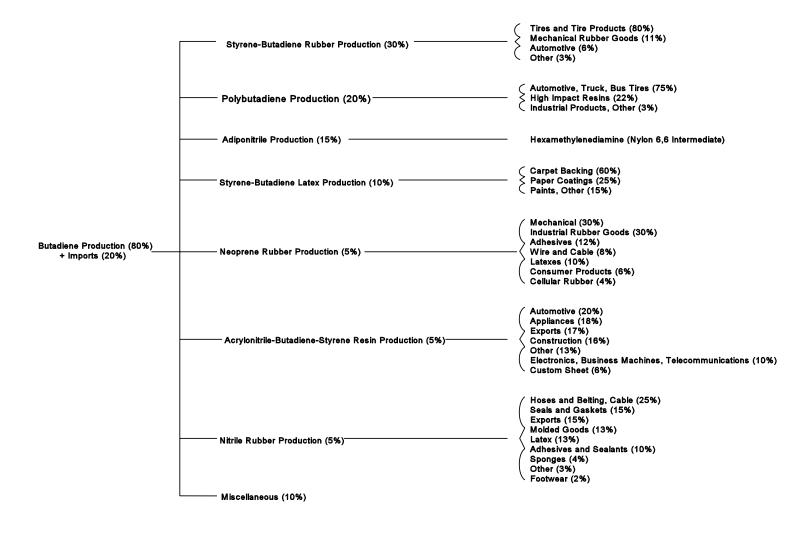


Figure 3-1. Chemical Production and Use Tree for 1,3-Butadiene

Long-term growth in demand for butadiene is expected to be modest, with reduced requirements for synthetic rubber because of quality and performance improvements in automobile and other road tires. There will be some newer butadiene applications (sealants, adhesives, processing aids for plastic industry) that will experience rapid growth in future years. However, overall U.S. butadiene demand growth is not expected to exceed 2 percent per year, and may well show a long term slow decline by 1995/1996. 10

3.3 OVERVIEW OF EMISSIONS

Sources of butadiene emissions from its production and uses are typical of those found at any chemical production facility:

- process vents,
- equipment leaks,
- waste streams (secondary sources),
- storage, and
- accidental or emergency releases.

Much of the available emissions data used to prepare this report were collected by EPA from industry in 1984. Use of these estimates to represent sources at different locations is of limited accuracy because of the differences in process configurations and plant operations. The equipment leak emission factors are based on a 1989 CMA study. The CMA Butadiene Panel collected monitoring data from nine of the facilities manufacturing butadiene to develop average component-specific emission factors. Although the accuracy of applying these emission factors to butadiene user facilities is undetermined, they are presented as an alternative to the SOCMI emission factors previously developed by EPA.

Emissions data from several butadiene sources, including mobile, petroleum refining, secondary lead smelting, tire burning, and biomass burning, have been added to this update of the document and are described in Section 7.0.

Estimated national emissions from on-road mobile sources amount to 56,786 tons (51,517 Mg) based on butadiene emission factors developed by the EPA Office of Mobile Sources¹⁷ and 1992 Department of Transportation data¹⁸ on vehicle miles travelled. For nonroad mobile sources, the EPA Nonroad Engine Vehicle Emission Study (NEVES) provides an average estimate of 41,883 tons (37,996 Mg). Three nonroad categories are not included in the NEVES--locomotives, aircraft, and rockets. Of these, only estimates for general aviation and air taxis have been developed. These account for 61 tons (55 Mg) and 46 tons (42 Mg), respectively. For the other mobile sources, activity data were not readily available.

Estimates of national butadiene emissions from mobile and stationary sources are shown in Figure 3-2, and Figure 3-3 shows a breakdown of stationary source emission estimates. The estimates from butadiene production, major butadiene users, petroleum refining, and miscellaneous "other" sources are based on SARA 313 Toxic Release Inventory data for 1992. As mentioned above, the mobile estimates are based on EPA studies and Department of Transportation data. The secondary lead smelting and biomass burning (forest fires and prescribed burning) emission estimates are based on available emission factors combined with activity data. Appendix B describes the basis for all of the national emission estimates.

Some butadiene sources discussed in this document did not have enough data to estimate national emissions and are, therefore, not included in Figures 3-2 and 3-3. For example, an emission factor for butadiene from open burning of tires was found in AP-42, but the only available activity data were for tire incineration, not open burning.

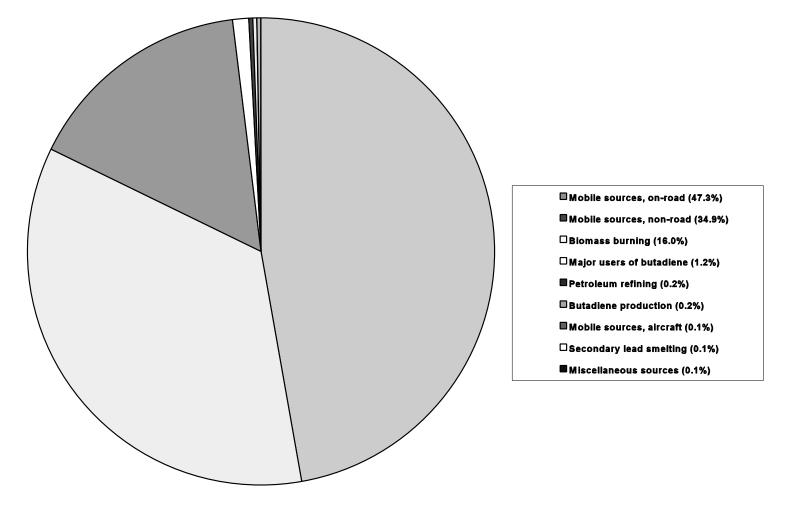


Figure 3-2. Relative Contributions to National Butadiene Emissions by Mobile and Point Source Categories

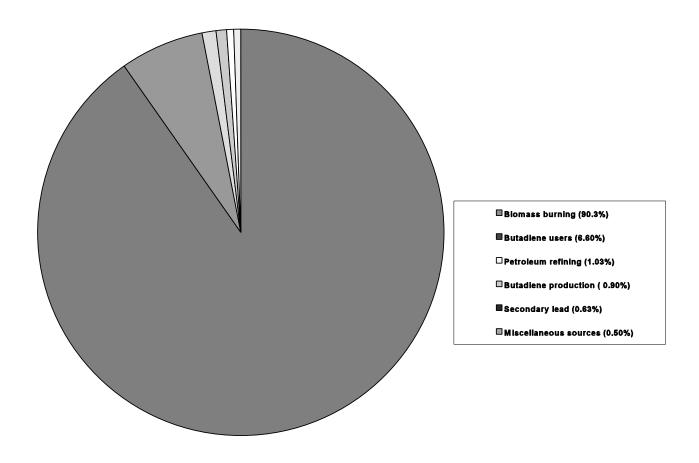


Figure 3-3. Relative Contributions to Stationary Butadiene Emissions by Point Source Categories

SECTION 4.0 EMISSIONS FROM BUTADIENE PRODUCTION

This section discusses emissions from sources associated with butadiene production. The information presented in this section includes identification of producers and descriptions of typical production processes. Process flow diagrams are given, as appropriate, with streams and vents labeled to correspond to the discussion in the text. Estimates of the associated butadiene emissions are provided in the form of emission factors when data were available to calculate them. Any known emission control practices are also discussed.

Much of the process vent and secondary source emissions data were taken from facility-reported information based on responses to Section 114 requests in 1984. In many cases, these responses were incomplete. Interested readers should therefore contact specific facilities directly to determine the process in use, production volume, and control techniques in place before applying any of the emission factors presented in this document. This document will be reviewed for the need to provide newer data as they become available.

The equipment leak emission factors given in this section were calculated from producer screening data collected by the Chemical Manufacturers' Association (CMA) in 1988. This study is briefly described and the results presented both in terms of average component-specific emissions factors and as annual emissions.

4.1 BUTADIENE PRODUCTION

The 1,3-isomer of butadiene, the only commercially significant isomer, is a high-volume intermediate organic chemical used to produce various types of rubber, resins, and plastics. Butadiene is produced by two different processes in the United States. One process involves the recovery of butadiene from a mixed- C_4 hydrocarbon stream generated during ethylene or other alkene production. The other process is the oxidative dehydrogenation of n-butenes to produce butadiene.

The 10 facilities currently producing finished butadiene in the United States are listed in Table 4-1. 10 All of these facilities recover butadiene from a mixed- C_4 stream. The mixed- C_4 streams feeding the recovery units are produced at olefins units co-located with the recovery units at these facilities, with the exception of one facility that receives its feedstock from an unidentified source. This facility also has the capacity to produce butadiene using the oxidative dehydrogenation of n-butenes process. However, this capacity is being utilized to dehydrogenate isobutane to isobutylene, for use in the manufacture of tert-butyl-methyl ether (MTBE). 10

4.1.1 <u>Process Descriptions</u>

Recovery of Butadiene from a Mixed-C₄ Stream

This process comprises two distinct steps. First, a mixed- C_4 stream containing butadiene is co-produced in an olefins plant during the cracking of large-molecule hydrocarbons to manufacture ethylene or other alkenes. The mixed- C_4 stream is then routed to a recovery unit, where the butadiene is separated.

The amount of butadiene produced during ethylene manufacture is dependent on both the type of hydrocarbon feedstock and the severity of the cracking operation. Typical butadiene yields from ethylene production, based on various feedstocks, are summarized in

TABLE 4-1. BUTADIENE PRODUCTION FACILITIES^a

Company	Location	Capacity in 1993 tons/yr (Mg/yr)
Amoco Chemicals Company	Chocolate Bayou, TX	91,100 (82,000)
Occidental Petrochemical	Chocolate Bayou, TX	67,800 (61,000)
	Corpus Christi, TX	111,100 (100,000)
Exxon Chemicals Company	Baton Rouge, LA	156,700 (141,000)
	Baytown, TX	121,100 (109,000)
Lyondell Petrochemical Company	Channelview, TX	310,000 (279,000)
Shell Chemical Company	Deer Park, TX	126,700 (114,000)
	Norco, LA	252,200 (227,000)
Texaco Chemical Company	Port Neches, TX	317,800 (295,000)
Texas Petrochemicals Corporation ^b	Houston, TX	403,300 (363,000)

Source: Reference 10.



^a The production process for all facilities is the recovery process. "Recovery" means butadiene as a coproduct in ethylene production is recovered from the mixed-C₄ stream.

Table 4-2.¹⁹ Heavier feedstocks (naphthas and gas oils) produce much larger quantities of butadiene than do the lighter feedstocks.

A generalized block flow diagram of an olefins unit producing a mixed- C_4 coproduct stream, excluding the ethylene separation process, is shown in Figure 4-1. In olefins production, a steam cracking furnace is used to crack the hydrocarbon feedstock (Step 1). The heavy hydrocarbons are broken into two or more fragments, forming a stream of mixed hydrocarbons. The concentration of butadiene in this mixed hydrocarbon stream varies with the type of feedstock. The flue gas from the cracking furnace is vented to the atmosphere (Vent A).

^b This facility is the only producer with on-purpose butylene dehydrogenation capacity, but this capacity is being utilized to dehydrogenate isobutane to isobutylene, for use in the manufacture of MTBE. This capacity is not included in the above totals. Effective January 1994, all of the Texas Petrochemicals operations will be owned by Huntsman Chemical.

TABLE 4-2. BUTADIENE YIELDS FROM RECOVERY USING A MIXED-C $_{\!\scriptscriptstyle 4}$ STREAM PRODUCED FROM VARIOUS FEEDSTOCKS^a

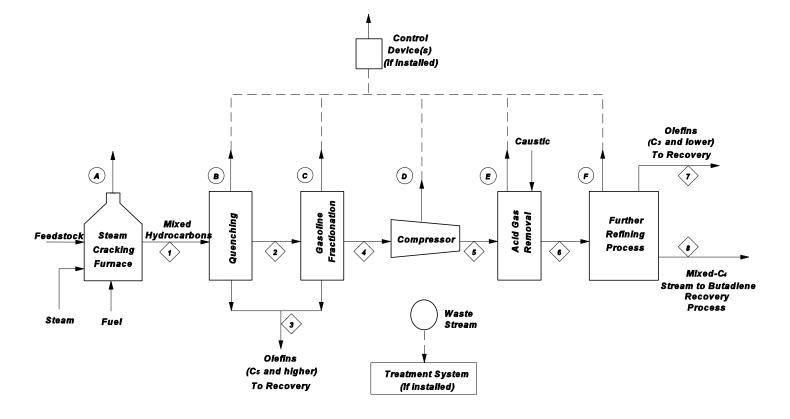
Feedstock	Yield Ratio (butadiene/ethylene produced on a weight basis)
Ethane	0.01 - 0.02
Refinery offgas	0.05
Propane	0.05 - 0.085
n-Butane	0.07 - 0.085
Naphthas	0.13 - 0.18
Gas oils	0.176 - 0.247

Source: Reference 19.

After the cracking step, the mixed hydrocarbon stream is cooled (Step 2) and, if naphtha or gas oils were the initial feedstock, the stream is sent to a gasoline fractionator (Step 3). The fractionator is used to recover heavy hydrocarbons (C₅ and higher). For some olefins units, the quenching step shown occurs after gasoline fractionation. The mixed stream is then compressed (Step 4) prior to removal of acid gas (hydrogen sulfide) (Step 5) and carbon monoxide. Acid removal usually involves a caustic wash step. The mixed hydrocarbon stream then goes through additional refining steps (Step 6), where it is separated from olefins (C₃ and lower).

The composition of a typical C₄ co-product stream from an ethylene plant using naphtha feedstocks is shown in Table 4-3.20 The mixed-C₄ stream may be sent directly to butadiene recovery at the same plant. Olefins plants that do not produce finished butadiene may (1) recover the crude butadiene from the byproduct mixed-C₄ streams and sell it to a butadiene producer, (2) recirculate the stream into the front of the ethylene process, and/or (3) use the stream to fuel the equipment (e.g., furnaces) in the ethylene process.

Refer to Figure 4-1 for a process diagram of mixed-C₄ production olefins unit. Refer to Figure 4-2 for a diagram of a butadiene recovery process.



Source: Reference 19

Figure 4-1. Process Diagram for Production of a Mixed- $\mathbf{C_4}$ Stream Containing Butadiene

TABLE 4-3. TYPICAL COMPOSITION OF MIXED-C₄ STREAM FORMED FROM NAPHTHA FEEDSTOCK USED TO PRODUCE ETHYLENE^a

Component	Molecular Formula	Composition (wt. %)
n-Butane	C_4H_{10}	6.80
Isobutane	C_4H_{10}	1.60
Isobutene	$\mathrm{C_4H_8}$	29.00
1-Butene	$\mathrm{C_4H_8}$	9.60
trans-2-Butene	$\mathrm{C_4H_8}$	7.50
cis-2-Butene	$\mathrm{C_4H_8}$	4.70
1,3-Butadiene	C_4H_6	39.30
1,2-Butadiene	C_4H_6	0.08
Propadiene	$\mathrm{C_4H_4}$	0.53
Methyl acetylene	$\mathrm{C_4H_4}$	0.65
Ethyl acetylene	C_4H_6	0.05
Dimethyl acetylene	$\mathrm{C_4H_6}$	0.08
Vinyl acetylene	$\mathrm{C_4H_4}$	<u>0.11</u>
TOTAL		100.0

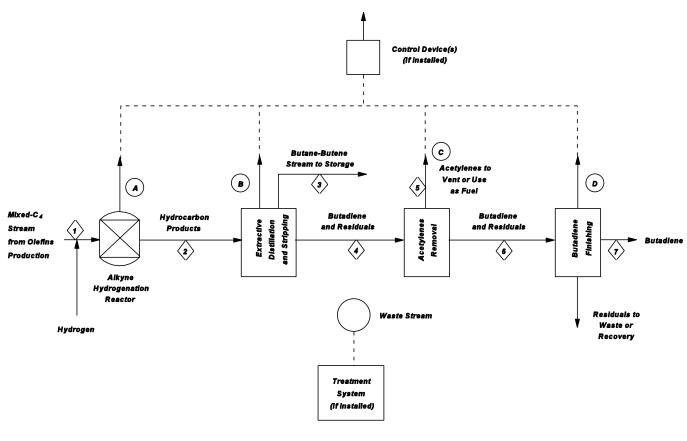


Source: Reference 20.

The second part of this butadiene production process involves recovering the butadiene from the mixed- C_4 stream. A generalized block flow diagram of a butadiene recovery unit is shown in Figure 4-2.¹⁹ The mixed- C_4 stream is fed from pressurized storage tanks into a hydrogen reactor along with hydrogen (Step 1) to convert some of the unsaturated hydrocarbons such as acetylene to olefins. The product C_4 stream from the hydrogenator is combined with a solvent (typically furfural) and fed into an extractive distillation operation (Step 2). In this operation, most of the butanes and butenes are separated from butadiene, which is absorbed in the solvent along with residual impurities. A stripping operation is then used to separate the butadiene from the solvent.

^a Refer to Figure 4-1 for process diagram of mixed-C₄ production.





Source: Reference 19

Figure 4-2. Process Diagram for Butadiene Production by Recovery from a Mixed-C $_4$ Stream

The stream containing butadiene typically has a small amount of residuals. Some of these residuals are alkynes that were not converted to olefins in the hydrogenation reactor. These residuals are removed from the butadiene stream by distillation (Step 3) and are usually vented to an emissions control device (Vent A). The bottom stream exiting the acetylenes removal operation contains butadiene and residuals such as polymer and 2-butene. The residuals are removed in the butadiene finishing operation (Step 4) and sent to a waste treatment system or recovery unit. The finished butadiene is then stored in pressurized tanks.

Oxidative Dehydrogenation of n-Butenes

The oxidative dehydrogenation of n-butenes (1- and 2-butenes) proceeds through the following primary reaction:

$$CH_2 = CH - CH_2 - CH_3$$
 (1-butene) or $+ 1/2 O_2 \longrightarrow CH_2 = CH - CH = CH_2 + H_2O$ $CH_3 - CH = CH - CH_3$ (1,3-butadiene) (2-butene)

Between 2.4 and 2.9 pounds (1.1 and 1.3 kilograms) of n-butenes are consumed per pound (kilogram) of butadiene formed.

A generalized block flow diagram of the butenes dehydrogenation process is shown in Figure 4-3.²¹ A feed stream of n-butenes is combined with steam and air, preheated, and passed through a dehydrogenation reactor (Step 1). Air is used as a source of oxygen to remove hydrogen from the butenes feed. The typical composition of a product stream is shown in Table 4-4.²¹ The product stream is compressed after exiting the reactor (Step 2) and sent to a hydrocarbon absorption and stripping process (Step 3). During compression and absorption, vent streams containing nitrogen, excess oxygen, and volatile organic compounds (VOCs) are

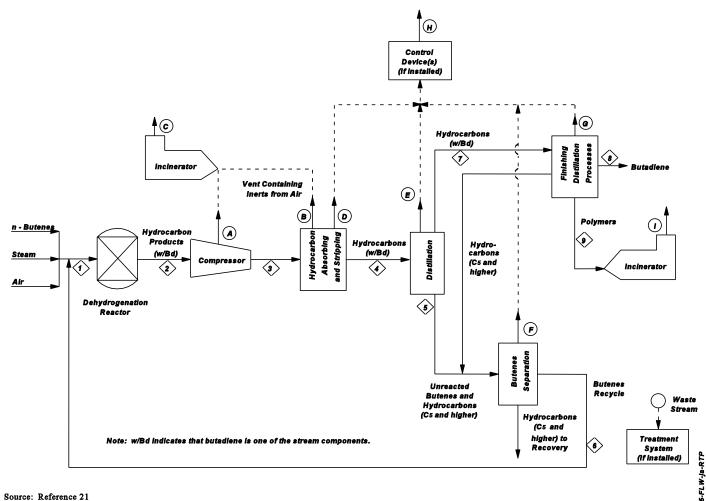


Figure 4-3. Process Diagram for Production of Butadiene by the Oxidative Dehydrogenation of Butene

TABLE 4-4. TYPICAL COMPOSITION OF n-BUTENES OXIDATIVE DEHYDROGENATION REACTOR PRODUCT STREAM $^{\rm a}$

Component	Molecular Formula	Composition (wt. %)
Oxygen	O_2	1.0
Nitrogen	N_2	15.8
Carbon oxides	CO, CO_2	3.0
Water	$\mathrm{H_{2}O}$	65.0
Methane	$\mathrm{CH_4}$	0.1
C ₂ 's		0.3
C ₃ 's		0.4
n-Butane	C_4H_{10}	0.4
Isobutane	C_4H_{10}	0.6
Isobutene	$\mathrm{C_4H_8}$	1.1
1-Butene	$\mathrm{C_4H_8}$	1.9
trans-2-Butene	$\mathrm{C_4H_8}$	1.7
cis-2-Butene	$\mathrm{C_4H_8}$	1.4
1,3-Butadiene	C_4H_6	7.2
C ₅ 's		0.1
1,2-Butadiene	C_4H_6	Trace
Propadiene	$\mathrm{C_4H_4}$	Trace
Methyl acetylene	$\mathrm{C_4H_4}$	Trace
Ethyl acetylene	C_4H_4	Trace
Dimethyl acetylene	C_4H_6	Trace
Vinyl acetylene	C_4H_4	Trace



Source: Reference 21.

^a Refer to Figure 4-3 for a process diagram of butadiene production by n-butenes oxidative dehydrogenation.

routed to an incinerator. The overhead stream from the hydrocarbon stripping column (not shown in Figure 4-3) is routed to a light-ends column for further separation.

The C_4 and heavier compounds (labeled hydrocarbons) exiting the absorption/stripping process are fed to a distillation operation (Step 4), where butadiene is separated from the unreacted n-butenes. The n-butenes stream exiting the distillation operation also contains C_5 and heavier hydrocarbons. This stream is routed to a separation process (Step 5), where n-butenes are recovered and recycled to the dehydrogenation reactor.

The stream containing butadiene from the distillation process (Step 4) is routed to a finishing distillation process (Step 7). At this point, finished butadiene is separated from other hydrocarbons and sent to pressurized storage. A polymer waste stream generated during the finishing process is routed to an incinerator. The hydrocarbons are sent to butene separation process units.

4.1.2 Emissions

Regardless of the process used to produce butadiene, emissions of butadiene at a production facility may be of five general types: process vent discharges, equipment leaks, emissions from secondary sources (wastewater, liquid waste, or solid waste discharges), storage-related releases, and emergency or accidental releases. In Figure 4-1, A through F are process vents, G represents an emission point after a control device. In Figure 4-2, the process vents are lettered A through D with E representing an emission point after a control device. In Figure 4-3, A through F are process vents, G, H, and I are emission points after control devices.

No information about emissions associated with storage or emergency/ accidental releases is available. Storage vessel discharges may be assumed to be negligible because butadiene is stored in pressure vessels that have no breathing or working losses. Some losses during transfer of butadiene are possible if the butadiene is not used on site. However, these losses should be low because the butadiene has to be transferred under pressure without release points.

Emissions are presented in the form of emission factor ranges for process vents and secondary sources. Individual emission factors having units of pounds (kilograms) of butadiene emitted per ton (megagram) of butadiene produced were first calculated for each facility by dividing facility-specific estimates by production, taken as 80 percent of capacity. From these facility-specific emission factors, a range for each source was established. The values of "n" indicate the number of facilities included. Because facilities reported varying levels of controls, two sets of emission factor ranges were developed. One range reflects actual facility emissions in which each facility may control all, some, or none of its sources. The second range incorporates both emissions from existing uncontrolled sources and potential emissions from controlled sources if controls had not been in place.

Equipment leak emissions are based on equipment count data collected by CMA in 1989 and average CMA emission factors for butadiene producers.

Facility-specific emissions estimates and capacity data appear in Appendix C, Tables C-1 through C-4. These emission factor ranges and annual emissions should be used only as order-of-magnitude approximations because differences in production processes and control levels, among other variables, may significantly influence actual emissions.

Process Vent Discharges

Process vent discharges occur from reactor vessels, recovery columns, and other process vessels. They may occur continuously (from a continuous process) or intermittently (from a batch process). Some continuous processes also have intermittent VOC emissions during startup and shutdown, or during control device malfunction or process upsets.

The possible locations of these process vents are shown in Figures 4-1 through 4-3. The actual locations and butadiene content may vary depending on the particular facility design. In many cases, process vents are directed to other parts of the plant or to a gas recovery system for use as fuel rather than discharged to the atmosphere.

Emissions data, including the use of control devices (six facilities use flares, of which two also have fuel gas recovery systems), were available for some facilities (see Appendix C). An emission factor range derived from these data is presented in Table 4-5. Also included in the table is an uncontrolled emission factor range to provide an indication of the extent to which controls are used. These were calculated from controlled emission factors using the emissions reduction efficiencies listed in Table 4-6.^{22,23,24} It should be noted that use of these factors introduces uncertainty. Many flares and incinerators achieve greater than 98 percent control. If 99 percent were used as a factor instead of 98, uncontrolled emissions estimates would double.

Processes for both olefins production and butadiene production via oxidative dehydrogenation are potential sources of emissions. However, the emissions data are limited to the olefins process at the two facilities. One of the facilities is reportedly controlling process vents on the oxidative dehydrogenation process at the hydrocarbon absorbing and stripping column and at the compressors (incinerator and flare) (see Figure 4-3).

Equipment Leak Emissions

Emissions from process equipment components occur when the liquid or gas process streams leak from the equipment. These components include pump seals, process valves, compressors, safety relief valves (pressure relief devices), flanges, open-ended lines, and sampling connections.

The emissions estimates shown in Table 4-5 are the results of a study conducted by CMA.²⁵ The study's objective was to develop industry-specific emission factors to replace SOCMI emission factors²⁶ because the SOCMI emission factors were thought to overestimate equipment leak emissions for butadiene producers. The study recommends, however, that screening data and correlation equations (also revised) be used to generate the most accurate estimates.

TABLE 4-5. SUMMARY OF EMISSION FACTORS FOR BUTADIENE PRODUCTION FACILITIES (FACTOR QUALITY RATING E)

	Facility Emission Fact	Facility Emission Factors ^{a,b,c}		Uncontrolled Emission Factors ^{a,b}	
Emission Sources	Range	Mean	Range	Mean	
Process Vents:					
C ₄ stream production 3-01-153			0.0054 lb/ton (0.0027 kg/Mg)		
Recovery process	0.0068 - 0.0550 lb/ton (n=3)	0.0314 lb/ton	0.0322 - 0.6872 lb/ton (n=3)	0.4652 lb/ton	
3-01-153-01	(0.0034 - 0.0275 kg/Mg)	(0.0157 kg/Mg)	(0.0161 - 0.3436 kg/Mg)	(0.2326 kg/Mg)	
Secondary Sources:					
Recovery process - wastewater	0.00068 - 4.4 lb/ton (n=6)	0.936 lb/ton			
3-01-153	(0.00034 - 2.2 kg/Mg)	(0.468 kg/Mg)			
Recovery process - solid waste 3-01-153	Negligible ^e (n=2)				

Source: References 19 and 25.

Note: Annual emissions from equipment leaks, recovery process (SCC 3-01-153-80), are 455 tons/yr (407 Mg/yr) (n=9) a.c.d

^aAssumes production capacity of 80 percent.

^bFactors are expressed as lb (kg) butadiene emitted per ton (Mg) produced.

^cRanges are based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.

^dTotal number of components is 79,430: 60 percent flanges, 29 percent liquid valves, 8 percent gas valves, and 3 percent all others combined.

 $^{^{\}circ}$ Defined as 0.4988 x 10^{-6} kg/Mg.

[&]quot;---" means no data available.

n = number of facilities.

TABLE 4-6. VOC EMISSIONS REDUCTION EFFICIENCIES OF CONTROL DEVICES USED TO ESTIMATE CURRENT BUTADIENE EMISSIONS

Control Device ^a	Reduction Efficiency (%)	Reference
Gas recovery (boiler)	99.9	21
Flare	98	22
Incinerator	98	23

^a Devices reported by industry to control vent streams and secondary emissions. Possible placement of control devices are shown in Figures 4-1 through 4-3.

The Butadiene Panel of CMA designed its study to closely adhere to EPA protocols for generating unit-specific emissions estimates as specified in the 1987 draft *Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP*. In addition to using the protocols, the Butadiene Panel sought EPA comments on the procedure before it began collecting data. Nine of the 11 finished butadiene producers in the United States participated in the study. The exceptions were the Shell facility in Norco, Louisiana, which was not in service, and the Texas Petrochemical facility in Houston, Texas. Four facilities that produce only crude butadiene also contributed data: three Union Carbide plants in Seadrift, Texas, Taft, Louisiana, and Texas City, Texas; and Dow Chemical in Freeport, Texas. All of these facilities produce butadiene by the recovery process. No estimate of equipment leak emissions from the oxidative dehydrogenation process was possible because of the lack of equipment component counts.

Based on facility data, ranges of butadiene concentrations through equipment components were established. Weighted average percents were calculated from the number of each component in each range. Approximately 20 percent of components were associated with butadiene streams having between 5-30 percent concentration, 47 percent with the 30-90 percent butadiene range, and 33 percent with the 90-100 percent butadiene range.

The screening data collected were similarly grouped into ranges of concentration [parts per million (ppm)] based on the instrument readout and the butadiene concentration in the stream. Five ranges from 0-9 to >9999 ppm were used. Upon calculating weighted average percents, about 76 percent of components fell in the 0-9 ppm range and 19 percent in the 10-99 ppm range. Fewer than 6 percent were found to be greater than 100 ppm. Table 4-7 summarizes the study results.²⁵

In addition to average emission rates, average butadiene concentration in the stream through each type of component is shown. These average concentrations were used to convert SOCMI emission factors from units of VOC emissions to butadiene emissions for purposes of comparison to the new emission rates. The results of this comparison are also given in Table 4-7.

In addition to compiling the data from all facilities, the study analyzed the data on a plant-specific level. Table 4-8 provides the variability among the plants by component type determined from this analysis.²⁵

The emissions shown in Table 4-7 include the reduction achieved by the various controls in place at the 13 facilities. The Butadiene Panel conducted a survey to identify and evaluate practices in the plants that would contribute to emissions reductions. Of the six respondents, all stated that they monitor fugitive emissions using a combination of visual observation and automatic audible alarm for specific equipment such as pumps and compressors. Three plants have routine leak inspection and maintenance programs. Two plants informally require immediate repair of leaks detected by the monitoring system. Five of the six plants reported combinations of visual inspections, pressure testing, VOC monitoring, use of double-sealed pumps, seals vented to a flare, bubble-testing flanges, tightness testing of valves, use of special packing material, closed-loop sampling points, and plugging of all open-ended lines. No estimate of the emissions reductions achieved by these practices was determined.

TABLE 4-7. AVERAGE BUTADIENE EMISSION RATES FOR PROCESS EQUIPMENT **COMPONENT LEAKS**

Equipment Component (Emission Source)	Average Emission Rate ^a (lb/hr/component)	Average Butadiene Concentration (%)	Reduction ^b (%)
Pumps - Liquid	0.05634		
	(0.02555)	64.1	19.3
Compressors	0.000004		
	(0.0000018)	27.9	99.9+
Flanges	0.000307		
	(0.000139)	61.0	72.5
Valves - Gas	0.001105		
	(0.000501)	60.2	85.1
Valves - Liquid ^c	0.003140		
	(0.001424)	59.7	66.3
Pressure Relief Devices	0.02996		
"Safety Valves"	(0.013590)	56.7	76.9
Sampling Point ^d	-	-	-
Open-ended Lines	0.000120		
	(0.000054)	67.9	95.2

Source: Reference 25.

^a The average emission rate has been derived from facility data, some of whom are using controls. Numbers in parentheses are in units of kg/hr/component.

b Calculated as [1 - <u>CMA emission factor</u>] x 100

SOCMI emission factor

^c Liquid refers to light liquid and is defined as a petroleum liquid with a vapor pressure greater than the vapor pressure of kerosene.

^d Sampling points were considered to be a subset of open-ended lines; therefore, data were incorporated in the open-ended line average emission factor.

TABLE 4-8. VARIABILITY IN FACILITY-SPECIFIC EMISSION RATES FOR EQUIPMENT LEAKS

Equipment Component	Relative Standard Deviation (%)
Pumps - Liquid	96.0 (n=13)
Compressors	137.4 (n=3)
Flanges	91.4 (n=13)
Valves - gas	84.3 (n=13)
Valves - liquid	45.2 (n=13)
Pressure Relief Devices	226.6 (n=10)
Open-ended Lines	117.8 (n=6)
Sample points	102.1 (n=4)

Source: Reference 25.



In the absence of specific information relating controls in use to reduction achieved, previously developed control efficiencies are presented in Table 4-9 to provide an indication of typical reductions achieved. For leak detection and repair programs, EPA has provided a method for estimating the emission reductions in *Protocol for Equipment Leak Emission Estimates*.¹ The reader is referred to this document for this information. To apply these efficiencies and determine emissions after controls, an estimate of uncontrolled emissions would be multiplied by [1-(efficiency/100)]. More information on estimating uncontrolled emissions is provided in Appendix D.

TABLE 4-9. CONTROL TECHNIQUES AND EFFICIENCIES APPLICABLE TO EQUIPMENT LEAK EMISSIONS

Equipment Type	Modification	Approximate Control Efficiency (%)
Pumps	Sealless design	100 ^a
	Closed-vent system	$90^{\rm b}$
	Dual mechanical seal with barrier fluid maintained at a higher pressure than the pumped fluid	100
Compressors	Closed-vent system	$90^{\rm b}$
	Dual mechanical seal with barrier fluid maintained at a higher pressure than the compressed gas	100
Pressure relief devices	Closed-vent system	c
	Rupture disk assembly	100
Valves	Sealless design	100^{a}
Connectors	Weld together	100
Open-ended lines	Blind, cap, plug, or second valve	100
Sampling connections	Closed-loop sampling	100

Note: Based on Reference 1. Butadiene emissions were assumed to be reduced by the same percentage as VOC emissions.

^a Sealless equipment can be a large source of emissions in the event of equipment failure.

Actual efficiency of a closed-vent system depends on percentage of vapors collected and efficiency of control device to which the vapors are routed.

^c Control efficiency of closed-vent systems installed on a pressure relief device may be lower than other closed-vent systems, because they must be designed to handle both potentially large and small volumes of vapor.

Secondary Emissions

Secondary emissions occur during the treatment and disposal of wastewater, other liquid waste, and solid waste. Few emissions estimates are available, and most of these data pertain to wastewater from the butadiene recovery process. Table 4-5 summarizes emission factors derived from the estimated wastewater and solid waste emissions in Appendix C. No factors are available for the olefins process, the oxidative dehydrogenation process, or for any liquid waste other than wastewater. The types of waste streams generating butadiene emissions include cooling water, wash water, solvent recovery wastewater, process unit wastewater, and waste polymer.

Because of its volatility and low solubility in water, butadiene in a waste stream is assumed to completely volatilize unless the vapor is routed to a control device. Some facilities use such emission control systems; others do not. Available information on facility control status and handling of the waste streams in 1984 is summarized in Appendix C.

SECTION 5.0 EMISSIONS FROM MAJOR USES OF BUTADIENE

Emissions from industrial processes using butadiene as a raw material are discussed in this section. Butadiene has six primary commercial uses, as illustrated in the chemical use tree in Figure 3-1. These uses are the production of styrene-butadiene (SB) copolymer, polybutadiene, adiponitrile, neoprene, acrylonitrile-butadiene-styrene (ABS) copolymer, and nitrile elastomer.

This section includes a subsection for each major use. Each subsection provides a general discussion of the production process, estimates of the associated butadiene emissions, and a description of any existing emissions control practices. These discussions are primarily based on summary memoranda of industry responses to EPA Section 114 questionnaires, National Institute for Occupational Safety and Health (NIOSH) survey reports, and various other reports as referenced, and represent information gathered prior to 1986. The level of detail varies according to the availability of information. In view of these limitations, the reader is advised to contact individual facilities or review State permit files for more complete and accurate information.

As with butadiene production sources, emission factor ranges in units of pounds (kilograms) butadiene emitted per ton (megagram) produced are provided for process vents and secondary sources, based on annual emissions estimates of tons/yr (Mg/yr). The same procedure described in Section 4.0 for calculating facility emission factors was followed to establish these ranges. Assumptions about production are provided in each subsection.

Equipment leak emissions are presented as annual emissions and were derived using the procedure in Appendix D and the CMA emission factors presented in Section 4.0. Although developed for butadiene producers, these emission factors were assumed to better represent practices of the user industries because all involve butadiene handling. Three alternative methods would be to (1) collect screening data and use correlation equations established in the CMA work, (2) apply SOCMI emission factors, weighted for the percent butadiene in the stream, or (3) apply other alternatives identified in the EPA document *1995 Protocols for Equipment Leak Emission Estimates*. The equipment leak emission estimates generally represent some level of control because the average emission rate is based on practices at butadiene producers.

The emission factors and annual emission values should be used only as estimates because facilities did not always provide complete information, and source characteristics cannot be assumed to be the same from location to location. The number of facilities included in establishing the range is indicated in parentheses; the individual values are reported in Appendix C.

Company identification and corresponding facility locations for the various production process are also given in each subsection. The production capacities supplied are, in most cases, taken from more recent (1992-1993) references.

5.1 STYRENE-BUTADIENE COPOLYMER PRODUCTION

Styrene-butadiene copolymers are composed of the monomer units butadiene and styrene. Depending upon the feed composition and extent of drying in the process, SB copolymers can be a solid or an emulsion.

Copolymers of styrene and butadiene that contain over 45 percent butadiene have rubber-like properties. The copolymers become more plastic-like when the styrene content is increased to above 45 percent.²⁷ Copolymers with more than 45 percent butadiene are sometimes referred to as styrene-butadiene rubber (SBR); products with more styrene may be

referred to as SB latex. No distinction is made in the following discussion because emissions data are not differentiated. The term elastomer will be used in a generic sense, meaning solid copolymer.

Styrene-butadiene latex is an elastomer emulsion. Styrene-butadiene rubber is also used as an emulsion. The emulsion process is the same process used for elastomers, except that it lacks the emulsion breaking (coagulation) and drying steps. The term latex is used here when referring to both SB and SBR emulsion.

Styrene-butadiene copolymers account for 40 percent of national butadiene consumption.⁸ The majority of SB elastomer produced is used by the tire industry. Latex has a wider variety of uses in industries such as textiles, paper, and adhesives manufacturing.

5.1.1 <u>Process Description</u>

Elastomer is manufactured by two processes: (1) the emulsion process, where monomer is dispersed in water, and (2) the solution process, where monomer is dissolved in a solvent. The emulsion process is more commonly used. Latex is similarly produced but is removed prior to the final processing that generates the solid copolymer.

A generalized block flow diagram of an elastomer and latex production process is shown in Figure 5-1.²⁷ Stored butadiene and styrene monomers are first washed to remove any inhibitors of the polymerization reaction (Step 1). The scrubbed monomers are then fed into polymerization reactors (Step 2) along with the ingredients listed in Table 5-1.²⁸ After the polymerization reaction has progressed to the desired extent, a polymer emulsion (latex) is removed from the reactors along with unreacted monomer (Step 3). Both styrene and butadiene are separated from the latex and recycled to the monomer feed tanks.

Source: Reference 27

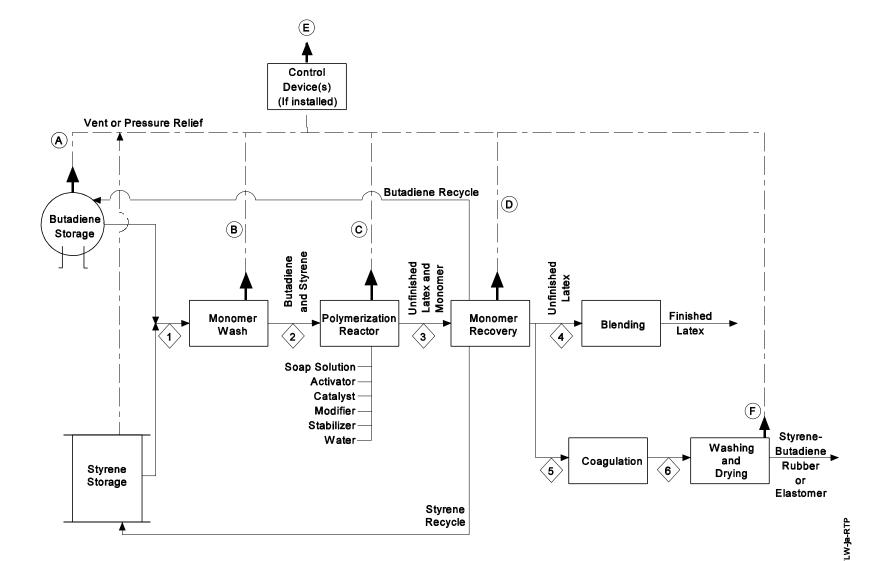


Figure 5-1. Process Diagram for Production of SB Copolymer

TABLE 5-1. TYPICAL RECIPE FOR EMULSION SBR

Components	Weight Percent	Function
Butadiene	25.0	Monomer
Styrene	10.0	Monomer
d-Isopropyl Benzene Hydroperoxide	<.1	Catalyst
Ferrous Sulfate	<.1	Activator
Tert-Dodecyl Mercaptan	.1	Modifier
Potassium Pyrophosphate	.1	Buffer
Rosin Acid Soap	1.4	Emulsifier
Water	63.0	



Source: Reference 28.

The unfinished latex may take one of two routes after monomer is removed. One route is for the latex to be blended into a homogenous emulsion (Step 4) and stored as finished latex. The other route involves a coagulation operation where the emulsion is broken (Step 5). This step is followed by washing and drying the polymer into a solid form (Step 6).

Table 5-2 lists the known production facilities, grouped by copolymer type.²⁹ Because three different latexes may be produced--SBR, SB, and styrene-butadiene-vinylpyridine (SBV)--the table indicates which copolymer(s) each facility manufactures.

5.1.2 <u>Emissions</u>

The emission sources at an SB copolymer facility are typical of those common to chemical production facilities: process vent discharges; equipment leaks; wastewater, liquid waste, or solid waste discharges (secondary emissions); storage-related releases; and accidental or emergency releases. Available emissions data are limited to emissions from process vents, equipment leaks, and secondary emissions, and are shown in Tables C-5 through C-8

TABLE 5-2. STYRENE-BUTADIENE ELASTOMER AND LATEX PRODUCTION FACILITIES

		G ' 1002	
Company	Location	Capacity in 1993 tons/yr (Mg/yr)	
Elastomer			
Ameripol Synpol	Port Neches, TX	372,200 (335,000)	
Copolymer Rubber	Baton Rouge, LA	138,900 (125,000)	
Dynagen, Inc.	Odessa, TX	100,000 (90,000)	
Firestone	Lake Charles, LA	166,600 (150,000)	
Goodyear	Houston, TX	338,900 (305,000)	
Goodyear	Beaumont, TX	22,200 (20,000)	
<u>Latex</u>		_	Type of Latex
Dow Chemical U.S.A.	Dalton, GA		
Dow Chemical U.S.A.	Freeport, TX		
Dow Chemical U.S.A.	Gales Ferry, CT	252,200 (227,000)	SB latex
Dow Chemical U.S.A.	Midland, MI		
Dow Chemical U.S.A.	Pittsburg, CA		
GenCorp	Howard, WI	40,000 (36,000)	SB latex
GenCorp	Mogadore, OH	101,100 (91,000)	SB latex; SBR latex; SBV latex
Goodyear	Akron, OH	4,400 (4,000)	SB latex; SBV latex
Goodyear	Calhoun, GA	55,500 (50,000)	SB latex; SBR latex; SBV latex
Goodyear	Houston, TX	28,900 (26,000)	SBR latex
Hampshire Chemical Corp.	Owensboro, KY	14,400 (13,000)	SB latex
BASF	Monaca, PA	25,500 (23,000)	SB latex
BASF	Chattanooga, TN	115,500 (104,000)	SB latex; SBR latex
Reichhold Chemicals, Inc.	Cheswold, DE		
Reichhold Chemicals, Inc.	Kensington, GA	93,300 (84,000)	SB latex
Rhône-Poulenc, Inc.	Gastonia, NC	25,600 (23,000)	SB latex
Rhône-Poulenc, Inc.	Charlotte, NC	30,000 (27,000)	SB latex
Rhône-Poulenc, Inc.	La Mirada, CA	13,300 (12,000)	SB latex
Rhône-Poulenc, Inc.	Kankakee, IL	10,000 (9,000)	SB latex



Source: Reference 29.

in Appendix C. In developing emission factors, the facilities were assumed to be operating at 80 percent production capacity.²⁷

Butadiene used in elastomer production is usually stored in pressurized vessels with some vented to a flare (point A in Figure 5-1). Storage, therefore, results in low emissions. Two facilities, however, store butadiene-containing material in fixed-roof storage tanks. Emissions are estimated to be low because of the low concentrations of butadiene (5 percent by weight or less).

Butadiene users do not transfer butadiene as a product onto tank trucks, so emissions from transfer operations are not of concern. Unloading emissions would be mostly emitted as storage tank working losses (already discussed under storage). Moving butadiene around within the plant is covered by equipment leak emission estimates.

Process Vent Emissions

As seen from the vent locations in Figure 5-1, process vent discharges occur from reactor vessels, recovery columns, and other process vessels. They may occur continuously (from a continuous process) or intermittently (from a batch process). Some continuous processes have emissions during startup and shutdown or during a control device malfunction or process upset.

The potential locations of these process vents (Vents B, C, D, F) are shown in Figure 5-1. Although the actual locations and butadiene content may vary depending on the facility design, process vents are typically located on absorption columns used to recover butadiene. In some cases, process vents are directed to other parts of the plant, or to a gas recovery system for use as fuel, rather than discharged to the atmosphere.

The available emissions data are presented in Table 5-3 as emission factor ranges. The facility emission factor range was calculated as described in Section 4.0 and reflects actual

TABLE 5-3. SUMMARY OF EMISSION FACTORS FOR SB COPOLYMER PRODUCTION FACILITIES^{a,b} (FACTOR QUALITY RATING D)

	Facility Emission Factors		Uncontrolled Emissio	n Factors
Emission Sources	Range ^c	Mean	Range	Mean
Process Vents 3-01-026	0.00024 - 94.34 lb/ton (n=18)	7.10 lb/ton	0.124 - 94.34 lb/ton (n=18)	14.20 lb/ton
	(0.00012 - 47.17 kg/Mg)	(3.55 kg/Mg)	(0.062 - 47.17 kg/Mg)	(7.10 kg/Mg)
Secondary Sources:				
Wastewater	0 - <10 lb/ton (n=18)	0.30 lb/ton		
3-01-026	$(0 - < 5 \text{ kg/Mg})^d$	(0.15 kg/Mg)		
Other liquid waste	<0.02 lb/ton (n=5)	<0.02 lb/ton		
3-01-026	(<0.01 kg/Mg)	(<0.01 kg/Mg)		
Solid waste	0 - <0.02 lb/ton (n=11)	<0.02 lb/ton		
3-01-026	$(0 - < 0.01 \text{ kg/Mg})^d$	<0.01 kg/Mg		

Source: Reference 27.

Note: Annual emissions from uncontrolled equipment leaks range 0.11 - 23.59 tons/yr (0.10 - 21.40 Mg/yr) and average 7.28 tons/yr (6.60 Mg/yr) (n=19).ac

NA = not available.

^a Assumes production capacity of 80 percent.

^b Factors are expressed as lb (kg) butadiene emitted per ton (Mg) produced.

^c Ranges are based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.

^d Upper value used to prevent disclosing confidential operating capacity.

n = number of facilities.

[&]quot;---" means no data specific to level or efficiency of controls were available.

emissions and the various levels of control reported. The second emission factor range incorporates both emissions from existing uncontrolled sources and potential emissions from controlled sources with controls removed.²⁷

Although 20 facilities supplied emissions data (Table C-6), production capacities for two were not available; therefore, these two were omitted from the emission factor range development. Control devices in use include absorbers, boilers, flares, scrubbers, and pressure condensers. Emissions after controls (Vent E) were calculated by applying appropriate reduction efficiencies. Standard control efficiencies from Table 4-6 were used to calculate controlled emissions unless alternate values were supplied by the companies and accompanied by quantitative documentation.

Equipment Leak Emissions

Emissions occur from process equipment components whenever the liquid or gas process streams leak from the equipment. Butadiene emissions were estimated for the following equipment components: pump seals, process valves, compressors, safety relief valves (pressure devices), flanges, open-ended lines, and sampling connections. For each facility where the number of equipment components was known, emissions were estimated using emission rates presented in Table 4-7. The method is described further in Appendix D. Although these emission rates include an unknown level of control at butadiene producer, the only controls reported in use by the industry are flares and/or rupture discs for pressure relief devices (PRD). Some facilities perform visual inspections, but with an unknown frequency. These estimates may not represent emissions at SB copolymer facilities where control practices differ. A summary of the available data is given in Table 5-3.

Secondary Emissions

Secondary emissions occur at the on-site and off-site facilities that treat and dispose of wastewater, liquid waste, or solid waste. Waste streams may be generated from any of the operations shown in Figure 5-1. Emissions data are available for 18 of the 21 facilities,

TABLE 5-4. POLYBUTADIENE PRODUCTION FACILITIES

Company	Location	Capacity in 1993 tons/yr (Mg/yr)
American Synthetic Rubber	Louisville, KY	121,300 ^a (110,000) ^a
Bridgestone/Firestone	Orange, TX	132,300 (120,000)
Bridgestone/Firestone	Lake Charles, LA	b
Goodyear	Beaumont, TX	237,000 ^a (215,000) ^a
Polysar	Orange, TX	126,800 (115,000)

Source: References 12 and 30.



^a Total includes some multipurpose SBR.

but are incomplete for each type of waste stream. These data are summarized in Table 5-3. The emission factor estimates were calculated from information on the flowrate of butadiene (kg/day) in the stream and facility production. Because of butadiene's volatility and low solubility, no reduction was included unless butadiene vapors were routed to a control device.

5.2 POLYBUTADIENE PRODUCTION

Polybutadiene production consumes approximately 20 percent of the butadiene produced.⁸ Like SB elastomer, polybutadiene is primarily used by the tire manufacturing industry, but also finds uses in the high-impact resins industry.

Four companies at five U.S. locations currently have the capacity to produce polybutadiene, two of which coproduce polybutadiene with SB copolymer. These four companies are listed in Table 5-4.^{12,30} Firestone in Lake Charles is primarily an SB copolymer producer, therefore emissions from this facility were included in the preceding section. Only emissions attributed to the polybutadiene production process are presented in this section.

^b Facility coproduces SB elastomer and polybutadiene rubber, but is primarily dedicated to SB elastomer.

5.2.1 <u>Process Description</u>

The polymerization of butadiene can yield several isomeric polymers. The two of commercial significance are the cis-1,4 isomer and, to a much lesser extent, the 1,2 isomer.³¹ The majority of polybutadiene is produced by a solution polymerization process. Smaller quantities are produced by an emulsion polymerization process. The relative proportions of the isomers formed are dependent on the catalyst system used and reaction conditions.

The cis-polybutadiene rubber process consists of five basic steps: (1) butadiene and solvent purification, (2) reaction, (3) concentrations, (4) solvent removal, and (5) drying and packaging. Figure 5-2 shows a diagram of this process.³¹ In Step 1, feed butadiene is dried and combined with a recycled butadiene stream. Solvent, typically hexane or cyclohexane, is also dried along with a recycled solvent stream. In Step 2, these streams are fed to the reactor, where polymerization takes place. With solution polymerization, a catalyst, such as lithium, sodium, or potassium, is used. The overall conversion of the process is greater than 98 percent.³¹

Reactor effluent is fed to the concentrator (Step 3), where any unreacted butadiene is removed for recycling. The product stream leaving the concentrator consists of polybutadiene dissolved in solvent, and is often referred to as "cement." The cement stream leaving the concentrator contains negligible butadiene. In Step 4, the cement is stripped of solvent, which is recycled to solvent purification. Stripping occurs through direct steam contact. The resulting polybutadiene crumb/water stream is dried, compressed, and packaged in Step 5. This process is run both continuously and in batch mode, but the majority of facilities operate continuously.

5.2.2 Emissions

Butadiene emissions from polybutadiene production are primarily of four types: process vent emissions, equipment leaks, secondary emissions, and accidental or emergency releases. Storage under pressure significantly reduces any potential for storage emissions

Source: Reference 31

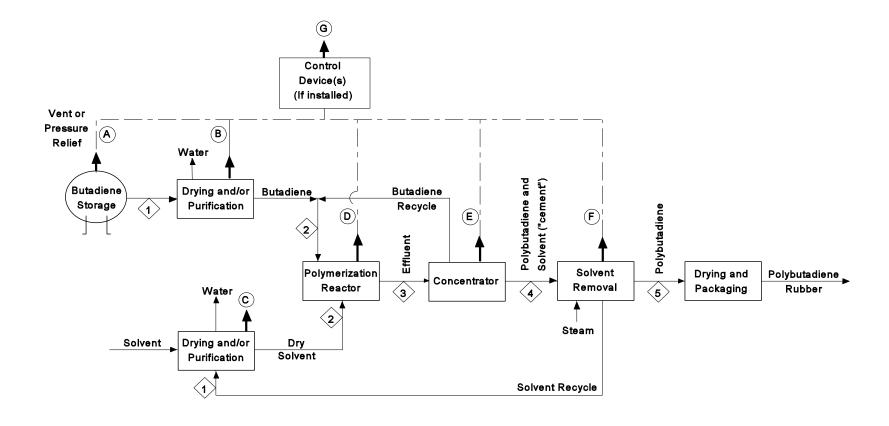


Figure 5-2. Process Diagram for Production of Polybutadiene Rubber

(point A in Figure 5-2), although source emissions during handling and transport of raw material are possible. Each emission type is discussed separately below. Typical production for the industry is estimated at 81 percent of capacity.³¹ This is incorporated into the emission factor calculations.

Process Vent Emissions

Process vent emissions occur during purging of noncondensible gases from reactors and other process vessels. The emissions may occur continuously or intermittently. Emission points indicated in Figure 5-2 as Vents B through F give the possible vent locations for butadiene releases. Emissions after the control device are denoted as Vent G in the process diagram.

Data on 1984 emissions, both uncontrolled and controlled, and the control type and efficiency are available for each facility and are summarized as emission factor ranges in Table 5-5 (for raw data, see Tables C-9 and C-10 in Appendix C). The two ranges were developed to represent actual emissions, where existing controls are taken into account, and potential emissions, where all reported sources are treated as uncontrolled sources.

In 1984, all facilities but one were controlling process vent emissions. Four used at least a flare, and one also used a butadiene absorber. The fifth used a butadiene recovery system. Two facilities reported control efficiencies greater than 98 percent; however, 98 percent was used as an upper limit in the absence of test data to support the higher numbers.

Equipment Leak Emissions

Equipment leak emissions were estimated by using the number of components, their time in service, and the weight percent butadiene in the stream. Estimated emissions were derived by applying the CMA method described in Appendix D to the facility-specific data

TABLE 5-5. SUMMARY OF EMISSION FACTORS FOR POLYBUTADIENE PRODUCTION FACILITIES a,b (FACTOR QUALITY RATING U)

	Facility Emission Factors		Uncontrolled Emission Factors	
Emission Sources	Range ^c	Mean	Range	Mean
Process Vents 3-01-026	0.00008 - 36.06 lb/ton (n=6)	6.14 lb/ton	0.0032 - 36.06 lb/ton (n=6)	8.96 lb/ton
	(0.00004 - 18.03 kg/Mg)	(3.07 kg/Mg)	(0.0016 - 18.03 kg/Mg)	(4.48 kg/Mg)
Secondary Sources:				
Wastewater 3-01-026	0 - 0.74 lb/ton (n=3)	0.24 lb/ton	0 - 0.74 lb/ton	0.24 lb/ton
	(0 - 0.38 kg/Mg)	(0.12 kg/Mg)	(0 - 0.38 kg/Mg)	(0.12 kg/Mg)
Solid Waste 3-01-026	0 lb/ton	0 lb/ton	0 lb/ton	0 lb/ton
	(0 kg/Mg)	(0 kg/Mg)	(0 kg/Mg)	(0 kg/Mg)

Source: Reference 31.

Note: Annual emissions from uncontrolled equipment leaks range from 4.04 - 31.42 tons/yr (3.66 - 28.50 Mg/yr) and average 10.41 tons/yr (9.44 Mg/yr) (n=6). For the facilities that reported emissions, none control equipment leaks.

n = number of facilities.

^a Assumes production capacity of 81 percent.

^b Factors are expressed as lb (kg) butadiene emitted per ton (Mg) produced.

^c Ranges are based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.

given in Appendix C, Table C-11, and component-specific emission factors from Table 4-7. These results are summarized in Table 5-5. They represent some level of control because the average emission rate is based on practices at butadiene producers. Although some facilities perform visual monitoring, none gave a specific frequency or scope of these programs; therefore, no estimate of reductions could have been made. A comparison to practices at butadiene producers was also not possible; therefore, users of the estimate should take this uncertainty into account.

Secondary Emissions

Only one facility reported a wastewater stream containing butadiene. Complete evaporation of butadiene from this stream, which is sent to a lagoon, was assumed because of butadiene's volatility and low water solubility. Secondary emissions are summarized in Table 5-5. One other facility reports that its wastewater contains no butadiene and, therefore, produces no emissions. One of the three facilities that indicated that they generate solid waste estimated that no butadiene emissions are released. Table C-12 in Appendix C summarizes the facility-specific data.

Accidental Release Emissions

Accidental release emissions include pressure relief events and accidental releases. Two of the four facilities reported no accidental release emissions; each of the other two facilities reported one accidental release. In the first case, the release was a result of a cracked valve; in the second, a loose flange. The estimated losses were 2,998 pounds (1,360 kg) over 30 hours and 11 pounds (5 kg) over 5 minutes, respectively.³²

5.3 ADIPONITRILE PRODUCTION

Adiponitrile (hexanedinitrile) is primarily used as an intermediate in the manufacture of hexamethylenediamine (HMDA) (1,6-diaminohexane), a principal ingredient in nylon 6,6 production.³³ Three facilities currently produce adiponitrile; Table 5-6 identifies their locations and capacities.²⁹ Only two facilities use butadiene, accounting for 12 percent of butadiene use in the United States.¹⁰ Monsanto uses acrylonitrile as the starting material and is, therefore, not a source of butadiene emissions and is omitted from further discussion.

5.3.1 <u>Process Description</u>

Both facilities that use butadiene run the adiponitrile process on a continuous basis. A generalized process diagram (Figure 5-3) illustrates the steps in adiponitrile production.³⁴ Butadiene is first converted to pentenenitriles by the addition of hydrogen cyanide in the presence of a catalyst (Step 1). The resulting pentenenitriles stream then continues through the butadiene column (Step 2) and catalyst removal (Step 3). The intermediary may be sold commercially or refined further. On-site processing begins with distillation of the pentenitriles for use in dinitrile synthesis (Step 4). In the dinitrile system unit (Step 5), the mononitriles are further hydrocyanated for conversion to dinitriles. The resulting mixture of six-carbon dinitriles is refined by distillation (Step 6). The final product, adiponitrile, is stored in tanks and then pumped via pipeline to the HMDA unit for hydrogenation. Most of the by-products of the process are burned in a boiler to recover their heating value. One of the mononitrile by-products is sold as a commercial product.

5.3.2 <u>Emissions</u>

From facility information, the sources of butadiene emissions are associated with production up to the point of catalyst removal. Test data of the butadiene column bottoms (at one location) show less than 0.02 percent by weight of butadiene.³⁴ The emission source types for which there are data include the process vents (denoted Vents B and C in Figure 5-3), equipment leaks, secondary sources, and one estimate of losses during butadiene storage railcar

TABLE 5-6. ADIPONITRILE PRODUCTION FACILITIES

Facility	Location	Capacity in 1993 tons/yr (Mg/yr)
DuPont	Orange, TX	244,400 (220,000)
DuPont	Victoria, TX	238,900 (215,000)
Monsanto ^a	Decatur, GA	228,900 (206,000)

Source: Reference 29.



^a Monsanto does not use butadiene as a raw material.

unloading at the facility. Other typical sources include emergency or accidental releases and emissions associated with butadiene storage (Vent A). No data are available for accidental releases and, because butadiene is stored under pressure, storage losses are assumed to be a small source of emissions. In order to develop emission factors, production values were needed. In the absence of facility-specific information, 80 percent of literature capacity values were assumed to represent production.³⁵

Process Vent Emissions

The emissions reported by the two facilities for process vents are given in Table 5-7 as emission factor ranges. All are controlled either by using a flare or by routing emissions to a boiler (see Tables C-13 and C-14 in Appendix C). Thus, facility emission factors represent controlled emissions. The uncontrolled emission factors represent potential emissions for the sources reported. Flares were assigned a 98-percent maximum removal efficiency unless supplementary data supported higher efficiencies. Because butadiene content in the process beyond the catalyst removal stage is low, emissions from process vents downstream of this stage were expected to be negligible.

Source: Reference 34

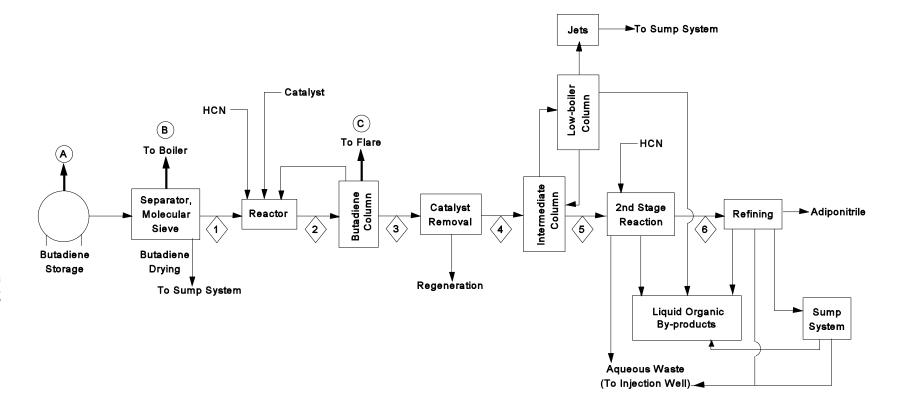


Figure 5-3. Process Diagram for Production of Adiponitrile

TABLE 5-7. SUMMARY OF EMISSION FACTORS FOR ADIPONITRILE PRODUCTION FACILITIES^{a,b} (FACTOR QUALITY RATING U)

	Facility Emission l	Factors	Uncontrolled Emission	Uncontrolled Emission Factors			
Emission Sources	Range ^c	Mean	Range	Mean			
Process Vents	0.12 lb/ton (n=2)	0.12 lb/ton	5.84 - 6.30 lb/ton (n=2)	6.08 lb/ton			
3-01-254	(0.06 kg/Mg)	(0.06 kg/Mg)	(2.92 - 3.15 kg/Mg)	(3.04 kg/Mg)			
Secondary Sources	0.016 - 0.024 lb/ton (n=2)	0.02 lb/ton	0.016 - 0.024 lb/ton (n=2)	0.02 lb/ton			
3-01-254	(0.008 - 0.012 kg/Mg)	(0.01 kg/Mg)	(0.008 - 0.012 kg/Mg)	(0.01 kg/Mg)			

Source: Reference 35.

Note: Annual emissions from uncontrolled equipment leaks (SCC 3-01-254-20) range 2.72 - 5.25 tons/yr (2.47 - 4.76 Mg/yr) and average 3.99 tons/yr (3.62 Mg/yr) (n=2).

n = number of facilities.

NA = not available.

^a Assumes production capacity of 80 percent.

^b Factors are expressed as lb (kg) butadiene emitted per ton (Mg) produced. Only incomplete data on emissions were available, therefore, values underestimate emissions.

^c Ranges are based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.

Equipment Leak Emissions

Equipment leak emissions were estimated by using the number of components, their time in service, and the weight percent butadiene in the stream. Estimated emissions were derived by applying the CMA method described in Appendix D to the facility-specific data given in Appendix C, Table C-11, and component-specific emission factors from Table 4-7. These results are summarized in Table 5-7. They represent some level of control because the average emission rate is based on practices at butadiene producers. Controls in use by the two facilities include ambient monitoring, quarterly leak detection and repair, double mechanical seals, and pressure relief devices, some of which are routed to a flare. No comparison to practices at butadiene producers is possible, however, so the user of the estimate should take this uncertainty into account.

Other Emissions

Although both facilities list various secondary sources, only two of the emission values are given, one for wastewater, the second for a waste tank (see Table C-16 in Appendix C). Emissions from these sources are reported to be uncontrolled. Other secondary sources reported include butadiene separator blowdown water, waste liquids, and a sump tank. Emissions from the latter two are routed to a boiler. Another source identified is the unloading of a storage railcar with a closed vapor balance system, estimated to emit 9.6 tons/yr (8.7 Mg/yr).

5.4 NEOPRENE PRODUCTION

Neoprene, also called polychloroprene, is a product of chloroprene (2-chloro-1,3-butadiene) polymerization. Consuming approximately 5 percent of butadiene produced,⁸ neoprene rubber is primarily used in the automotive industry in such applications as belts, cables, hoses, and wires.³⁶ Three facilities currently produce neoprene; these are listed in Table 5-8, along with 1993 capacities.²⁹ Only two facilities use butadiene as a raw material.

TABLE 5-8. CHLOROPRENE/NEOPRENE PRODUCTION FACILITIES

Company	Location	Capacity in 1993 tons/yr (Mg/yr)
DuPont	Louisville, KY ^a	171 100 (10 100)
DuPont	La Place, LA	151,100 (136,000)
Polysar	Houston, TX	30,000 (27,000)



Source: Reference 30.

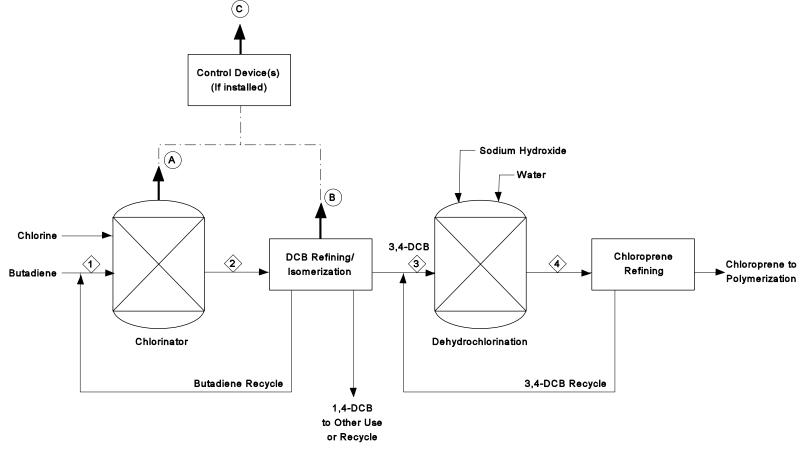
Because the DuPont plant in Louisville, Kentucky, starts with chloroprene, it is not included in the subsequent discussion of process and emissions information.²⁹

5.4.1 <u>Process Description</u>

The production of neoprene is a continuous process that starts with the chlorination of butadiene to form chloroprene. Figure 5-4 shows this process schematically.³⁷ The initial chlorination (Step 1) takes place in a vapor-phase reactor. This produces a mixture of 3,4-dichloro-1-butene (3,4-DCB) and the cis and trans isomers of 1,4-dichloro-2-butene (1,4-DCB), along with unreacted butadiene. The next process step (Step 2) involves the isomerization of 1,4-DCB to 3,4-DCB and the removal of any unreacted butadiene. This is performed in a combined reactor/distillation column under reduced pressure and the presence of a catalyst. Butadiene is recycled to the chlorinator and 1,4-DCB can be recycled or used elsewhere.

The final steps in the synthesis of chloroprene involve the dehydrochlorination of 3,4-DCB in a solution of sodium hydroxide and water (Step 3) and further refining (Step 4). The chloroprene is isolated from the unreacted 3,4-DCB, which is recycled to the reactor. The overall chemical yield of chloroprene is generally greater than 95 percent.³⁸

^aThis facility does not use butadiene as the raw material. The facility also has an additional 44,000 tons (39,900 Mg) of idle capacity, which does not use any butadiene either.



DCB = Dichlorobutenes

1,4-DCB = 1,4-Dichloro-2-Butene

3,4-DCB = 3,4-Dichloro-1-Butene

Figure 5-4. Process Diagram for Production of Chloroprene Monomer

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The chloroprene produced is then used in the production of neoprene elastomers. A schematic of this process is shown in Figure 5-5.³⁹ Chloroprene proceeds to emulsification (Step 1), then to initiation, catalysis, and monomer conversion in Step 2. The polymer continues with short-stopping and stabilization, monomer recovery, and polymer isolation. The resulting latex can be sold as product or dried and compressed to form neoprene rubber.³⁹

5.4.2 <u>Emissions</u>

Of the five general emission types, information is only available for three: process vent releases, equipment leaks, and emergency and accidental release emissions. These sources are discussed in more detail below. Although secondary sources and storage-related emissions were not characterized, butadiene emissions from pressurized storage tanks were assumed to be negligible. Some losses during transfer and handling are likely. For purposes of emission factor development, both facilities were assumed to be operating at full capacity.³⁹

Process Vent Emissions

The two facilities using butadiene report that process vent emissions are limited to the chloroprene production process. These vents are associated with the chlorination, DCB refining, and isomerization steps (identified as Vents A and B in Figure 5-4) and are used to vent noncondensible gases such as nitrogen. Unreacted butadiene is removed after chlorination is complete and, therefore, is only present in low quantities in subsequent process steps. A summary of the data collected in 1985 appears in Table 5-9. The raw data are shown in Tables C-17 and C-18 in Appendix C. Calculated as described in Section 4.0, the facility emission factor range reflects the use of some controls by both facilities. The uncontrolled emission factor ranges represent potential emissions if the sources reported were not controlled.

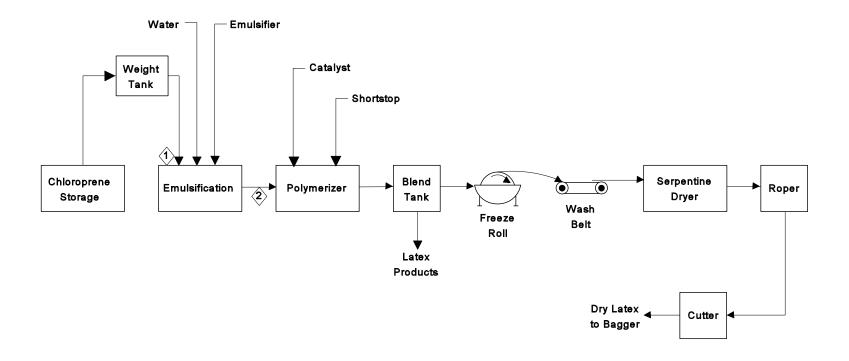


Figure 5-5. Flow Sheet for the Production of Neoprene

TABLE 5-9. SUMMARY OF EMISSION FACTORS FOR NEOPRENE PRODUCTION FACILITIES^{a,b} (FACTOR QUALITY RATING E)

	Facility Emission	Factors	Uncontrolled Emission Factors		
Emission Sources	Range ^c Mean		Range	Mean	
Process Vents	0.32 - 6.78 lb/ton (n=2)	4.04 lb/ton	0.40 - 24.18 lb/ton (n=2)	12.28 lb/ton	
3-01-026	(0.16 - 3.89 kg/Mg)	(2.02 kg/Mg)	(0.20 - 12.09 kg/Mg)	(6.14 kg/Mg)	
Secondary Sources 3-01-026	NA	NA	NA	NA	

Source: Reference 39.

Note: Annual emissions from uncontrolled equipment leaks range 1.03 - 4.88 tons/yr (0.93 - 4.43 Mg/yr) and average 2.95 tons/yr (2.68 Mg/yr) (n=2).^a For the facilities that reported emissions, none control equipment leaks.

n = number of facilities.

NA = not available.

 ^a Assumes production capacity of 100 percent.
 ^b Factors are expressed as lb (kg) butadiene emitted per ton (Mg) produced.
 ^c Ranges are based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.

Both facilities use controls, but the water-cooled condenser at one facility affords no emissions reduction. Also, the control efficiency of a flare in use was assigned a 98-percent removal efficiency, despite a higher value reported, because of the lack of supporting test data. Emissions from control devices are identified as Vent C on the process diagram.

Equipment Leak Emissions

Using facility-supplied information on the number of equipment components and the CMA procedure in Appendix D, equipment leak emissions estimates were calculated (see Table C-18 in Appendix C) and are summarized in Table 5-9. Although both facilities perform visual and area monitoring, neither provided specific information about these programs. No other controls were reported to be in use. The estimates include some level of control because the average emission rates are based on practices at butadiene producers.

Short-term Emissions

As a result of specific requests by the EPA for emissions data, short-term emissions are relatively well characterized. The data fall into four categories: short-term process vent emissions, pressure relief events, short-term emissions from equipment openings, and emissions from accidental releases.³⁷ No emissions were routed to a control device. A summary of the estimated emissions is given in Table 5-10.³⁷ Additional emissions are possible because companies were only asked to report the larger releases for that year.

5.5 ACRYLONITRILE-BUTADIENE-STYRENE COPOLYMER PRODUCTION

Acrylonitrile-butadiene-styrene (ABS) resins are currently produced by four companies at 10 locations.¹⁴ Table 5-11 presents a list of these facilities with their approximate capacities.²⁹ At least four of the ten facilities producing ABS do not use butadiene. They start instead from polybutadiene and proceed either through the suspension process or the continuous mass process. Therefore, no butadiene emissions are expected from these production processes.

TABLE 5-10. SHORT-TERM EMISSIONS FROM NEOPRENE PRODUCTION FACILITIES

Facility	Event Description	Number of Events per Year	Duration (minutes)	Amount Released per Event lb (kg)
Polysar	Butadiene vent shutdown	1	30	150 (68)
	Chlorinator shutdown	4/month	30	24 (11)
	Chlorinator shutdown	2/month	30	51 (23)
	Pressure relief	0		
	Equipment opening	1	Unknown	<150 (<68)
	Accidental releases	0		
DuPont	Vent	1	360	291 (132)
	Caustic scrubber relief valve	1	Unknown	40 (18)
	Equipment opening	0		
-	Accidental releases	0		



Source: Reference 37.

ABS resins are used to make plastic components for a variety of uses, including automotive parts, pipe and fittings, appliances, telephones, and business machines. Butadiene use in resin production accounts for about 5 percent of total butadiene consumption.⁸

5.5.1 <u>Process Description</u>

ABS resins are synthesized by three polymerization processes: an emulsion process, a suspension process, and a continuous mass (bulk) process. The majority of production is done by batch emulsions. Specialized resins are produced by the suspension process. These two processes are based on an aqueous-phase reaction. In contrast, the continuous mass process, the newest technology, does not proceed in water. This eliminates the need for dewatering and polymer drying, and reduces the volume of wastewater treatment required.

TABLE 5-11. ACRYLONITRILE-BUTADIENE-STYRENE RESIN PRODUCTION FACILITIES

Company	Location	Capacity in 1993 tons/yr (Mg/yr)
GE	Washington, WV	133,300 (120,000)
GE^{a}	Ottowa, IL	173,300 (156,000)
GE	Port Bienville, MS	101,100 (91,000)
Dow^a	Midland, MI	71,100 (64,000)
Dow	Hanging Rock, OH	45,600 (41,000)
$\mathrm{Dow}^{\mathrm{a}}$	Allyn's Point, CT	30,000 (27,000)
Dow^a	Torrance, CA	20,000 (18,000)
Monsanto	Addyston, OH	226,700 (204,000)
Monsanto	Muscatine, IA	75,600 (68,000)
Diamond Polymers	Akron, OH	8,900 (8,000)



Source: Reference 29.

Emulsion Process

A block diagram of the ABS emulsion process is shown in Figure 5-6.⁴¹ This process is referred to as the ABS/styrene-acrylonitrile (ABS/SAN) process because SAN is prepared in a side step and mixed with graft ABS. Some companies also produce SAN as a separate product.

The emulsion process involves several steps, from combining the raw materials with water for aqueous-phase reaction to purification and packaging of the product resins. Three distinct polymerizations occur in the first few steps: (1) butadiene polymerizes to form a polybutadiene substrate latex; (2) styrene and acrylonitrile are grafted to the polybutadiene substrate; and (3) styrene-acrylonitrile copolymer forms.

About 70 to 90 percent of butadiene monomer is converted to polybutadiene in the first step (Figure 5-6). The unreacted butadiene monomer is removed from the latex in a

^a Facility has used polybutadiene as raw material for ABS production since 1985.

Source: Reference 41

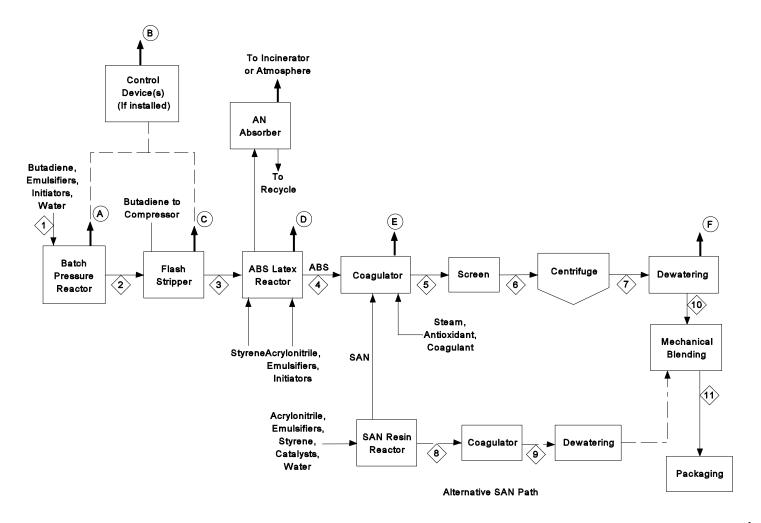


Figure 5-6. Process Diagram for Production of ABS/SAN Via the Emulsion Process

flash stripper (Step 2) and usually recovered. The reactor, stripper, and recovery system vents are usually directed to a flare or other combustion device. The grafting of acrylonitrile and styrene to the polybutadiene substrate (Step 3) may be either a batch or continuous process. Reaction conversion of monomers is 90 to 95 percent. Vapors from the reactors are usually vented to an acrylonitrile absorber. The absorber is vented to the atmosphere or to an incinerator.

The ABS plastic is a blend of graft ABS rubber and SAN resin. The blend of these compounds determines the properties for the ABS product. The copolymer SAN is prepared in a separate side step. The prepared SAN and graft ABS are mixed at either of two points in the process. The SAN latex may be blended with graft rubber latex in the coagulator (Step 4). The agglomerated polymer is dewatered by screening (Step 5), centrifuging (Step 6), and vacuum filtration (Step 7). No drying step is required. However, some facilities employ a dryer in place of the centrifuge and vacuum filter.

Alternatively, the SAN latex may be coagulated (Step 8) and dewatered (Step 9) separately, with the resulting solid resins being mechanically mixed with ABS rubber (Step 10). In a compounding step, solids are mechanically blended with dyes, antioxidants, and other additives (Step 10). In the final step (11), the polymer sheets from these operations are pelletized and packaged.

Suspension Process

A block diagram of the suspension ABS process is shown in Figure 5-7.⁴¹ This process begins with polybutadiene rubber, which is so lightly cross-linked that it is soluble in the acrylonitrile and styrene monomers. Polybutadiene synthesis is previously described in this section.

Polybutadiene is first dissolved in styrene and acrylonitrile monomers to produce a solution free of cross-linked rubber gels. A free radical is added to the solution along with chain-transfer agents in a prepolymerizer (Step 2). After 25 to 35 percent monomer conversion,

the polymer syrup is transferred to a suspension reactor, where it is dispersed in water with agitation (Step 3).

After achieving the desired monomer conversion, the products are transferred to a washing/dewatering system (Step 4), usually a continuous centrifuge. The polymer beads are then dried in a hot-air dryer (Step 5).

Continuous Mass Process

A block flow diagram for the continuous mass ABS process is shown in Figure 5-8.⁴¹ This process begins with polybutadiene rubber, which is dissolved in styrene and acrylonitrile monomers (Step 1), along with initiators and modifiers. The ABS polymer is then formed through phase inversion. Conversion begins in the prepolymerizer (Step 2), where the reaction causes the ABS rubber to precipitate out of solution. When monomer conversion is about 30 percent complete, the resulting syrup is transferred to the bulk polymerizer, where monomer conversion is taken to between 50 and 80 percent (Step 3). Unreacted monomer is removed under vacuum from the polymer melt in the devolatilizer (Step 4). The monomer vapors are condensed and recycled to the prepolymerizer. The ABS polymer is then extruded, cooled in a water bath (Step 5), and chopped into pellets (Step 6).

5.5.2 Emissions

As mentioned previously, at least four of the ten facilities producing ABS do not use butadiene. They start instead from polybutadiene and proceed either through the suspension process or the continuous mass process. Therefore, no butadiene emissions are expected from these production processes. Of the four remaining plants in operation, data are only available for three locations and are limited to information on process vents and equipment leaks associated with the emulsion process. Calculated emission factors are summarized in Table 5-12 as ranges and are based on data from 1984 appearing in Tables C-19 and C-20 in Appendix C.

Source: Reference 41

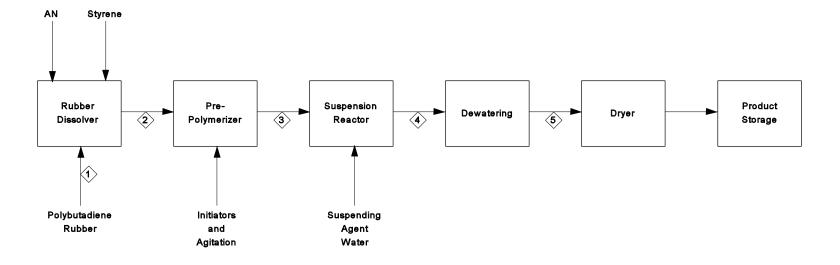


Figure 5-7. Process Diagram for Production of ABS via the Suspension Process (not a source of butadiene emissions)



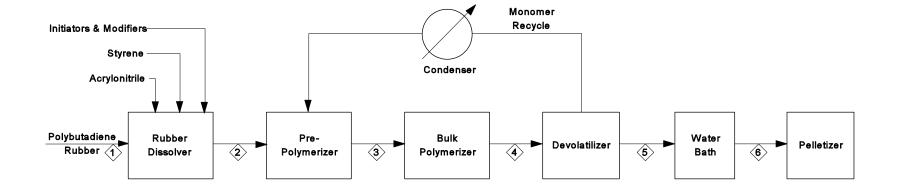


Figure 5-8. Process Diagram for Production of Bulk ABS (not a source of butadiene emissions)

Source: Reference 41

The facility emission factor range for process vents includes existing sources, some of which are controlled. The uncontrolled range represents potential emissions if the sources reported were not controlled.⁴⁰

One estimate of emissions from butadiene storage was reported as zero because butadiene is stored under pressure. Some emissions are possible from secondary sources, emergency and accidental releases, and transfer and handling raw material losses, but estimates for these sources are currently unavailable.

Process Vent Emissions

Based on available data, process vent emissions of butadiene occur mainly from the flash-stripping of the latex from the polymerization reactor in the ABS emulsion process. The vent emissions from the batch reactors are highly variable, with changing compositions. Most of these vents are controlled by a flare (control efficiency of 99.9 percent).

Butadiene emissions also occur during the coagulation and dewatering stages and from intermediate process latex tanks. In 1984, only one facility used a control device. In this plant, one of the downstream vents was controlled by routing the vent to the plant boiler. Figure 5-6 shows the process vent locations: Vents A and C through F for emissions directly associated with the process and Vent B for emissions from a control device.

Equipment Leak Emissions

The estimates for uncontrolled equipment leaks at the two facilities appearing in Table 5-12 are based on equipment counts provided by the facilities. The CMA estimation procedure is described in Appendix D. One location reported daily inspection of equipment; however, no further details on follow-up for any leaks discovered during these inspections were given. The estimates include some level of control because the average emission rates are based on practices at butadiene producers.

TABLE 5-12. SUMMARY OF EMISSION FACTORS FOR ABS PRODUCTION FACILITIES, EMULSION PROCESS^{a,b} (FACTOR QUALITY RATING E)

	Facility Emission	Factors	Uncontrolled Emission Factors			
Emission Sources	Range ^c	Mean	Range	Mean		
Process Vents	0.16 - 10.66 lb/ton (n=3)	4.22 lb/ton	6.50 - 11.28 lb/ton (n=3)	9.48 lb/ton		
6-41	(0.08 - 5.33 kg/Mg)	(2.11 kg/Mg)	(3.25 - 5.64 kg/Mg)	(4.74 kg/Mg)		
Secondary Sources 6-41	NA	NA	NA	NA		

Source: Reference 40.

Note: Annual emissions from uncontrolled equipment leaks range from 1.21 - 3.50 tons/yr (1.10 - 3.17 Mg/yr) and average 2.36 tons/yr (2.14 Mg/yr) (n=2). For facilities that reported emissions, none control equipment leaks.

n = number of facilities.

NA = not available.

^a Assumes production capacity of 100 percent.

^b Factors are expressed as lb (kg) butadiene emitted per ton (Mg) produced. Data from two facilities are specific to the emulsion process; the third is assumed to use the same.

^c Ranges are based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.

5.6 NITRILE ELASTOMER PRODUCTION

Nitrile elastomer or nitrile-butyl rubber (NBR) is produced by nine facilities.²⁹ The location of the facilities, the type of elastomer produced, and their approximate capacities are presented in Table 5-13.²⁹

Nitrile elastomer is considered a specialty elastomer and is primarily used for its oil-, solvent-, and chemical-resistant properties by a variety of manufacturers. ⁴² Some uses include hose, belting, and cable manufacturing, and molded goods such as seals and gaskets. Nitrile elastomer production accounts for about 5 percent of total annual butadiene consumption. ⁸

Several of the facilities involved in NBR production also produce other elastomers. Goodyear in Texas, Polysar in Tennessee and Texas, Copolymer, and Reichhold all produce SB copolymers. Because of the common use of butadiene in these production processes, emissions data often represent total rather than individual process emissions. Whenever possible, the portion of butadiene emissions directly attributable to nitrile rubber is shown.

5.6.1 <u>Process Description</u>

Nitrile elastomers are copolymers of acrylonitrile and butadiene. They are produced by emulsion polymerization in batch or continuous processes. The process is illustrated in the block flow diagram in Figure 5-9.⁴¹

The emulsion polymerization process uses water as a carrier medium. Butadiene and acrylonitrile monomers are piped to agitated polymerization reactors (Step 1) along with additives and soap. The water not only serves as a reaction medium, but also effectively transfers the heat of reaction to the cooled reactor surfaces. The additives include a catalyst

TABLE 5-13. NITRILE ELASTOMER PRODUCTION FACILITIES

Company	Location	Elastomer Type	Capacity in 1993 dry rubber or latex tons/yr (Mg/yr)
Copolymer	Baton Rouge, LA	Solid rubber	11,100 (10,000)
Zeon Chemicals	Pasadena, TX	Hydrogenated	2,200 (2,000)
	Louisville, KY	Solid rubber	33,300 (30,000)
Goodyear	Houston, TX	Solid rubber	34,400 (31,000)
Polysar Ltd.	Orange, TX	Solid rubber	2,200 (2,000)
BASF	Chattanooga, TN	Latex	
Reichhold Chemicals	Cheswold, DE	Latex	
Uniroyal Chemical Co.	Painesville, OH	Solid rubber	22,200 (20,000)
W. R. Grace	Owensboro, KY	Latex	



Source: Reference 29.

(cumene hydroperoxide as an oxidizing component), sodium formaldehyde sulfoxylate with EDTA (ferrous sulfate complexed with ethylenediamine-tetraacetic acid as the reducing component), and modifiers (alkyl mercaptans).

The reaction is allowed to proceed for 5 to 12 hours. A shortstop solution (sodium bisulfate or potassium dimethyl dithiocarbonate) is added to terminate the reaction at a predetermined point, usually after 75 to 90 percent conversion (depending on the desired molecular weight of the product). The reaction latex is then sent to a blowdown tank (Step 2), where antioxidants are normally added.

The latex is subjected to several vacuum flash steps (3), where most of the unreacted butadiene is released. It is then steam-stripped under vacuum (Step 4) to remove the remaining butadiene and most of the unreacted acrylonitrile. The unreacted monomers are sent to recovery and recycling. Stripped latex at about 110 to 130°F (43 to 54°C) is pumped to blend tanks (Step 5).

[&]quot;--" means capacity not known.

Source: Reference 41

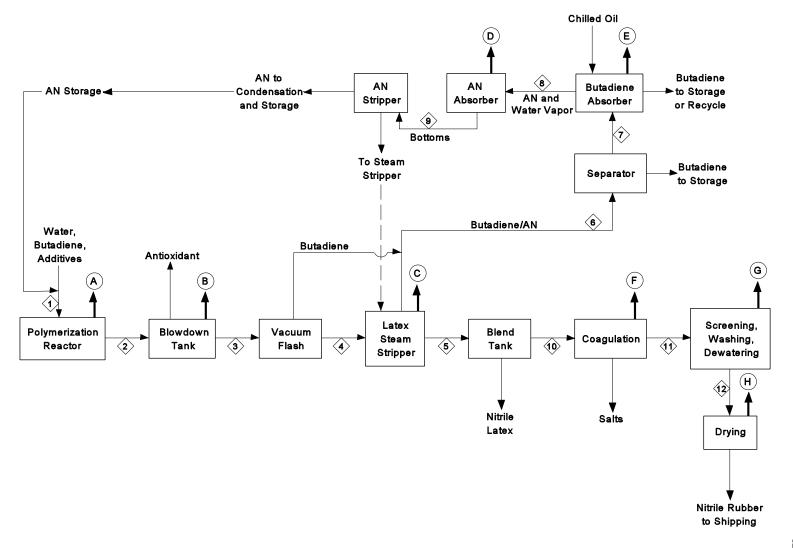


Figure 5-9. Process Diagram for Production of Nitrile Elastomer

Gases released in the flash steps and stripped overhead contain butadiene. These gases are sent to a partial condenser (not shown) and separator (Step 6), where butadiene vapor is condensed and sent to liquid storage. Uncondensed butadiene vapor from the separator flows to an absorber (Step 7), where it is absorbed by countercurrent contact with chilled oil. The absorber bottoms are pumped to a flash tank (not shown), and dissolved butadiene is released and returned to the compressor. The hot lean oil is then cooled, chilled, and returned to the top of the absorber.

Unreacted acrylonitrile in flash vapors and latex stripper overhead is recovered by sending these gases to a water absorber (Step 8). Absorber bottoms and the liquid phase of the latex stripper overhead are pumped to a steam stripper (Step 9). The overhead vapor stream from this stripper is condensed in a decanter. Phase separation is allowed to take place and the acrylonitrile phase is decanted to storage. The water-rich phase with residual acrylonitrile is returned to the stripper.

Latex is pumped from the blend tanks (Step 5) to a coagulation tank (Step 10), where the emulsion is broken by the addition of dilute inorganic salt solution (sodium chloride or aluminum sulfate) or a weak organic acid. The slurry of fine polymer crumb is then filtered to remove coagulating chemicals (liquor is recycled) and may be reslurried for further purification. Crumb is dewatered in an extruder (Step 11), then hot-air dried (Step 12). Dried rubber is weighed, pressed into bales, and prepared for shipment.

If latex is the desired end product, the final processing steps (coagulation, screening, washing, and drying) are omitted. The initial steps are essentially identical to those for solid rubber production.⁴⁰

5.6.2 Emissions

The availability of emissions data for nitrile elastomer is somewhat limited. At coproduction facilities, the estimated butadiene emissions include releases from other elastomer production processes. For the two facilities that are also SB copolymer producers, the percent of

the total reported emissions assigned to the NBR process was based on the percent of total production resulting in nitrile elastomer in 1984. Table 5-14 summarizes emissions for process vents, equipment leaks, and secondary sources. All nitrile elastomer production was assumed to be operating at full capacity. Emissions from emergency and accidental releases and transfer/handling were not known and storage vent emissions from butadiene storage were expected to be low because of the use of tanks under pressure.

Process Vent Emissions

All six facilities for which emissions data were reported use some level of emissions control. Many of the controls that are designed to reduce acrylonitrile emissions are also effective in reducing butadiene emissions (flares, for example). Data from 1984 for four of these facilities are summarized as emission factor ranges in Table 5-14 (see Tables C-21 and C-22 in Appendix C for facility-specific data). The fifth is not used because calculation of an emission factor might reveal confidential business information on production capacity. Potential vent locations, shown in Figure 5-9 as Vents A through H, are based on information on the vent locations supplied by five facilities.

The emission factor ranges were developed as described in Section 4.0. The facility emission factor range includes the various levels of control that each facility has in place. Control efficiencies varied from 89 percent to 99.9 percent. The uncontrolled emission factor range represents potential emissions if controls were not in use.

Equipment Leak Emissions

The estimates for equipment leaks provided by three facilities span three orders of magnitude (Table 5-14). These estimates include the level of control at butadiene producers because of how the average emission rates were derived. The only known control devices currently in use are rupture discs and a flare for pressure relief devices by one facility. The other three facilities indicate daily visual inspection of equipment; however, no repair programs were described for any of the leaks found. Although some controls are in place, detailed information that could be used to compare practices with those at butadiene producers was not available.

TABLE 5-14. SUMMARY OF EMISSION FACTORS FOR NITRILE ELASTOMER PRODUCTION FACILITIES a,b (FACTOR QUALITY RATING E)

	Facility Emission F	Uncontrolled Emissi	Uncontrolled Emission Factors			
Emission Sources	Range ^c	Mean	Range	Mean		
Process Vents	0.0004 - 17.80 lb/ton (n=6)	~ 4 lb/ton	0.030 - <50 lb/ton (n=6)	~ 16 lb/ton		
3-01-026	(0.0001 - 8.90 kg/Mg)	$(\sim 2 \text{ kg/Mg})$	(0.01 - <25 kg/Mg)	$(\sim 8 \text{ kg/Mg})$		
Secondary Sources ^e	0.002 - 0.018 lb/ton (n=2)	0.010 lb/ton	0.002 - 0.018 lb/ton (n=2)	0.010 lb/ton		
3-01-026	(0.001 - 0.009 kg/Mg)	(0.005 kg/Mg)	(0.001 - 0.009 kg/Mg)	(0.005 kg/Mg)		

Source: Reference 40.

Note: Annual emissions from uncontrolled equipment leaks range 0.43 - 18.67 tons/yr (0.39 - 16.93 Mg/yr) and average 8.74 tons/yr (7.93 Mg/yr) (n=3).

n = number of facilities.

NA = not available.

^a Assumes production capacity of 100 percent.

^b Factors are expressed as lb (kg) butadiene emitted per ton (Mg) produced. Only incomplete data on emissions were available, therefore, values underestimate emissions.

^c Ranges are based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.

^d Upper value used to prevent disclosing confidential operating capacity.

^e Lower end of range is for one solid waste stream; upper end includes solid waste, wastewater and contaminated cooling water.

Secondary Emissions

One emissions estimate of 132 lb/yr (60 kg/yr) was provided from secondary sources. This estimate includes wastewater, solid waste, and contaminated cooling water. A second facility also indicated wastewater and solid waste as potential secondary sources. The butadiene content in the wastewater was undetermined; therefore, emissions could not be estimated. However, the solid waste stream contains 4 ppm butadiene. Based on a generation rate of 1063 lb/day (483 kg/day) and assumptions of continuous operation and total volatilization, the source's emissions potential is approximately 0.02 tons/yr (20 kg/yr).

SECTION 6.0

BUTADIENE EMISSIONS FROM MOBILE SOURCES

This section describes estimation methods for butadiene as one component of mobile source hydrocarbon emissions, based on work by EPA's Office of Mobile Sources (OMS). Butadiene emissions are formed in engine exhaust by the incomplete combustion of the fuel. Based on the available data, butadiene emissions appear to increase roughly in proportion to hydrocarbon emissions. Because hydrocarbon emissions are greater from noncatalyst-controlled engines than from catalyst-equipped engines, butadiene emissions are expected to be higher from noncatalyst-controlled engines, such as those in lawnmowers and chainsaws.¹⁷

Levels of butadiene in gasoline and diesel fuel are expected to be insignificant because butadiene tends to readily form a varnish that can be harmful to engines; therefore, refiners try to minimize the butadiene content. As a result, it was assumed that butadiene is not present in evaporative, refueling, or resting emissions.¹⁷

6.1 ON-ROAD MOBILE SOURCES

Results of work by the OMS on toxic emissions from on-road motor vehicles are presented in the 1993 report *Motor Vehicle-Related Air Toxics Study* (MVATS).¹⁷ This report was prepared in response to Section 202(l)(1) of the 1990 Clean Air Act Amendments which directs EPA to complete a study of the need for, and feasibility of, controlling emissions of toxic air pollutants that are unregulated under the Act and are associated with motor vehicles and motor vehicle fuels. The report presents composite emission factors for several toxic air pollutants, including butadiene.

The emission factors presented in the MVATS were developed using currently available emissions data in a modified version of the EPA's MOBILE4.1 emission model (designated MOBTOX) to estimate toxic emissions as a fraction of total organic gas (TOG) emissions. All exhaust mass fractions were calculated on a vehicle by vehicle basis for six vehicle types: light-duty gasoline vehicles, light-duty gasoline trucks, heavy-duty gasoline trucks, light-duty diesel vehicles, light-duty diesel trucks and heavy-duty diesel trucks. It was assumed that light-duty gas and diesel trucks have the same mass fractions as light-duty gas vehicles and diesel vehicles, respectively. For light duty gas vehicles and trucks, mass fractions were disaggregated for four different catalytic types for running emissions and two different fuel systems. Heavy-duty gas vehicles were assumed to have a carbureted fuel system with either no catalyst or three-way catalyst. These mass fractions were applied to TOG emission factors developed to calculate in-use toxics emission factors.

A number of important assumptions were made in the development of these inuse toxic emission factors. They include:

- 1. Increase in air toxics due to vehicle deterioration with increased mileage is proportional to increase in TOG.
- 2. Toxics fractions remain constant with ambient temperature changes.
- 3. The fractions are adequate to use for the excess hydrocarbons that come from malfunction and tampering/misfueling.

It should be noted that in specific situations, the EPA Mobile models may over or underestimate actual emissions.

The butadiene emission factors by vehicle class in grams of butadiene emitted per mile driven are shown in Table 6-1.⁴⁴ The OMS also performed multiple runs of the MOBTOX program to derive a pollutant-specific, composite emission factor that represented all vehicle classes, based on the percent of total vehicle miles traveled (VMT) attributable to each vehicle class. Table 6-1 also presents the composite emission factor in pounds (grams) of butadiene emitted per mile driven.¹⁷

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TABLE 6-1. BUTADIENE EMISSION FACTORS FOR 1990 TAKING INTO CONSIDERATION VEHICLE AGING (g/mi)

	LDGV	LDGT1	LDGT2	LDGT	HDGV	LDDV	LDDT	HDDV	MC	Weighted VMT Mix
Exhaust										
Areas with no I/M	0.017	0.026	0.042	0.029	0.087	0.007	0.011	0.057	0.029	0.024
Areas with basic I/M	0.013	0.026	0.042	0.029	0.087	0.007	0.011	0.057	0.029	0.022

Source: Reference 44.

LDGV = Light-Duty Gasoline Vehicle

LDGT1 = Light-Duty Gasoline Truck [pick-ups and vans with gross vehicle weight

of 0 to 6000 lb (0 to 272 kg)]

LDGT2 = Light-Duty Gasoline Truck [pick-ups and vans with gross vehicle weight

of 6001 to 8500 lb (273 to 3,856 kg)]

LDGT = Light-Duty Gasoline Truck (combined category of LDGT1 and LDGT2)

HDGV = Heavy-Duty Gasoline Vehicle LDDV = Light-Duty Diesel Vehicle LDDT = Light-Duty Diesel Truck HDDV = Heavy-Duty Diesel Vehicle

MC = Motorcycle

The OMS continues to update the on-road mobile sources model. As of the date of preparation of this report, MOBILE5a was available, but butadiene-specific emission factors had not been generated. Emissions based on this newer model, however, are estimated to be about 20 percent higher on average than those from MOBTOX. Due to the higher VOC emission rates associated with the newer model, the emission rates for 1,3-butadiene may also be incrementally higher.

Use of methanol in motor vehicles will result in substantial 1,3-butadiene emission reductions. Projected reductions in butadiene levels of approximately 93 percent were given in a recent comparison of gasoline and 85-percent methanol (M85) emissions from flexible fuel and variable fuel vehicles. Also, butadiene emissions reductions of 99 percent for optimized flexible fuel vehicles running on 100-percent methanol (M100) fuel were estimated in EPA's Methanol Special Report. Substantial reductions in butadiene emissions are also expected with use of ethanol as a clean fuel. Finally, butadiene emissions with the use of compressed natural gas are extremely low.

6.2 OFF-ROAD MOBILE SOURCES

For off-road mobile sources, EPA prepared the 1991 report *Non-road Engine Vehicle Emission Study* (NEVES),⁵⁰ which presents emission factors for 79 equipment types, ranging from small equipment such as lawnmowers and chain saws, to large agricultural, industrial, and construction machinery (see Table 6-2). Locomotives, aircraft, and rockets are not included. The equipment types were evaluated based on three engine designs: 2-stroke gasoline, 4-stroke gasoline, and diesel. Sources for the data include earlier EPA studies and testing and new information supplied by the engine manufacturers for tailpipe exhaust and crankcase emission. For test data on new engines, adjustments were made to better represent emissions from in-use equipment because EPA believes the new engine data do not take into consideration increase in emissions due to engine deterioration associated with increased equipment age; therefore, new engine data underestimate in-use emissions.⁵⁰

TABLE 6-2. OFF-ROAD EQUIPMENT TYPES AND BUTADIENE EMISSION FACTORS INCLUDED IN THE NEVES (g/hp-hr) (FACTOR QUALITY RATING E)

	2-Stroke Gasoline Engines		4-Stroke Eng		Diesel Engines		
Equipment type, AMS Code (2-stroke gas/4-stroke gas/diesel)	Exhaust	Crank Case	Exhaust	Crank Case	Exhaust	Crank Case	
Lawn and Garden, 22-60/65/70-004-							
025 Trimmers/Edgers/Brush Cutters	6.13^{a}	N/A	0.66^{a}	0.104^{a}	N/A	N/A	
010 Lawn Mowers	5.68^{a}	N/A	1.03 ^a	0.162^{a}	N/A	N/A	
030 Leaf Blowers/Vacuums	5.88^{a}	N/A	0.53^{a}	0.083^{a}	N/A	N/A	
040 Rear Engine Riding Mowers	N/A	N/A	0.25^{a}	0.040^{a}	0.02	N/A	
045 Front Mowers	N/A	N/A	0.25^{a}	0.040^{a}	N/A	N/A	
020 Chain Saws <4 hp	8.14^{a}	N/A	N/A	N/A	N/A	N/A	
050 Shredders < 5 hp	5.68 ^a	N/A	1.03 ^a	0.162^{a}	N/A	N/A	
015 Tillers < 5 hp	5.68^{a}	N/A	1.03 ^a	0.162^{a}	N/A	N/A	
055 Lawn and Garden Tractors	N/A	N/A	0.26^{a}	0.040^{a}	0.02	N/A	
060 Wood Splitters	N/A	N/A	1.03 ^a	0.162^{a}	0.02	N/A	
035 Snowblowers	5.68 ^a	N/A	1.03 ^a	0.162^{a}	N/A	N/A	
065 Chippers/Stump Grinders	N/A	N/A	0.74^{b}	0.162^{b}	0.02	N/A	
070 Commercial Turf Equipment	5.68^{a}	N/A	0.26^{a}	0.040^{a}	N/A	N/A	
075 Other Lawn and Garden Equipment	5.68 ^a	N/A	1.03ª	0.162 ^a	0.02	N/A	
Airport Service, 22-60/65/70-008-							
005 Aircraft Support Equipment	N/A	N/A	0.13^{b}	0.029^{b}	0.03^{c}	N/A^c	
010 Terminal Tractors	$0.06^{b,d}$	$0.013^{b,d}$	0.13 ^b	0.029^{b}	0.03^{c}	N/A ^c	
Recreational, 22-60/65/70-001-							
030 All Terrain Vehicles (ATVs)	16.38 ^{a,e}	N/A	$2.73^{a,e}$	$0.429^{a,e}$	N/A	N/A	
040 Minibikes	N/A	N/A	$2.73^{a,e}$	$0.429^{a,e}$	N/A	N/A	
010 Off-Road Motorcycles	16.38 ^{a,e}	N/A	1.95 ^{b,e}	$0.429^{b,e}$	N/A	N/A	
050 Golf Carts	16.38 ^{a,e}	N/A	$2.73^{a,e}$	$0.429^{a,e}$	N/A	N/A	
020 Snowmobiles	2.98^{a}	N/A	N/A	N/A	N/A	N/A	
060 Specialty Vehicles Carts	16.38 ^{a,e}	N/A	$2.73^{a,e}$	$0.429^{a,e}$	0.02^{e}	N/A^{e}	

TABLE 6-2. CONTINUED

	2-Stroke Eng		4-Stroke Eng	Gasoline ines	Diesel Engines	
Equipment type, AMS Code (2-stroke gas/4-stroke gas/diesel)	Exhaust	Crank Case	Exhaust	Crank Case	Exhaust	Crank Case
Recreational Marine Vessels, 22-82-005/010/020-						
005 Vessels w/Inboard Engines	11.36 ^{b,f}	N/A	$1.41^{b,f}$	N/A	0.39^{f}	N/A
010 Vessels w/Outboard Engines	11.36 ^{b,f}	N/A	$1.71^{b,f}$	$0.376^{\mathrm{b,f}}$	$0.39^{\rm f}$	$0.008^{\rm f}$
Vessels w/Sterndrive Engines	11.36 ^{b,f}	N/A	$1.41^{b,f}$	N/A	$0.39^{\rm f}$	N/A
020 Sailboat Auxiliary Inboard Engines	N/A	N/A	1.41 ^{b,f}	N/A	1.96 ^f	N/A
025 Sailboat Auxiliary Outboard Engines	11.36 ^{b,f}	N/A	1.71 ^{b,f}	0.376 ^{b,f}	1.96 ^f	0.039 ^f
Light Commercial, less than 50 HP, 22-60/65/70-006-						
005 Generator Sets	5.68 ^a	N/A	0.26^{a}	0.041^{a}	0.02	N/A
010 Pumps	$0.12^{a,d}$	$0.018^{a,d}$	0.26^{a}	0.041 ^a	0.02	N/A
015 Air Compressors	N/A	N/A	0.26^{a}	0.041^{a}	0.02	N/A
020 Gas Compressors	$0.08^{b,d}$	$0.018^{b,d}$	N/A	N/A	N/A	N/A
025 Welders	N/A	N/A	0.26^{a}	0.041 ^a	0.02	N/A
030 Pressure Washers	N/A	N/A	0.26^{a}	0.041 ^a	0.02	N/A
Industrial, 22-60/65/70-003-						
010 Aerial Lifts	$0.06^{b,d}$	$0.019^{b,d}$	0.13^{b}	0.029^{b}	0.03°	N/A ^c
102 Forklifts	$0.06^{b,d}$	$0.019^{b,d}$	0.13 ^b	0.029^{b}	0.03°	N/A ^c
030 Sweepers/Scrubbers	$0.06^{b,d}$	$0.019^{b,d}$	0.13^{b}	0.029^{b}	0.03°	N/Ac
040 Other General Industrial Equipment	4.06 ^b	N/A	0.13 ^b	0.029^{b}	0.03°	N/A ^c
050 Other Material Handling Equipment	N/A	N/A	0.13 ^b	0.029 ^b	0.03°	N/A ^c
Construction, 22-60/65/70-002-						
003 Asphalt Pavers	N/A	N/A	0.13^{b}	0.028^{b}	0.01	N/A
006 Tampers/Rammers	5.68 ^a	N/A	0.18^{a}	0.028^{a}	0.00	0.00
009 Plate Compactors	5.68 ^a	N/A	0.18^{a}	0.028^{a}	0.01	N/A
012 Concrete Pavers	N/A	N/A	N/A	N/A	0.02	N/A
015 Rollers	N/A	N/A	0.25^{a}	0.040^{a}	0.01	N/A
018 Scrapers	N/A	N/A	N/A	N/A	$0.01^{\rm c}$	N/Ac
021 Paving Equipment	5.68 ^a	N/A	0.18^{a}	0.028^{a}	0.02	N/A

TABLE 6-2. CONTINUED

	2-Stroke (Engi		4-Stroke Eng		Diesel E	Diesel Engines	
Equipment type, AMS Code (2-stroke gas/4-stroke gas/diesel)	Exhaust	Crank Case	Exhaust	Crank Case	Exhaust	Crank Case	
Construction, 22-60/65/70-002- (con't)							
024 Surfacing Equipment	N/A	N/A	0.18^{a}	0.028^{a}	0.00	0.00	
027 Signal Boards	N/A	N/A	0.18^{a}	0.028^{a}	0.02	N/A	
030 Trenchers	N/A	N/A	0.13^{b}	0.028^{b}	0.02^{c}	N/A^c	
033 Bore/Drill Rigs	5.68 ^a	N/A	0.13^{b}	0.028^{b}	0.02^{c}	N/A^c	
036 Excavators	N/A	N/A	0.13^{b}	0.028^{b}	$0.01^{\rm c}$	N/A^c	
039 Concrete/Industrial Saws	N/A	N/A	0.18^{a}	0.028^{a}	0.02°	N/Ac	
042 Cement and Mortar Mixers	N/A	N/A	0.18^{a}	0.028^{a}	0.02	N/A	
045 Cranes	N/A	N/A	0.13^{b}	0.028^{b}	0.02^{c}	N/A^{c}	
048 Graders	N/A	N/A	N/A	N/A	0.02°	N/Ac	
051 Off-Highway Trucks	N/A	N/A	N/A	N/A	0.01°	N/Ac	
054 Crushing/Proc. Equipment	N/A	N/A	0.13^{b}	0.028^{b}	$0.02^{\rm c}$	N/Ac	
057 Rough Terrain Forklifts	N/A	N/A	0.13^{b}	0.028^{b}	0.03°	N/A ^c	
060 Rubber Tire Loaders	N/A	N/A	0.11^{b}	0.024^{b}	$0.01^{\rm c}$	N/A ^c	
063 Rubber Tire Dozers	N/A	N/A	N/A	N/A	$0.01^{\rm c}$	N/A ^c	
066 Tractors/Loaders/Backhoes	N/A	N/A	0.13^{b}	0.028^{b}	0.02°	N/A ^c	
069 Crawler Tractors	N/A	N/A	N/A	N/A	0.02°	N/A ^c	
072 Skid Steer Loaders	N/A	N/A	0.13^{b}	0.028^{b}	0.03°	0.001°	
075 Off-Highway Tractors	N/A	N/A	N/A	N/A	$0.04^{\rm c}$	0.001^{c}	
078 Dumpers/Tenders	N/A	N/A	0.18^{a}	0.028^{a}	0.01°	N/Ac	
081 Other Construction Equipment	N/A	N/A	0.13 ^b	0.028^{b}	$0.02^{\rm c}$	N/A°	
Agricultural, 22-60/65/70-005-							
010 2-Wheel Tractors	N/A	N/A	0.15^{a}	0.024^{a}	N/A	N/A	
015 Agricultural Tractors	N/A	N/A	0.11^{b}	0.024^{b}	$0.04^{\rm c}$	0.001°	
030 Agricultural Mowers	N/A	N/A	0.20^{a}	0.031 ^a	N/A	N/A	
020 Combines	N/A	N/A	0.14^{b}	0.031^{b}	0.02°	N/Ac	
035 Sprayers	N/A	N/A	0.14^{b}	0.031^{b}	0.04	0.001	
025 Balers	N/A	N/A	N/A	N/A	0.04	0.001	
040 Tillers > 5 hp	N/A	N/A	1.03 ^a	0.162 ^a	0.02	N/A	
045 Swathers	N/A	N/A	0.14^{b}	0.031 ^b	0.01	N/A	
050 Hydro Power Units	N/A	N/A	0.20^{a}	0.031 ^a	0.04	0.001	
055 Other Agricultural Equipment	N/A	N/A	0.14^{b}	0.031 ^b	0.03	0.001	

TABLE 6-2. CONTINUED

	2-Stroke Gasoline Engines		4-Stroke Gasoline Engines		Diesel Engines	
Equipment type, AMS Code (2-stroke gas/4-stroke gas/diesel)	Exhaust	Crank Case	Exhaust	Crank Case	Exhaust	Crank Case
Logging, 22-60/65/70-007-						
005 Chain Saws >4 hp	4.15 ^a	N/A	N/A	N/A	N/A	N/A
010 Shredders > 5 hp	N/A	N/A	0.25^{a}	0.040^{a}	N/A	N/A
015 Skidders	N/A	N/A	N/A	N/A	0.01°	N/A^{c}
020 Fellers/Bunchers	N/A	N/A	N/A	N/A	0.01°	N/A ^c

Source: Reference 50.

N/A = Not applicable.

Although these emission factors were intended for calculating criteria pollutant (VOCs, NO_x, CO) emissions for SIP emissions inventories, emission factors for several hazardous air pollutants (HAPs), including butadiene, were derived so that national air toxics emissions could be estimated. To estimate butadiene emissions, EPA expressed butadiene emissions as a weight percent of tailpipe exhaust hydrocarbons plus crank case hydrocarbons and combined the weight percents with existing hydrocarbon emission factors. The weight percents butadiene applied to all categories of equipment were 1.6 and 1.3 for diesel and gasoline engines, respectively. These are based on the recommendations from an EPA report Non-road Emission Factors of Air Toxics⁵¹ that are based on automobile test data. For emissions from diesel-fueled marine vessels, high-speed, agricultural, construction and large utility equipment, the report suggests use of weight factors 1.5 percent for direct injection, and 1.7 percent for indirect injection diesel engines. For emissions from unleaded non-catalyst gasoline-powered marine vessels, agricultural, construction and large utility equipment, a 1.3 percent weight factor is recommended.⁵¹ The NEVES distinguished between off-road diesel and gasoline engines and applied the diesel and gasoline weight percents to all equipment types. Future work may provide equipment-specific values and the use of these should be considered instead.

^a Adjusted for in-use effects using small utility engine data.

^b Adjusted for in-use effects using heavy duty engine data.

^c Exhaust HC adjusted for transient speed and/or transient load operation.

^d Emission factors for 4-stroke propane-fueled equipment.

e g/hr.

f g/gallon.

The most accurate emission estimate requires that the emission factors be used with local activity data. If these data are unavailable, a state may elect to approximate emissions using estimates from the NEVES for 24 nonattainment areas. Taking this approach, the state chooses one of the 24 nonattainment areas which best represents the state's offroad activity. The corresponding emission estimate is then adjusted by applying a ratio of the population for the two areas to more closely approximate the state's emissions. The NEVES report also provides estimates for counties in the 24 nonattainment areas; therefore, state and local agencies may prepare regional or county inventories by applying a population ratio to the NEVES estimates. For further details on the estimation procedure, the reader should refer to the NEVES report.

6.2.1 Marine Vessels

For commercial marine vessels, the NEVES report includes VOC emissions for six nonattainment areas taken from a 1991 EPA study *Commercial Marine Vessel Contribution to Emission Inventories*. This study provided hydrocarbon emission factors for ocean-going commercial vessels and harbor and fishing vessels. The emission factors are shown in Table 6-3.

Ocean-going marine vessels fall into one of two categories--those with steam propulsion and those with motor propulsion. Furthermore, they emit pollution under two modes of operation: underway and at dockside (hotelling). Most steamships use boilers rather than auxiliary diesel engines while hotelling. Currently, there are no butadiene toxic emission fractions for steamship boiler burner emissions. The emission factors for motor propulsion systems are based on emission fractions for heavy-duty diesel vehicle engines. For auxiliary diesel generators, emission factors are available only for 500 KW engines, since the 1991 Booz-Allen and Hamilton⁵² report indicated that almost all generators were rated at 500 KW or more.

For harbor and fishing vessels, butadiene emission factors for diesel engines are provided for the following horsepower categories -- less than 500 hp, 500 to 1,000 hp, 1,000 to

1,500 hp, 1,500 to 2,000 hp, and greater than 2,000 hp. In each of these categories, emission factors are developed for full, cruise, and slow operating modes. Butadiene emission factors are also provided for gasoline engines in this category. These emission factors are not broken down by horsepower rating, and are expressed in grams per brake horsepower hour rather than pounds per thousand gallons of fuel consumed.

6.2.2 Locomotives

As noted in the U.S. EPA's *Procedures for Emission Inventory Preparation*, *Volume IV: Mobile Sources*, ⁵³ locomotive activity can be defined as either line haul or yard activities. Line haul locomotives, which perform line haul operation, generally travel between distant locations, such as from one city to another. Yard locomotives, which perform yard operations, are primarily responsible for moving railcars within a particular railway yard.

The OMS has included locomotive emissions in its *Motor Vehicle-Related Air Toxic Study*.¹⁷ The emission factors used for locomotives in this report are derived from the heavy-duty diesel on-road vehicles as there are no emission factors specifically for locomotives. To derive toxic emission factors for heavy duty diesel on-road vehicles, hydrocarbon emission factors were speciated. The emission factors provided in this study (shown in Table 6-4) are based on fuel consumption.⁵⁴

6.2.3 Aircraft

There are two main types of aircraft engines in use: turbojet and piston. A kerosene-like jet fuel is used in the jet engines, whereas aviation gasoline with a lower vapor pressure than automotive gasoline is used for piston engines. The aircraft fleet in the United States numbers about 198,000, including civilian and military aircraft. Most of the fleet is of the single- and twin-engine piston type and is used for general aviation. However, most of the

TABLE 6-4. BUTADIENE EMISSION FACTORS FOR LOCOMOTIVES

Source	Toxic Emission Fraction	Emission Factor (lb/gal)
Line Haul Locomotive	0.0158^{a}	0.00033
Yard Locomotive	0.0158^{a}	0.00080

Source: Reference 54.

fuel is consumed by commercial jets and military aircraft; thus, these types of aircraft contribute more to combustion emissions than does general aviation. Most commercial jets have two, three, or four engines. Military aircraft range from single or dual jet engines, as in fighters, to multi-engine transport aircraft with turbojet or turboprop engines.⁵⁶

Despite the great diversity of aircraft types and engines, there are considerable data available to aid in calculating aircraft- and engine-specific hydrocarbon emissions, such as the database maintained by the Federal Aviation Administration (FAA) Office of Environment and Energy, FAA Aircraft Engine Emissions Database (FAEED).⁵⁷ These hydrocarbon emission factors may be used with weight percent factors of butadiene in hydrocarbon emissions to estimate butadiene emissions from this source. Butadiene weight percent factors in aircraft hydrocarbon emissions are listed in the EPA SPECIATE database⁵⁸ and are presented inTable 6-5.⁵⁹

Current guidance from EPA for estimating hydrocarbon emissions from aircraft appears in *Procedures for Emission Inventory Preparation, Volume IV: Mobile Sources.*⁶⁰ The landing/takeoff (LTO) cycle is the basis for calculating aircraft emissions. The operating modes in an LTO cycle are: (1) approach, (2) taxi/idle in, (3) taxi/idle out, (4) takeoff, and (5) climbout. Emission rates by engine type and operating mode are given and require that the fleet be

^a These fractions are found in Appendix B6 of Reference 55, and represent toxic emission fractions for heavy-duty diesel vehicles. Toxic fractions for locomotives are assumed to be the same, since no fractions specific for locomotives are available. It should be noted

TABLE 6-5. BUTADIENE CONTENT IN AIRCRAFT LANDING AND TAKEOFF EMISSIONS

SPECIATE Profile #	Description	AMS Code	Weight Percent Butadiene	Factor Quality
1097	Military Aircraft	22-75-001-000	1.89	В
1098	Commercial Aircraft	22-75-020-000	1.80	В
1099	General Aviation Pistons Turbines	22-75-050-000	1.57 0.98 1.57	C C C
1214	Composite of 6 engines burning JP-4 fuel at 75% power	22-75-001-000	3.85	С
1215	Composite of 6 engines burning JP-4 fuel at 30% power	22-75-001-000	1.00	С
1216	Composite of 6 engines burning JP-4 fuel across all powers	22-75-001-000	2.08	С
1217	Composite of 6 engines burning JP-4 fuel at idle power	22-75-001-000	2.20	С
1218	Composite - TF-39 engine burning JP-5 fuel across all powers	22-75-001-000	2.86	С
1219	Composite - CTM-56 engine burning JP-5 fuel across all powers	22-75-001-000	2.47	С
1220	Composite - J79 engine burning JP-4 fuel across all powers	22-75-001-000	2.01	C

Source: References 58 and 59.



characterized and the time in each of the operating modes determined. From this information, hydrocarbon emissions can be calculated for one LTO for each aircraft type in the fleet. To determine total hydrocarbon emissions from the fleet, the emissions from a single LTO for the aircraft type must be multiplied by the number of LTOs for each aircraft type. The weight percent factor for butadiene can be applied to the total hydrocarbon emissions to estimate the butadiene emissions.

The emission estimating method noted above is the preferred approach as it takes into consideration differences between new and old aircraft. If detailed aircraft information is unavailable, hydrocarbon emission indices for representative fleet mixes are provided in the emissions inventory guidance document *Procedures for Emissions Inventory Preparation, Volume IV: Mobile Sources.* The hydrocarbon emission indices are 0.394 pounds per LTO (0.179 kg per LTO) for general aviation and 1.234 pounds per LTO (0.560 kg per LTO) for air taxis.

The butadiene fraction of the hydrocarbon total can be estimated by using the percent weight factors from SPECIATE. Because air taxis have larger engines and more of the fleet is equipped with turboprop and turbojet engines than is the general aviation fleet, the percent weight factor is somewhat different from the general aviation emission factor. To approximate a butadiene percent weight factor for air taxis, the commercial and general aviation percent weight factors were averaged (see Table 6-6). ^{58,60,61} 6.2.4

Rocket Engines

Butadiene has also been detected from rocket engines tested or used for space travel. Source testing of booster rocket engines using RP-1 (kerosene) and liquid oxygen have been completed at an engine test site. Tests for butadiene were taken for eight test runs sampling four locations within the plume envelope below the test stand. Results from these tests yielded a range of butadiene emission factors--0.0368 to 0.47 lbs/ton (0.0151 to 0.193 kg/Mg) of fuel combusted (factor quality rating C)--providing an average emission factor of 0.14 lb/ton

TABLE 6-6. BUTADIENE EMISSION FACTORS FOR GENERAL AVIATION AND AIR TAXIS^a

Aircraft Type	1990 National LTOs ^b	Hydrocarbon Emission Indices ^c	Hydrocarbon Total in tons (Mg)	Butadiene Weight Percent ^d	Butadiene Emissions in tons (Mg)
General Aviation	19,584,898	0.394 lb/LTO	3,858 (3,472)	1.57	61 (55)
Air Taxis	4,418,836	1.234 lb/LTO	2,726 (2,454)	1.69	46 (42)

^a From Federal Aviation Administration-Controlled Towers.
^b Source: Reference 61.
^c Source: Reference 60.

(0.058 kg/Mg) of fuel combusted. It should be noted that booster fuel consumption is approximately five times that of sustainer rocket engines. 4,62

^d Source: Reference 58.

SECTION 7.0

EMISSIONS FROM MISCELLANEOUS SOURCES OF BUTADIENE

This section provides an overview of the miscellaneous sources of butadiene emissions. These sources can be divided into the following categories: miscellaneous chemical production; secondary lead smelting; petroleum refining; combustion sources (biomass burning, scrap tire burning, and stationary internal combustion sources); and "other." With regard to the chemical production category, the major uses of butadiene were discussed in Section 5.0. Section 7.0 identifies the smaller consumers, which account for about 8 percent of butadiene use in the United States. Available details of the production process and associated emissions are provided, where known. Often these details are incomplete; therefore, readers should contact the facilities directly for the most accurate information.

The biomass burning and scrap tire burning categories are extremely diverse sources and are therefore difficult to quantify. This section describes the various types of burning and any associated emissions. The "other" category contains sources that have been identified as possible butadiene sources, but for which specific emissions data are lacking.

7.1 MISCELLANEOUS USES OF BUTADIENE IN CHEMICAL PRODUCTION

Eighteen companies at 19 locations are producing 14 different products from butadiene. Originally identified in a summary report on miscellaneous butadiene uses,³⁵ this list of facilities has been updated using the *1993 Directory of Chemical Producers - U.S.A.* These facilities are summarized in Table 7-1, along with estimated capacities.^{19,29} Because data corresponding to each location are not readily available, all the production process descriptions, current as of 1984, appear first, followed by a summary of any emissions estimates.

7.1.1 <u>Product and Process Descriptions</u>

Styrene-Butadiene-Vinylpyridine (SBV) Latex

No information on the production process or the use of styrene-butadiene-vinylpyridine latex is available. As a copolymer, its production process is likely to be similar to that of other copolymers.

Tetrahydrophthalic (THP) Anhydride and Acid

Tetrahydrophthalic anhydride and acid (the acid is the hydrate form of the chemical) may be used either as a curing agent for epoxy resins or as an intermediate in the manufacture of Captan®, an agricultural fungicide.

In the manufacture of the anhydride as a curing agent, Mobay Synthetics (formerly Denka) is reported to use the following process. Liquid butadiene is first pressure-fed to a vaporizer. The resulting vapor is then pressure-fed to the reactor, where reaction with molten maleic anhydride occurs. Maleic anhydride is consumed over a period of 6 to 10 hours. The product, molten THP anhydride, is crystallized onto a chill roller at the bagging operation. Solidified anhydride is cut from the roller by a doctor blade into a weighed container, either a bag or drum. Because ArChem also uses THP anhydride in epoxy resins, use of a process similar to Mobay Synthetics' was assumed.

ICI American Holdings, Inc. (formerly Calhio) was reported to generate the anhydride for captive use as an intermediate for Captan®. In the generation process, butadiene is charged to reactors along with maleic anhydride to produce THP anhydride. The reaction is a Diels-Alder reaction, run under moderate temperature and pressure.⁶⁴

TABLE 7-1. MISCELLANEOUS USES OF BUTADIENE IN CHEMICAL PRODUCTION

Company	Location	Product	Mode of Operation	Capacity in 1993 tons/yr (Mg/yr)
Ameripol Synpol	Port Neches, TX	Styrene-butadiene- vinylpyridine (SBV) Latex	Unknown	
ArChem Company	Houston, TX	Tetrahydrophthalic (THP) Anhydride	Batch	572 (515)
B. F. Goodrich Company	Akron, OH	Butadiene-vinylpyridine Latex	Batch (on demand)	
ICI American Holdings, Inc.	Perry, OH	Captan®	Batch	
Chevron Chemical	Richmond, CA	Captafol®	Continuous	
DuPont	Beaumont, TX	1,4-Hexadiene	Continuous	
DuPont	Victoria, TX	Dodecanedioic Acid	Continuous (2 weeks per month due to low demand)	
		Butadiene Dimers	Unknown	
Dixie Chemical Company	Bayport, TX	THP Anhydride	Unknown	
GenCorp	Mogadore, OH	SBV Latex	Unknown	
Goodrich	Akron, OH	SBV Latex	Unknown	
Goodyear	Calhoun, GA	SBV Latex	Unknown	
Kaneka Texas Corporation	Bayport, TX	Methyl Methacrylate-butadiene- styrene (MBS) Resins	Batch	25,600 (23,000)
Metco America	Axis, AL	MBS Resins	Unknown	20,000 (18,000)

(continued)

TABLE 7-1. CONTINUED

Company	Location	Product	Mode of Operation	Capacity in 1993 tons/yr (Mg/yr)
Mobay Synthetics Corporation ^a	Houston, TX	THP Acid	Batch	1,700 (1,500)
Phillips Chemical	Borger, TX	Butadiene Cylinders	Batch	539 (485)
Company		Butadiene-furfural Cotrimer ^b	Continuous, intermittent, about 65% of the time	50 (45)
		Sulfolane	Batch	
Rohm and Haas Company	Louisville, KY	MBS Resins	Batch	25,500 (23,000)
Shell Oil Company	Norco, LA	Sulfolane	Unknown	
Standard Oil Chemical Company	Lima, OH	Methyl Methacrylate- acrylonitrile-butadiene-styrene (MABS) Polymer	Unknown	
Union Carbide	Institute, WV	Butadiene Dimers	Continuous	7,200 (6,500)
		Ethylidene Norbornene	Continuous	

Source: References 19 and 29.

^a Formerly Denka.
^b Process in operation in 1984, status unknown in 1994.

[&]quot;___" means capacity not known.
"----" means company-confidential.

Butadiene-Vinylpyridine Latex

Butadiene-vinylpyridine latex is produced at the B. F. Goodrich, Akron, Ohio, facility as an ingredient in an adhesive promoter. As a copolymer, the production process is similar to that of other copolymers, usually involving an emulsion polymerization process.⁶⁵ B. F. Goodrich operates the process in a batch mode, on a schedule that depends on demand.

The finished latex is blended with SB latex and a phenol-formaldehyde mixture to form a "dip" or an adhesive promoter. Dip is used with fabrics in geared rubber goods manufacturing. This includes fabric used in tires, hoses, and belting production.⁶⁶

Methyl Methacrylate-Butadiene-Styrene Terpolymers

Methyl methacrylate-butadiene-styrene (MBS) terpolymers are produced in resin form by four companies at four locations. This resin is used as an impact modifier in rigid polyvinyl chloride products for applications in packaging, building, and construction.³⁵

Production of MBS terpolymers is achieved using an emulsion process in which methyl methacrylate and styrene are grafted onto an SB rubber. The product is a two-phase polymer.⁶⁶

Captan®

In Captan® production, tetrahydrophthalic anhydride is passed through an ammonia scrubber to produce tetrahydrophthalimide (THPI). Molten THPI is coated onto a chill roller, where it solidifies into a quasi-crystalline state. THPI is then conveyed into a reactor containing perchloromethyl mercaptan (PMM). Caustic is charged to the reactor, initiating the reaction that produces Captan®. Captan® is brought to a higher temperature in the heat

treatment tank to remove residual PMM, after which the material passes through a vacuum filter to remove salt and water. The product cake is dried and collected in a baghouse.⁶⁴

Captafol®

Chevron produces Captafol®, a fungicide, under the trade name Difolatan® at its Richmond, California, facility. The only information on the process is that production occurs on a continuous basis and is carried out in a pressurized system vented to an incinerator.³⁵

1,4-Hexadiene

DuPont produces 1,4-hexadiene for use in manufacturing Nordel® synthetic rubber. Nordel® polymer is used in the manufacture of rubber goods, wire and cable insulation, automobile bumpers, and as an oil additive.⁶⁷

In the reactor, butadiene reacts with ethylene to form 1,4-hexadiene. After reaction, unreacted 1,3-butadiene and ethylene, along with 1,4-hexadiene and by-products, are flashed from the catalyst and solvent. The maximum temperature in the process is approximately 250°F (121°C). The catalyst solution is pumped back to the reactor; vaporized components are sent to a stripper column. The column separates ethylene and 1,3-butadiene from the 1,4-hexadiene product and by-products; unreacted components are pumped back to the reactor. The 1,4-hexadiene and by-products are sent to crude product storage before transfer to refining. The 1,4-hexadiene is refined in low-boiler and high-boiler removal columns and transferred to the Nordel® polymerization process.⁶⁸

Dodecanedioic Acid

Dodecanedioic acid (DDDA) is produced by DuPont for use as an intermediate in the production of 1,5,9-cyclodecatriene, a constituent in the manufacture of DuPont's Quiana® fabric. Butadiene can be converted into several different cyclic or open-chain dimers and trimers, depending upon the reaction conditions and catalysts. Although vinylcyclohexene and

1,5-cyclooctadiene are the predominant products, 1,2-divinylcyclobutane may be formed under suitable reaction conditions. Nickel catalysts are often used in the cyclodimerization and cyclotrimerization of butadiene; however, complexes of iron, copper (I), zeolite, and compositions also promote cyclodimerization, often giving cyclooctadiene as the principal product.⁶⁸

Butadiene Cylinders

Phillips Chemical Company fills cylinders with butadiene monomer at its Borger, Texas, facility. A NIOSH survey report on this facility indicates that these cylinders may be samples of butadiene taken for process quality control.⁶⁹ The report describes routine quality control sampling in the tank farm area in which the samples are collected using pressure cylinders. Operators connect the sample containers to a process line and open valves to fill the cylinder. Butadiene fills the container and is purged out of the rear of the cylinder before the valve is closed, resulting in emissions from the cylinder. The sample container is subjected to vacuum exhaust under a laboratory hood at the conclusion of sampling.³⁵

Butadiene Furfural Cotrimer

Butadiene furfural cotrimer or 2,3,4,5-bis(butadiene)tetrahydrofurfural, commonly known as R-11, is used as an insect repellant and as a delousing agent for cows in the dairy industry. The concentrations of R-11 in commercial insecticide spray are generally less than 1 percent.⁶⁹

Production of R-11 at Phillips' Borger, Texas, facility, occurs intermittently throughout the year; however, when operating, the production process is a continuous operation. In the process, butadiene reacts with an excess of furfural in a liquid-phase reactor. The reaction proceeds under moderate conditions of temperature and pressure and consumes 1 mole of furfural for 2 moles of butadiene. After a period of 4 to 5 hours, the reaction mixture is transferred to the reactor effluent surge tank. The mixture proceeds to a vertical column that separates butadiene dimer by distillation. Butadiene dimer, or 4-vinyl-1-cyclohexane, is

recovered from the column and later transported to a refinery for reprocessing in crude catalytic cracking units.⁶⁹

Furfural is removed from the reaction products by distillation in a similar column and recycled to the reactor. The last column in the R-11 process runs as a batch operation, and separates R-11 from the polymer kettle product. The kettle product is a crystalline solid that is disposed of in an on-site landfill. R-11, which is in the form of a yellow liquid, is transferred to storage tanks and shipped to customers in drums.⁶⁹

Sulfolane

Sulfolane is a common trade name for tetrahydrothiophene 1,1-dioxide. It is used principally as a solvent for extracting aromatic hydrocarbons from mixtures containing straight-chained hydrocarbons. Sulfolane is produced by first reacting butadiene and sulfur dioxide to form 3-sulfolene. The 3-sulfolene is then hydrogenated to produce sulfolane. Phillips' Borger, Texas, facility is assumed to be using a similar process. The Shell facility at Norco, Louisiana, has a sulfolane production unit downstream of the butadiene recovery process that is included as part of the butadiene production facility.¹⁹

Methyl Methacrylate-Acrylonitrile-Butadiene-Styrene (MABS) Polymers

MABS polymers are produced by Standard Oil Company under the trade name Barex®. The MABS copolymers are prepared by dissolving or dispersing polybutadiene rubber in a mixture of methyl methacrylate-acrylonitrile-styrene and butadiene monomer. The graft copolymerization is carried out by a bulk or a suspension process. The final polymer is two-phase, with the continuous phase terpolymer of methyl methacrylate, acrylonitrile, and styrene grafted onto the dispersed polybutadiene phase.⁶⁶

These polymers are used in the plastics industry in applications requiring a tough, transparent, highly impact-resistant, and thermally-formable material. Except for their transparency, the MABS polymers are similar to the opaque ABS plastics. The primary function

of methyl methacrylate is to match the refractive indices of the two phases, thereby imparting transparency. ⁶⁶

Butadiene Dimers

Tetrahydrobenzaldehyde (THBA), a butadiene dimer, is produced by Union Carbide and DuPont (Victoria, Texas). At Union Carbide, butadiene is reacted with acrolein and cyclohexane to produce THB anhydride in +90-percent yields over a short period of time when the reaction is carried out at temperatures up to 392°F (200°C). The reaction will also take place at room temperature in the presence of an aluminum-titanium catalyst. A by-product of the reaction is 4-vinyl-1-cyclohexane. At the Union Carbide facility, THBA is recovered and the unreacted raw materials are recycled to the feed pot. The feed pot, reactor, recovery stills, and refined product storage tanks are all vented to a flare header. In the absence of process information at the DuPont facility, it is assumed to be using a similar production process.

Ethylidene Norbornene (ENB)

ENB, produced by Union Carbide, is a diene that is used as a third monomer in the production of ethylene-propylene-dimethacrylates. Ethylene-propylene-dimethacrylate elastomers are unique in that they are always unsaturated in the side chain pendant to the main or backbone chain. Therefore, any oxidation or chemical reaction with residual unsaturation has only a limited effect on the properties of the elastomer.⁷⁰

7.1.2 <u>Emissions</u>

No emissions data are available for the following products: SBV latex, Captan®, Captafol®, THP acid, and ethylidene norbornene. For processes where emissions information is available, it is limited to three sources: process vents, equipment leaks, and secondary sources. Butadiene emissions from raw material storage are expected to be negligible because butadiene is usually stored under pressure. Some emissions resulting from accidental

and emergency releases and transfer and handling of raw materials are likely; however, they have not generally been quantified.

Data are available for process vent emissions from production processes at eight facilities. At five of these facilities, flares or boilers are used on some vents to control emissions. At a sixth facility, emissions reduction is achieved by recovery of the vented stream off the butadiene-furfural cotrimer process, one of the two process vents identified. Because every facility did not report an emissions estimate for each process vent listed, emissions data are incomplete.

The emission factors for process vents and secondary sources are summarized in Table 7-2, 19,35,65 with facility-specific data appearing in Tables C-23 through C-25 in Appendix C. Ranges are provided if more than one data point was available. The facility emission factors include the control that each facility providing the data has in place. The uncontrolled emission factors represent potential emissions if controls were not in use.

Because equipment count data were not readily available, no calculations of equipment leak emissions using average CMA factors were done. Instead, equipment leak estimates for eight processes at eight facilities were taken from memoranda prepared for EPA in 1986. Because information on emissions control through leak detection and repair programs was incomplete, adjustments to estimated emissions could not be made. The only other controls in use were double mechanical pump seals and rupture discs on pressure relief devices.

Based on information on secondary sources from eight facilities, emissions generally appear to be negligible from these sources, despite different end products. One exception is the butadiene-vinylpyridine process. The facility estimated butadiene emissions from wastewater volatilization to be approximately 1.3 tons/yr (1.2 Mg/yr).⁶⁵

Two estimates for emergency vent releases during upsets, startups, and shutdowns of the 1,4-hexadiene process are 0.2 tons/yr (0.2 Mg/yr) (uncontrolled) off the abatement collection system for waste liquid and vapors and 47.5 tons/yr (43.1 Mg/yr) from the reactor

TABLE 7-2. SUMMARY OF EMISSION FACTORS AND ANNUAL EMISSIONSFROM EQUIPMENT LEAKS FOR MISCELLANEOUS CHEMICALSPRODUCTIONFACILITIES^{a,b} (FACTOR QUALITY RATING U)

Chemical Produced	Source		cility n Factors		trolled 1 Factors
Butadiene Cylinders	Process Vents	43.2 lb/ton	(21.6 kg/Mg)	43.2 lb/ton	(21.6 kg/Mg)
3-01-153	Equipment Leaks	<0.11 tons/yr	(<0.1 Mg/yr)	<0.11 tons/yr	(<0.1 Mg/yr)
	Secondary Sources	NA		NA	
Butadiene Dimers	Process Vents	0.030 lb/ton	(0.015 kg/Mg)	1.54 lb/ton	(0.77 kg/Mg)
3-01	Equipment Leaks	4.3 tons/yr	(3.9 Mg/yr)		
	Secondary Sources	0		0	
Butadiene-furfural	Process Vents	440 lb/ton	(220 kg/Mg)	440 lb/ton	(220 kg/Mg)
Cotrimers 3-01	Equipment Leaks	1.1 tons/yr	(0.5 Mg/yr)		
	Secondary Sources	0		0	
Butadiene-vinylpyridine Latex 3-01-026	Process Vents				
	Equipment Leaks	0.61 tons/yr	(0.55 Mg/yr)	NA	
	Secondary Sources (Wastewater)	NA			
Dodecanedioic Acid	Process Vents				
6-84-350	Equipment Leaks	5.73 tons/yr	(5.2 Mg/yr)	5.73 tons/yr	(5.2 Mg/yr)
	Secondary Sources	NA		NA	
1,4-Hexadiene	Process Vents				
3-01	Equipment Leaks	59.3 tons/yr	(53.8 Mg/yr)	67.7 tons/yr	(61.4 Mg/yr)
	Secondary Sources	0		0	

(Continued)

TABLE 7-2. Continued

Chemical Produced	Source		cility on Factors		ntrolled n Factors
Methylmethacrylate-	Process Vents	1.8 lb/ton	(0.9 kg/Mg)	17.2 lb/ton	(8.6 kg/Mg)
butadiene-styrene Resins 6-41	Equipment Leaks	4.0 - 17.4 tons/yr (n=2)	(3.6 - 15.8 Mg/yr) ^c	17.4 tons/yr (n=2)	(15.8 Mg/yr)
	Secondary Sources	0 (n=2)		0 (n=2)	
Sulfolane	Process Vents				
3-01	Equipment Leaks	1.8 - 14.7 tons/yr (n=2)	(1.6 - 13.3 Mg/yr) ^c	1.8 - 14.7 tons/yr ^c (n=2)	(1.6 - 13.3 Mg/yr) ^c
	Secondary Sources	NA		NA	
Tetrahydrophthalic Anhydride/Acid 3-01	Process Vents				
	Equipment Leaks	2.4 tons/yr	(2.2 Mg/yr)	2.4 tons/yr	(2.2 Mg/yr)
	Secondary Sources	0 (n=2)		0 (n=2)	

Source: References 19, 35, and 65.

NA = not available.

 ^a Assumes production capacity of 100 percent.
 ^b Factors are expressed as lb (kg) butadiene emitted per ton (Mg) produced and tons (Mg) emitted per year.
 ^c Range is based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.

[&]quot;---" means not calculated because production capacity was not available.

emergency vent. A brine refrigerated condenser on the reactor emergency vent may afford some emissions reduction, but an efficiency was not indicated.³⁵

7.2 INDIRECT SOURCES OF BUTADIENE

A number of indirect sources of butadiene emissions have been identified. Each is described briefly below. Where emissions information was available, this is also provided. Because of EPA's increasing interest in air toxics, emissions information may be available in the future; therefore, the reader should consider a literature search to identify new sources of butadiene and locate emissions data.

7.2.1 <u>Vinyl Chloride Monomer and Polyvinyl Chloride Production</u>

In vinyl chloride monomer (VCM) production, butadiene appears as an impurity in the final product at a maximum level of 6.0 ppm.⁷¹ An emission factor developed for overall production of polyvinyl chloride (PVC) (SCC 6-46-300-01) at a representative PVC plant was calculated and is given as 4.6×10^{-4} lb/ton (2.1×10^{-4} g/kg) PVC produced.

7.2.2 <u>Publicly Owned Treatment Works</u>

Some estimates for emissions from wastewater sent to publicly owned treatment works (POTWs) by SB copolymer producers, considered a secondary source, were made based on three industry responses to EPA Section 114 requests. Using data on the butadiene content of wastewater sent to a POTW for each of these facilities and air emission models developed by EPA's Office of Air Quality Planning and Standards (OAQPS) for treatment, storage, and disposal facilities, estimated emissions for all three facilities are 21 tons/yr (19 Mg/yr). This approach did not account for volatilization from wastewater during transport to the POTW.

An emission factor developed for butadiene in influent in a representative POTW was calculated and is given as 1.7×10^3 lb/ton (771 g/kg) butadiene in influent.^{4,72}

7.2.3 <u>Secondary Lead Smelting</u>

Although not a significant source, secondary lead smelters are a source of 1,3-butadiene emissions. The secondary lead smelting industry produces elemental and lead alloys by reclaiming lead mainly from scrap automobile batteries. There are approximately 23 secondary lead smelters in the United States.⁷³

Lead-acid batteries represent about 90 percent of the raw materials at a typical secondary lead smelter. A typical automotive lead-acid battery is made up of lead, sulfuric acid electrolyte, plastic separators, and a plastic casing. Older batteries may have a hard rubber casing instead of plastic. The plastic battery separators and hard rubber casings on older batteries are the sources of butadiene emissions from secondary lead smelting.

The secondary lead smelting process consists of (1) breaking lead-acid batteries and separating the lead-bearing materials from the other materials (including plastic and acid electrolyte); (2) melting lead metal and reducing lead compounds to lead metal in the smelting furnace (reverberatory, blast, rotary, or electric); and (3) refining and alloying the lead to customer specifications.⁷³

The vast majority of butadiene emissions come from the smelting furnace process. Because of the lower exhaust temperature from the charge column, blast furnaces are substantially greater sources of organic HAP (including butadiene) and related emissions than are reverberatory or rotary furnaces. From uncontrolled concentrations of butadiene measured during testing of a blast furnace outlet, an average emission factor of 1.16 lb/ton, range 0.78 - 1.54 lb/ton (0.48 kg/Mg, range 0.32 - 0.63 kg/Mg) was developed.⁷³ For the rotary furnace, the calculated emission factor was 0.13 lb/ton (0.05 kg/Mg).

On June 23, 1995, EPA promulgated a NESHAP for the secondary lead production industry. The regulation rquires a reduction of hazardous air pollutant emissions from blast furnaces which will include butadiene emissions. All the requirements are to be

implemented by June 1997. Users of this document should review the requirements to determine what the emission reductions are.

7.2.4 <u>Petroleum Refining</u>

According to 1992 Toxic Release Inventory (TRI) data, petroleum refineries are the fourth largest emitters of butadiene following the production of organic chemicals, synthetic rubber, and plastics and resins. However, besides the TRI figure of 437,590 lb/yr (397,000 Mg/yr) of butadiene emitted, no other emissions numbers were located. The Petroleum Refineries NESHAP was promulgated on August 18, 1995. Information Collection Request (ICR) questionnaires supporting that work reported that butadiene is released from blowdown vents, catalyst regeneration process vents, and miscellaneous vents at vacuum distillation, alkylation, and thermal cracking units. However, Clean Air Act Section 114 questionnaires for that NESHAP did not require the reporting of butadiene emissions. For equipment leaks, EPA has prepared average emission rates. These are provided in Appendix D along with a description of equipment leak estimation methods.

Requirements of this NESHAP and the earlier Benzene NESHAP will reduce butadiene emissions by an estimated 60 percent, assuming reductions are similar to those for HAPs and VOCs overall. However, the reader is referred to the regulations to evaluate the exact impact at a particular facility.

7.2.5 <u>Combustion Sources</u>

Butadiene is produced in the combustion of diverse materials such as gasoline, diesel oil, wood, and tobacco. Therefore, all combustion processes are potential sources of butadiene. A brief description of biomass burning, tire burning, and stationary internal combustion sources and their potential butadiene emissions follow.

Biomass Burning

Fires are known to produce respirable particulate matter and toxic substances. Concern has even been voiced regarding the effect of emissions from biomass burning on climate change. Burning wood, leaves, and vegetation can be a source of butadiene emissions. In this document, the burning of any wood, leaves, and vegetation is categorized as biomass burning, and includes yard waste burning, land clearing/burning and slash burning, and forest fires/prescribed burning. The source of butadiene emissions.

Part of the complexity of fires as a source of emissions results from the complex chemical composition of the fuel source. Different woods and vegetation are composed of varying amounts of cellulose, lignin, and extractives such as tannins, and other polyphenolics, oils, fats, resins, waxes, and starches. General fuel type categories in the National Fire-Danger Rating (NFDR) System include grasses, brush, timber, and slash (residue that remains on a site after timber harvesting). The flammability of these fuel types depends upon plant species, moisture content, whether the plant is alive at the time of burning, weather, and seasonal variations.

Pollutants from the combustion of biomass include carbon monoxide (CO), nitrogen oxides, sulfur oxides, oxidants, polycyclic organic matter, hydrocarbons, and particulate matter. The large number of combustion products is due, in part, to the diversity of combustion processes occurring simultaneously within fire--flaming, smoldering, and glowing combustion. These processes are distinct combustion processes that involve different chemical reactions that affect when and what pollutants will be emitted during burning.⁷⁸

Emission factor models based on field and laboratory data were developed by the U.S. Forest Service. These models incorporate variables such as fuel type and combustion types (flaming or smoldering). Because air toxic substances are correlated with the release of other primary products of incomplete combustion [CO and carbon dioxide (CO₂)], the models correlate butadiene with CO emissions.⁷⁸ These emission factor models were used to develop emission factors for the biomass burning sub-categories described in the following sections.⁷⁷

TABLE 7-3. EMISSION FACTORS FOR 1,3-BUTADIENE FOR BURNING OF YARD WASTE, LAND CLEARING/BURNING, AND SLASH BURNING (FACTOR QUALITY RATING U)

Yard Waste (AMS 26-10-030-000)	Land Clearing/Burning (AMS 28-01-500-000)	Slash (pile) Burning (AMS 28-10-005-000)
0.40 lb/ton	0.32 lb/ton	0.32 lb/ton
(0.198 g/kg)	(0.163 g/kg)	(0.163 g/kg)

Source: References 77 and 78.

Because of the potential variety in the fuel source and the limited availability of emission factors to match all possible fuel sources, emission estimates may not necessarily represent the combustion practices occurring at every location in the United States. Therefore, localized practices of such parameters as type of wood being burned and control strategies should be carefully compared.⁷⁷

Yard Waste Burning--Yard waste burning is the open burning of such materials as landscape refuse, wood refuse, and leaves in urban, suburban, and residential areas.⁷⁷ Yard waste is often burned in open drums, piles, or baskets located in yards or fields. Ground-level open burning emissions are affected by many variables, including wind, ambient temperature, composition and moisture content of the material burned, and compactness of the pile. It should be noted that this type of outdoor burning has been banned in certain areas of the United States, thereby reducing emissions from this subcategory.^{77,79} An emission factor for yard waste is shown in Table 7-3.^{77,78}

Land Clearing and Slash Burning--This subcategory includes the burning of organic refuse (field crops, wood, and leaves) in fields (agricultural burning) and wooded areas (slash burning) in order to clear the land. Burning as part of commercial land clearing often requires a permit.⁷⁷ Emissions from organic agricultural refuse burning are dependent primarily on the moisture content of the refuse and, in the case of field crops, on whether the refuse is burned in a headfire or a backfire.⁷⁹ Other variables, such as fuel loading (how much refuse

material is burned per unit of land area) and how the refuse is arranged (in piles, rows, or spread out), are also important in certain instances. Emission factors for land clearing/burning and slash burning are shown in Table 7-3.^{77,78}

Forest Fires/Prescribed Burning--A forest fire (or wildfire) is a large-scale natural combustion process that consumes various ages, sizes, and types of outdoor vegetation. ⁸⁰ The size, intensity, and even occurrence of a forest fire depend on such variables as meteorological conditions, the species and moisture content of vegetation involved, and the weight of consumable fuel per acre (fuel loading). ⁸⁰

Prescribed or broadcast burning is the intentional burning of forest acres as part of forest management practices to achieve specific wildland management objectives. Controlled burning can be used to reduce fire hazard, encourage wildlife habitat, control insects, and enhance the vigor of the ecosystem.⁷⁸ Prescribed burning occurs thousands of times annually in the United States, and individual fires vary in size from a fraction of an acre to several thousand acres. Prescribed fire use is often seasonal, which can greatly affect the quantity of emissions produced.⁷⁸

HAP emission factors for forest fires and prescribed burning were developed using the same basic approach as for yard waste and land clearing burning, with an additional step to further classify fuel types into woody fuels (branches, logs, stumps, and limbs), live vegetation, and duff (layers of partially decomposed organic matter).⁷⁷ In addition to the fuel type, the methodology was altered to account for different phases of burning, namely, flaming and smoldering.⁷⁷ The resulting emission factors are shown in Table 7-4.^{77,78}

TABLE 7-4. EMISSION FACTORS FOR 1,3-BUTADIENE FOR FOREST FIRES AND PRESCRIBED BURNING BY FUEL TYPE (FACTOR QUALITY RATING U)

Fuel Type	Forest Fires (AMS 28-10-001-000) lb/ton (g/kg)	Prescribed Burning (Broadcast) (AMS 28-10-015-000) lb/ton (g/kg)
Fine wood	0.24 (0.12)	0.24 (0.12)
Small wood	0.24 (0.12)	0.24 (0.12)
Large wood (flaming)	0.24 (0.12)	0.24 (0.12)
Large wood (smoldering)	0.90 (0.45)	0.90 (0.45)
Live vegetation	0.52 (0.26)	0.52 (0.26)
Duff (flaming)	0.24 (0.12)	0.24 (0.12)
Duff (smoldering)	0.90 (0.45)	0.90 (0.45)

Source: References 77 and 78.

Tire Burning

Approximately 240 million vehicle tires are discarded annually.⁸¹ Although viable methods for recycling exist, less than 25 percent of discarded tires are recycled; the remaining 175 million are discarded in landfills, stockpiles, or illegal dumps.⁸¹ Although it is illegal in many states to dispose of tires using open burning, fires often occur at tire stockpiles and through illegal burning activities.⁷⁹ These fires generate a huge amount of heat and are difficult to extinguish (some tire fires continue for months). Butadiene is a major constituent of the tire fabrication process and is, therefore, present in emissions from tire burning.

Table 7-5 contains emission factors for chunk tires and shredded tires.^{79,81} When estimating emissions from an accidental tire fire, it should be kept in mind that emissions from burning tires are generally dependent on the burn rate of the tire. A greater potential for emissions exists at lower burn rates, such as when a tire is smoldering rather than burning out of control.⁷⁹ The fact that the shredded tires have a lower burn rate indicates that the gaps between

TABLE 7-5. EMISSION FACTORS FOR 1,3-BUTADIENE FROM OPEN BURNING OF TIRES (SCC 5-03-002-03)^{a,b} (FACTOR QUALITY RATING C)

Chunk Tires	Shredded Tires
234.28 lb/1000 tons	277.95 lb/1000 tons
(117.14 mg/kg)	(138.97 mg/kg)

Source: References 79 and 81.

tire materials provide the major avenue of oxygen transport. Oxygen transport appears to be a major, if not the controlling mechanism for sustaining the combustion process.⁸¹

Besides accidental or illegal open burning of tires, waste tires are incinerated for energy recovery and disposal purposes. Tires are combusted at tire-to-energy facilities, cement kilns, tire manufacturing facilities, and as supplemental fuel in boilers, especially in the pulp and paper industry. No emission factors for butadiene from tire incineration have been located.

Other Stationary Combustion Sources

Because butadiene has been detected from mobile combustion sources and biomass and tire burning, stationary external and internal combustion sources are potential sources as well. External combustion sources include utility boilers and residential wood combustion. No emission factors were identified for these sources. Internal combustion sources include gasoline and diesel engines used for industrial and commercial activities, as well as gas turbines applied in electric power generation. Available emissions information is summarized below.

^a Values are weighted averages because of differing burn rates.

^b Emissions determined using system response to toluene. Data averaged over six sets of VOST tubes per day taken over 2 days.

Gasoline and diesel internal combustion engines are used in aerial lifts, fork lifts, mobile refrigeration units, generators, pumps, industrial sweepers/scrubbers, and material handling equipment (such as conveyors). The rated power of these engines covers a substantial range, up to 250 hp (186 kW) for gasoline engines and up to 600 hp (445 kW) for diesel engines. These have been included in the off-road sources in Section 6.0. Diesel engines larger than 600 hp (445 kW) are used primarily in oil and gas exploration and production, supplying mechanical power to operate drilling, mud pumping, and hoisting equipment generators. These larger diesel engines are frequently used for electrical generation, irrigation, and nuclear power plant emergency cooling water pump operations. 82

Even though butadiene emissions have been quantified for both gasoline and diesel mobile combustion engines, butadiene emission factors for stationary internal combustion engines have only been developed for uncontrolled diesel engines (SCCs 2-02-001-02 and 2-03-001-01, industrial and commercial/institutional reciprocating IC engines, respectively, fueled with either distillate oil or diesel). The current emission factor provided in the fifth edition of AP-42 is <0.0000391 lbs/MMBtu of fuel (<0.017 ng/J of fuel). This emission factor is rated E due to a limited data set (one diesel engine), and/or a lack of documentation of test results. Such an emission factor may not be suitable for estimating emissions from specific facilities and should be used with care. ⁸²

Gas turbines greater than 3 MW are primarily used in electrical generation for continuous, peaking, or standby power. They are also used as gas pipeline pumps, compressor drivers, and in various process industries. This diversity of uses has lead to the development of a diversity of engine designs and models using a wide range of fuels, including natural gas, distillate (No. 2) fuel oil, and in a few cases, residual fuel oil. Although butadiene emissions from gas turbines are presently being investigated, there are currently no emission factors to quantify butadiene emissions.⁸²

7.3 OTHER BUTADIENE SOURCES

Other potential sources of butadiene emissions have been identified by OAQPS, which has collected information to assist State and local agencies in their toxic air pollutant programs. The Crosswalk/Air Toxic Emission Factor (XATEF) database⁸³ provides a list of possible sources for a number of toxic air pollutants. The Standard Industrial Classification (SIC) Codes identified in the report as possible butadiene sources are shown in Table 7-6.

Data collected by NIOSH during the 1972-1974 National Occupational Health (NOH) survey^{84,85} identify additional potential emission sources, which are also listed in Table 7-6. This work was designed specifically to estimate the number of workers (grouped by SIC Code) potentially exposed to butadiene. In some cases, the "potential exposure" determination was supported by observing butadiene in use. However, many of these cases were based on trade name product use; that is, the product used was derived from butadiene or may otherwise have a potential to contain butadiene.⁸⁴ In a 1981-1983 NOH survey, six additional industries were identified as posing a potential for worker exposure. These industries are also included in Table 7-6.

It is important to remember that these data were collected by NIOSH to assess worker exposure. They do not necessarily translate directly into atmospheric emission sources because of possible in-plant controls and butadiene removal as a result of its reactivity. However, the list represents several possible sources that may not otherwise be immediately identified as having a butadiene emissions potential.

Another reference for butadiene sources was the 1992 Toxic Chemical Release Inventory Data Base,⁷⁴ in which industry reporting of butadiene releases for 1993 were identified by SIC Code and are included in Table 7-6.

TABLE 7-6. POTENTIAL SOURCE CATEGORIES OF BUTADIENE EMISSIONS

1990 SIC Code	1990 Description
2269 ^a	Dyeing and finishing of textiles (except wool fabrics and unit-finishers of textiles) not elsewhere classified
2273 ^b (2272 ^c)	Carpets and rugs
2621 ^d	Paper and allied products - paper mills
2631°	Paperboard mills
2652 ^b	Paperboard containers and boxes - set up paperboard boxes
2812 ^d	Industrial inorganic chemicals - alkalis and chlorine
2819 ^d	Industrial inorganic chemicals not elsewhere classified
2821 ^d	Plastics materials and resins
2822 ^d	Synthetic rubber
2851 ^b	Paints and allied products
2865 ^d	Cyclic crudes and intermediates
2869 ^d	Industrial organic chemicals not elsewhere classified
2879 ^d	Pesticides and agricultural chemicals not elsewhere classified
2899 ^d	Chemicals and chemical preparations not elsewhere classified
2911 ^d	Petroleum refining
2951 ^b	Asphalt paving and roofing materials - paving mixtures and blocks
2992 ^d	Miscellaneous products of petroleum and coal - lubricating oils and greases
3011 ^b	Rubber and miscellaneous plastics products - tires and inner tubes
3021 ^a	Rubber and plastics footwear
3052 ^{b,e} (3041)	Rubber and plastics hose and belting
3069 ^{b,e} (3031)	Fabricated rubber products not elsewhere classified
308 ^b , 3432 ^b (3079)	Miscellaneous plastics products, plumbing fixtures fitting and trim
3357 ^b	Nonferrous wire drawing and insulating
3494 ^b	Miscellaneous fabricated metal products - valves and pipe fittings not elsewhere classified
3499 ^{b,e}	Fabricated metal products not elsewhere classified
3533 ^b	Construction, mining, and material handling machinery and equipment - oil and gas field machinery
3569 ^b	General industry machinery and equipment not elsewhere classified
3585 ^b	Air-conditioning and warm air heating equipment and commercial and industrial refrigeration equipment
3621 ^b	Electrical industrial apparatus - motors and generators
3643 ^b	Electric lighting and wiring equipment - current-carrying wiring devices
3651 ^b	Household audio and video equipment

TABLE 7-6. CONTINUED

1990 SIC Code	1990 Description
3721 ^b	Aircraft and parts - aircraft
3799 ^b	Transportation equipment not elsewhere classified
3841 ^b	Surgical and medical instruments
3996 ^b	Linoleum, asphalted felt-base, and other hard surface floor coverings not elsewhere classified
4226 ^a	Special warehousing and storage, not elsewhere classified
5014°	Motor vehicles and motor vehicle parts and supplies - tires and tubes
5162 ^b , 5169 ^b	Chemicals and allied products - plastic materials and (5161 ^a) basic forms and shapes not elsewhere classified
5171 ^b	Petroleum and petroleum products - petroleum bulk stations and terminals
5541 ^b	Gasoline service stations
6513 ^b	Real estate operators - apartment buildings
7319 ^b	Advertising not elsewhere classified
7538°	Automotive repair shops - general
806 ^b	Hospitals
8372, 8741- 8743 ^b , 8748 ^b (7392)	Commercial economic, sociological, and educational research, management, and public relations services except facilities support
8731 ^d (7391 ^c)	Research, development and testing services - commercial physical and biological research

^a SIC Code is listed as a potential source in the EPA XATEF document, Reference 83.

^b This source is from the NIOSH NOH 1972-1974 survey, Reference 85. This is the current SIC Code for this category; the code in parentheses was the code for the category at the time of the survey.

^c SIC Code was identified as possible butadiene source during the NIOSH NOH 1981-1983 survey, Reference 85.

^d SIC Code was identified from the Toxic Release Chemical Inventory Database for 1993 submittals by industry, Reference 74.

^e SIC Code is listed by both EPA and NIOSH.

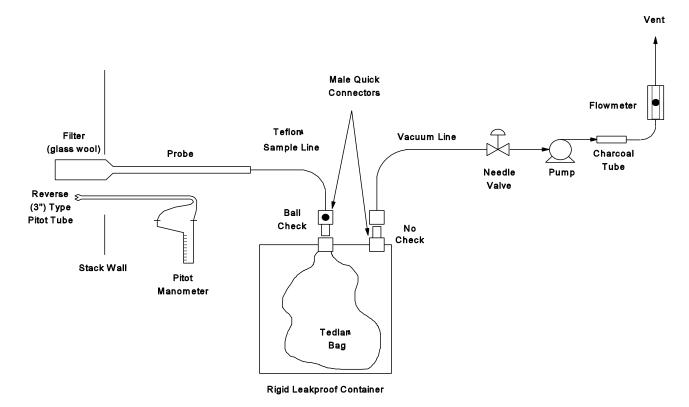
SECTION 8.0 SOURCE TEST PROCEDURES

1,3-Butadiene emissions can be measured by a number of methods. The following methods are applicable for measuring emissions from stationary sources, ambient air, and vehicle exhaust: (1) EPA Reference Method 18;⁸⁶ (2) NIOSH Analytical Method 1024;⁸⁷ (3) EPA Exhaust Gas Sampling System, Federal Test Procedure (FTP);⁸⁸ and (4) Auto/Oil Air Quality Improvement Research Program (AQIRP) speciation methodology.⁸⁹

EPA Reference Method 18 applies to the sampling and analysis of approximately 90 percent of the total gaseous organics emitted from an industrial source, whereas NIOSH Method 1024 applies specifically to the collection and analysis of 1,3-butadiene from ambient air. The FTP and AQIRP methods measure vehicle exhaust by bag sampling and gas chromatography/flame ionization detector (GC/FID) analysis. All four methods are described in the following sections.

8.1 EPA REFERENCE METHOD 18

In Method 18, a sample of the exhaust gas to be analyzed is drawn into a Tedlar® or aluminized Mylar® bag as shown in Figure 8-1. The Tedlar® bag has been used for some time in the sampling and analysis of source emissions for pollutants. The cost of the Tedlar® bag is relatively low, and analysis by GC is easier than with a stainless steel cylinder sampler, because pressurization is not required to extract the air sample in the gas chromatographic analysis process. The bag is placed inside a rigid, leakproof container and evacuated. The bag is then connected by a Teflon® sampling line to a sampling probe (stainless steel, Pyrex® glass,



Source: Reference 86

Figure 8-1. Integrated Bag Sampling Train

or Teflon®) at the center of the stack. The sample is drawn into the bag by pumping air out of the rigid container.

The sample is then analyzed by GC coupled with FID. Based on field and laboratory validation studies, the recommended time limit for analysis is within 30 days of sample collection. One recommended column is the 6-ft (1.82-m) Supelco Porapak QS. However, the GC operator should select the column and GC conditions that provide good resolution and minimum analysis time for 1,3-butadiene. Zero helium or nitrogen should be used as the carrier gas at a flow rate that optimizes the resolution.

The peak areas corresponding to the retention times of 1,3-butadiene are measured and compared to peak areas for a set of standard gas mixtures to determine the 1,3-butadiene concentrations. The detection limit of this method ranges from about 1 ppm to an upper limit governed by the FID saturation or column overloading. However, the upper limit can be extended by diluting the stack gases with an inert gas or by using smaller gas sampling loops.

Recent work by EPA's Atmospheric Research and Exposure Assessment Laboratory has produced a modified version of Method 18 for stationary source sampling. ^{90,93} One difference is in the sampling rate, which is reduced to allow collection of more manageable gas volumes. By reducing the gas volumes, smaller Tedlar® bags (5 to 7L) can be used instead of the traditional 25-L or larger bags, which are not very practical in the field, especially when a large number of samples is required. ⁹⁰ A second difference is the introduction of a filtering medium to remove entrained liquids, which improves the butadiene quantitation precision.

Two other changes involve the analytical procedure. The first uses picric acid in a second column (2 m x 1/8" stainless steel column, 0.19 percent picric acid on 80/100 mesh Carbopak C) to minimize the interference by butane and butene isomers that are also present in the stream. The second uses a backflush-to-vent configuration to remove any high-boiling compounds that have been collected before they reach the picric acid column. These

modifications allow more accurate quantitation of butadiene to be performed in a shorter time period than with Method 18.

8.2 NIOSH METHOD 1024

NIOSH Method 1024 is appropriate for measuring ambient emissions of 1,3-butadiene in the workplace. In this NIOSH method, samples are collected with adsorbent tubes containing charcoal that has been washed and coated with 10 percent by weight 4-tert-butylcatechol (TBC-charcoal), a chemical known to inhibit the polymerization of 1,3-butadiene. Three-liter air samples should be collected with the use of a personal sampling pump at a flow rate of 0.05 L/min.^{87,94}

Samples are desorbed with carbon disulfide and analyzed by GC equipped with an FID and a column capable of resolving 1,3-butadiene from the solvent front and other interferences. The column specified in NIOSH Method 1024 is a 50-m x 32-mm internal diameter, fused-silica, porous-layer, open-tubular column coated with aluminum oxide and potassium chloride (Al₂O₃/KCl).⁸⁷ Degradation of compound separation may be eliminated by using a back flushable precolumn [e.g., 10-m x 0.5-mm interior diameter fused-silica (CP Wax 57 CB)]. The precolumn allows light hydrocarbons to pass through, but water, methylene chloride, and polar or high-boiling components are retained and can be backflushed.^{87,93}

The amount of 1,3-butadiene in a sample is obtained from the calibration curve in units of micrograms per sample. Collected samples are sufficiently stable to permit 6 days of ambient sample storage before analysis. If samples are refrigerated, they are stable for 18 days. Butadiene can dimerize during handling and storage. The rate of dimerization is a function of temperature, increasing with increasing temperature. Consequently, samples should be stored at low temperatures.

This procedure is applicable for monitoring 1,3-butadiene air concentrations ranging from 0.16 ppm to 36 ppm, and is more sensitive and selective than the previously-used

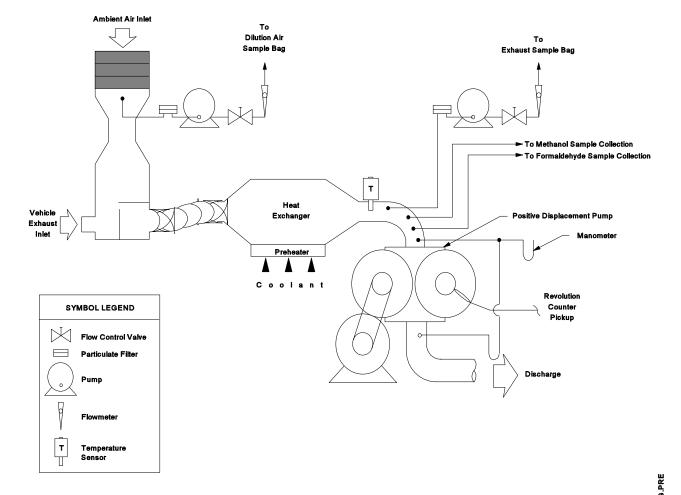
NIOSH Method S-91.⁹⁵ The GC column and operating conditions should provide good resolution and minimum analysis time.

8.3 FEDERAL TEST PROCEDURE

The most widely-used test procedure for sampling emissions from vehicle exhaust is the FTP, which was initially developed in 1974. 88,96,97 The FTP uses the Urban Dynamometer Driving Schedule (UDDS), which is 1,372 seconds in duration. An automobile is placed on a chassis dynamometer where it is run according to the following schedule: 505 seconds of a cold-start; 867 seconds of hot transient; and 505 seconds of a hot-start. (The definitions of the above terms can be found in the FTP description in the 40 CFR, Section 86). The vehicle exhaust is collected in Tedlar® bags during the three testing stages. It should be noted that, in most cases, the majority of 1,3-butadiene is generated in bag one, the first 505-second segment of the cold-start UDDS cycle. 98

The most widely used method for transporting the vehicle exhaust from the vehicle to the bags is a dilution tube sampling arrangement identical to the system used for measuring criteria pollutants from mobile sources. Dilution techniques are used for sampling auto exhaust because in theory, dilution helps simulate the conditions under which exhaust gases condense and react in the atmosphere. Figure 8-2 shows a diagram of a vehicle exhaust sampling system. Vehicle exhausts are introduced at an orifice where the gases are cooled and mixed with a supply of filtered dilution air. The diluted exhaust stream flows at a measured velocity through the dilution tube and is sampled isokinetically.

The major advantage in using a dilution tube approach is that exhaust gases are allowed to react and condense onto particle surfaces prior to sample collection, providing a truer composition of exhaust emissions as they occur in the atmosphere. Another advantage is that the dilution tube configuration allows simultaneous monitoring of hydrocarbons, carbon monoxide, carbon dioxide, and nitrogen oxides. Back-up sampling techniques, such as filtration/adsorption, are generally recommended for collection of both particulate- and gas-phase emissions.⁹⁷



Source: Reference 99 Figure 8-2. Vehicle Exhaust Gas Sampling System

8.4AUTO/OIL AIR QUALITY IMPROVEMENT RESEARCH PROGRAM SPECIATION METHOD

Although there is no EPA-recommended analytical method for measuring 1,3-butadiene from vehicle exhaust, the AQIRP method for the speciation of hydrocarbons and oxygenates is widely used. ^{89,97} This analytical method calls for a dual column GC with FID. A pre-column, 15-m x 0.53-mm interior diameter, 1 µm film, such as the DB-WAX (J & W Scientific Co, Folsom, CA), is recommended to retain water and alcohols while allowing the lower molecular weight hydrocarbons to pass rapidly through to the analytical column. ⁸⁹ A backflush valve can be activated to prevent the polar species and higher hydrocarbons from entering the analytical column, and to backflush these species from the pre-column. The recommended analytical column is a 50-m x 0.53-mm interior diameter, 10 µm film, porous layer open tubular (PLOT) column of alumina deactivated by potassium chloride. ⁸⁹

The peak areas corresponding to the retention times of 1,3-butadiene are measured and compared to peak areas for a set of standard gas mixtures to determine the 1,3-butadiene concentrations. The detection limit for this method is on the order of 0.03 ppmC in dilute exhaust for 1,3-butadiene (0.5 mg/mile for the FTP). 98

It should be noted that sample instability has been shown to be a problem for 1,3-butadiene in exhaust mixtures. Therefore, to minimize concerns about sample integrity, exhaust emissions should be analyzed promptly (within 1 hour of collection). 98,100

SECTION 9.0

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APPENDIX A EMISSION FACTOR SUMMARY TABLE

TABLE A-1. SUMMARY OF EMISSION FACTORS BY SOURCE CLASSIFICATION CODE

SCC/AMS Code and			Emiss	Emission Factor ^a		
Description	Emissions Source	Control Device	Range ^b	Mean	Factor Rating	
2-02-001-01 Internal Combustion Engines - Industrial	Distillate Oil/Diesel, Reciprocating	Uncontrolled		<.0000391 lb/MMBtu (<0.017 ng/J)	Е	
2-03-001-01 Internal Combustion Engines - Commercial/ Industrial	Distillate Oil/Diesel, Reciprocating	Uncontrolled		<.0000391 lb/MMBtu (<0.017 ng/J)	E	
3-01 Butadiene Dimers	Process Vents	Controlled		0.030 lb/ton ^c (0.015 kg/Mg)	U5	
		Uncontrolled		1.54 lb/ton ^c (0.77 kg/Mg)	U5	
	Equipment Leaks	Controlled		4.3 tons/yr ^c (3.9 Mg/yr)	U5	
3-01 Butadiene-furfural	Process Vents	Controlled		440 lb/ton ^c (220 kg/Mg)	U5	
Cotrimers		Uncontrolled		440 lb/ton ^c (220 kg/Mg)	U5	
	Equipment Leaks	Controlled		1.1 tons/yr ^c (0.5 Mg/yr)	U5	
3-01 1,4-Hexadiene	Equipment Leaks	Controlled		59.3 tons/yr ^c (53.8 Mg/yr)	U5	
		Uncontrolled		67.7 tons/yr ^c (61.4 Mg/yr)	U5	

TABLE A-1. CONTINUED

	Emissions Source			Emission Fa	Emission Factor ^a	
		Control Device	Range ^b	Mean	FactorRating	
3-01 Sulfolane	Equipment Leaks	Controlled	1.8 - 14.7 tons/yr ^c (1.6 - 13.3 Mg/yr)		U5	
		Uncontrolled	1.8 - 14.7 tons/yr ^c (1.6 - 13.3 Mg/yr)		U5	
3-01 Tetrahydrophthalic	Equipment Leaks	Controlled		2.4 tons/yr ^c (2.2 Mg/yr)	U5	
Anhydride/Acid		Uncontrolled		2.4 tons/yr ^c (2.2 Mg/yr)	U5	
3-01-026 SB Copolymer	Process vents	Controlled	0.00024 - 94.34 lb/ton ^d (0.00012 - 47.17 kg/Mg)	7.10 lb/ton ^d (3.55 kg/Mg)	D	
Production		Uncontrolled	0.124 - 94.34 lb/ton ^d (0.062 - 47.17 kg/Mg)	14.20 lb/ton ^d (7.10 kg/Mg)	D	
3-01-026 SB Copolymer Production	Equipment leaks	Uncontrolled	0.11 - 23.59 tons/yr ^d (0.10 - 21.40 Mg/yr)	7.28 tons/yr ^d (6.60 Mg/yr)	D	
3-01-026 SB Copolymer Production	Wastewater	Controlled	0 - <10 lb/ton ^d (0 - <5 kg/Mg) ^e	0.30 lb/ton ^d (0.15 kg/Mg)	D	
3-01-026 SB Copolymer Production	Other liquid waste	Controlled	<0.02 lb/ton ^d (<0.01 kg/Mg)	<0.02 lb/ton ^d (<0.01 kg/Mg)	D	
3-01-026 SB Copolymer Production	Solid waste	Controlled	0 - <0.02 lb/ton ^d (0 - <0.01 kg/Mg) ^e	<0.02 lb/ton ^d (<0.01 kg/Mg)	D	

TABLE A-1. CONTINUED

SCC/AMS Code and			Emission Factor ^a		— Factor
Description Description	Emissions Source	Control Device	Range ^b	Mean	Rating
3-01-026 Polybutadiene	Process vents	Controlled	0.00008 - 36.06 lb/ton ^f (0.00004 - 18.03 kg/Mg)	6.14 lb/ton ^f (3.07 kg/Mg)	U5
Production		Uncontrolled	0.0032 - 36.06 lb/ton ^f (0.0016 - 18.03 kg/Mg)	8.96 lb/ton ^f (4.48 kg/Mg)	U5
3-01-026 Polybutadiene	Equipment leaks	Controlled	4.04 - 31.42 tons/yr ^f (3.66 - 28.50 Mg/yr)	10.41 tons/yr ^f (9.44 Mg/yr)	U5
Production		Uncontrolled	4.04 - 31.42 tons/yr ^f (3.66 - 28.50 Mg/yr)	10.41 tons/yr ^f (9.44 Mg/yr)	U5
3-01-026 Polybutadiene	Wastewater	Controlled	0 - 0.74 lb/ton ^f (0 - 0.38 kg/Mg)	0.24 lb/ton ^f (0.12 kg/Mg)	U5
Production		Uncontrolled	0 - 0.74 lb/ton ^f (0 - 0.38 kg/Mg)	(0.12 kg/Mg) 0.24 lb/ton ^f (0.12 kg/Mg)	U5
3-01-026 Polybutadiene	Solid waste	Controlled	0 lb/ton ^f (0 kg/Mg)	0 lb/ton ^f (0 kg/Mg)	U5
Production		Uncontrolled	0 lb/ton ^f (0 kg/Mg)	0 lb/ton ^f (0 kg/Mg)	U5
3-01-026 Neoprene Production	Process vents	Controlled	0.32 - 6.78 lb/ton ^c (0.16 - 3.89 kg/Mg)	4.04 lb/ton ^c (2.02 kg/Mg)	E
		Uncontrolled	0.40 - 24.18 lb/ton ^c (0.20 - 12.09 kg/Mg)	12.28 lb/ton ^c (6.14 kg/Mg)	E
3-01-026 Neoprene Production	Equipment leaks	Controlled	1.03 - 4.88 tons/yr ^c (0.93 - 4.43 Mg/yr)	2.95 tons/yr ^c (2.68 Mg/yr)	Е
		Uncontrolled	1.03 - 4.88 tons/yr ^c (0.93 - 4.43 Mg/yr)	2.95 tons/yr ^c (2.68 Mg/yr)	E

TABLE A-1. CONTINUED

SCC/AMS Code and			Emission F	actor ^a	Factor
Description	Emissions Source	Control Device	Range ^b	Mean	Rating
3-01-026 Nitrile Elastomer	Process vents	Controlled	0.0004 - 17.80 lb/ton ^{c,g} (0.0001 - 8.90 kg/Mg)	~ 4 lb/ton ^{c,g,h} (~ 2 kg/Mg)	Е
Production		Uncontrolled	0.030 - <50 lb/ton ^{c,g} (0.01 - <25 kg/Mg)	~ 16 lb/ton ^{c,g,h} (~ 8 kg/Mg)	E
3-01-026 Nitrile Elastomer Production	Equipment leaks	Uncontrolled	0.43 - 18.67 tons/yr ^{c.g} (0.39 - 16.93 Mg/yr)	8.74 tons/yr ^{c,g} (7.93 Mg/yr)	E
3-01-026 Nitrile Elastomer	Secondary sources	Controlled	0.002 - 0.018 lb/ton ^{c.g,i} (0.001 - 0.009 kg/Mg)	0.010 lb/ton ^{c,g,i} (0.005 kg/Mg)	Е
Production		Uncontrolled	0.002 - 0.018 lb/ton ^{c,g,i} (0.001 - 0.009 kg/Mg)	0.010 lb/ton ^{c,g,i} (0.005 kg/Mg)	E
3-01-026 Butadiene-vinylpyridine Latex	Equipment Leaks	Controlled		0.61 tons/yr ^c (0.55 Mg/yr)	U5
3-01-153 Butadiene Cylinders	Process Vents	Controlled		43.2 lb/ton ^c (21.6 kg/Mg)	U5
		Uncontrolled		43.2 lb/ton ^c (21.6 kg/Mg)	U5
	Equipment Leaks	Controlled		<0.11 tons/yr ^c (<0.1 Mg/yr)	U5
		Uncontrolled		<0.11 tons/yr ^c (<0.1 Mg/yr)	U5
3-01-153 Butadiene Production - C ₄ Stream Production	Process vents	Uncontrolled	0.0054 lb/ton ^d (0.0027 kg/Mg)		Е

SCC/AMS Code and			Emission 1	Factor ^a	- Factor
Description	Emissions Source	Control Device	Range ^b	Mean	Rating
3-01-153 Butadiene Production - Recovery Process	Wastewater	Controlled	0.00068 - 4.4 lb/ton ^d (0.00034 - 2.2 kg/Mg)	0.936 lb/ton ^d (0.468 kg/Mg)	Е
3-01-153 Butadiene Production - Recovery Process	Solid waste	Controlled		5.542x10 ⁻⁷ lb/ton ^d (4.988x10 ⁻⁷ kg/Mg)	Е
3-01-153-01 Butadiene Production -	Process vents	Controlled	0.0068 - 0.0550 lb/ton ^d (0.0034 - 0.0275 kg/Mg)	0.0314 lb/ton ^d (0.0157 kg/Mg)	Е
Recovery Process		Uncontrolled	0.0322 - 0.6872 lb/ton ^d (0.0161 - 0.3436 kg/Mg)	0.4652 lb/ton ^d (0.2326 kg/Mg)	E
3-01-153-80 Butadiene Production - Recovery Process	Equipment leaks ⁱ	Controlled	455 tons/yr ^d (407 Mg/yr)		Е
3-01-254 Adiponitrile Production	Process vents	Controlled	0.12 lb/ton ^{d,g} (0.06 kg/Mg)	0.12 lb/ton ^{d,g} (0.06 kg/Mg)	U5
		Uncontrolled	5.84 - 6.30 lb/ton ^{d.g} (2.92 - 3.15 kg/Mg)	6.08 lb/ton ^{d,g} (3.04 kg/Mg)	U5
3-01-254 Adiponitrile Production	Secondary sources	Controlled	0.016 - 0.024 lb/ton ^{d,g} (0.008 - 0.012 kg/Mg)	0.02 lb/ton ^{d,g} (0.01 kg/Mg)	U5
		Uncontrolled	0.016 - 0.024 lb/ton ^{d,g} (0.008 - 0.012 kg/Mg)	0.02 lb/ton ^{d,g} (0.01 kg/Mg)	U5
3-01-254-20 Adiponitrile Production	Equipment leaks	Uncontrolled	2.72 - 5.25 tons/yr ^{d,g} (2.47 - 4.76 Mg/yr)	3.99 tons/yr ^{d,g} (3.62 Mg/yr)	U5

TABLE A-1. CONTINUED

SCC/AMS Code and			Emission	Factor ^a	Factor
Description	Emissions Source	Control Device	Range ^b	Mean	Rating
3-04-004-03 Secondary lead	Blast furnace outlet	Uncontrolled	0.78 - 1.54 lb/ton (0.32 - 0.63 kg/Mg)	1.16 lb/ton (0.48 kg/Mg)	С
production	Rotary furnace outlet	Uncontrolled		0.13 lb/ton (0.05 kg/Mg)	С
5-01-007-01 Wastewater treatment facility	Influent	Uncontrolled		1.7 x 10 ³ lb/ton (771 g/kg)	U5
5-03-002-03 Open Burning of Tires	Chunk tires	Uncontrolled		234.28 lb/1,000 tons (117.14 mg/kg)	С
	Shredded tires	Uncontrolled		277.95 lb/1,000 tons (138.97 mg/kg)	С
6-41 Methylmethacrylate-	Process Vents	Controlled		1.8 lb/ton ^c (0.9 kg/Mg)	U5
butadiene-styrene Resins		Uncontrolled		17.2 lb/ton ^c (8.6 kg/Mg)	U5
	Equipment Leaks	Controlled	4.0 - 17.4 tons/yr ^c (3.6 - 15.8 Mg/yr)		U5
		Uncontrolled		17.4 tons/yr ^c (15.8 Mg/yr)	U5
6-41 ABS Production	Process vents	Controlled	0.16 - 10.66 lb/ton ^{c,k} (0.08 - 5.33 kg/Mg)	4.22 lb/ton ^{c,k} (2.11 kg/Mg)	Е
		Uncontrolled	6.50 - 11.28 lb/ton ^{c,k} (3.25 - 5.64 kg/Mg)	9.48 lb/ton ^{c,k} (4.74 kg/Mg)	Е
6-41 ABS Production	Equipment leaks	Controlled	1.21 - 3.50 tons/yr ^{c,k} (1.10 - 3.17 Mg/yr)	2.36 tons/yr ^{c,k} (2.14 Mg/yr)	Е
		Uncontrolled	1.21 - 3.50 tons/yr ^{c,k} (1.10 - 3.17 Mg/yr)	2.36 tons/yr ^{c,k} (2.14 Mg/yr)	E

TABLE A-1. CONTINUED

SCC/AMS Code and			Emissi	on Factor ^a	Factor
Description	Emissions Source	Control Device	Range ^b	Mean	Rating
6-46-300-01 Polyvinyl chloride	Suspension process, entire plant	Uncontrolled		4.6 x 10 ⁻⁴ lb/ton (2.1 x 10 ⁻⁴ g/kg)	U5
6-84-350 Dodecanedioic Acid	Equipment Leaks	Controlled		5.73 tons/yr ^c (5.2 Mg/yr)	U5
		Uncontrolled		5.73 tons/yr ^c (5.2 Mg/yr)	U5
22-01-001-000 Light-Duty Gas Vehicle	Mobile	Uncontrolled		2 x 10 ⁻⁵ lb/mile (0.01 g/mile)	D
22-01-020-000 Light-Duty Gas Truck 1	Mobile	Uncontrolled		4 x 10 ⁻⁵ lb/mile (0.02 g/mile)	D
22-01-040-000 Light-Duty Gas Truck 2	Mobile	Uncontrolled		6 x 10 ⁻⁵ lb/mile (0.03 g/mile)	D
22-01-060-000 Light-Duty Gas Truck	Mobile	Uncontrolled		4 x 10 ⁻⁵ lb/mile (0.02 g/mile)	D
22-01-070-000 Heavy-Duty Gas Vehicle	Mobile	Uncontrolled		1 x 10 ⁻⁴ lb/mile (0.06 g/mile)	D
22-01-080-000 Motorcycle	Mobile	Uncontrolled		6 x 10 ⁻⁵ lb/mile (0.03 g/mile)	D
22-30-001-000 Light-Duty Diesel Vehicle	Mobile	Uncontrolled		2 x 10 ⁻⁵ lb/mile (0.01 g/mile)	D

TABLE A-1. CONTINUED

SCC/AMS Code and			Emissi	on Factor ^a	Factor
Description Description	Emissions Source	Control Device	Range ^b	Mean	Rating
22-30-060-000 Light-Duty Diesel Truck	Mobile	Uncontrolled		2 x 10 ⁻⁵ lb/mile (0.01 g/mile)	D
22-30-070-000 Heavy-Duty Diesel Vehicle	Mobile	Uncontrolled		1 x 10 ⁻⁴ lb/mile (0.05 g/mile)	D
22-60-001-010 Off-Road Motorcycles	2-stroke gas, exhaust	Uncontrolled		16.38 g/hr ^l	Е
22-60-001-020 Snowmobiles	2-stroke gas, exhaust	Uncontrolled		2.978 g/hp-hr ^l	Е
22-60-001-030 All Terrain Vehicles (ATV's)	2-stroke gas, exhaust	Uncontrolled		16.38 g/hr ^l	E
22-60-001-050 Golf Carts	2-stroke gas, exhaust	Uncontrolled		16.38 g/hr ^l	Е
22-60-001-060 Specialty Vehicles Carts	2-stroke gas, exhaust	Uncontrolled		16.38 g/hr ^l	Е
22-60-002-006 Tampers/Rammers	2-stroke gas, exhaust	Uncontrolled		5.678 g/hp-hr ^l	Е
22-60-002-009 Plate Compactors	2-stroke gas, exhaust	Uncontrolled		5.678 g/hp-hr ^l	Е
22-60-002-021 Paving Equipment	2-stroke gas, exhaust	Uncontrolled		5.678 g/hp-hr ^l	Е
22-60-002-033 Bore/Drill Rigs	2-stroke gas, exhaust	Uncontrolled		5.678 g/hp-hr ¹	Е

SCC/AMS Code and			Emissi	on Factor ^a	Factor
Description	Emissions Source	Control Device	Range ^b	Mean	Rating
22-60-003-010	2-stroke gas, exhaust	Uncontrolled		0.059 g/hp-hr ^{m,n}	Е
Aerial Lifts	2-stroke gas, crank case	Uncontrolled		$0.019 \text{ g/hp-hr}^{m,n}$	E
22-60-003-020	2-stroke gas, exhaust	Uncontrolled		$0.059~g/hp\text{-}hr^{m,n}$	E
Forklifts	2-stroke gas, crank case	Uncontrolled		$0.019 \text{ g/hp-hr}^{m,n}$	E
22-60-003-030	2-stroke gas, exhaust	Uncontrolled		$0.056 \text{ g/hp-hr}^{m,n}$	E
Sweepers/Scrubbers	2-stroke gas, crank case	Uncontrolled		$0.019 \text{ g/hp-hr}^{\text{m,n}}$	E
22-60-003-040 Other General Industrial Equipment	2-stroke gas, exhaust	Uncontrolled		4.056 g/hp-hr ⁿ	Е
22-60-004-010 Lawn Mowers	2-stroke gas, exhaust	Uncontrolled		5.678 g/hp-hr	Е
22-60-004-015 Tillers <5 hp	2-stroke gas, exhaust	Uncontrolled		5.678 g/hp-hr ^l	Е
22-60-004-020 Chain Saws <4 hp	2-stroke gas, exhaust	Uncontrolled		8.135 g/hp-hr ^l	Е
22-60-004-025 Trimmers/Edgers/ Brush Cutters	2-stroke gas, exhaust	Uncontrolled		6.131 g/hp-hr ^l	Е
22-60-004-030 Leaf Blowers/ Vacuums	2-stroke gas, exhaust	Uncontrolled		5.878 g/hp-hr ^l	Е
22-60-004-035 Snowblowers	2-stroke gas, exhaust	Uncontrolled		5.678 g/hp-hr ^l	Е
22-60-004-050 Shredders <5 hp	2-stroke gas, exhaust	Uncontrolled		5.678 g/hp-hr ^l	Е
22-60-004-070 Commercial Turf Equipment	2-stroke gas, exhaust	Uncontrolled		5.678 g/hp-hr ^l	E

TABLE A-1. CONTINUED

SCC/AMS Code and			Emissi	on Factor ^a	Factor
Description	Emissions Source C	Control Device	Range ^b	Mean	Rating
22-60-004-075 Other Lawn and Garden Equipment	2-stroke gas, exhaust	Uncontrolled		5.678 g/hp-hr ¹	Е
22-60-006-005 Generator Sets	2-stroke gas, exhaust	Uncontrolled		5.678 g/hp-hr ^l	E
22-60-006-010	2-stroke gas, exhaust	Uncontrolled		0.117 g/hp-hr ^l	Е
Pumps	2-stroke gas, crank case	Uncontrolled		0.018 g/hp-hr ^l	Е
22-60-006-020	2-stroke gas, exhaust	Uncontrolled		$0.084 \text{ g/hp-hr}^{m,n}$	Е
Gas Compressors	2-stroke gas, crank case	Uncontrolled		0.084 g/hp-hr ^{m,n}	E
22-60-007-005 Chain Saws >4 hp	2-stroke gas, exhaust	Uncontrolled		4.15 g/hp-hr ^l	E
22-60-008-010	2-stroke gas, exhaust	Uncontrolled		0.059 g/hp-hr ^{m,n}	Е
Terminal Tractors	2-stroke gas, crank case	Uncontrolled		$0.013 \text{ g/hp-hr}^{m,n}$	E
22-65-001-010	4-stroke gas, exhaust	Uncontrolled		5.678 g/hp-hr ^l 0.117 g/hp-hr ^l 0.018 g/hp-hr ^l 0.084 g/hp-hr ^{m,n} 0.018 g/hp-hr ^{m,n} 4.15 g/hp-hr ^l	Е
Off-Road Motorcycles	4-stroke gas, crank case	Uncontrolled		0.429 g/hr ⁿ	E
22-65-001-030	4-stroke gas, exhaust	Uncontrolled		2.73 g/hr ^l	Е
All Terrain Vehicles (ATV's)	4-stroke gas, crank case	Uncontrolled		0.429 g/hr ^l	E
22-65-001-040	4-stroke gas, exhaust	Uncontrolled		2.73 g/hr ¹	Е
Minibikes	4-stroke gas, crank case	Uncontrolled		$0.429~\mathrm{g/hr^1}$	E
22-65-001-050	4-stroke gas, exhaust	Uncontrolled		2.73 g/hr ¹	Е
Golf Carts	4-stroke gas, crank case	Uncontrolled		$0.429~g/hr^l$	E

TABLE A-1. CONTINUED

SCC/AMS Code and			Emission Factor ^a		— Factor
Description	Emissions Source	Control Device	Range ^b	Mean	Rating
22-65-001-060	4-stroke gas, exhaust	Uncontrolled		2.73 g/hr ¹	Е
Specialty Vehicles Carts	4-stroke gas, crank case	Uncontrolled		0.429 g/hr^{1}	E
22-65-002-003	4-stroke gas, exhaust	Uncontrolled		0.127 g/hp-hr ⁿ	Е
Asphalt Pavers	4-stroke gas, crank case	Uncontrolled		$0.028~g/hp-hr^n$	E
22-65-002-006	4-stroke gas, exhaust	Uncontrolled		0.177 g/hp-hr ¹	Е
Tampers/Rammers	4-stroke gas, crank case	Uncontrolled		$0.028~\mathrm{g/hp-hr^l}$	E
22-65-002-009	4-stroke gas, exhaust	Uncontrolled		0.177 g/hp-hr ^l	Е
Plate Compactors	4-stroke gas, crank case	Uncontrolled		$0.028~\mathrm{g/hp-hr^l}$	E
22-65-002-015	4-stroke gas, exhaust	Uncontrolled		0.253 g/hp-hr ^l	Е
Rollers	4-stroke gas, crank case	Uncontrolled		$0.04 \text{ g/hp-hr}^{\text{l}}$	E
22-65-002-021	4-stroke gas, exhaust	Uncontrolled		0.177 g/hp-hr ¹	Е
Paving Equipment	4-stroke gas, crank case	Uncontrolled		$0.028 \text{ g/hp-hr}^{\text{l}}$	E
22-65-002-024	4-stroke gas, exhaust	Uncontrolled		0.429 g/hr ¹ 0.127 g/hp-hr ⁿ 0.028 g/hp-hr ⁿ 0.177 g/hp-hr ¹ 0.028 g/hp-hr ¹ 0.177 g/hp-hr ¹ 0.028 g/hp-hr ¹ 0.028 g/hp-hr ¹ 0.028 g/hp-hr ¹ 0.04 g/hp-hr ¹ 0.177 g/hp-hr ¹ 0.177 g/hp-hr ¹ 0.177 g/hp-hr ¹ 0.177 g/hp-hr ¹ 0.128 g/hp-hr ¹ 0.127 g/hp-hr ⁿ 0.028 g/hp-hr ⁿ 0.127 g/hp-hr ⁿ	Е
Surfacing Equipment	4-stroke gas, crank case	Uncontrolled		$0.028~\mathrm{g/hp-hr^l}$	E
22-65-002-027	4-stroke gas, exhaust	Uncontrolled		0.429 g/hr¹ 0.127 g/hp-hr¹ 0.028 g/hp-hr¹ 0.177 g/hp-hr¹ 0.028 g/hp-hr¹ 0.177 g/hp-hr¹ 0.028 g/hp-hr¹ 0.028 g/hp-hr¹ 0.04 g/hp-hr¹ 0.177 g/hp-hr¹ 0.077 g/hp-hr¹ 0.177 g/hp-hr¹ 0.177 g/hp-hr¹ 0.177 g/hp-hr¹ 0.177 g/hp-hr¹ 0.177 g/hp-hr¹ 0.177 g/hp-hr¹ 0.127 g/hp-hr¹ 0.127 g/hp-hr³	Е
Signal Boards	4-stroke gas, crank case	Uncontrolled			E
22-65-002-030	4-stroke gas, exhaust	Uncontrolled		0.127 g/hp-hr ⁿ	Е
Trenchers	4-stroke gas, crank case	Uncontrolled		0.028 g/hp-hr ⁿ	E
22-65-002-033	4-stroke gas, exhaust	Uncontrolled		0.127 g/hp-hr ⁿ	Е
Bore/Drill Rigs	4-stroke gas, crank case	Uncontrolled		0.028 g/hp-hr ⁿ	E
22-65-002-036	4-stroke gas, exhaust	Uncontrolled		0.127 g/hp-hr ⁿ	Е
Excavators	4-stroke gas, crank case	Uncontrolled		0.028 g/hp-hr ⁿ	E

TABLE A-1. CONTINUED

SCC/AMS Code and			Emission Factor ^a		Factor
Description Description	Emissions Source	Control Device	Range ^b	Mean	Rating
22-65-002-039	4-stroke gas, exhaust	Uncontrolled		0.177 g/hp-hr ¹	Е
Concrete/Industrial Saws	4-stroke gas, crank case	Uncontrolled		$0.028~\mathrm{g/hp-hr^l}$	Е
22-65-002-042	4-stroke gas, exhaust	Uncontrolled		0.177 g/hp-hr ¹	Е
Cement and Mortar Mixers	4-stroke gas, crank case	Uncontrolled		$0.028~\mathrm{g/hp-hr^l}$	E
22-65-002-045	4-stroke gas, exhaust	Uncontrolled		0.127 g/hp-hr ⁿ	E
Cranes	4-stroke gas, crank case	Uncontrolled		$0.028 \text{ g/hp-hr}^{\text{n}}$	E
22-65-002-054	4-stroke gas, exhaust	Uncontrolled		0.127 g/hp-hr ⁿ	E
Crushing/Proc. Equipment	4-stroke gas, crank case	Uncontrolled		$0.028~g/hp-hr^n$	Е
22-65-002-057	4-stroke gas, exhaust	Uncontrolled		0.127 g/hp-hr ⁿ	Е
Rough Terrain Forklifts	4-stroke gas, crank case	Uncontrolled		$0.028~g/hp-hr^n$	E
22-65-002-060	4-stroke gas, exhaust	Uncontrolled		0.108 g/hp-hr ⁿ	Е
Rubber Tire Loaders	4-stroke gas, crank case	Uncontrolled		$0.024 \text{ g/hp-hr}^{\text{n}}$	E
22-65-002-066	4-stroke gas, exhaust	Uncontrolled		0.127 g/hp-hr ⁿ	E
Tractors/Loaders/ Backhoes	4-stroke gas, crank case	Uncontrolled		0.028 g/hp-hr ⁿ	Е
22-65-002-072	4-stroke gas, exhaust	Uncontrolled		0.127 g/hp-hr ⁿ	Е
Skid Steer Loaders	4-stroke gas, crank case	Uncontrolled		$0.028~g/hp-hr^n$	E
22-65-002-078	4-stroke gas, exhaust	Uncontrolled		0.177 g/hp-hr ^l	Е
Dumpers/Tenders	4-stroke gas, crank case	Uncontrolled		$0.028~g/hp-hr^1$	E
22-65-002-081	4-stroke gas, exhaust	Uncontrolled		0.127 g/hp-hr ⁿ	Е
Other Construction Equipment	4-stroke gas, crank case	Uncontrolled		0.028 g/hp-hr ⁿ	Е

TABLE A-1. CONTINUED

SCC/AMS Code and			Emission Factor ^a		— Factor
Description	Emissions Source	Control Device	Range ^b	Mean	Rating
22-65-003-010	4-stroke gas, exhaust	Uncontrolled		0.13 g/hp-hr ⁿ	Е
Aerial Lifts	4-stroke gas, crank case	Uncontrolled		0.029 g/hp-hr ⁿ	E
22-65-003-020	4-stroke gas, exhaust	Uncontrolled		0.13 g/hp-hr ⁿ	Е
Forklifts	4-stroke gas, crank case	Uncontrolled		0.029 g/hp-hr ⁿ	E
22-65-003-030	4-stroke gas, exhaust	Uncontrolled		0.13 g/hp-hr ⁿ	Е
Sweepers/Scrubbers	4-stroke gas, crank case	Uncontrolled		0.13 g/hp-hr ⁿ 0.029 g/hp-hr ⁿ 0.13 g/hp-hr ⁿ 0.029 g/hp-hr ⁿ	E
22-65-003-040	4-stroke gas, exhaust	Uncontrolled		0.13 g/hp-hr ⁿ	Е
Other General Industrial Equipment	4-stroke gas, crank case	Uncontrolled		0.027 g/hp-hr ⁿ	Е
22-65-003-050	4-stroke gas, exhaust	Uncontrolled		0.13 g/hp-hr ⁿ	E
Other Material Handling Equipment	4-stroke gas, crank case	Uncontrolled		$0.027 \text{ g/hp-hr}^{\text{n}}$	E
22-65-004-010	4-stroke gas, exhaust	Uncontrolled		1.029 g/hp-hr ¹	Е
Lawn Mowers	4-stroke gas, crank case	Uncontrolled		$0.162 \text{ g/hp-hr}^{\text{l}}$	E
22-65-004-015	4-stroke gas, exhaust	Uncontrolled		1.029 g/hp-hr ¹	Е
Tillers < 5 hp	4-stroke gas, crank case	Uncontrolled		$0.162 \text{ g/hp-hr}^{1}$	E
22-65-004-025	4-stroke gas, exhaust	Uncontrolled		0.66 g/hp-hr ¹	Е
Trimmers/Edgers/ Brush Cutters	4-stroke gas, crank case	Uncontrolled		$0.104 \text{ g/hp-hr}^{\text{l}}$	Е
22-65-004-030	4-stroke gas, exhaust	Uncontrolled		0.53 g/hp-hr ¹	E
Leaf Blowers/ Vacuums	4-stroke gas, crank case	Uncontrolled		0.083 g/hp-hr ^l	E
22-65-004-035	4-stroke gas, exhaust	Uncontrolled		1.029 g/hp-hr ¹	E
Snowblowers	4-stroke gas, crank case	Uncontrolled		$0.162 \text{ g/hp-hr}^{1}$	E

TABLE A-1. CONTINUED

SCC/AMS Code and			Emissio	on Factor ^a	Factor
Description Description	Emissions Source	Control Device	Range ^b	Mean	Rating
22-65-004-040	4-stroke gas, exhaust	Uncontrolled		0.254 g/hp-hr ¹	Е
Rear Engine Riding Mowers	4-stroke gas, crank case	Uncontrolled		0.04 g/hp-hr ^l	E
22-65-004-045	4-stroke gas, exhaust	Uncontrolled		0.254 g/hp-hr ¹	Е
Front Mowers	4-stroke gas, crank case	Uncontrolled		0.04 g/hp-hr ¹	E
22-65-004-050	4-stroke gas, exhaust	Uncontrolled		1.029 g/hp-hr ¹	Е
Shredders <5 hp	4-stroke gas, crank case	Uncontrolled		0.254 g/hp-hr ¹ 0.04 g/hp-hr ¹ 0.254 g/hp-hr ¹ 0.04 g/hp-hr ¹	E
22-65-004-055	4-stroke gas, exhaust	Uncontrolled		0.257 g/hp-hr ¹	Е
Lawn and Garden Tractors	4-stroke gas, crank case	Uncontrolled		0.04 g/hp-hr ^l	E
22-65-004-060	4-stroke gas, exhaust	Uncontrolled		1.029 g/hp-hr ¹	Е
Wood Splitters	4-stroke gas, crank case	Uncontrolled		• •	E
22-65-004-065	4-stroke gas, exhaust	Uncontrolled		0.735 g/hp-hr ⁿ	Е
Chippers/Stump Grinders	4-stroke gas, crank case	Uncontrolled		0.162 g/hp-hr ⁿ	E
22-65-004-070	4-stroke gas, exhaust	Uncontrolled		0.257 g/hp-hr ¹	Е
Commercial Turf Equipment	4-stroke gas, crank case	Uncontrolled		0.04 g/hp-hr ^l	E
22-65-004-075	4-stroke gas, exhaust	Uncontrolled		1.029 g/hp-hr ^l	Е
Other Lawn and Garden Equipment	4-stroke gas, crank case	Uncontrolled		0.162 g/hp-hr ^l	Е
22-65-005-010	4-stroke gas, exhaust	Uncontrolled		0.15 g/hp-hr ¹	Е
2-Wheel Tractors	4-stroke gas, crank case	Uncontrolled		0.024 g/hp-hr ¹	E
22-65-005-015	4-stroke gas, exhaust	Uncontrolled		0.107 g/hp-hr ⁿ	Е
Agricultural Tractors	4-stroke gas, crank case	Uncontrolled		$0.024 \text{ g/hp-hr}^{\text{n}}$	E

TABLE A-1. CONTINUED

SCC/AMS Code and			Emissio	on Factor ^a	Factor
Description Description	Emissions Source	Control Device	Range ^b	Mean	Rating
22-65-005-020	4-stroke gas, exhaust	Uncontrolled		0.14 g/hp-hr ⁿ	Е
Combines	4-stroke gas, crank case	Uncontrolled		$0.031 \text{ g/hp-hr}^{\text{n}}$	E
22-65-005-030	4-stroke gas, exhaust	Uncontrolled		0.199 g/hp-hr ¹	Е
Agricultural Mowers	4-stroke gas, crank case	Uncontrolled		0.031 g/hp-hr^1	E
22-65-005-035	4-stroke gas, exhaust	Uncontrolled		0.14 g/hp-hr ⁿ	Е
Sprayers	4-stroke gas, crank case	Uncontrolled		$0.031 \text{ g/hp-hr}^{\text{n}}$	E
22-65-005-040	4-stroke gas, exhaust	Uncontrolled		1.029 g/hp-hr ^l	E
Tillers >5 hp	4-stroke gas, crank case	Uncontrolled		$0.162 \text{ g/hp-hr}^{1}$	E
22-65-005-045	4-stroke gas, exhaust	Uncontrolled		0.14 g/hp-hr ⁿ	E
Swathers	4-stroke gas, crank case	Uncontrolled		0.031 g/hp-hr ⁿ 0.199 g/hp-hr ^l 0.031 g/hp-hr ^l 0.031 g/hp-hr ⁿ 0.14 g/hp-hr ⁿ 1.029 g/hp-hr ^l 0.162 g/hp-hr ^l 0.14 g/hp-hr ⁿ 0.031 g/hp-hr ⁿ 0.031 g/hp-hr ⁿ 0.196 g/hp-hr ^l 0.14 g/hp-hr ⁿ 0.031 g/hp-hr ^l 0.14 g/hp-hr ⁿ 0.041 g/hp-hr ^l 0.259 g/hp-hr ^l 0.041 g/hp-hr ^l 0.041 g/hp-hr ^l 0.259 g/hp-hr ^l 0.259 g/hp-hr ^l	E
22-65-005-050	4-stroke gas, exhaust	Uncontrolled		0.196 g/hp-hr ¹	Е
Hydro Power Units	4-stroke gas, crank case	Uncontrolled		Mean 0.14 g/hp-hr ⁿ 0.031 g/hp-hr ⁿ 0.199 g/hp-hr ^l 0.031 g/hp-hr ^l 0.031 g/hp-hr ^l 0.14 g/hp-hr ⁿ 1.029 g/hp-hr ^l 0.162 g/hp-hr ^l 0.14 g/hp-hr ⁿ 0.196 g/hp-hr ^l 0.259 g/hp-hr ^l	E
22-65-005-055	4-stroke gas, exhaust	Uncontrolled		0.14 g/hp-hr ⁿ	E
Other Agricultural Equipment	4-stroke gas, crank case	Uncontrolled		0.031 g/hp-hr ⁿ	E
22-65-006-005	4-stroke gas, exhaust	Uncontrolled		0.259 g/hp-hr ¹	Е
Generator Sets	4-stroke gas, crank case	Uncontrolled		0.041 g/hp-hr^1	E
22-65-006-010	4-stroke gas, exhaust	Uncontrolled		0.259 g/hp-hr ¹	Е
Pumps	4-stroke gas, crank case	Uncontrolled		0.041 g/hp-hr^1	E
22-65-006-015	4-stroke gas, exhaust	Uncontrolled		0.259 g/hp-hr ¹	E
Air Compressors	4-stroke gas, crank case	Uncontrolled		$0.041~g/hp-hr^1$	E
22-65-006-025	4-stroke gas, exhaust	Uncontrolled		0.259 g/hp-hr ¹	Е
Welders	4-stroke gas, crank case	Uncontrolled		$0.041 \text{ g/hp-hr}^{1}$	Е

TABLE A-1. CONTINUED

SCC/AMS Code and			Emissio	on Factor ^a	Factor
Description Description	Emissions Source	Control Device	Range ^b	Mean	Rating
22-65-006-030	4-stroke gas, exhaust	Uncontrolled		0.259 g/hp-hr ^l	Е
Pressure Washers	4-stroke gas, crank case	Uncontrolled		$0.041 \text{ g/hp-hr}^{1}$	E
22-65-007-010	4-stroke gas, exhaust	Uncontrolled		0.254 g/hp-hr ^l	Е
Shredders >5 hp	4-stroke gas, crank case	Uncontrolled		0.04 g/hp-hr^1	E
22-65-008-005	4-stroke gas, exhaust	Uncontrolled		0.13 g/hp-hr ⁿ	Е
Aircraft Support Equipment	4-stroke gas, crank case	Uncontrolled		0.029 g/hp-hr ⁿ	E
22-65-008-010	4-stroke gas, exhaust	Uncontrolled		0.13 g/hp-hr ⁿ	Е
Terminal Tractors	4-stroke gas, crank case	Uncontrolled		0.259 g/hp-hr ¹ 0.041 g/hp-hr ¹ 0.254 g/hp-hr ¹ 0.04 g/hp-hr ¹ 0.13 g/hp-hr ⁿ 0.029 g/hp-hr ⁿ 0.13 g/hp-hr ⁿ 0.029 g/hp-hr ⁿ 0.019 g/hr 0.0003 g/hr 0.01 g/hp-hr 0.000 g/hp-hr 0.00 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.003 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr	Е
22-70-001-060	Diesel, exhaust	Uncontrolled		0.019 g/hr	Е
Specialty Vehicles Carts	Diesel, crank case	Uncontrolled		0.259 g/hp-hr ¹ 0.041 g/hp-hr ¹ 0.254 g/hp-hr ¹ 0.04 g/hp-hr ¹ 0.04 g/hp-hr ¹ 0.13 g/hp-hr ⁿ 0.029 g/hp-hr ⁿ 0.13 g/hp-hr ⁿ 0.019 g/hr 0.009 g/hp-hr 0.0003 g/hr 0.000 g/hp-hr 0.000 g/hp-hr 0.013 g/hp-hr	E
22-70-002-003	Diesel, exhaust	Uncontrolled		0.01 g/hp-hr	Е
Asphalt Pavers	Diesel, crank case	Uncontrolled		0.04 g/hp-hr ¹ 0.13 g/hp-hr ⁿ 0.029 g/hp-hr ⁿ 0.13 g/hp-hr ⁿ 0.029 g/hp-hr ⁿ 0.019 g/hr 0.019 g/hr 0.0003 g/hr 0.0002 g/hp-hr 0.00 g/hp-hr 0.00 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr	E
22-70-002-006	Diesel, exhaust	Uncontrolled		0.00 g/hp-hr	Е
Tampers/Rammers	Diesel, crank case	Uncontrolled		0.00 g/hp-hr	E
22-70-002-009	Diesel, exhaust	Uncontrolled		0.013 g/hp-hr	Е
Plate Compactors	Diesel, crank case	Uncontrolled		0.0003 g/hp-hr	E
22-70-002-012	Diesel, exhaust	Uncontrolled		0.018 g/hp-hr	Е
Concrete Pavers	Diesel, crank case	Uncontrolled		0.0003 g/hp-hr	Е
22-70-002-015	Diesel, exhaust	Uncontrolled		0.013 g/hp-hr	Е
Rollers	Diesel, crank case	Uncontrolled		0.0003 g/hp-hr	E

TABLE A-1. CONTINUED

SCC/AMS Code and			Emissi	on Factor ^a	Factor
Description	Emissions Source	Control Device	Range ^b	Mean	Rating
22-70-002-018	Diesel, exhaust	Uncontrolled		0.011 g/hp-hr°	Е
Scrapers	Diesel, crank case	Uncontrolled		$0.0002~g/hp-hr^{\circ}$	E
22-70-002-021	Diesel, exhaust	Uncontrolled		0.016 g/hp-hr	Е
Paving Equipment	Diesel, crank case	Uncontrolled		0.0003 g/hp-hr	E
22-70-002-024	Diesel, exhaust	Uncontrolled		0.00 g/hp-hr	Е
Surfacing Equipment	Diesel, crank case	Uncontrolled		0.00 g/hp-hr	E
22-70-002-027	Diesel, exhaust	Uncontrolled		0.019 g/hp-hr	Е
Signal Boards	Diesel, crank case	Uncontrolled		0.0003 g/hp-hr	E
22-70-002-030	Diesel, exhaust	Uncontrolled		0.025 g/hp-hr°	Е
Trenchers	Diesel, crank case	Uncontrolled		0.011 g/hp-hr° 0.0002 g/hp-hr° 0.016 g/hp-hr 0.0003 g/hp-hr 0.00 g/hp-hr 0.00 g/hp-hr 0.019 g/hp-hr 0.0003 g/hp-hr° 0.0005 g/hp-hr° 0.0005 g/hp-hr° 0.011 g/hp-hr° 0.0002 g/hp-hr° 0.0003 g/hp-hr° 0.016 g/hp-hr° 0.016 g/hp-hr	E
22-70-002-033	Diesel, exhaust	Uncontrolled		0.023 g/hp-hr°	Е
Bore/Drill Rigs	Diesel, crank case	Uncontrolled		$0.0005~g/hp-hr^{\circ}$	E
22-70-002-036	Diesel, exhaust	Uncontrolled		0.011 g/hp-hr°	Е
Excavators	Diesel, crank case	Uncontrolled		$0.0002~g/hp-hr^{\circ}$	E
22-70-002-039	Diesel, exhaust	Uncontrolled		0.023 g/hp-hr°	E
Concrete/Industrial Saws	Diesel, crank case	Uncontrolled		$0.0005~\mathrm{g/hp\text{-}hr^o}$	E
22-70-002-042	Diesel, exhaust	Uncontrolled		0.016 g/hp-hr	Е
Cement and Mortar Mixers	Diesel, crank case	Uncontrolled		0.0003 g/hp-hr	E
22-70-002-045	Diesel, exhaust	Uncontrolled		0.02 g/hp-hr°	Е
Cranes	Diesel, crank case	Uncontrolled		$0.0005~g/hp-hr^{\circ}$	E

TABLE A-1. CONTINUED

SCC/AMS Code and			Emissi	Emission Factor ^a	
Description	Emissions Source	Control Device	Range ^b	Mean	FactorRating
22-70-002-048	Diesel, exhaust	Uncontrolled		0.025 g/hp-hr°	Е
Graders	Diesel, crank case	Uncontrolled		$0.0005~g/hp-hr^{\circ}$	E
22-70-002-051	Diesel, exhaust	Uncontrolled		0.013 g/hp-hr°	Е
Off-Highway Trucks	Diesel, crank case	Uncontrolled		$0.0003~g/hp-hr^{\circ}$	E
22-70-002-054	Diesel, exhaust	Uncontrolled		0.023 g/hp-hr°	Е
Crushing/Proc. Equipment	Diesel, crank case	Uncontrolled		$0.0005~\mathrm{g/hp\text{-}hr^o}$	E
22-70-002-057	Diesel, exhaust	Uncontrolled		0.027 g/hp-hr°	Е
Rough Terrain Forklifts	Diesel, crank case	Uncontrolled		$0.0005~g/hp-hr^{\circ}$	E
22-70-002-060	Diesel, exhaust	Uncontrolled		0.013 g/hp-hr°	Е
Rubber Tire Loaders	Diesel, crank case	Uncontrolled		$0.0003~g/hp-hr^{\circ}$	E
22-70-002-063	Diesel, exhaust	Uncontrolled		0.013 g/hp-hr° 0.0003 g/hp-hr° 0.013 g/hp-hr°	Е
Rubber Tire Dozers	Diesel, crank case	Uncontrolled		$0.0003~g/hp-hr^{\circ}$	E
22-70-002-066	Diesel, exhaust	Uncontrolled		0.022 g/hp-hr°	E
Tractors/Loaders/ Backhoes	Diesel, crank case	Uncontrolled		$0.0005~g/hp-hr^{\circ}$	E
22-70-002-069	Diesel, exhaust	Uncontrolled		0.02 g/hp-hr°	Е
Crawler Tractors	Diesel, crank case	Uncontrolled		$0.0005~\mathrm{g/hp}\text{-hr}^{\mathrm{o}}$	E
22-70-002-072	Diesel, exhaust	Uncontrolled		0.034 g/hp-hr°	Е
Skid Steer Loaders	Diesel, crank case	Uncontrolled		$0.0006~\mathrm{g/hp\text{-}hr^o}$	E
22-70-002-075	Diesel, exhaust	Uncontrolled		0.039 g/hp-hr°	Е
Off-Highway Tractors	Diesel, crank case	Uncontrolled		$0.0008~\mathrm{g/hp}\text{-hr}^{\circ}$	E

TABLE A-1. CONTINUED

SCC/AMS Code and			Emission Factor ^a		Factor
Description	Emissions Source	Control Device	Range ^b	Mean	Rating
22-70-002-078	Diesel, exhaust	Uncontrolled		0.013 g/hp-hr°	Е
Dumpers/Tenders	Diesel, crank case	Uncontrolled		$0.0003~g/hp-hr^{\circ}$	E
22-70-002-081	Diesel, exhaust	Uncontrolled		0.023 g/hp-hr°	Е
Other Construction Equipment	Diesel, crank case	Uncontrolled		$0.0005~g/hp-hr^{\circ}$	E
22-70-003-010	Diesel, exhaust	Uncontrolled		$0.025~\mathrm{g/hp-hr^o}$	E
Aerial Lifts	Diesel, crank case	Uncontrolled		Mean 0.013 g/hp-hr° 0.0003 g/hp-hr° 0.0023 g/hp-hr° 0.0005 g/hp-hr° 0.0025 g/hp-hr° 0.0005 g/hp-hr° 0.0025 g/hp-hr° 0.0019 g/hp-hr 0.0003 g/hp-hr 0.019 g/hp-hr 0.0003 g/hp-hr	E
22-70-003-020	Diesel, exhaust	Uncontrolled		$0.025~g/hp-hr^o$	Е
Forklifts	Diesel, crank case	Uncontrolled		Mean 0.013 g/hp-hr° 0.0003 g/hp-hr° 0.0003 g/hp-hr° 0.0005 g/hp-hr° 0.019 g/hp-hr 0.019 g/hp-hr 0.019 g/hp-hr 0.0003 g/hp-hr	E
22-70-003-030	Diesel, exhaust	Uncontrolled		Mean 0.013 g/hp-hr° 0.0003 g/hp-hr° 0.0003 g/hp-hr° 0.0025 g/hp-hr° 0.0025 g/hp-hr° 0.0005 g/hp-hr° 0.0025 g/hp-hr° 0.0025 g/hp-hr° 0.0025 g/hp-hr° 0.0005 g/hp-hr° 0.0005 g/hp-hr° 0.0005 g/hp-hr° 0.0005 g/hp-hr° 0.019 g/hp-hr 0.019 g/hp-hr 0.0003 g/hp-hr 0.0003 g/hp-hr	Е
Sweepers/Scrubbers	Diesel, crank case	Uncontrolled			E
22-70-003-040	Diesel, exhaust	Uncontrolled		$0.025~g/hp-hr^{\circ}$	E
Other General Industrial Equipment	Diesel, crank case	Uncontrolled		$0.0005~g/hp\text{-}hr^{\rm o}$	E
22-70-003-050	Diesel, exhaust	Uncontrolled		$0.025~g/hp-hr^o$	E
Other Material Handling Equipment	Diesel, crank case	Uncontrolled		$0.0005~g/hp\text{-}hr^{\rm o}$	E
22-70-004-040	Diesel, exhaust	Uncontrolled		0.019 g/hp-hr	Е
Rear Engine Riding Mowers	Diesel, crank case	Uncontrolled		0.0003 g/hp-hr	Е
22-70-004-055	Diesel, exhaust	Uncontrolled		0.019 g/hp-hr	E
Lawn and Garden Tractors	Diesel, crank case	Uncontrolled		0.0003 g/hp-hr	E
22-70-004-060	Diesel, exhaust	Uncontrolled		0.0192 g/hp-hr	Е
Wood Splitters	Diesel, crank case	Uncontrolled		0.0003 g/hp-hr	E

TABLE A-1. CONTINUED

SCC/AMS Code and			Emission Factor ^a		— Factor
Description	Emissions Source	Control Device	Range ^b	Mean	Rating
22-70-004-065	Diesel, exhaust	Uncontrolled		0.019 g/hp-hr	Е
Chippers/Stump Grinders	Diesel, crank case	Uncontrolled		0.0003 g/hp-hr	Е
22-70-004-075	Diesel, exhaust	Uncontrolled		0.019 g/hp-hr	Е
Other Lawn and Garden Equipment	Diesel, crank case	Uncontrolled		0.0003 g/hp-hr	Е
22-70-005-015	Diesel, exhaust	Uncontrolled		0.0003 g/hp-hr 0.019 g/hp-hr 0.0003 g/hp-hr 0.0003 g/hp-hr 0.0006 g/hp-hr 0.002 g/hp-hr 0.0005 g/hp-hr 0.0038 g/hp-hr 0.0006 g/hp-hr 0.0006 g/hp-hr 0.0006 g/hp-hr 0.019 g/hp-hr 0.0003 g/hp-hr 0.014 g/hp-hr 0.0003 g/hp-hr 0.0003 g/hp-hr	E
Agricultural Tractors	Diesel, crank case	Uncontrolled		$0.0006~g/hp\text{-}hr^{\circ}$	E
22-70-005-020	Diesel, exhaust	Uncontrolled		$0.02~\mathrm{g/hp}\text{-hr}^{\mathrm{o}}$	E
Combines	Diesel, crank case	Uncontrolled		$0.0005~g/hp\text{-}hr^{\circ}$	E
22-70-005-025	Diesel, exhaust	Uncontrolled			Е
Balers	Diesel, crank case	Uncontrolled		0.0006 g/hp-hr	E
22-70-005-035	Diesel, exhaust	Uncontrolled		0.038 g/hp-hr	Е
Sprayers	Diesel, crank case	Uncontrolled		0.019 g/hp-hr 0.0003 g/hp-hr 0.019 g/hp-hr 0.0003 g/hp-hr 0.0006 g/hp-hr 0.0006 g/hp-hr 0.0005 g/hp-hr 0.0006 g/hp-hr 0.0006 g/hp-hr 0.0006 g/hp-hr 0.0006 g/hp-hr 0.019 g/hp-hr 0.019 g/hp-hr 0.019 g/hp-hr 0.014 g/hp-hr 0.0003 g/hp-hr 0.0003 g/hp-hr 0.0003 g/hp-hr 0.0006 g/hp-hr 0.0009 g/hp-hr	E
22-70-005-040	Diesel, exhaust	Uncontrolled		0.019 g/hp-hr	Е
Tillers >5 hp	Diesel, crank case	Uncontrolled		0.0003 g/hp-hr	E
22-70-005-045	Diesel, exhaust	Uncontrolled		0.014 g/hp-hr	Е
Swathers	Diesel, crank case	Uncontrolled		0.0003 g/hp-hr	E
22-70-005-050	Diesel, exhaust	Uncontrolled		0.036 g/hp-hr	Е
Hydro Power Units	Diesel, crank case	Uncontrolled		0.0006 g/hp-hr	E
22-70-005-055	Diesel, exhaust	Uncontrolled		0.029 g/hp-hr	Е
Other Agricultural Equipment	Diesel, crank case	Uncontrolled		0.0006 g/hp-hr	E

TABLE A-1. CONTINUED

SCC/AMS Code and			Emission Factor ^a		Factor
Description	Emissions Source	Control Device	Range ^b	Mean	Rating
22-70-006-005	Diesel, exhaust	Uncontrolled		0.019 g/hp-hr	Е
Generator Sets	Diesel, crank case	Uncontrolled		0.0003 g/hp-hr	E
22-70-006-010	Diesel, exhaust	Uncontrolled		0.019 g/hp-hr	Е
Pumps	Diesel, crank case	Uncontrolled		0.0003 g/hp-hr	E
22-70-006-015	Diesel, exhaust	Uncontrolled		0.019 g/hp-hr	Е
Air Compressors	Diesel, crank case	Uncontrolled		Mean 0.019 g/hp-hr 0.0003 g/hp-hr 0.019 g/hp-hr 0.0003 g/hp-hr	E
22-70-006-025	Diesel, exhaust	Uncontrolled		Mean 0.019 g/hp-hr 0.0003 g/hp-hr 0.019 g/hp-hr 0.0003 g/hp-hr 0.019 g/hp-hr 0.019 g/hp-hr 0.019 g/hp-hr 0.019 g/hp-hr 0.019 g/hp-hr 0.019 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.015 g/hp-hr 0.025 g/hp-hr 0.0005 g/hp-hr 0.0005 g/hp-hr	Е
Welders	Diesel, crank case	Uncontrolled		0.0003 g/hp-hr	E
22-70-006-030	Diesel, exhaust	Uncontrolled		0.019 g/hp-hr	Е
Pressure Washers	Diesel, crank case	Uncontrolled		0.019 g/hp-hr 0.0003 g/hp-hr 0.019 g/hp-hr 0.0003 g/hp-hr 0.019 g/hp-hr 0.019 g/hp-hr 0.019 g/hp-hr 0.019 g/hp-hr 0.019 g/hp-hr 0.019 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.0003 g/hp-hr 0.0003 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.0005 g/hp-hr 0.0005 g/hp-hr 0.0005 g/hp-hr	E
22-70-007-015	Diesel, exhaust	Uncontrolled		0.013 g/hp-hr°	Е
Skidders	Diesel, crank case	Uncontrolled		0.019 g/hp-hr 0.0003 g/hp-hr 0.019 g/hp-hr 0.0003 g/hp-hr 0.019 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.0003 g/hp-hr 0.0003 g/hp-hr 0.013 g/hp-hr 0.0005 g/hp-hr 0.0005 g/hp-hr 0.0005 g/hp-hr	E
22-70-007-020	Diesel, exhaust	Uncontrolled		0.013 g/hp-hr°	Е
Fellers/Bunchers	Diesel, crank case	Uncontrolled		$0.0003~g/hp-hr^{\circ}$	E
22-70-008-005	Diesel, exhaust	Uncontrolled		0.025 g/hp-hr°	Е
Aircraft Support Equipment	Diesel, crank case	Uncontrolled		0.0003 g/hp-hr 0.019 g/hp-hr 0.0003 g/hp-hr 0.019 g/hp-hr 0.019 g/hp-hr 0.019 g/hp-hr 0.019 g/hp-hr 0.0003 g/hp-hr 0.019 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.0003 g/hp-hr 0.0003 g/hp-hr 0.0005 g/hp-hr 0.0005 g/hp-hr 0.0005 g/hp-hr	E
22-70-008-010	Diesel, exhaust	Uncontrolled		0.025 g/hp-hr°	Е
Terminal Tractors	Diesel, crank case	Uncontrolled		0.019 g/hp-hr 0.0003 g/hp-hr 0.019 g/hp-hr 0.0003 g/hp-hr 0.019 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.0003 g/hp-hr 0.0003 g/hp-hr 0.0003 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.013 g/hp-hr 0.0005 g/hp-hr 0.0005 g/hp-hr 0.0005 g/hp-hr	E
22-82-005-005 Vessels w/Inboard Engines	2-stroke gas, exhaust	Uncontrolled		11.358 g/gal ⁿ	Е

SCC/AMS Code and			Emissio	on Factor ^a	— Factor
Description	Emissions Source	Control Device	Range ^b	Mean	Rating
22-82-005-010 Vessels w/Outboard Engines	2-stroke gas, exhaust	Uncontrolled		11.358 g/gal ⁿ	Е
22-82-005-015 Vessels w/Sterndrive Engines	2-stroke gas, exhaust	Uncontrolled		11.358 g/gal ⁿ	Е
22-82-005-025 Sailboat Auxiliary Outboard Engines	2-stroke gas, exhaust	Uncontrolled		11.358 g/gal ⁿ	Е
22-82-010-005 Vessels w/Inboard Engines	4-stroke gas, exhaust	Uncontrolled		1.413 g/gal ⁿ	Е
22-82-010-010	4-stroke gas, exhaust	Uncontrolled		1.71 g/gal ⁿ	Е
Vessels w/Outboard Engines	4-stroke gas, crank case	Uncontrolled		0.376 g/gal ⁿ	E
22-82-010-015 Vessels w/Sterndrive Engines	4-stroke gas, exhaust	Uncontrolled		1.413 g/gal ⁿ	Е
22-82-010-020 Sailboat Auxiliary Inboard Engines	4-stroke gas, exhaust	Uncontrolled		1.413 g/gal ⁿ	Е
22-82-010-025	4-stroke gas, exhaust	Uncontrolled		1.71 g/gal ⁿ	Е
Sailboat Auxiliary Outboard Engines	4-stroke gas, crank case	Uncontrolled		0.376 g/gal ⁿ	E
22-82-020-005 Vessels w/Inboard Engines	Diesel, exhaust	Uncontrolled		0.39 g/gal	E

TABLE A-1. CONTINUED

SCC/AMS Code and			Emission Factor ^a		
Description Description	Emissions Source	Control Device	Range ^b	Mean	Factor Rating
22-82-020-010	Diesel, exhaust	Uncontrolled		0.39 g/gal	Е
Vessels w/Outboard Engines	Diesel, crank case	Uncontrolled		0.008 g/gal	Е
22-82-020-015 Vessels w/Sterndrive Engines	Diesel, exhaust	Uncontrolled		0.39 g/gal	E
22-82-020-020 Sailboat Auxiliary Inboard Engines	Diesel, exhaust	Uncontrolled		1.959 g/gal	E
22-82-020-025	Diesel, exhaust	Uncontrolled		1.959 g/gal	Е
Sailboat Auxiliary Outboard Engines	Diesel, crank case	Uncontrolled		0.039 g/gal	Е
26-10-030-000 Yard Waste	Biomass burning	Uncontrolled		0.40 lb/ton (0.198 g/kg)	U4
28-01-500-000 Land Clearing/Burning	Biomass burning	Uncontrolled		0.32 lb/ton (0.163 g/kg)	U4
28-10-001-000 Forest Fires	Fine wood	Uncontrolled		0.24 lb/ton (0.12 g/kg)	U4
	Small wood			0.24 lb/ton (0.12 g/kg)	U4
	Large wood (flaming)			0.24 lb/ton (0.12 g/kg)	U4
	Large wood (smoldering)			0.90 lb/ton (0.45 g/kg)	U4
	Live vegetation			0.52 lb/ton (0.26 g/kg)	U4

SCC/AMS Code and			Emiss	sion Factor ^a	Factor
Description Description	Emissions Source	Control Device	Range ^b	Mean	Rating
28-10-001-000	Duff (flaming)			0.24 lb/ton (0.12 g/kg)	U4
Forest Fires (continued)	Duff (smoldering)			0.90 lb/ton (0.45 g/kg)	U4
28-10-005-000 Slash (pile) Burning	Biomass burning	Uncontrolled		0.32 lb/ton (0.163 g/kg)	U4
28-10-015-000	Fine wood	Uncontrolled		0.24 lb/ton (0.12 g/kg)	U4
Prescribed Burning (Broadcast)	Small wood			0.24 lb/ton (0.12 g/kg)	U4
	Large wood (flaming)			0.24 lb/ton (0.12 g/kg)	U4
	Large wood (smoldering)			0.90 lb/ton (0.45 g/kg)	U4
	Live vegetation			0.52 lb/ton (0.26 g/kg)	U4
	Duff (flaming)			0.24 lb/ton (0.12 g/kg)	U4
	Duff (smoldering)			0.90 lb/ton (0.45 g/kg)	U4
28-10-040-000 Rocket engine testing	Mobile	Uncontrolled		0.14 lb/ton (0.057 kg/Mg)	С

^aFactors are generally expressed as lb (kg) butadiene emitted per ton (Mg) produced and tons (Mg) emitted per year, unless otherwise noted.

^bRanges are based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.

^cAssumes production capacity of 100 percent.

^dAssumes production capacity of 80 percent.

^eUpper value used to prevent disclosing confidential operating capacity.

^fAssumes production capacity of 81 percent.

^gOnly incomplete data on emissions were available, therefore, values underestimate emissions.

^hUpper value used to prevent disclosing confidential operating capacity.

ⁱLower end of range is for one solid waste stream; upper end includes solid waste, wastewater and contaminated cooling water.

^jTotal number of components is 79,430: 60 percent flanges, 29 percent liquid valves, 8 percent gas valves, and 3 percent all others combined.

^kData from two facilities are specific to the emulsion process; the third is assumed to use the same.

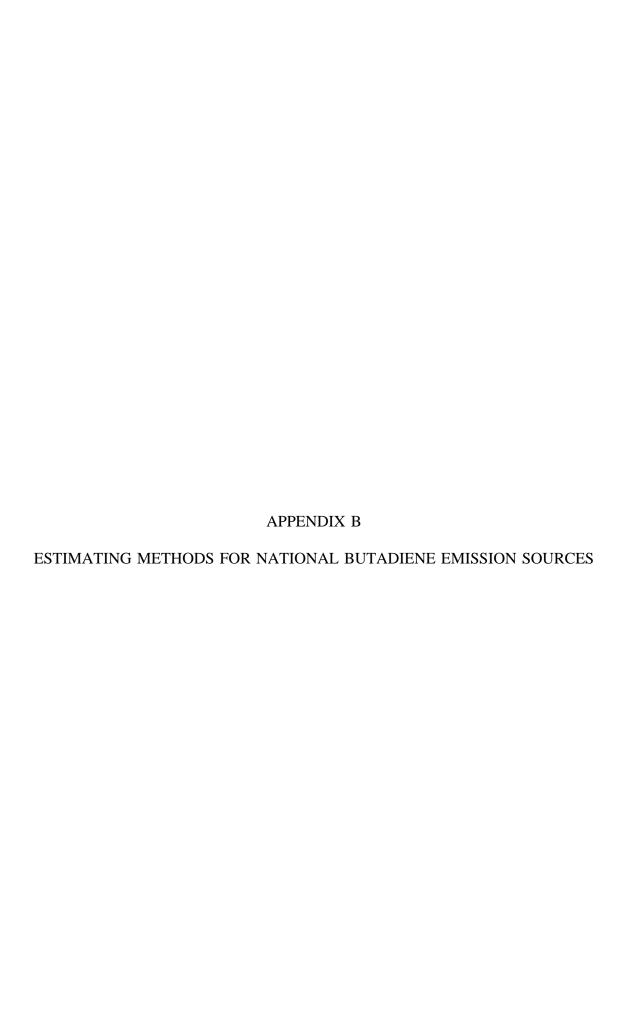
¹Adjusted for in-use effects using small utility engine data.

^mEmission factors for 4-stroke propane-fueled equipment.

ⁿAdjusted for in-use effects using heavy duty engine data.

°Exhaust HC adjusted for transient speed and/or transient load operation.

"---" means no data available.



EMISSIONS FROM ON-ROAD MOBILE SOURCES

Basis for Calculation

To estimate national butadiene emissions for this report, the butadiene emission factor presented in the MVATS¹ was used with VMT data from the Federal Highway Administration's *Highway Statistics 1992*.² This approach is similar to the one used to estimate emissions from on-road mobile sources for State Implementation Plan (SIP) inventories (*Procedures for Emission Inventory Preparation Volume IV: Mobile Sources*, 1992³). Table B-1 summarizes 1992 VMT data and butadiene emissions estimates for each State using the OMS's composite emission factor of 0.023 g of butadiene/mile.

Example Calculation

Annual Emissions = $(0.023 \text{ g butadiene/VMT}) \text{ x } (4.5762 \text{x} 10^{10} \text{ VMT}) \text{ x}$

for Alabama (1.10231136 ton/Mg)

= 1,161 ton of butadiene

TABLE B-1. 1992 ON-ROAD BUTADIENE EMISSIONS

State	1992 Vehicle Miles Travelled (millions)	Emissions in tons (Mg)
Alabama	45,762	1,161 (1,053)
Alaska	3,841	97 (88)
Arizona	35,047	888 (806)
Arkansas	23,081	584 (530)
California	262,548	6,657 (6,039)
Colorado	28,927	733 (665)
Connecticut	26,459	671 (609)
Delaware	6,892	175 (159)
Dist. of Columbia	3,562	90 (82)
Florida	114,311	2,898 (2,629)
Georgia	77,904	1,975 (1,792)
Hawaii	8,066	205 (186)
Idaho	10,764	273 (248)
Illinois	87,642	2,222 (2,016)
Indiana	57,072	1,447 (1,313)
Iowa	23,926	606 (550)
Kansas	24,163	613 (556)
Kentucky	38,062	965 (875)
Louisiana	33,853	859 (779)
Maine	12,151	308 (279)
Maryland	41,896	1,063 (964)
Massachusetts	47,348	1,200 (1,089)
Michigan	84,219	2,135 (1,937)
Minnesota	41,162	1,044 (947)
Mississippi	26,239	665 (603)
Missouri	53,254	1,350 (1,225)
Montana	8,525	216 (196)

(continued)

TABLE B-1. CONTINUED

State	1992 Vehicle Miles Travelled (millions)	Emissions in tons (Mg)
Nebraska	14,621	370 (336)
Nevada	10,897	277 (251)
New Hampshire	10,067	256 (232)
New Jersey	59,410	1,506 (1,366)
New Mexico	18,452	467 (424)
New York	109,881	2,786 (2,527)
North Carolina	67,538	1,712 (1,553)
North Dakota	6,072	154 (140)
Ohio	95,221	2,414 (2,190)
Oklahoma	35,119	891 (808)
Oregon	27,926	708 (642)
Pennsylvania	89,200	2,262 (2,052)
Rhode Island	7,676	195 (177)
South Carolina	35,049	888 (806)
South Dakota	7,218	183 (166)
Tennessee	49,994	1,268 (1,150)
Гexas	163,329	4,141 (3,757)
Utah	16,307	413 (375)
Vermont	6,019	152 (138)
Virginia	63,447	1,608 (1,459)
Washington	49,386	1,252 (1,136)
West Virginia	16,478	418 (379)
Wisconsin	47,628	1,207 (1,095)
Wyoming	6,217	158 (143)
Total	2,239,828	56,786 (51,517)

Source: Reference 2.

EMISSIONS FROM NON-ROAD MOBILE SOURCES

Basis for Calculation:

National emissions for butadiene were taken directly from the NEVES report.⁴ "In use" estimates for butadiene were taken from two inventories: A, which is an EPA-developed inventory; and B, which is an inventory prepared by trade associations. The values were averaged to calculate the national emission estimates.

Calculation:

Butadiene estimate for the:

A inventory - 47,816 tons/year

B inventory - 35,949 tons/year

National Annual Emissions =
$$\frac{47,816 + 35,949}{2}$$
$$= 41,883 \text{ tons/year}$$

EMISSIONS FROM AIRCRAFT

Basis for Calculation

To estimate national emissions from aircraft, hydrocarbon emission indices for representative fleet mixes are provided in the emissions inventory guidance document *Procedures for Emissions Inventory Preparation; Volume IV: Mobile Sources.*⁵ The hydrocarbon emission indices are 0.394 pounds per LTO (0.179 kg per LTO) for general aviation and 1.234 pounds per LTO (0.560 kg per LTO) for air taxis.

The butadiene fraction of the hydrocarbon total can be estimated by using the percent weight factors from SPECIATE.⁶ It is assumed in this report that half of the general aviation fleet is equipped with piston engines and the other half is equipped with turbine engines, such that these two emission factors are averaged. Because air taxis have larger engines and more of the fleet is equipped with turboprop and turbojet engines than is the general aviation fleet, the percent weight factor is somewhat different from the general aviation emission factor. To approximate a butadiene percent weight factor for air taxis, the commercial and general aviation (piston) percent weight factors were averaged.

Because there are no aggregated hydrocarbon emission indices for commercial or military aircraft, national emissions estimates for butadiene for these aircraft categories cannot be estimated without considerable detailed activity data (i.e., fleet mix and associated LTOs).

To estimate national butadiene emissions for general aviation and air taxis, FAA air traffic activity data⁷ (LTO) were applied to the hydrocarbon emission indices to estimate total national hydrocarbon emissions. The appropriate weight percent butadiene factor were applied to the total national hydrocarbon emission values, yielding the national butadiene emission estimate for general aviation and air taxis. These emission estimates are presented in Table 6-6. Note that in this approach emissions were estimated for aircraft airport activity

EMISSIONS FROM AIRCRAFT, CONTINUED

only; in-flight emissions cannot be calculated without considerable detailed data. In addition, this estimate does not include any aircraft activity occurring at non-FAA control towered airports.

Calculation - General Aviation

General Aviation

= (0.394 lbs hydrocarbon/LTO) x (ton/2,000 lbs) x

Emissions

(19,584,898 LTOs in 1993) x (1.57 weight % butadiene)

= 61 tons

Calculation - Air Taxis

Air Taxi Emissions = $(1.234 \text{ lbs hydrocarbon/LTO}) \times (\text{ton/2000 lbs}) \times (4,418,836 \text{ LTOs in})$

1993) x (1.69 weight % butadiene)

= 46 tons

<u>Calculation - Total</u>

National Butadiene

= 61 ton/yr of butadiene + 46 ton/yr of butadiene

Emissions Estimate

= 107 ton/yr of butadiene

EMISSIONS FROM BUTADIENE PRODUCTION

Basis for Calculation

The 1992 TRI data were used as an estimate of national emissions from butadiene production facilities.⁸ The TRI butadiene values (in lb/yr) reported by the 11 butadiene production facilities listed in Table 4-1 of this document were summed to give an estimate of the butadiene emissions from production facilities nationwide. The estimated national emissions of butadiene from butadiene production facilities are 191 tons/yr (163 Mg/yr).

EMISSIONS FROM MAJOR BUTADIENE USERS

Basis for Calculation

The 1992 TRI data were used to estimate national emissions from major butadiene users. All facilities with their primary SIC Codes reported as 28XX, industries within the Chemicals and Allied Products classification, were assumed to represent major users of butadiene. Some of the miscellaneous butadiene uses described in Section 7.0 may also be included, but because differentiating would be difficult and the contribution to national emissions from the miscellaneous uses is considered to be small, extracting these from the TRI data was not done.

The facility SIC Codes reported included the following:

- 28 Chemicals and allied products
- 2812 Alkalies and chlorine
- 2819 Industrial inorganic chemicals, nec
- 2821 Plastics materials, synthetic resins, and nonvulcanizable elastomers
- 2822 Synthetic rubber (vulcanizable elastomers)
- 2865 Cyclic organic crudes and intermediates, and organic dyes and pigments
- 2869 Industrial organic chemicals, nec
- 2879 Pesticides and agricultural chemicals, nec
- 2891 Adhesives and sealants
- 2899 Chemicals and chemical preparations, nec

To avoid double-counting butadiene production facility emissions (butadiene production facilities also fall under the 2869 SIC Code), the total for the 11 facilities (191 tons/yr (163 Mg/yr)) was subtracted from the total for the 28XX SIC Codes (1,596 tons/yr (1,448 Mg/yr)). The estimated national emissions of butadiene from major butadiene users are 1,405 tons/yr (1,275 Mg/yr).

EMISSIONS FROM MISCELLANEOUS OTHER BUTADIENE SOURCES

Basis for Calculation

The 1992 TRI data also included other source categories that were not otherwise identified as butadiene sources during the revision of this document.⁸ These facilities fall into one of the following SIC Codes. There were two facilities for which no SIC Code was reported, and one facility used an SIC Code, 2641, for which the 1987 Standard Industrial Classification Manual⁹ has no description.

- 2046 Wet corn milling
- 2369 Girl's, children's, and infant's outerwear, nec
- 2621 Paper mills
- 3312 Steel works, blast furnaces (including coke ovens), and rolling mills
- 3579 Office machines, nec
- 8731 Commercial physical and biological research

The butadiene emissions reported by each of these facilities were summed to total national emissions of butadiene from miscellaneous other butadiene sources of 106 tons/yr (96 Mg/yr).

EMISSIONS FROM PETROLEUM REFINING

Basis for Calculation

While the Petroleum Refineries NESHAP provides emissions estimates for VOCs and total HAPs at 190 facilities, emission estimates are not available for specific HAPs, such as butadiene. Therefore, 1992 TRI data were used as estimates of national emissions from petroleum refining. Petroleum refining is represented by SIC Code 2911. Based on the TRI data, the estimated national emissions of butadiene from petroleum refining are 219 tons/yr (241 Mg/yr).

EMISSIONS FROM SECONDARY LEAD SMELTING

Basis for Calculation

As part of the background information for developing the proposed and final NESHAP for the secondary lead smelting industry, emissions data were collected for 1,3-butadiene and other species of organic HAP during an EPA-sponsored test program at three representative smelters.¹¹ These data were used to calculate total controlled organic HAP emissions for each of the 23 secondary lead smelters known to exist in the United States.

The emission estimates assumed that organic HAP emissions from each smelter were controlled to the level required by the final NESHAP. Total estimated organic HAP emissions from this industry under the final NESHAP are 552 ton/yr (508 Mg/yr). The final NESHAP will reduce organic HAP emissions 71 percent from a 1990 baseline of 1,905 ton/yr (1,728 Mg/yr).

The emissions test data were also used to estimate a ratio of 1,3-butadiene to total organic HAP emissions for each of the three smelters for which test data were available:

ton 1,3-butadiene/ton organic HAP

East Penn Manufacturing Company:	0.337
Schuylkill Metals:	0.252
Tejas Resources:	0.131
Average:	0.240

The data from East Penn and Schuylkill are from blast furnaces and the data from Tejas are from a rotary furnace. The difference in ratios cannot be explained by any of the parameters that were monitored during the testing program or any of the differences in

EMISSIONS FROM SECONDARY LEAD SMELTING, CONTINUED

feed stocks used at these smelters; all three smelters used essentially the same feed stocks.

Example Calculation

National Emissions = (0.240 tons of 1,3-butadiene/ton organic HAP) x

Estimate (560 tons organic HAP/yr)

= 134.4 ton/yr (121.9 Mg/yr)

EMISSIONS FROM OPEN BURNING OF BIOMASS

Basis for Calculation

Emission factors for butadiene emissions from forest fires and prescribed burning were obtained from a 1993 Office of Research and Development project on Puget Sound and an inventory prepared by Darold Ward and Janice Peterson for the USDA Forest Service. ^{12,13} The emission factors vary according to fuel type (i.e., flaming versus smoldering wood or duff or live vegetation) and are presented in Section 7.0 of this document.

A national activity level for biomass burning (i.e., prescribed burning and forest fires) was obtained from a final report for the national emission inventories compiled for Section 112(c)(6) pollutants, prepared by Radian Corporation for the EPA.¹⁴ The total biomass burning in prescribed burning was documented as 42 million tons, and the total biomass burned in forest fires was documented as 53 million tons.¹⁴ Because no information was available to characterize, on a national basis, the percentages of the specific types of fuels burned in forest fires and prescribed burning, certain assumptions were made in calculating national emissions from the emission factors. The national estimate is calculated based on flaming wood and duff and smoldering wood and duff. It was assumed that, on a national basis, during prescribed burns and forest fires 75 percent of the biomass (wood and duff) is burned under flaming conditions and 25 percent of the biomass (wood and duff) is burned under smoldering conditions.

The following calculations were carried out to determine national butadiene emissions from forest fires. However, the national emissions from prescribed burning were obtained from a prescribed fire emissions inventory developed from Ward and Peterson's methodology.¹³

EMISSIONS FROM OPEN BURNING OF BIOMASS, CONTINUED

Example Calculation:

Annual = emissions from forest fires

National Emissions = $[(1.2 \times 10^{-4} \text{ tons/ton flaming wood and duff burned}) \times$

(39,750,000 tons flaming wood and duff burned in forest fires/yr)] +

[(4.5 x 10⁻⁴ tons/ton smoldering wood and duff burned) x (13,250,000 tons smoldering wood and duff burned in forest

fires/yr)]

= 10,733 tons/yr (9,737 Mg/yr)

Annual = emissions from prescribed burning

National Emissions = 9,198 tons/yr (8,345 Mg/yr)

Annual = emissions from biomass burning National Emissions = 10,733 tons/yr + 9,198 tons/yr

= 19,931 tons/yr (18,082 Mg/yr)

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APPENDIX C FACILITY-SPECIFIC EMISSIONS DATA FROM EPA SECTION 114 RESPONSES

APPENDIX C

FACILITY-SPECIFIC EMISSIONS DATA FROM EPA SECTION 114 RESPONSES

Tables C-1 through C-25 contain the capacity and emissions data that formed the basis for the emission factor ranges and ranges of annual emissions presented in the main text. Capacity data were compiled from responses to Section 114 requests or literature values if available. Most of the emissions data are from responses to Section 114 requests in 1984. Inconsistencies with the text are due to facility changes in ownership and/or in the production process since 1984. The emission values, therefore, may no longer reflect the current status of the industry. Furthermore, reported emissions were not supplied for every emission point identified, nor were all emission points identified by each facility.

Emission factors for each emission point were calculated by dividing the reported emissions by the facility's capacity, modified to reflect actual production. In instances where the use of facility production capacity in an emission factor might reveal company-confidential information, the emissions data were not used to calculate the ranges. In the absence of facility-reported capacity values, literature values may have been used.

Equipment leak emission estimates were derived from 1984 data supplied by facilities in Section 114 responses. Using the procedure described in Appendix D and average CMA emission factors, ranges of annual emissions were calculated. Equipment count data for the miscellaneous category were unavailable, therefore estimates are based on the SOCMI emission factors as reported in the summary memoranda.

TABLE C-1. BUTADIENE PRODUCTION FACILITIES FOR WHICH 1984 EMISSION DATA ARE AVAILABLE

Company	Location	Capacity in 1984 tons/yr (Mg/yr)
Amoco Chemicals Company	Chocolate Bayou, TX	90,400 (82,000) ^a
	Channelview, TX	350,500 (318,000)
Cain Chemical Company ^b	Chocolate Bayou, TX	67,200 (61,000) ^a
Cain Chemical Company ^c	Corpus Christi, TX	110,200 (100,000) ^a
Exxon Chemicals Company	Baton Rouge, LA	155,400 (141,000)
	Baytown, TX	120,200 (109,000)
Mobil Chemical Company	Beaumont, TX	29,800 (27,000) ^a
Shell Chemical Company	Deer Park, TX	400,100 (363,000)
	Norco, LA	250,200 (227,000)
Texas Chemical Company	Port Neches, TX	179,700 (163,000)
Texas Petrochemicals Corp.	Houston, TX	400,100 (363,000) ^d

Source: Reference 1.

^aValues taken from the literature.

^bFormerly DuPont de Nemours and Company.

^cFormerly El Paso Products Company.

 $^{^{\}rm d}$ 250,200 tons/yr (227,000 Mg/yr) from the recovery process, 149,900 tons/yr (136,000 Mg/yr) from the dehydrogenation process.

TABLE C-2. BUTADIENE EMISSIONS (1984) FROM PROCESS VENTS AT OLEFINS AND BUTADIENE PRODUCTION FACILITIES ¹

	C ₄ Stream Production Emissions in tons/yr (Mg/yr) ^a				overy Process Emin tons/yr (Mg/y	
Company	Uncontrolled	Controlled	Control Device	Uncontrolled	Controlled	Control Device
Facility A						Flare
Facility B			Flare			Flare
Facility C						Flare
Facility D	0.3 (0.3)	N/A	None			
Facility E				1.5 (1.4)	N/A	None
Facility F						Flare
Facility G				67.7 (61.4)	0.7 (0.6)	Boiler/Flare
Facility H ^d				68.8 (62.4)	5.5 (5.0)	Boiler/Flare

Source: Reference 1.

N/A means not applicable.

 $^{{}^{}a}C_{4}$ stream production means production of a mixed- C_{4} stream as a coproduct from the manufacturer of ethylene and other alkenes in an olefins plant.

^bRecovery process means recovery of butadiene from a mixed-C₄ stream.

^{&#}x27;The combination was assigned an overall efficiency of 99 percent.

^dSource of the mixed-C₄ stream is unknown.

^eReduction efficiency based on facility reported information.

[&]quot;---" means no data available.

TABLE C-3. SUMMARY OF BUTADIENE EMISSIONS (1987) FROM EQUIPMENT LEAKS AT NINE PRODUCTION FACILITIES

	Number of	Emissions ^a		
Equipment Component	Components	(tons/yr)	(Mg/yr)	
Pumps - liquid	376	74	67	
Compressors	17	0.0002	0.0002	
Flanges	47,277 ^b	51	46	
Valves - gas	6,315	24	22	
Valves - liquid	23,233	260	230	
Pressure relief devices	428	45	41	
Open-ended lines	1,744	0.73	0.67	
Sample points ^c	40	0.37	0.34	
Total:	79,430	460	410	

^aAssumes 80 percent of production capacity (taken as 8,760 hours of operations per year). Emissions rounded to two significant figures.

^bAlthough only 11,428 flanges were included in the study, a ratio of 1.6:1 flanges:valves is generally accepted. The total number of flanges upon which the emissions estimate is based is, therefore, $[(6,315+23,233) \times 1.6] = 47,277$.

^cEmission factor was taken from reference 1, p.5-16.

TABLE C-4. BUTADIENE EMISSIONS (1984) FROM SECONDARY SOURCES AT BUTADIENE PRODUCTION FACILITIES USING THE RECOVERY FROM A MIXED-C₄ STREAM PROCESS ¹

	Emissions in tons/yr (Mg/yr)		Controls/Dest	ination
Company	Wastewater	Solid Waste	Wastewater	Solid Waste
Facility B	Negligible	Negligible ^a		
Facility D	6.1 (5.5)		Emissions routed to flare, air strip or steam strip	Incineration
Facility E	0.03 (0.03)	Negligible	Emissions routed to flare, air strip or steam strip for recovery or to flare	Incineration
Facility G			Onsite NPDES, disposal wells	Offsite landfill
Facility H	18.1 (16.4)		Aeration lagoon	Offsite landfill
Facility I	0.18 (0.16)		Biological treatment	
Facility J	320 (290)		Biological treatment, discharge	
Facility K			Biological treatment	Landfill, disposal well

Source: Reference 1.

^aReported as "minor."

^bEstimated at 4.43 x 10⁻⁵ lb/yr (3.99 x 10⁻⁵ Mg/yr).

[&]quot;---" means no data available.

TABLE C-5. STYRENE-BUTADIENE ELASTOMER AND LATEX PRODUCTION FACILITIES FOR WHICH 1984 EMISSIONS DATA ARE AVAILABLE

Company	Location	Capacity in 1984 tons/yr (Mg/yr)
<u>Elastomer</u>		
American Synthetic ^a	Louisville, KY	111,200 ^b (100,000) ^b
B. F. Goodrich ^c	Port Neches, TX	d
Copolymer Rubber	Baton Rouge, LA	232,600 ^b (211,000) ^b
Firestone	Lake Charles, LA	$132,300^{b} (120,000)^{b}$
GenCorp	Odessa, TX	95,900 ^b (87,000) ^b
Goodyear	Houston, TX	d
Uniroyal ^c	Port Neches, TX	$201,700^{b} (183,000)^{b}$
<u>Latex</u>		
Borg-Warner ^e	Washington, WV	d
Dow Chemical	Dalton, GA	d
Dow Chemical	Freeport, TX	d
Dow Chemical	Gates Ferry, CT	d
Dow Chemical	Midland, MI	d
Dow Chemical	Pittsburgh, CA	d
GenCorp	Mogadore, OH	66,100 (60,000)
Goodyear ^e	Akron, OH	d
Goodyear	Calhoun, GA	d
W. R. Grace	Owensboro, KY	3,300 (3,000)
Polysar	Chattanooga, TN	167,500 (152,000)
Reichhold (DE)	Cheswold, DE	65,000 (59,000)
Reichhold (GA)	Kensington, GA	58,400 (53,000)
Unocal	La Mirada, CA	19,800 (18,000)

Source: Reference 2.

^aFacility was mothballed in 1984.

^bDry weight.

[°]B.F. Goodrich and Uniroyal are now Ameripol Synpol.

^dCompany-confidential.

^eFacility's operating status in 1988 unknown.

TABLE C-6. BUTADIENE EMISSIONS (1984) FROM PROCESS VENTS AT SB COPOLYMER PRODUCTION FACILITIES²

Company	Vent Location	Uncontrolled Emissions tons/yr (Mg/yr)	Controlled Emissions tons/yr (Mg/yr)	Control Device	Control Efficiency (%)
<u>Elastomer</u>					
Facility A	Recovery process	29 (26)	2.9 (2.6)	Absorber	90
Facility B	Butadiene recovery	463 (420)	23.1 (21.0)	Kerosene absorber	95
Facility C	Butadiene absorber vent	22 (20)	$0.02 (0.02)^a$	Boiler	99.9
Facility D	Tank farm, purification reactor, desolventization	88 (80) ^b	1.8 (1.6) ^b	Flare	98 °
Facility E	Recovery area absorber vent	4.7 (4.3)	0.7 (0.6)	Absorber	86
Facility F	Process vessels (storage blending, coagulation, crumb washing)	66 (60.0) ^a	N/A	None	0
	Dryers	11 (10.0) a	N/A	None	0
Facility G	Butadiene recovery	139 (126)	7.0 (6.3) ^b	Kerosene scrubbers	95
<u>Latex</u>					
Facility H	Latex A1	127 (115)	N/A	None	0
	Latex A2	127 (115)	N/A	None	0
	Latex B	518 (469.8)	44.5 (40.4)	Pressure condenser	91.4
Facility I	Vent stack	d	285 (259)	d	d
Facility J	Monomer mix tanks, recovery tank	d	11.4 (10.3)	d	d

<u>-</u>

TABLE C-6. CONTINUED

Company	Vent Location	Uncontrolled Emissions tons/yr (Mg/yr)	Controlled Emissions tons/yr (Mg/yr)	Control Device	Control Efficiency (%)
<u>Elastomer</u>					
Facility K	Reactors, strippers	d	10.8 (9.8)	d	d
Facility L	Process scrubber	d	30.0 (27.0)	d	d
	Latex process	d	5.3 (4.8)		
Facility M	Latex process and tanks	d	5.6 (5.1)	d	d
Facility N	Central vacuum flare stack	628 (570)	12.6 (11.4)	Flare	98
	Latex stripping	0.6 (0.5)	N/A	None	0
Facility O	Butadiene recovery	36 (33)	3.7 (3.3)	Condenser	90
Facility P	Vent gas absorber	17 (15)	0.3 (0.3)	Scrubber	98
Facility Q	Reactor	104.7 (95.0)	N/A	None	0
	Mix tank	20.1 (18.2)	N/A	None	0
Facility R	Reactor recovery storage	5.5 (5.0)	0.1 (0.1)	Flare	e 98
	Recycle butadiene receiver	15.4 (14.0)	N/A e	None	0
	Stripping vacuum pump exhaust	45.0 (40.8)	N/A	None	0
Facility S	Process	325 (295)	6.5 (5.9)	Flare	98

TABLE C-6. (CONTINUED)

Company	Vent Location	Uncontrolled Emissions tons/yr (Mg/yr)	Controlled Emissions tons/yr (Mg/yr)	Control Device	Control Efficiency (%)
<u>Elastomer</u>					
Facility T	Waste vent gas	60 (54.0)	N/A	None	0
	Vacuum pump discharge	226.3 (205.3)	N/A	None	0
	Stream jet discharge	11.9 (10.8)	N/A	None	0
Facility U	Unknown	Unknown	Unknown	Incineration	Unknown

Source: Reference 2.

N/A = not applicable.

^aEmissions shown are for both SB copolymer and nitrile rubber production.

^bEmissions shown are for both SB copolymer and polybutadiene production.

^cFacility reported a higher efficiency but did not support it with test data. ^dInformation for facilities on control devices is considered confidential.

^eEstimates exclude reported emissions for pressure relief discharges of 0.1 tons/yr (0.1 Mg/yr).

TABLE C-7. BUTADIENE EMISSIONS (1984) FROM EQUIPMENT LEAKS AT SB COPOLYMER PRODUCTION FACILITIES

	Uncontrolled Emissions ^a	
Company	tons/yr (Mg/yr)	Control Status
<u>Elastomer</u>		
Facility A	6.2 (5.6)	PRDs vented to a flare
Facility B	8.5 (7.7)	Rupture discs for PRDs
Facility C	14.3 (13) ^b	Rupture discs
Facility D	4.0 (3.6)	Rupture discs and flare for PRDs
Facility E	74 (67)	None reported
Facility F	23 (21) ^b	Rupture discs and flare for PRDs
Facility G	14 (13) ^c	Most PRDs have rupture discs vented
<u>Latex</u>		
Facility H	15 (14)	None reported
Facility I	5.0 (4.5)	None reported
Facility J	1.5 (1.4)	None reported
Facility K	0.98 (0.89)	None reported
Facility L	2.9 (2.6)	Some rupture discs
Facility M	2.1 (1.9)	Rupture discs
Facility N	5.8 (5.3)	None reported
Facility O	4.6 (4.2)	Rupture discs for PRDs
Facility P	4.7 (4.3)	None reported
Facility Q	0.11 (0.10)	None reported
Facility R	14 (13)	Some rupture discs
Facility T	2.2 (2.0)	Most PRDs have rupture discs

Source: References 2 and 3.

PRDs= Pressure relief devices.

^aCalculated using 1984 equipment counts and average CMA emission factor. Emissions rounded to two significant figures.

^bThe emissions are for both SB copolymer and nitrile rubber production.

^cThe emissions are for both SB copolymer and polybutadiene production.

TABLE C-8. BUTADIENE EMISSIONS (1984) FROM SECONDARY SOURCES AT SB COPOLYMER PRODUCTION FACILITIES ²

	Emis	ssions in tons/yr (Mg/yr)		
Company	Wastewater	Other Liquid Waste	Solid Waste	Waste Treatment
Elastomer				
Facility A	0	0	0	None
Facility B	0.4 (0.4)			Landfill, primary and secondary treatment
Facility C	0.9 (0.8) a	a	0.0007 (0.0006)	^a Biotreafment, incineration, landfill
Facility D	0	0	0	Unknown
Facility E	13.8 (12.5) ^a	a	2.2 (2.0)	^a Biotreatment, landfill
Facility G	0		0	Unknown
<u>Latex</u>				
Facility H	0	0	0	Unknown
Facility I	0		0	NPDES permit, landfill
Facility J	0		0	Unknown
Facility K	0	0.008 (0.007)	0	 Biotreatment incineration of liquid waste, landfarm solids
Facility L	0		0	Biotreatment, landfill
Facility M	0			Solar pond
Facility N	0.00002 (0.00002)			Equalization, settling, discharge to POTW

TABLE C-8. CONTINUED

	Emissions in tons/yr (Mg/yr) from:			
Company	Wastewater	Other Liquid Waste	Solid Waste	Waste Treatment
Elastomer				
Facility O	14.4 (13.1) ^c	c c	c	Discharge to POTW
Facility P	8.6 (7.8)			Aerated lagoon
Facility Q	Negligible	d		Biotreatment, aerated lagoon
Facility R	26.4 (24.0)			City sewer
Facility T	Negligible	d Negligibled	Negligible ^d	Biotreatment

Source: Reference 2.

^aEmissions are for both SB copolymer and nitrile rubber production.

^bEmissions occur off-site from an incinerator stack.

^cFacility did not report emissions separately for each of the four production processes on-site. ^dOnly trace amounts of butadiene reported in waste. ^eFacility had two units in production; waste treatment at Unit #2 is confidential.

[&]quot;---" means no information available on the source.

TABLE C-9. POLYBUTADIENE PRODUCTION FACILITIES FOR WHICH 1984 EMISSIONS DATA ARE AVAILABLE

Company	Location	Capacity in 1985 tons/yr (Mg/Yr)
American Synthetic Rubber	Louisville, KY	69,400 ^a (63,000) ^a
Arco Chemical ^b	Channelview, TX	7,500 (6,800)
Borg-Warner	Ottawa, IL	c
Firestone	Orange, TX and Lake Charles, LA ^d	121,300 ^a (110,000) ^a
Goodyear	Beaumont, TX	c
Phillips	Borger, TX	70,500 ^a (64,000) ^a
Polysar	Orange, TX	c

Source: Reference 4.

^aValue taken from the literature.

^bFacility's operating status in 1988 unknown.

^cCompany confidential.

^dFacility coproduced SBS elastomer and polybutadiene rubber, but was primarily dedicated to SB elastomer.

TABLE C-10. BUTADIENE EMISSIONS (1984) FROM PROCESS VENTS AT POLYBUTADIENE PRODUCTION FACILITIES⁴

Company	Vent Locations	Uncontrolled Emissions tons/yr (Mg/yr)	Controlled Emissions tons/yr (Mg/yr)	Control Device	Control Efficiency (%)
Facility A	Recovery process	0.09 (0.08)	0.002 (0.002)	Butadiene absorber, flare	97.5
Facility B	Acetone column vent	36.5 (33.1)	N/A	None	N/A
	Vacuum system vent	73.0 (66.2)	N/A	None	N/A
Facility C	Flashers	48.9 (44.4)	4.4 (4.0)	Butadiene recovery	91
Facility D	Plantwide	22.0 (20)	0.4 (0.4)	Flare	98
Facility E	Two plant vents	568 (515)	11.4 (10.3)	Flare	98
Facility F	Polymerization reactors	5.5 (5)	0.1 (0.1)	Flare	98
	Kerosene scrubbing	27.6 (25)	0.6 (0.5)	Flare	98

Source: Reference 4.

^aCompany reported greater than 98-percent control efficiency, but did not provide supporting test data.

N/A = not applicable.

TABLE C-11. BUTADIENE EMISSIONS (1984) FROM EQUIPMENT LEAKS AT POLYBUTADIENE PRODUCTION FACILITIES

Company	Uncontrolled Emissions tons/yr (Mg/Yr) ^a
Facility A	4.1 (3.7)
Facility B	5.8 (5.3)
Facility D	32.0 (29)
Facility E	10.5 (9.5)
Facility F	5.7 (5.2)
Facility G	4.9 (4.4)

Source: References 3 and 4.

^aCalculated using 1984 equipment counts and average CMA emission factors. Emissions rounded to two significant figures.

TABLE C-12. BUTADIENE EMISSIONS (1984) FROM SECONDARY SOURCES AT POLYBUTADIENE PRODUCTION FACILITIES

	Source tons/yr (Mg/yr)		
Company	Wastewater	Solid Waste	Waste Treatment
Facility B		0	Landfill
Facility C	0	a	Activated sludge
Facility F	21.3 (19.3)		Lagoon

Source: Reference 4.

^aFacility listed solid waste as a source but provided no data.

[&]quot;---" means no data available.

TABLE C-13. ADIPONITRILE PRODUCTION FACILITIES FOR WHICH 1984 EMISSIONS DATA ARE AVAILABLE

Facility	Location	Capacity in 1984 tons/yr (Mg/Yr)
DuPont	Orange, TX	231,500 (210,000) ^a
DuPont	Victoria, TX	146,500 (132,900)

Source: Reference 5.

^aValue taken from the literature.

TABLE C-14. BUTADIENE EMISSIONS (1984) FROM PROCESS VENTS AT ADIPONITRILE PRODUCTION FACILITIES⁵

Company	Vent Location	Uncontrolled Emissions tons/yr (Mg/yr)	Controlled Emissions tons/yr (Mg/yr)	Control Device	Control Efficiency (%)
Facility A	Recycle purge	540.1 (490)	10.8 (9.8)	Flare	98
	Butadiene dryer			Boiler	
Facility B	Recycle purge	363.8 (330)	7.3 (6.6)	Flare	98
	Butadiene dryer	4.9 (4.4)	0.004 (0.004)	Boiler	99.9
	Jets			Boiler	99.9
	Second reactor			Boiler	99.9
	Refining			Boiler	99.9

Source: Reference 5.

^aFacility reported a higher efficiency but did not provide supporting test data.

[&]quot;---" means no data available.

TABLE C-15. BUTADIENE EMISSIONS (1984) FROM EQUIPMENT LEAKS AT ADIPONITRILE PRODUCTION FACILITIES

Company	Uncontrolled Emissions tons/yr (Mg/yr) ^a	Controls
Facility A	5.3 (4.8)	Ambient monitoring, ^b double mechanical seals, some PRDs routed to a flare.
Facility B	2.8 (2.5)	Quarterly LDAR, ambient monitoring, double mechanical seals.

Source: References 3 and 5.

PRDs = pressure relief devices.

LDAR = leak detection and repair program.

^aCalculated using 1984 equipment counts and average CMA emission factors. Emissions rounded to two significant figures.

^bAmbient monitoring in the vicinity was being used to detect elevated VOCs, potentially indicating leaks.

TABLE C-16. BUTADIENE EMISSIONS (1984) FROM SECONDARY SOURCES AT ADIPONITRILE PRODUCTION FACILITIES

Facility	Source Description	Uncontrolled Emissions tons/yr (Mg/Yr)
Facility A	Waste tank	2.2 (2.0)
	Butadiene separator blowdown water	
Facility B	Sump tank ^a	
	Waste liquids ^a	
	Wastewater	1.0 (0.9)

Source: Reference 5.

^aSource was routed to a boiler with a 99.9-percent reduction efficiency.

[&]quot;---" means no data reported.

TABLE C-17. CHLOROPRENE/NEOPRENE PRODUCTION FACILITIES FOR WHICH 1984 EMISSIONS DATA ARE AVAILABLE

Company	Capacity in 1985 ^a tons/yr (Mg/Yr)
Denka	37,500 (34,000)
DuPont	47,400 (43,000)

^aValues taken from the literature.

TABLE C-18. BUTADIENE EMISSIONS (1984) FROM NEOPRENE PRODUCTION FACILITIES⁶

		Process Vent tons/yr (_	Control	Equipment Leaks -
Company	Vent Location	Uncontrolled	Controlled	Control Device	Efficiency (%)	Uncontrolled ^a tons/yr (Mg/yr)
Facility A	DCB refining	5.3 (4.8)	N/A	None	0	1.03 (0.93)
	DCB refining	0.96 (0.87)	0.1 (0.1)	Absorber/-20°F condenser	88.6	
	DCB refining	1.06 (0.96)	0.6 (0.5)	-20°F condenser	48.0	
Facility B	DCB refining	176 (160)	N/A	Water-cooled condenser	0	4.9 (4.4)
	DCB synthesis	397 (360)	7.9 (7.2)	Flare	98	

^aCalculated using 1984 equipment counts and average CMA emission factors. Emissions rounded to two significant figures. ^bCompany estimated a higher efficiency but did not provide supportive data.

N/A = Not applicable.

TABLE C-19. ACRYLONITRILE-BUTADIENE-STYRENE RESIN PRODUCTION FACILITIES FOR WHICH 1984 EMISSIONS DATA ARE AVAILABLE

Company	Location	Capacity in 1985 ^a tons/yr (Mg/Yr)
Goodyear ^b	Akron, OH	165 (150)
Monsanto	Addyston, OH	177,500 (161,000)
Monsanto	Muscatine, IA	57,500 (52,200)

^aValues taken from the literature.

^bGoodyear coproduced ABS with nitrile elastomer. About 3 percent was dedicated to production.

TABLE C-20. BUTADIENE EMISSIONS (1984) FROM ABS PRODUCTION FACILITIES 7

	Process Vent Emission tons/yr (Mg/yr)			-	Control	Equipment Leaks -	
Company	Vent Location	Uncontrolled	Controlled	Control Device	Efficiency (%)	Uncontrolled tons/yr (Mg/yr)	
Facility A	Spray dryer	0.9 (0.8)	N/A	None	0	Unknown	
	Dewatering (1)	Unknown	N/A	None	0		
Facility B	Polymerization (9)	661 (500)	0.6 (0.5)	Flare	99.9	3.5 (3.2)	
	Dewatering (1)	<11 (<10)	<0.01 (<0.01)	Boiler	99.9		
	Dewatering (1)	2.1 (1.9)	N/A	None	0		
	Dewatering (1)	2.1 (1.9)	N/A	None	0		
	Tanks (3)	10.0 (9.0)	N/A	None	0		
	Tanks (6)	Unknown	Unknown	Unknown	Unknown		
	Coagul/Wash (7)	Unknown	Unknown	Unknown	Unknown		
	Compounding (9)	0	N/A	None	0		
Facility C	Polymerization (1)	276 (250)	2.8 (2.5)	Flare	99	1.2 (1.1)	
	Polymerization (1)	6.8 (6.2)	N/A	None	0		

(Continued)

TABLE C-20. CONTINUED

		Process Ven tons/yr (_	Control	Equipment Leaks - Uncontrolled
Company	Vent Location	Uncontrolled	Controlled	Control Device	Efficiency (%)	tons/yr (Mg/yr)
	Coagul/Wash (2)	18.5 (16.8)	N/A	None	0	
	Dewatering (4)	10.7 (9.7)	N/A	None	0	
	Compounding (1)	6.9 (6.3)	N/A	None	0	
	Tanks (5)	6.2 (5.6)	N/A	None	0	

^aNumber in parenthesis indicates number of vents.

^bCalculated from 1984 equipment counts and average CMA emission factors. Emissions rounded to two significant figures.

TABLE C-21. NITRILE ELASTOMER PRODUCTION FACILITIES FOR WHICH 1984 EMISSIONS DATA ARE AVAILABLE

Company	Location	Capacity in 1985, dry rubber or latex tons/yr (Mg/Yr)
B. F. Goodrich ^a	Akron, OH	0
Copolymer	Baton Rouge, LA	$7,500^{\rm b} (6,800)^{\rm b}$
Goodyear	Houston, TX	17,600 (16,000)
Goodyear ^c	Akron, OH	5,500 (5,000)
Sohio ^d	Lima, OH	e
Uniroyal Chemical Co.	Painesville, OH	18,000 (16,300)

 $^{^{\}mathrm{a}}$ B. F. Goodrich closed its NBR facility in 1983. Facility still produced 8,377 tons/yr (7,600 Mg/yr) of vinyl pyridine.

^bValue taken from the literature.

^cFacility also produced about 165 tons/yr (150 Mg/yr) of ABS copolymer (3 percent of production).

^dFacility's operating status in 1988 unknown.

^eCompany confidential.

TABLE C-22. BUTADIENE EMISSIONS (1984) FROM NITRILE ELASTOMER PRODUCTION FACILITIES 7

		Process Vent Emissions tons/yr (Mg/yr)		_	Control	Equipment Leaks -
Company	Vent Location	Uncontrolled	Controlled	Control Device	Efficiency (%)	Uncontrolled ^b tons/yr (Mg/yr)
Facility A	Process A (46)	60.6 (55)	2.4 (2.2)	Boiler	96	
Facility B ^c	Butadiene absorber	<0.07 (<0.06)	<0.001 (<0.001)	Boiler	99+	18.7 (17)
Facility C ^d	Blowdown tank (1)	35.3 (32)	3.5 (3.2)	Condenser	90	
	Coagulator (1)	42.3 (38.4)		Chemical treatment	Unknown	
	Building (1)	3.2 (2.9)		None	0	
	Screening (1)			Chemical treatment	Unknown	
	Dewatering (1)			None	0	
	Dryer (2)			None	0	
Facility D ^f	Reactor (1)			Flare	99.9	
	Absorber (1)			Flare	99.9	
	Distillation (1)			Flare	99.9	
	Screen/coagulation (2)	16.5 (15)	1.7 (1.5)	Steam stripper for acrylonitrile	90	
Facility E	Reactor (1)	220.0 (200)	0.2 (0.2)	Thermal oxidation	99.9	0.43 (0.39)

TABLE C-22. CONTINUED

		Process Vent Emissions tons/yr (Mg/yr)		_	Control Efficiency	Equipment Leaks - Uncontrolled ^b
Company	Vent Location	Uncontrolled	Controlled	Control Device	(%)	tons/yr (Mg/yr)
Facility Fg	Recycle receiver (1)	3.3 (3.0)	0.36 (0.33)	Scrubber	89	7.2 (6.5)
	Steam jets (2)			Steam stripper for acrylonitrile	90	
	Dryer (1)			Steam stripper for acrylonitrile	90	
	Tanks (8)			Steam stripper for acrylonitrile	90	

^aNumber in parentheses indicates the number of vents of this type.

^bCalculated from 1984 equipment counts and average CMA emission factors. Emissions rounded to two significant figures.

^cFacility was also an SB copolymer producer; total facility emissions were reported. Emissions apportioned to NBR production based on percent production resulting in nitrile elastomer--3 percent.

^dFacility was also an ABS copolymer producer; total facility emissions were reported. Emissions apportioned to NBR production based on percent production resulting in nitrile elastomer--97 percent.

^eChemical treatment destroys residual acrylonitrile. The effect on butadiene is not known.

^fOnly equipment leaks emissions were apportioned using percent of capacity dedicated to nitrile elastomer.

^gFacility was also an SB copolymer producer; total facility emissions were reported. Emissions apportioned to NBR production based on percent production resulting in nitrile elastomer--5 percent.

[&]quot;---" means no data available.

TABLE C-23. MISCELLANEOUS USES OF BUTADIENE FOR WHICH EMISSIONS DATA ARE AVAILABLE $^{\rm 5}$

Company	Location	Product	Mode of Operation	1986 Design Capacity tons/yr (Mg/yr)
ArChem Company	Houston, TX	Tetrahydrophthalic (THP) Anhydride	Batch	568 (515)
B. F. Goodrich Company	Akron, OH	Butadiene-vinylpyridine Latex	Batch (on demand)	Unknown
Denka (Mobay Synthetics Corporation)	Houston, TX	THP Acid	Batch	1,650 (1,500)
DuPont	Beaumont, TX	1,4-Hexadiene	Continuous	a
DuPont	Victoria, TX	Dodecanedioic Acid	Continuous (2 weeks per month due to low demand)	a
Kaneka Texas Corporation	Bayport, TX	MBS Resins	Batch	14,300 (13,000)
Phillips Chemical Company	Borger, TX	Butadiene Cylinders	Batch	535 (485)
		Butadiene-furfural Cotrimer ^c	Continuous, intermittent, about 65% of the time	50 (45)
		Sulfolane	Batch	Unknown
Rohm and Haas Company	Louisville, KY	MBS Resins	Batch	a
Shell Oil Company	Norco, LA	Sulfolane	Unknown	Unknown
Union Carbide	Institute, WV	Butadiene Dimers	Continuous	7,200 (6,500)

^aCompany confidential.

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TABLE C-24. BUTADIENE EMISSIONS FROM PROCESS VENTS ASSOCIATED WITH MISCELLANEOUS USES OF BUTADIENE 5,8,9

Chemical Produced	Company	Vent Location	Uncontrolled Emissions tons/yr (Mg/yr)	Controlled Emissions tons/yr (Mg/yr)	Control Device	Control Efficiency (%)
Butadiene cylinders	Facility A	Process vents	11.6 (10.5)	N/A	None	0
Butadiene dimers	Facility B	Feedpot, recycle pot, reactor, and three recovery stills	5.6 (5)	0.1 (0.1)	Flare	98
Butadiene-furfural cotrimer	Facility A	Reactor	Unknown	0	By-product butadiene dimer recovery	100
		Crude storage	10.9 (9.9)	N/A	None	0
Butadiene-	Facility C	Process vents	353 (320)	0.35 (0.32)	Boiler	99.9
vinylpyridine latex		Dryer	6.6 (6.0)	N/A	None	0
Dodecanedioic	Facility D	Butadiene dryer + two jets	<110 (<100)	<0.1 (<0.1)	Boiler	99.9
acid		Reactor	220 (200)	0.2 (0.2)	Boiler	99.9
1,4-Hexadiene	Facility E	Knockout pot	27.2 (24.7)	N/A	None	0
		Reactor, stripper, recycle condenser	Unknown	Unknown	Abatement collection system for waste liquids and vapors routed to a boiler	99.9
Methyl	Facility F	Reactor	110 (100)	0.1 (0.1)	Boiler	99.9
methacrylate-		Coagulator	6.6 (6.0)	N/A	None	0
butadiene-styrene resins		Dryer	6.6 (6.0)	N/A	None	0
	Facility G	Reactor	1.0 (0.9)	N/A	None	0

TABLE C-24. CONTINUED

Chemical Produced	Company	Vent Location	Uncontrolled Emissions tons/yr (Mg/yr)	Controlled Emissions tons/yr (Mg/yr)		Control Device	Control Efficiency (%)
Sulfolane	Facility H	Reactant recycle accumulator	1.73 (1.57)	0.034 (0.031)	Flare		98
		Light ends stripper	7.57 (6.87)	0.15 (0.14)	Flare		98
Sulfolane	Facility A	Caustic scrubber	99 (90)	N/A	None		0
		Sulfolene flakes caustic scrubber	32.3 (29.3)	N/A	None		0
		Sulfolane reactor	0	N/A	None		0

Sources: References 5, 8, and 9.

TABLE C-25. BUTADIENE EMISSIONS FROM EQUIPMENT LEAKS ASSOCIATED WITH MISCELLANEOUS USES OF BUTADIENE 5,8,9

Chemical Produced	Company	Uncontrolled Emissions tons/yr (Mg/yr)	Controlled Emissions tons/yr (Mg/yr)	Controls	Control Efficiency (%)
Butadiene cylinders	Facility A	<0.1 (<0.1)	N/A	None	0
Butadiene dimers	Facility B	4.3 (3.9)		Ambient monitoring, double mechanical seals	0, 100
Butadiene-furfural cotrimer	Facility A	0.6 (0.5)		Rupture discs c c	100
Butadiene-vinylpyridine latex	Facility C	Unknown	0.61 (0.55)	Quarterly LDAR, some rupture discs	32, 100
1,4-Hexadiene	Facility D	67.7 (61.4)	59.3 (53.8)	Some double mechanical seals, some rupture discs, some closed sampling	e
Dodecanedioic acid	Facility E	5.7 (5.2)		Visual inspections	0
Methyl methacrylate-butadiene-	Facility F	4.0 (3.6)		Unknown	
styrene resins	Facility G	17.4 (15.8)		Ambient monitoring	0

TABLE C-25. CONTINUED

Chemical Produced	Company	Uncontrolled Emissions tons/yr (Mg/yr)	Controlled Emissions tons/yr (Mg/yr)	Controls	Control Efficiency (%)
Sulfolane	Facility A	14.7 (13.3)	N/A	None	0
	Facility H	1.8 (1.6)	N/A	None	0
Tetrahydrophthalic anhydride/acid	Facility I	2.4 (2.2)		Visual inspections	0

Source: References 5, 8, and 9.

LDAR = leak detection and repair program.

^aExcludes pumps with double mechanical seals.

^bAmbient monitoring in the vicinity was being used to detect elevated VOC levels, a potential indication of equipment leaks.

^eExcludes pressure relief devices since all are controlled.

^dExcludes pumps with double mechanical seals and closed sampling ports.

^eEach control is 100-percent effective; however, not all components are controlled, so overall reduction is not equal to 100 percent.

^fFor visual inspections, no reduction was given due to inadequate information.

[&]quot;---" means no data available.

REFERENCES FOR APPENDIX C

- 1. Memorandum from K. Q. Kuhn and R. A. Wassel, Radian Corporation, to the Butadiene Source Category Concurrence File, March 25, 1986. "Estimate of 1,3-Butadiene Emissions from Production Facilities and Emissions Reductions Achievable with Additional Controls."
- 2. Memorandum from R. A. Wassel and K. Q. Kuhn, Radian Corporation, to the Butadiene Source Category Concurrence File, April 8, 1986. "Estimates of 1,3-Butadiene Emissions from Styrene-Butadiene Copolymer Facilities and Emissions Reductions Achievable with Additional Controls."
- 3. Randall, J. L. et al., April 1989. Fugitive Emissions from the 1,3-Butadiene Production Industry: A Field Study, Final Report. Radian Corporation. Prepared for the 1,3-Butadiene Panel of the Chemical Manufacturers Association. p. 5-11.
- 4. Memorandum from E. P. Epner, Radian Corporation, to the Butadiene Source Category Concurrence File, March 27, 1986. "Estimates of 1,3-Butadiene from Polybutadiene Facilities and Emissions Reductions Achievable with Additional Controls."
- 5. Memorandum from K. Q. Kuhn and R. C. Burt, Radian Corporation, to the Butadiene Source Category Concurrence File, December 12, 1986. "Estimates of 1,3-Butadiene Emissions from Miscellaneous Sources and Emissions Reductions Achievable with Candidate NESHAP Controls."
- 6. Memorandum from E. P. Epner, Radian Corporation, to L. B. Evans, U.S. Environmental Protection Agency, Chemicals and Petroleum Branch, December 23, 1985. "Estimates of 1,3-Butadiene Emissions from Neoprene Facilities and Emissions Reductions Achievable with Additional Controls."
- 7. Memorandum from R. Burt and R. Howle, Radian Corporation, to L. B. Evans, U.S. Environmental Protection Agency, Chemicals and Petroleum Branch, January 29, 1986. "Estimates of Acrylonitrile, Butadiene, and Other VOC Emissions and Controls for ABS and NBR Facilities."

APPENDIX D ESTIMATION METHODS FOR EQUIPMENT LEAKS

APPENDIX D

ESTIMATION METHODS FOR EQUIPMENT LEAKS

An estimate of equipment leak emissions of butadiene depends on the equipment type (e.g., pump seals, flanges, valves, etc.), the associated emission factor, and the number of process components. For batch processes, the hours per year that butadiene actually flows through the component is estimated from the reported percent of the year the equipment operates. For continuous processes, butadiene is assumed to flow through the equipment 8,760 hours per year.

In 1988 and 1989, the Chemical Manufacturer's Association established a panel to study butadiene emissions from equipment leaks. Out of this study, the panel produced average butadiene emission rates (see Table 4-7). These emission rates represent a range of controls at the facility in the study, thus they cannot be used to calculate uncontrolled emissions. For butadiene producers and major users of butadiene, these emission rates can be used to calculate emissions where the number of equipment components and time in service is known. The estimate for each component type is the product of the emission rate, the number of components, and the time in service.

$$\left[\begin{array}{c} component-specific \\ emission \ rate, \\ lb/hr/component \end{array} \right] x \left[\begin{array}{c} no. \ of \ equipment \\ components \ in \\ butadiene \ service \end{array} \right] x \left[\begin{array}{c} no. \ of \ hrs/yr \\ in \ butadiene \\ service \end{array} \right]$$

The estimate for all equipment leaks is the sum of the total for each component type.

Where an uncontrolled estimate is of interest, EPA methods have been published in *Protocol for Equipment Leak Emission Estimates*.¹ These include:

- an average emission factor approach;
- a screening ranges approach;
- an EPA correlation approach; and
- a unit-specific correlation approach.

The approaches differ in complexity; however, greater complexity usually yields more accurate emissions estimates.

The simplest method, the average emission factor approach, requires that the number of each component type be known. For each component, the type of service (gas, light or heavy liquid), the butadiene content of the stream, and the time the component is in service are needed. This information is then multiplied by the EPA's average emission factors. Emission factors for SOCMI process units and refineries are shown in Tables D-1 and D-2. Emission factors for marketing terminals and oil and gas production are also provided in the document. However, these are not provided here as no data on butadiene from these industries were identified. This method is an improvement on using generic emissions developed from source test data, inventory data, and/or engineering judgement. However, this method should only be used if no other data are available because it may result in an overestimation of actual equipment leak emissions. For each component, estimated emissions are calculated as follows:

$$\begin{bmatrix} & \text{No. of} \\ & \text{equipment} \\ & \text{components} \end{bmatrix} x \begin{bmatrix} & \text{Weight \%} \\ & \text{butadiene} \\ & \text{in the stream} \end{bmatrix} x \begin{bmatrix} & \text{Component-} \\ & \text{specific} \\ & \text{emission factor} \end{bmatrix} x \begin{bmatrix} & \text{No. of hrs/yr in} \\ & \text{butadiene service} \end{bmatrix}$$

TABLE D-1. SOCMI AVERAGE TOTAL ORGANIC COMPOUND EMISSION FACTORS FOR EQUIPMENT LEAKS

	_	Emission Factor ^{a,b}
Equipment Type	Service	lb/hr/source (kg/hr/source)
Valves	Gas Light liquid Heavy liquid	0.01313 (0.00597) 0.00887 (0.00403) 0.00051 (0.00023)
Pump seals ^c	Light liquid Heavy liquid	0.0438 (0.0199) 0.01896 (0.00862)
Compressor seals	Gas	0.502 (0.228)
Pressure relief valves	Gas	0.229 (0.104)
Connectors	All	0.00403 (0.00183)
Open-ended lines	All	0.0037 (0.0017)
Sampling connections	All	0.0330 (0.0150)

To obtain more accurate equipment leak emission estimates, one of the more complex estimation approaches should be used. These approaches require that some level of emissions measurement for the facility's equipment components be collected. These are described briefly, and the reader is referred to the EPA protocol document for the calculation details.

The screening ranges approach (formerly known as the leak/no leak approach) is based on a determination of the number of leaking and non-leaking components. This approach may be applied when screening data are available as either "greater than or equal to 10,000 ppmv" or as "less than 10,000 ppmv." Emission factors for SOCMI facilities for these two ranges of screening values are presented in Table D-3; Table D-4 contains emission

^a The emission factors presented in this table for gas valves, light liquid valves, light liquid pumps, and connectors are revised SOCMI average emission factors.

b These factors are for total organic compound emission rates.

^c The light liquid pump seal factor can be used to estimate the leak rate from agitator seals.

TABLE D-2. REFINERY AVERAGE EMISSION FACTORS

Equipment type	Service	Emission Factor (kg/hr/source) ^a
Valves	Gas	0.0268
	Light Liquid	0.0109
	Heavy Liquid	0.00023
Pump seals ^b	Light Liquid	0.114
	Heavy Liquid	0.021
Compressor seals	Gas	0.636
Pressure relief valves	Gas	0.16
Connectors	All	0.00025
Open-ended lines	All	0.0023
Sampling connections	All	0.0150

The EPA correlation approach offers an additional refinement to estimating equipment leak emissions by providing an equation to predict mass emission rate as a function of screening value for a specific equipment type. Correlation equations for SOCMI process units and for petroleum process units are provided in Reference 1, along with their respective correlation curves. The EPA correlation approach is preferred when actual screening values are available.¹

The unit-specific correlation approach requires the facility to develop its own correlation equations and requires more rigorous testing, bagging, and analyzing of equipment leaks to determine mass emission rates.

^a These factors are for non-methane organic compound emission rates.

^b The light liquid pump seal factor can be used to estimate the leak rate from agitator seals. factors for refineries. Emission factors for marketing terminals and oil and gas production are also available from Reference 1; however, as noted above, no data on whether these industries are emission sources are available.

TABLE D-3. SOCMI SCREENING VALUE RANGE TOTAL ORGANIC COMPOUND EMISSION FACTORS FOR EQUIPMENT LEAK EMISSIONS^a

		≥10,000 ppmv Emission Factor ^b	<10,000 ppmv Emission Factor ^b
Equipment Type	Service	lb/hr/source(kg/hr/source)	lb/hr/source(kg/hr/source)
Valves	Gas Light liquid	0.1720 (0.0782) 0.1962 (0.0892)	0.000288 (0.000131) 0.000363 (0.000165)
	Heavy liquid	0.00051 (0.00023)	0.00051 (0.00023)
Pump seals ^c	Light liquid Heavy liquid	0.535 (0.243) 0.475 (0.216)	0.00411 (0.00187) 0.00462 (0.00210)
Compressor seals	Gas	3.538 (1.608)	0.1967 (0.0894)
Pressure relief valves	Gas	3.720 (1.691)	0.0983 (0.0447)
Connectors	All	0.249 (0.113)	0.0001782 (0.0000810)
Open-ended lines	All	0.02629 (0.01195)	0.00330 (0.00150)

The emission factors presented in this table for gas valves, light liquid valves, light liquid pumps, and connectors are revised SOCMI≥ 10,000/< 10,000 ppmv emission factors.

These factors are for total organic compound emission rates.

The light liquid pump seal factors can be applied to estimate the leak rate from agitator seals.

TABLE D-4. REFINERY SCREENING RANGES EMISSION FACTORS

Equipment Type	Service	≥10,000 ppmv Emission Factor (kg/hr/source) ^a	<10,000 ppmv Emission Factor (kg/hr/source) ^a
Valves	Gas Light Liquid Heavy Liquid	0.2626 0.0852 0.00023	0.0006 0.0017 0.00023
Pump seals ^b	Light Liquid Heavy Liquid	0.437 0.3885	0.0120 0.0135
Compressor seals	Gas	1.608	0.0894
Pressure relief valves	Gas	1.691	0.0447
Connectors	All	0.0375	0.00006
Open-ended lines	All	0.01195	0.00150

Appendix A of the EPA protocol document provides example calculations for each of the approaches described above.

Adjusting any of the estimates derived from the EPA approaches requires that facility control practices be known. Table 4-9 presents control techniques and typical efficiencies by equipment component that may be applied to emission estimates for each component type.

^a These factors are for non-methane organic compound emission rates.

^b The light liquid pump seal factors can be applied to estimate the leak rate from agitator seals.

REFERENCES FOR APPENDIX D

1. U.S. EPA. *Protocol for Equipment Leak Emission Estimates*. EPA-453/R-95-017. Research Triangle Park, North Carolina: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, 1995. p. 2-10.

APPENDIX E

SUMMARY OF 1992 TRI AIR EMISSIONS DATA FOR 1,3-BUTADIENE

TABLE E-1. SUMMARY OF 1992 TRI AIR EMISSIONS DATA FOR 1,3-BUTADIENE

									Point Air	Non-point		
									Release	Air Release	Total	
SIC1	SIC2	SIC3	SIC4	SIC5	SIC6	Facility Name	City	State	(lb/yr) ^a	(lb/yr) ^a	(lb/yr) ^a	Notes
NA						Goodyear Tire & Rubber Co. Plant 5	Akron	ОН	324	3,500	3,824	Assumed SIC Code 28
No	data		1	1	1	Rohm & Haas Kentucky Inc.	Louisville	KY	2,300	8,600	10,900	
28	2819	2821	2834	2869	2979	Dow Chemical USA Midland Site	Midland	MI	5,720	14,009	19,729	2979 is an invalid code
2046	NA					Penford Prods. Co.	Cedar Rapids	IA	250	250	500	Point and non-point are avgs ^b
2369	2821	NA				Texas Eastman Company	Longview	TX	49,000	11,000	60,000	
2621	2672	2821	3081	NA		W.R. Grace & Co.	Owensboro	KY	115,300	18,500	133,800	2672 is an invalid code
2641	2821	3479	NA			Nashua Corp. Computer Products Div.	Merrimack	NH	36	36	72	
2812	2813	2819	2821	2822	2865	Dow Chemical Co. Texas Operations	Freeport	TX	52,000	46,000	98,000	
2812	2821	2869	NA			Dow Chemical Co. Louisiana Div.	Plaquemine	LA	41,000	12,000	53,000	
2812	2821	2869	NA			BF Goodrich BFG Intermediates Co. Inc.	Calvert City	KY	170	5,100	5,270	
2819	2821	2869	NA			Elf Atochem N.A. Inc	Axis	AL	12,886	2,325	15,211	
2821	2822	NA				BASF Corp.	Chattanooga	TN	150,000	1,600	151,600	
2821	NA					GE Chemicals Inc.	Washington	WV	20,000	60,000	80,000	
2821	NA					Reichhold Chemicals Inc.	Cheswold	DE	64,688	5,383	70,071	
2821	2869	NA				Rexene Corp. Polypropylene Plant	Odessa	TX	10,766	34,479	45,245	
2821	2869	NA				Phillips Petroleum Co. Houston Chemical Complex	Pasadena	TX	11,000	26,000	37,000	
2821	NA					Goodyear Tire & Rubber Co.	Calhoun	GA	12,332	19,552	31,884	
2821	NA					GE Chemicals Inc. Chemicals	Ottawa	IL	12,100	18,513	30,613	
2821	2869	NA				Union Carbide Chemicals & Plastics Co. Texas City Plant	Texas City	TX	19,696	10,409	30,105	
2821	2822	2865	NA			Uniroyal Chemical Co. Inc.	Painesville	ОН	3,066	14,452	17,518	
2821	NA					Reichhold Chemicals Inc.	Chickamauga	GA	8,100	8,900	17,000	
2821	2869	NA				Quantum Chemical Corp. USI Div.	Clinton	IA	6,900	9,800	16,700	
2821						Kaneka Texas Corp.	Pasadena	TX	3,200	12,000	15,200	
2821						Rohm & Haas Unocal Chemical Division	Charlotte	NC	6,470	6,140	12,610	
2821	2869	2813	NA			Quantum Chemical Corp. La Porte	La Porte	TX	5,744	5,380	11,124	

TABLE E-1. CONTINUED

SIC1	SIC2	SIC3	SIC4	SIC5	SIC6	Facility Name	City	State	Point Air Release (lb/yr) ^a	Non-point Air Release (lb/yr) ^a	Total	Notes
2821	2869	NA				Quantum Chemical Corp. USI Div.	Morris	IL	3,000	7,200	10,200	
2821	3086	NA				Monsanto Co.	Addyston	ОН	6,000	860	6,860	
2821	NA					Goodyear Tire & Rubber Co. Akron Polymer Plant	Akron	ОН	892	2,979	3,871	
2821	3086	NA				Dow Chemical Dalton Site	Dalton	GA	40	1,800	1,840	
2821	3086	NA				Dow North America Allyn's Point Plant	Gales Ferry	СТ	45	1,340	1,385	
2821	2899	2822	NA			Rhone-Poulenc Inc. Walsh Div.	Gastonia	NC	242	807	1,049	
2821	NA					Ricon Resins Inc.	Grand Junction	СО	750	250	1,000	Point and non-point are avgs ^b
2821	2869					Amoco Chemical Co.	Whiting	IN	250	750	1,000	Point and non-point are avgs ^b
2821	2822	NA				Rohm & Haas Delaware Valley Inc.	Kankakee	IL	120	300	420	
2821						Rohm & Haas Delaware Valley Inc.	La Mirada	CA	0	242	242	
2822	NA					Miles Inc. Polysar Rubber Div.	Orange	TX	4,400	350,000	354,400	
2822						Firestone Synthetic Rubber & Latex Co.	Orange	TX	7,000	93,000	100,000	
2822	NA					Ameripol Synpol Corporation	Port Neches	TX	2,300	81,500	83,800	
2822	NA					Goodyear Tire & Rubber Co. Houston Chemical Plant	Houston	TX	9,000	60,724	69,724	
2822	2869					Du Pont Pontchartrain Works	La Place	LA	56,000	5,200	61,200	
2822	NA					Zeon Chemicals Kentucky Inc.	Louisville	KY	26,841	33,844	60,685	
2822	2821	2869	NA			Goodyear Tire & Rubber Co. Beaumont Chemical Plant	Beaumont	TX	6,600	42,000	48,600	
2822	2821					BASF Corp.	Monaca	PA	38,000	17	38,017	
2822	2865	NA				Miles Inc.	Houston	TX	14,300	15,600	29,900	
2822						Firestone Synthetic Rubber & Latex Co.	Lake Charles	LA	4,000	24,540	28,540	
2822						Dynagen Inc. of General Tire Inc.	Odessa	TX	11,150	15,222	26,372	
2822	2865	2869	2873			Du Pont Beaumont Plant Beaumont Works	Beaumont	TX	8,997	6,568	15,565	
2822	NA					American Synthetic Rubber Corp.	Louisville	KY	0	14,000	14,000	
2822	3087					Shell Chemical Co.	Belpre	ОН	2,300	8,400	10,700	

TABLE E-1. CONTINUED

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SIC1	SIC2	SIC3	SIC4	SIC5	SIC6	Facility Name	City	State	Point Air Release (lb/yr) ^a	Non-point Air Release (lb/yr) ^a	Total (lb/yr)ª	Notes
2822	NA					Copolymer Rubber & Chemical Corp.	Baton Rouge	LA	500	10,000	10,500	
2822	2891					Gencorp Polymer Prods. Latex	Mogadore	ОН	650	5,000	5,650	
2822	NA					BASF Corp.	Chattanooga	TN	150	750	900	Non-point is avg ^b
2822						Enichem Elastomers Americas Inc.	Baytown	TX	250	250	500	Point and non-point are avgs ^b
2822	NA					Firestone Synthetic Rubber & Latex Co.	Akron	ОН	39	117	156	
2865						Buffalo Color Corp.	Buffalo	NY	1,800	36,000	37,800	
2865	NA					Amoco Chemical Co. Plant B	Texas City	TX	14	173	187	
2869	2821	NA				Lyondell Petrochemical Co.	Channelview	TX	245,000	61,000	306,000	
2869	NA					Texas Petrochemicals Corporation	Houston	TX	37,240	125,710	162,950	
2869	NA					Occidental Chemical Corp.	Alvin	TX	13,000	95,400	108,400	
2869	NA					Amoco Chemical Co. Chocolate Bayou Plant	Alvin	TX	250	102,000	102,250	Point is avg ^b
2869	NA					Texaco Chemical Co.	Port Neches	TX	15,000	55,000	70,000	
2869	2865	2822				Exxon Chemical Co. Baton Rouge Chemical Plant	Baton Rouge	LA	5,900	55,000	60,900	
2869	2821	NA				Phillips 66 Co. Philtex/Ryton Complex	Borger	TX	33,000	25,000	58,000	
2869	2822	2821				BF Goodrich Co. Akron Chemical Plant	Akron	ОН	25,000	21,000	46,000	
2869						Union Carbide Chemicals & Plastics Co. Institute WV Plant Ops.	Institute	WV	15,751	20,611	36,362	
2869						Oxy Petrochemical Inc. Corpus Christi Plant	Corpus Christi	TX	26,300	9,700	36,000	
2869						Exxon Chemical Co. Baytown Olefins Plant	Baytown	TX	15,000	19,000	34,000	
2869						Union Carbide Chemicals & Plastics Co. Seadrift Plant	Port Lavaca	TX	12,929	20,965	33,894	
2869	NA					Mobil Chemical Co. Olefins/Aromatics Plant	Beaumont	TX	2,547	29,005	31,552	
2869						Du Pont Sabine River Works	Orange	TX	26,522	3,428	29,950	
2869	2865	2819	NA			Texaco Chemical Co. Port Arthur Chemical Plant	Port Arthur	TX	12,000	8,300	20,300	
2869	NA					Union Texas Prods. Corp. Geismar Ethylene Plant	Geismar	LA	1,300	14,600	15,900	

SIC1	SIC2	SIC3	SIC4	SIC5	SIC6	Facility Name	City	State	Point Air Release (lb/yr) ^a	Non-point Air Release (lb/yr) ^a	Total	Notes
2869					0.00	Du Pont Victoria Plant	Victoria	TX	10,158	5,250	15,408	
2869	NA					Oxy Petrochemicals Inc.	Sulphur	LA	90	14,073	14,163	
2869	NA					Mobil Chemical Corp.	Houston	TX	5,000	5,500	10,500	
2869	4463	NA				Union Carbide Chemicals & Plastics Co. Marine Terminal	Texas City	TX	9,905	0	9,905	
2869	2865	2819	NA			Vista Chemical Co. Lake Charles Chemical Complex	Westlake	LA	2,980	5,475	8,455	
2869	2821	2895				Chevron Chemical Co.	Baytowm	TX	0	6,159	6,159	
2869						Lubrizol Petroleum Chemicals Co.	Painesville	ОН	3,922	853	4,775	
2869	NA					Lindau Chemicals Inc.	Columbia	SC	4,200	250	4,450	Non-point is avg ^b
2869	NA					Hoescht-Celanese Corp. Pampa Plant	Pampa	TX	1,600	0	1,600	
2869	NA					Westlake Petrochemicals Corp.	Sulphur	LA	1,033	83	1,116	
2869	2821					Exxon Chemical Americas Baytown Chemical Plant	Baytown	TX	87	810	897	
2869						Union Carbide Corp. Indl. Chemicals	Hahnville	LA	105	507	612	
2869	2821	2822	NA			Morton Intl. Inc. MPM	Moss Point	MS	250	250	500	Point and non-point are avgs ^b
2869	2879	3083	2087	2821		Phillips Research Center	Bartlesville	OK	24	243	267	
2869						Sea Lion Tech. Inc.	Texas City	TX	250	5	255	Point and non-point are avgs ^b
2869	2821	NA				Dixie Chemical Co. Inc.	Pasadena	TX	0	15	15	
2869	NA					Lubrizol Corp. Deer Park Plant	Deer Park	TX	0	5	5	Non-point is avg ^b
2879	2821	2869	NA			Monsanto Co.	Muscatine	IA	160,000	4,000	164,000	
2879	NA					Zeneca Inc. Perry Plant	Perry	ОН	9,800	80	9,880	
2879	2822	NA				Dow Chemical Co.	Pittsburg	CA	310	1,500	1,810	
2891						Roberts Consolidated Ind. Inc.	Mexico	МО	250	0	250	Point is avg ^b
2899	3081	2822	NA			ЗМ	Decatur	AL	1,400	740	2,140	
2911	NA					Chevron USA Products Co. Port Arthur Refinery	Port Arthur	TX	14,000	120,000	134,000	
2911	2869	NA				Shell Norco Manufacturing Complex E. Site	Norco	LA	3,200	92,000	95,200	

TABLE E-1. CONTINUED

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									Point Air Release	Non-point Air Release	Total	
SIC1	SIC2	SIC3	SIC4	SIC5	SIC6	Facility Name	City	State	(lb/yr) ^a	(lb/yr) ^a	(lb/yr) ^a	Notes
2911	2869	2865	2821			Shell Oil Co. Deer Park Mfg. Complex	Deer Park	TX	10,960	57,679	68,639	
2911	NA					Texaco Refining & Marketing Inc. Puget Sound Plant	Anacortes	WA	23,000	10,000	33,000	
2911	NA					Ashland Petroleum Co. St. Paul Park Refinery	Saint Paul Park	MN	17,046	0	17,046	
2911	NA					Mobil Oil Beaumont Refinery	Beaumont	TX	13,000	1,300	14,300	
2911						Star Ent. Inc. Delaware City Refinery	Delaware City	DE	0	13,000	13,000	
2911	2951	2992	NA			Amoco Oil Co. Whiting Refinery	Whiting	IN	0	8,600	8,600	
2911	NA					Hess Oil Virgin Islands Corp. (HOVIC)	Kingshill	VI	0	7,394	7,394	
2911	NA					Arco Cherry Point Refinery	Ferndale	WA	0	6,900	6,900	
2911	NA					Kerr-McGee Refining Corp.	Wynnewood	OK	320	3,900	4,220	
2911	2869	NA				Phillips 66 Co.	Sweeny	TX	0	3,402	3,402	
2911	NA					Star Ent. Inc. Port Arthur Plant	Port Arthur	TX	2,803	9	2,812	
2911	5171	NA				Exxon Baytown Refinery	Baytown	TX	2,580	174	2,754	
2911	NA					Ashland Petroleum Co. Canton Refinery	Canton	ОН	256	2,162	2,418	
2911	NA					Conoco Lake Charles Refinery	Westlake	LA	130	1,500	1,630	
2911	2819	2869	NA			Citgo Petroleum Corp.	Lake Charles	LA	31	1,500	1,531	
2911	NA					Conoco Billings Refinery	Billings	MT	27	1,400	1,427	
2911	NA					Ultramar Inc.	Wilmington	CA	270	750	1,020	Non-point is avg ^b
2911	NA					Marathon Oil Co.	Texas City	TX	830	180	1,010	
2911	NA					Lion Oil Co.	El Dorado	AR	0	1,006	1,006	
2911	NA					Exxon Co. USA Benicia Refinery	Benicia	CA	580	400	980	
2911	5171	NA				Exxon Baton Rouge Refinery	Baton Rouge	LA	440	460	900	
2911	NA					BP Oil Co. Toledo Refinery	Oregon	ОН	210	690	900	
2911	2819	NA				Phillips 66 Co.	Borger	TX	18	870	888	
2911	2999	NA				Conoco Ponca City Refinery	Ponca City	ОК	510	350	860	

SIC1	SIC2	SIC3	SIC4	SIC5	SIC6	Facility Name	City	State	Point Air Release (lb/yr) ^a	Non-point Air Release (lb/yr) ^a	Total (lb/yr) ^a	Notes
2911	NA					Chevron USA Products Co. Hawaiian Refinery	Kapolei	H	5	750	755	Point and non-point are avgs ^b
2911	NA					Mobil Joliet Refinery Corp.	Joliet	L	350	200	550	
2911	NA					Texaco Refining & Marketing Inc. Lap	Wilmington	CA	0	540	540	
2911	NA					Ashland Petroleum Co. Catlettsburg Refinery	Catlettsburg	KY	455	70	525	
2911	2951	NA				Chevron USA Inc. El Paso Refinery	El Paso	TX	400	110	510	
2911						Shell Oil Co. Anacortes Refinery	Anacortes	WA	2	500	502	
2911	NA					Cenex Refinery	Laurel	MT	250	250	500	Point and non-point are avgs ^b
2911	NA					Southwestern Refining Co. Inc.	Corpus Christi	TX	250	250	500	Point and non-point are avgs ^b
2911						Crown Central Petroleum Corp. Houston Refinery	Pasadena	TX	5	482	487	
2911	5171	NA				Exxon Billings Refinery	Billings	MT	0	460	460	
2911	NA					Amerada Hess Corp.	Purvis	MS	0	415	415	
2911	NA					Amoco Oil Co.	Mandan	ND	0	410	410	
2911	2869	2873	NA			Chevron Products Co. Pascagoula Refinery	Pascagoula	MS	0	390	390	
2911	NA					Phibro Refining Krotz Springs	Krotz Springs	LA	90	242	332	
2911	NA					Conoco Denver Refinery	Commerce City	СО	0	320	320	
2911	NA					Amoco Oil Co. Texas City Refinery	Texas City	TX	0	310	310	
2911	NA					Chevron USA Products Co. El Segundo Refinery	El Segundo	CA	0	310	310	
2911	NA					Chevron USA Products Co.	Philadelphia	PA	0	301	301	
2911						Fletcher Oil & Refining Co.	Carson	CA	250	5	255	Point and non-point are avgs ^b
2911	2869	2992	NA			Lyondell Petrochemical Co. Houston Refinery	Houston	TX	0	250	250	Non-point is avg ^b
2911	NA					Mobil Oil Paulsboro Refinery	Paulsboro	NJ	0	250	250	Non-point is avg ^b
2911	4613	NA				Total Petroleum Inc. Alma Refinery	Alma	MI	0	250	250	Non-point is avg ^b
2911	NA					Arco Prods. Co. LA Refinery	Carson	CA	4	240	244	

TABLE E-1. CONTINUED

									Point Air	Non-point		
SIC1	SIC2	SIC3	SIC4	SIC5	SIC6	Facility Name	City	State	Release (lb/yr) ^a	Air Release (lb/yr) ^a	Total (lb/yr)ª	Notes
2911	NA					Shell Oil Co. Wood River Mfg. Complex	Roxana	IL	0	230	230	
2911						Phibro Energy USA Inc.	Texas City	TX	171	58	229	
2911	NA					Tosco Refining Co.	Martinez	CA	17	200	217	
2911	NA					Total Petroleum Inc.	Ardmore	OK	0	150	150	
2911	NA					Mobil Oil Corp. Chalmette Refinery	Chalmette	LA	9	140	149	
2911	NA					Valero Refining Co.	Corpus Christi	TX	98	38	136	
2911	NA					Sun Refining & Marketing Co.	Marcus Hook	PA	0	120	120	
2911	NA					Giant Refining Co. Ciniza	Jamestown	NM	100	10	110	
2911	NA					Texaco Refining & Marketing Inc.	Bakersfield	CA	80	29	109	
2911	NA					Diamond Shamrock Refining & Marketing Co. Three Rivers	Three Rivers	TX	0	100	100	
2911	NA					BP Oil Co. Ferndale Refinery	Ferndale	WA	51	46	97	
2911	5171					Exxon Eastside Chemical Plant	Linden	NJ	34	63	97	
2911	2869	NA				Texaco Refining & Marketing Inc.	El Dorado	KS	0	91	91	
2911	5171					Exxon Refining & Marketing Terminal	Linden	NJ	0	88	88	
2911	NA					Sun Refining & Marketing Co.	Oregon	ОН	0	77	77	
2911	NA					Chevron USA Products Co. Richmond Refinery	Richmond	CA	0	74	74	
2911	NA					Sun Refining & Marketing Co.	Philadelphia	PA	0	58	58	
2911	NA					Phibro Energy USA Inc.	Houston	TX	7	49	56	
2911						Fina Oil & Chemical Co.	Port Arthur	TX	0	42	42	
2911	NA					Mobil Oil Corp. Torrence Refinery	Torrence	CA	16	15	31	
2911	NA					Texaco Refining & Marketing Inc.	Bakersfield	CA	9	22	31	
2911						Marathon Oil Co.	Detroit	MI	0	22	22	
2911	NA					Unocal Corp. Carson Plant	Carson	CA	1	20	21	
2911						Uno-Ven Co. Chicago Refinery	Lemont	IL	0	19	19	

TABLE E-1. CONTINUED

SIC1	SIC2	SIC3	SIC4	SIC5	SIC6	Facility Name	City	State	Point Air Release (lb/yr) ^a	Non-point Air Release (lb/yr) ^a	Total (lb/yr) ^a	Notes
2911	NA					Marathon Oil Co. Louisiana Refinery	Garyville	LA	5	12	17	Point is avg ^b
2911	NA					Sun Refining & Marketing Co.	Tulsa	ОК	0	8	8	
2911	NA					Countrymark Cooperative Inc. Assn. Inc. Mt. Vernon Refinery	Mount Vernon	IN	0	5	5	Non-point is avg ^b
2911	2819	2869	NA			Shell Oil Co. Martinez Mfg. Complex	Martinez	CA	0	2	2	
2911	NA					Star Ent. Inc. PAAC	Port Neches	TX	1	0	1	
3312	NA					Bethlehem Steel Corp. Burns Harbor Div.	Burns Harbor	IN	0	250	250	Non-point is avg ^b
3579	NA					Xerox	Oklahoma City	OK	4,200	0	4,200	
8731	8711	8734	NA			Chevron Research & Technology Co.	Richmond	CA	1	0	1	

^aIncludes any controls in place at the facility.
^bAir releases were given as a range. The data were averaged for the table.