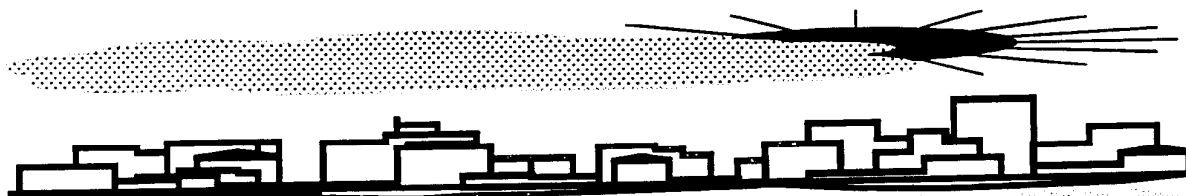




**LOCATING AND ESTIMATING
AIR EMISSIONS
FROM SOURCES OF
CHLOROBENZENES
(REVISED)**



L & E

EPA-454/R-93-044

LOCATING AND ESTIMATING AIR EMISSIONS
FROM SOURCES OF CHLOROBENZENES (REVISED)

Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

March 1994

This report has been reviewed by the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, and has been approved for publication. Any mention of trade names or commercial products is not intended to constitute endorsement or recommendation for use.

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EXECUTIVE SUMMARY

Emissions of chlorobenzenes into the atmosphere are of special significance because of the 1990 Clean Air Act Amendments. These amendments mandate that chlorobenzenes emissions be subject to standards that allow for the maximum degree of reduction of emissions and that, by 1995, a list of source categories be established that accounts for no less than 90 percent of chlorobenzenes emissions. This document is designed to assist groups interested in inventorying air emissions of chlorobenzenes by providing a compilation of available information on sources and emissions of these substances.

The chlorinated derivatives of benzene are a group of stable, colorless and pleasant smelling compounds. Only the mono-, di-, and trichlorobenzenes have important industrial applications. Information on hexachlorobenzene is included due to its past usage and generation as a byproduct in other manufacturing processes.

In the U.S., chlorobenzenes are produced by three companies at three locations. In 1989, the production capacity for monochlorobenzene was 168,000 megagrams (371 million pounds), for ortho-dichlorobenzene, 36,700 megagrams (80.9 million pounds), and for para-dichlorobenzene, 60,000 megagrams (132 million pounds). Few data are available on production of more highly chlorinated benzenes.

Major uses for monochlorobenzene are in the manufacture of phenol and ortho- and para-nitrochlorobenzenes, diphenyl oxide, dye and herbicide intermediates, and sulfone polymers.

Ortho-dichlorobenzene is used primarily in the synthesis of 3,4-dichloroaniline, which is used in the production of herbicides. It is also used in the manufacture of dyes, as a solvent in paint removers and engine cleaners, and as a de-inking solvent.

Para-dichlorobenzene is used in the manufacture of 1,2,4-trichlorobenzene, polyphenylene

sulfide resins, room deodorants, moth proofing products and as an intermediate in the dye and

insecticide industries.

1,2,4-trichlorobenzene is used in pesticide formulation, as a process solvent, chemical intermediate, lubricant and heat transfer medium.

Hexachlorobenzene is no longer produced or imported in the U.S. for commercial use. It is formed as a process waste byproduct during the manufacture of specific chlorinated solvents and pesticides.

At the time of publication of this document, estimates of nationwide chlorobenzenes emissions were not available. Updates to this document will attempt to incorporate any nationwide emissions information subsequently available.

SECTION 1.0
PURPOSE OF DOCUMENT

The Environmental Protection Agency (EPA) and 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, very little information is available on the ambient air concentrations of these substances or on the sources that may be discharging them to the atmosphere.

To assist groups interested in inventorying air emissions of various potentially toxic substances, the EPA is preparing a series of documents which compile available information on sources and emissions of these substances. The primary purpose of this document is to revise and update the information presented in the *Locating and Estimating Emissions From Sources of Chlorobenzenes* (EPA-450/4-84-007m) document which was originally published in 1984. Prior documents in the series are listed below:

<u>Substance</u>	<u>EPA Publication Number</u>
Acrylonitrile	EPA-450/4-84-007a
Carbon Tetrachloride	EPA-450/4-84-007b
Chloroform	EPA-450/4-84-007c
Ethylene Dichloride	EPA-450/4-84-007d
Formaldehyde (Revised)	EPA-450/2-91-012
Nickel	EPA-450/4-84-007f
Chromium	EPA-450/4-84-007g
Manganese	EPA-450/4-84-007h
Phosgene	EPA-450/4-84-007i
Epichlorohydrin	EPA-450/4-84-007j
Vinylidene Chloride	EPA-450/4-84-007k
Ethylene Oxide	EPA-450/4-84-007l
Chlorobenzenes	EPA-450/4-84-007m
Polychlorinated Biphenyls (PCBs)	EPA-450/4-84-007n
Polycyclic Organic Matter (POM)	EPA-450/4-84-007p
Benzene	EPA-450/4-84-007q
Organic Liquid Storage Tanks	EPA-450/4-88-004
Coal and Oil Combustion Sources	EPA-450/2-89-001
Municipal Waste Combustors	EPA-450/2-89-006

<u>Substance</u>	<u>EPA Publication Number</u>
Perchloroethylene and Trichlorethylene	EPA-450/2-90-013
1,3-Butadiene	EPA-450/2-89-021
Chromium (supplement)	EPA-450/2-89-002
Sewage Sludge	EPA-450/2-90-009
Styrene	EPA-450/4-91-029
Methylene Chloride	EPA-454/R-93-006

This document deals specifically with chlorobenzenes. Its intended audience includes Federal, State, and local air pollution personnel and others who are interested in locating potential emitters of chlorobenzenes, and making gross estimates of air emissions therefrom.

Because of the limited amounts of data available on some potential sources of chlorobenzenes emissions, and since the configurations of many sources will not be the same as those described here, this document is best used as a primer to inform air pollution personnel about (1) the types of sources that may emit chlorobenzenes, (2) process variations and release points that may be expected within these sources, and (3) available emissions information indicating the potential for chlorobenzenes to be released into the air from each operation.

The reader is strongly cautioned against using the emissions information contained in this document to try to develop an exact assessment of emissions from any particular facility. Because insufficient data are available to develop statistical estimates of the accuracy of these emission factors, no estimate can be made of the error that could result when these factors are used to calculate emissions from any given facility. It is possible, in some extreme cases, that order-of-magnitude differences could result between actual and calculated emissions, depending on differences in source configurations, control equipment, and operating practices. Thus, in situations where an accurate assessment of chlorobenzenes emissions is necessary, source-specific information should be obtained to confirm the existence of particular emitting operations, the types and effectiveness of control measures, and the impact of operating practices. A source test and/or material balance should be considered as the best means to determine air emissions directly from an operation.

In addition to the information presented in this document, another potential source of emissions data for chlorobenzenes is the Toxic Chemical Release Inventory (TRI) form required by Section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA 313).¹ SARA 313 requires owners and operators of certain facilities that manufacture, import, process or otherwise use certain toxic chemicals to report annually their releases of these chemicals to any 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, broken out into fugitive and point components. No individual process or stack data are provided to the EPA. The TRI requires the use of available stack monitoring or measurement of emissions to comply with SARA 313. If monitoring data are unavailable, emissions are to be quantified based on best estimates of releases to the environment.

The reader is cautioned that the 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 balances, engineering judgement). The reader is urged to obtain TRI data in addition to information provided in this document to locate potential emitters of chlorobenzenes, and to make preliminary estimates of air emissions from these facilities. To obtain an exact assessment of air emissions from processes at a specific facility, source tests or detailed material balance calculations should be conducted, and detailed plant site information should be compiled.

Each L&E document, as standard procedure, is sent to government, industry, and environmental groups wherever EPA is aware of expertise. These groups are given the opportunity to review the document, comment, and provide additional data where applicable. Where necessary, the documents are then revised to incorporate these comments. Although these documents have 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 is welcome on process descriptions, operating parameters, control measures, and emissions information that would enable EPA to improve the contents of this document. Comments and information may be sent to the following address:

Chief, Emission Factor and Methodologies Section
Emission Inventory Branch, (MD-14)
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

1.1 REFERENCE FOR SECTION 1.0

1. Toxic Chemical Release Reporting: Community Right-To-Know. Federal Register 52(107): 21152-21208. June 4, 1987.

SECTION 2.0 OVERVIEW OF DOCUMENT CONTENTS

As stated in Section 1.0, the purpose of this document is to assist Federal, State and local air pollution agencies and others who are interested in locating potential air emitters of chlorobenzenes and making gross estimates of air emissions therefrom. Because of the limited available background data, the information summarized in this document does not and should not be assumed to represent the source configuration or emissions associated with any particular facility.

This section provides an overview of the contents of this document. It briefly outlines the nature, extent, and format of the material presented in the remaining sections of this report.

Section 3.0 of this document briefly summarizes the physical and chemical characteristics of chlorobenzenes, and provides an overview of their production and use. This background section may be useful to someone who needs to develop a general perspective on the nature of this substance and how it is manufactured and consumed.

Section 4.0 of this document focuses on major production source categories that may discharge air emissions containing chlorobenzenes. Section 5.0 discusses emissions from major uses of chlorobenzenes. Section 6.0 addresses emissions as a result of releases after manufacture from products containing chlorobenzenes. Section 7.0 describes sources of emissions as a result of the manufacture of another product, or as a by-product of another process (*e.g.*, burning of fuel oil). Example process descriptions and flow diagrams are given in addition to available emission factor estimates for each major industrial source category described in Sections 4.0, 5.0, 6.0, and 7.0. Individual companies involved with either the production or use of chlorobenzenes are reported throughout the document. Information reported is extracted primarily from trade publications.

Section 8.0 of this document summarizes available procedures for source sampling and analysis of chlorobenzenes. The summaries provide an overview of applicable sampling and analytical procedures, citing references for those interested in conducting source tests.

Appendix A identifies potential source categories of chlorobenzenes emissions by Standard Industrial Classification (SIC) code and associated description. These potential source categories do not necessarily denote significant sources of chlorobenzene emissions. The readers interested in cross referencing SICs with Source Classification Codes (SCCs) and associated descriptions should consult the *Crosswalk/Air Toxic Emission Factor Database Management System*, Version 2.0 (October 1992) and/or the *Volatile Organic Compound (VOC)/Particulate Matter (PM) Speciation Database Management System*, Version 1.4 (October 1992).^{1,2} Appendix B lists textile dyeing facilities with sales greater than \$1,000,000. Appendix C summarizes, in table format, all emission factors listed in this document.

Each emission factor listed in Sections 3.0 through 7.0 has been assigned an emission factor grade based on the criteria for assigning data quality and emission factor ratings as required in the document *Technical Procedures for Developing AP-42 Emission Factors and Preparing AP-42 Sections*.³ These criteria for rating test data used to develop emission factors are presented below. The data used to develop emission factors are rated as follows:

- A - Tests 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 - Tests that are performed by a generally sound methodology but lack enough detail for adequate validation.
- C - Tests that are based on a nonvalidated or draft methodology or that lack a significant amount of background data.
- D - Tests that are based on a generally unacceptable method but may provide an order-of-magnitude value for the source.

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 an emission factor is not practical. Therefore, some subjective quality rating is necessary. The following emission factor quality ratings are applied to the emission factor tables.

A - Excellent. 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.

B - Above average. 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 industries. As in the A rating, the source category is specific enough to minimize variability within the source category population.

C - Average. 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 in the A rating, the source category is specific enough to minimize variability within the source category population.

D - Below average. 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. Limitations on the use of the emission factor are footnoted in the emission factor table.

E - 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. Limitations on the use of these factors are always footnoted.

U - Unrated or Unratable. 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:

- a gross mass balance estimation
- QA/QC deficiencies found with C- and D-rated test data
- gross engineering judgement
- technology transfer

*Source category: A category in the emission factor table for which an emission factor has been calculated; generally a single process.

This document does not contain any discussion of health or other environmental effects of chlorobenzenes. It does include a discussion of ambient air monitoring techniques; however, these ambient air monitoring methods may require modifications for stack sampling and may affect data quality.

2.1 REFERENCES FOR SECTION 2.0

1. U.S. Environmental Protection Agency, *Crosswalk/Air Toxic Emission Factor Database Management System, Version 2.0*, Office of Air Quality Planning and Standards, Research Triangle Park, NC, October 1992.
2. U.S. Environmental Protection Agency, *Volatile Organic Compound (VOC)/Particulate Matter (PM) Speciation Database Management System, Version 1.4*, Office of Air Quality Planning and Standards, Research Triangle Park, NC, October 1992.
3. U.S. Environmental Protection Agency, *Technical Procedures for Developing AP-42 Emission Factors and Preparing AP-42 Sections*, Draft Document, Office of Air Quality Planning and Standards, Research Triangle Park, NC, March 1992.
4. Group discussion meeting on applying "U" rating to emission factors. Anne Pope, EIB; Robin Baker Jones, Midwest Research Institute; Garry Brooks, Radian Corporation; and Theresa Moody, TRC Environmental Corporation.

SECTION 3.0 BACKGROUND

3.1 NATURE OF POLLUTANT

The chlorinated derivatives of benzene, $C_6H_{(6-x)}Cl_x$, form a group of stable, colorless, pleasant smelling compounds. Chlorine can be substituted for the six hydrogen atoms on the benzene ring, forming twelve different chlorinated compounds:

- monochlorobenzene
- ortho-dichlorobenzene
- meta-dichlorobenzene
- para-dichlorobenzene
- 1,2,3-trichlorobenzene
- 1,2,4-trichlorobenzene
- 1,3,5-trichlorobenzene
- 1,2,3,4-tetrachlorobenzene
- 1,3,4,5-tetrachlorobenzene
- 1,2,4,5-tetrachlorobenzene
- pentachlorobenzene
- hexachlorobenzene

Only the mono-, di-, and trichlorobenzenes have important industrial applications. Thus, relevant information on each of these groups is discussed in this report. Although it has no current commercial applications, information on hexachlorobenzene is included due to its past usage and generation as a byproduct in other manufacturing processes. Synonyms and trade names for these chlorinated products are presented in Table 3-1. The physical properties of the industrially significant chlorobenzenes are listed in Table 3-2.

**TABLE 3-1.
SYNONYMS AND TRADE NAMES FOR
CHLOROBENZENES**

Pollutant	Synonyms
Monochlorobenzene	benzene chloride; chlorobenzene; chlorobenzol; phenyl chloride; MCB; NCI-C54886
o-Dichlorobenzene	orthodichlorobenzene; ortho-dichlorobenzene; ortho-dichlorobenzol; 1,2-dichlorobenzene; ODB; ODCB; Dizene [®] ; Chloroben [®] ; Dowtherm [®] E; "Special termite fluid"; Termitkil; Dilatin DB
m-Dichlorobenzene	metadichlorobenzene; meta-dichlorobenzol; meta-dichlorobenzene; 1,3-dichlorobenzene; m-phenylenedichloride
p-Dichlorobenzene	paradichlorobenzene; para-dichlorobenzene; para-dichlorobenzol; 1,4-dichlorobenzene; PDB; PDCB; Di-chloricide [®] ; Paracide [®] ; Paradi [®] ; Paradow [®] ; Paramoth [®] ; Santochlor [®] ; Parazene; Paranuggets; paraCrystals; p-chlorophenyl chloride; Evola; Persia-Perazol
1,2,3-Trichlorobenzene	1,2,3-trichlorobenzol; 1,2,3-TCB; 1,2,6-trichlorobenzene; vic-trichlorobenzene
1,2,4-Trichlorobenzene	1,2,4-trichlorobenzol; 1,2,4-TCB; unsymtrichlorobenzene
1,3,5-Trichlorobenzene	1,3,5-trichlorobenzol; 1,3,5-TCB; sym-trichlorobenzene; s-trichlorobenzene; TCBA
Hexachlorobenzene	Amatin; Anticarie; Bunt-Cure; Bunt-No-More; Co-op Hexa; Granox NM; HCB; HEXA C.B.; Julin's Carbon Chloride; No Bunt Liquid; pentachlorophenyl chloride; perchlorobenzene; phenyl perchloryl; Sanocide; Smut-Go; Snieciotox

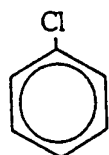
Source: References 1-3.

TABLE 3-2.
PROPERTIES OF INDUSTRIALLY SIGNIFICANT CHLOROBENZENES

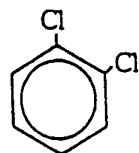
	MCB	o-DCB	m-DCB	p-DCB	1,2,3-TCB	1,2,4-TCB	1,3,5-TCB	HCB
Chemical Abstracts Service Registry Number	108-90-7	95-50-1	541-73-1	106-46-7	87-61-6	120-82-1	108-70-3	118-74-1
Molecular Weight (g) Molecular Formula	112.56 C ₆ H ₅ Cl	147.0 C ₆ H ₄ Cl ₂	147.0 C ₆ H ₄ Cl ₂	147.0 C ₆ H ₄ Cl ₂	181.5 C ₆ H ₃ Cl ₃	181.5 C ₆ H ₃ Cl ₃	181.5 C ₆ H ₃ Cl ₃	284.76 C ₆ Cl ₆
Physical Properties								
Physical State at standard temperature and pressure	liquid colorless	liquid colorless	liquid colorless	monoclinic crystals (volatile)	solid crystalline	liquid	solid crystalline	solid crystalline
Boiling Point (at 760mm)	131.7°C	180.5°C	173.0°C	174.12°C	218.0°C	213.0°C	208.0°C	323°C
Melting Point	-45.5°C	-17.0°C	-24.7°C	53.5°C	52.4°C	16.6°C	63.0°C	230°C
Density (g/mL) (at 20°C/4°C)	1.1058	1.305	1.288	1.458	1.69	1.46	---	1.57 (at 23°C)
Vapor Pressure (mmHg at 25°C)	11.8	1.28	0.4	1.89	---	0.29	0.15	1.68 x 10 ⁻⁵
Vapor Density	3.88	5.05	5.08	5.08	6.26	6.26	6.26	9.8
Solubility	insoluble	slightly (0.145g/L H ₂ O)	insoluble	nearly insol. (0.079g/L H ₂ O)	insoluble	insoluble	insoluble	insoluble
Log Partition Coefficient (Octanol/H ₂ O)	2.84	3.38	---	---	---	---	---	---
Atmospheric Reactivity								
Transformation Products								
Reactivity toward OH ⁻	1/3 Butane	1/2 Butane	---	1/2 Butane	---	---	---	---
Reactivity toward O ₃	No reaction	5% Propylene	---	5% Propylene	---	---	---	---

Source: References 1, 4-8.
Dashes indicate data not found.

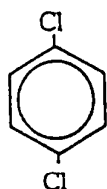
Molecular structures for the chlorobenzenes discussed in this document are presented below:



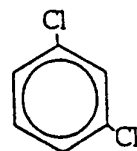
monochlorobenzene



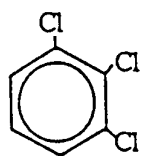
ortho-dichlorobenzene



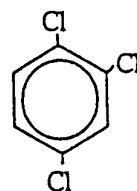
para-dichlorobenzene



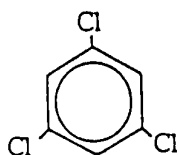
meta-dichlorobenzene



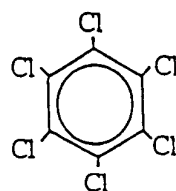
1,2,3-trichlorobenzene



1,2,4-trichlorobenzene



1,3,5-trichlorobenzene



hexachlorobenzene

3.1.1 Properties of Chlorobenzenes

As a group, chlorobenzenes are much less reactive than the corresponding chlorinated derivatives of alkyl compounds and are similar in reactivity to the vinyl halides. They are very stable to nucleophilic attack due to resonance in the molecule resulting in a shortening of the carbon-chlorine bond distance and an increase in bond strength.¹

At room temperature and pressure, chlorobenzenes are not attacked by air, moisture, or light. They are not affected by steam, prolonged boiling with aqueous or alcoholic ammonia, other alkalis, hydrochloric acid, or dilute sulfuric acid. Hydrolysis takes place at elevated temperatures in the presence of a catalyst to form phenols.¹

Chlorobenzenes are subject to attack by hot concentrated sulfuric acid to form chlorobenzene-p-sulfonic acid. Nitric acid will react with chlorobenzenes at the meta- and para-positions on the ring to form chloronitrobenzenes at -30°C to 0°C (-22°C to 32°F). At higher temperatures, the nitration will either proceed further to form a dinitrochloro-compound, chloronitrophenol, or a nitrophenol.¹ Chlorobenzenes are attacked by electrophilic agents. Substitution for monochlorobenzene is predominantly para-; with some ortho-substitution. The higher chlorinated benzenes tend to resist electrophilic substitution but can be substituted under extreme conditions.¹

Chlorobenzenes also undergo some free radical reactions. Formation of organometallic compounds (grignards, aryl-lithium compounds) provides a useful route to many organic intermediates. Photochemical transformations occur on irradiation of chlorinated benzenes, which are much less stable to radiation than benzene. When subjected to ultraviolet irradiation or pulse hydrolysis in solution, chlorobenzenes may polymerize to biphenyls, chloronaphthalenes, or more complex products.¹ The ability of chlorobenzenes to undergo wide varieties of chemical reactions makes chlorinated benzenes useful as reactants in numerous commercial processes to produce varied products. All chlorinated derivatives of benzene are soluble in lipids. Partition coefficient data for chlorobenzenes show an increase in partition coefficient with an increase in

the degree of chlorination. In general, a positive correlation exists between partition coefficient and degree of bioaccumulation.¹

3.1.2 Properties of Monochlorobenzene

Monochlorobenzene has a high solubility in nonpolar solvents, however, it is almost insoluble in water. If it accumulates in water systems, it tends to sink due to its density. There may be a greater tendency for monochlorobenzene to accumulate in still lake waters rather than fast moving streams and rivers because of its comparatively high volatility.¹

Monochlorobenzene is most likely to enter the atmosphere from fugitive emission sources, including solvent evaporation. Monochlorobenzene will exist in the atmosphere in the vapor phase and will react with hydroxyl radicals, producing chlorophenol byproducts of decomposition. The atmospheric half-life of monochlorobenzene is 17 days. Atmospheric half-life will decrease in polluted air containing nitric oxide. Products of decomposition will include chloronitrobenzene and chloronitrophenols. Photolysis in the atmosphere is expected to be slower (30 days), resulting in monochlorobiphenyl production.⁴

3.1.3 Properties of Dichlorobenzenes

Ortho- and meta-dichlorobenzene are neutral, mobile, colorless liquids with similar characteristics and odors. Para-dichlorobenzene is a pleasant smelling white crystalline solid. The crystals readily sublime at room temperature. Solubilities of the dichlorobenzenes are similar to those of monochlorobenzene, and the dichlorobenzenes also form a number of azeotropes.¹

Solvent evaporation is the major source of o-dichlorobenzene in the atmosphere. Approximately 25 percent of annual solvent production using o-dichlorobenzene is expected to be lost to the atmosphere. It will exist in the atmosphere in the vapor phase and will react with hydroxyl radicals for an estimated half-life of 24 days.⁴ Meta-dichlorobenzene is most likely to enter the atmosphere from fumigation products application, as well as chemical intermediate and solvent use. It exists in the atmosphere in the vapor phase and can react with hydroxyl

radicals for an estimated half-life of 14 days.⁴ Para-dichlorobenzene is most likely to enter the atmosphere from the volatilization of household deodorant products and moth flakes. Approximately 70 to 90 percent of p-dichlorobenzene's annual production may eventually be released to the atmosphere. It exists in the atmosphere in the vapor phase and reacts with hydroxyl radicals for an estimated half-life of 31 days. Byproducts of decomposition in the presence of smog include dichloronitriphenol, dichloronitrobenzene, and dichlorophenol.⁴

3.1.4 Properties of Trichlorobenzenes

The trichlorinated benzenes are white crystalline solids, except for 1,2,4-trichlorobenzene, which is a colorless liquid. Solubilities are similar, with insolubility in water, generally good solubility in alcohol, ether, benzene, and chloroform, and relatively high lipid solubility.¹

1,2,4-Trichlorobenzene may enter the atmosphere through its use in the manufacture of dye carriers, herbicides, chlorinated benzenes, dielectric fluids, and a variety of other applications. It exists in the atmosphere in the vapor phase and reacts with hydroxyl radicals for an estimated half-life of 18.5 days. Byproducts of photodegradation in the atmosphere include 1,3- and 1,4-dichlorobenzene.⁴ 1,3,5-Trichlorobenzene may enter the atmosphere through its use as an industrial chemical, chemical intermediate, solvent, and emulsifier. It exists in the atmosphere in the vapor phase and will react with hydroxyl radicals for an estimated half-life of 6.17 months.⁴

3.1.5 Properties of Hexachlorobenzene

Hexachlorobenzene is a colorless crystalline solid at normal temperatures which slowly degrades in the environment. Although insoluble in water, it is slightly soluble in cold alcohol and soluble in benzene, chloroform, and ethyl ether. Rapid sublimation of the crystals occurs in the temperature range of 0°C to 30°C (32° to 86°F).⁶

Hexachlorobenzene may enter the atmosphere through waste incineration or chlorinated hydrocarbon manufacture. Hexachlorobenzene is extremely resistant to biodegradation and is

therefore very persistent in the environment. It exists in the atmosphere in the vapor phase and the adsorbed phase. Hexachlorobenzene degradation in the atmosphere has an estimated half-life of 2 years. Due to the stable characteristics of hexachlorobenzene, long range transport in the atmosphere is likely.⁴

3.2 OVERVIEW OF PRODUCTION AND USE

Twelve chlorinated benzenes can be formed by replacing some or all of the hydrogen atoms on the benzene ring with chlorine atoms. With the exceptions of 1,3-dichlorobenzene, 1,3,5-trichlorobenzene, and 1,2,3,5-tetrachlorobenzene, the chlorinated benzenes are produced in the presence of a Friedel-Crafts catalyst. The usual catalyst is ferric chloride (FeCl_3), which can be added to the reaction mixture or generated *in situ* by exposing a large iron surface to the liquid being chlorinated. Each compound, except hexachlorobenzene, can be chlorinated further; hence, the product is always a mixture of chlorinated benzenes. Pure compounds are obtained by distillation and crystallization.⁸

Currently, there are three known domestic producers of chlorobenzenes, each operating at a single location. Individual plants producing chlorobenzenes vary in capacity from 0.5 million to 80 million kilograms (1 to 176 million pounds). In 1989, the total production capacity for monochlorobenzene was 168 million kilograms (371 million pounds), for o-dichlorobenzene it was 36.7 million kilograms (81 million pounds), and for p-dichlorobenzene, 60 million kilograms (132 million pounds).⁹ Few data are available on production of more highly chlorinated benzenes.

Processes for the manufacture of chlorobenzenes include various chemistry and product separation methods. The process currently used by industry is direct chlorination of benzene in the presence of a FeCl_3 catalyst to produce monochlorobenzene. The monochlorobenzene reacts with the remaining chlorine to form dichlorobenzenes. Hydrogen chloride is a byproduct in both reactions. In addition to the two major isomers of dichlorobenzene, ortho- and para-, a very small amount of the meta-isomer is formed. As chlorination is continued, tri-, tetra-, penta-, and hexachlorobenzenes are formed. Usually, trichlorobenzene is the only highly chlorinated product

found in significant amounts. The degree of chlorination of benzene can be controlled by the choice of the catalyst, temperature, and benzene:chlorine ratio in the reactor feed. Hydrogen chloride, a byproduct of the reaction, is processed under anhydrous conditions before it is absorbed in water. The reaction and the recovery operations, in most cases, are continuous.

Demand for monochlorobenzene as a feedstock comes mostly from the synthetic organic chemical manufacturing industries. Accordingly, the simple manufacturing process often allows monochlorobenzene to be manufactured in the same plant in which it is consumed. Historically, the two major markets for monochlorobenzene have been in the manufacture of phenol and o- and p- nitrochlorobenzenes. However, the use of monochlorobenzene as a feedstock in phenol manufacturing has been phased out and replaced by cumene.¹⁰ Other feedstock uses for monochlorobenzene include use in the manufacture of diphenyl oxide, dye and herbicide intermediates, and sulfone polymers.

Ortho-dichlorobenzene is used primarily in organic synthesis of 3,4-dichloroaniline, which is used as an intermediate in the production of herbicides. Demand for o-dichlorobenzene as a solvent carrier in the manufacture of toluene diisocyanate for polyurethane manufacture has increased, and is expected to grow faster than any other use. It is also used as a solvent in paint removers and engine cleaners, in de-inking solvents, and in dye manufacture.¹¹

Para-dichlorobenzene is used predominantly in the manufacture of polyphenylene sulfide resins. In 1988, polyphenylene sulfide resin manufacturing consumed 22 percent of all the p-dichlorobenzene manufactured for that year. In addition to the manufacture of polyphenylene sulfide, p-dichlorobenzene is used in the manufacture of room deodorants, moth proofing products, and 1,2,4-trichlorobenzene. Para-dichlorobenzene is also used as an intermediate in the dyes and insecticide industries.¹²

1,2,4-Trichlorobenzene is primarily used in pesticide formulation. The manufacture of the pesticide Banvel[®] consumed approximately 15 million pounds of trichlorobenzene in 1988. 1,2,4-Trichlorobenzene is also used as a process solvent, chemical intermediate, lubricant, and a heat transfer medium.¹³

Hexachlorobenzene is no longer produced or imported into the United States for commercial usage. Formerly, hexachlorobenzene was used as an active ingredient in fungicidal preparations, but this use has been nearly eliminated due to the cancellation of registry of HCB-containing fungicides. Currently, hexachlorobenzene is formed as a process waste byproduct during the manufacture of specific chlorinated solvents and pesticides.¹³

Meta-dichlorobenzene, 1,2,3-trichlorobenzene, and 1,3,5-trichlorobenzene, pentachlorobenzene, and all three tetrachlorobenzenes are not discussed here due to their limited production and use. Summaries of the current uses of each of the industrially significant chlorobenzenes are presented in Figures 3-1 through 3-4, along with the percentage of total product devoted to each use.

Table 3-3 shows some of the end products from chlorobenzenes. These products and some of their production processes will be covered in detail in Sections 5.0 and 6.0.

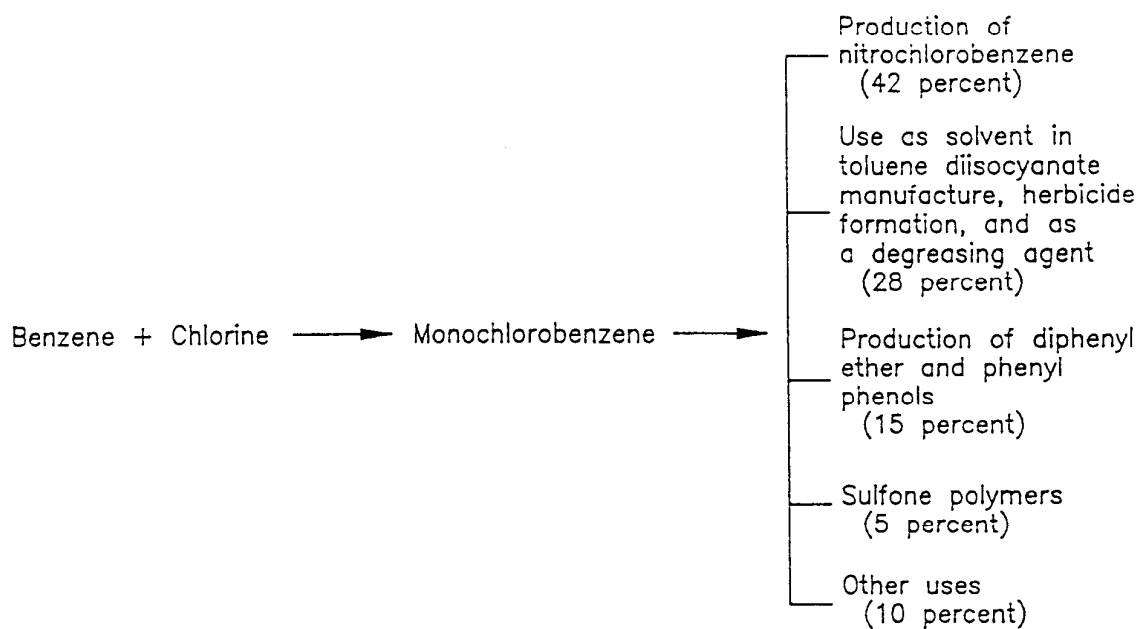


Figure 3-1. End uses of monochlorobenzene¹²

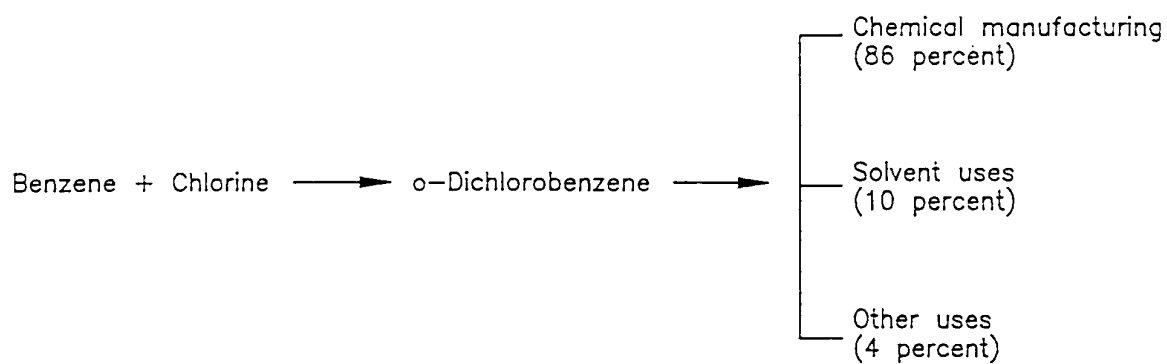


Figure 3-2. End uses of o-dichlorobenzene¹²

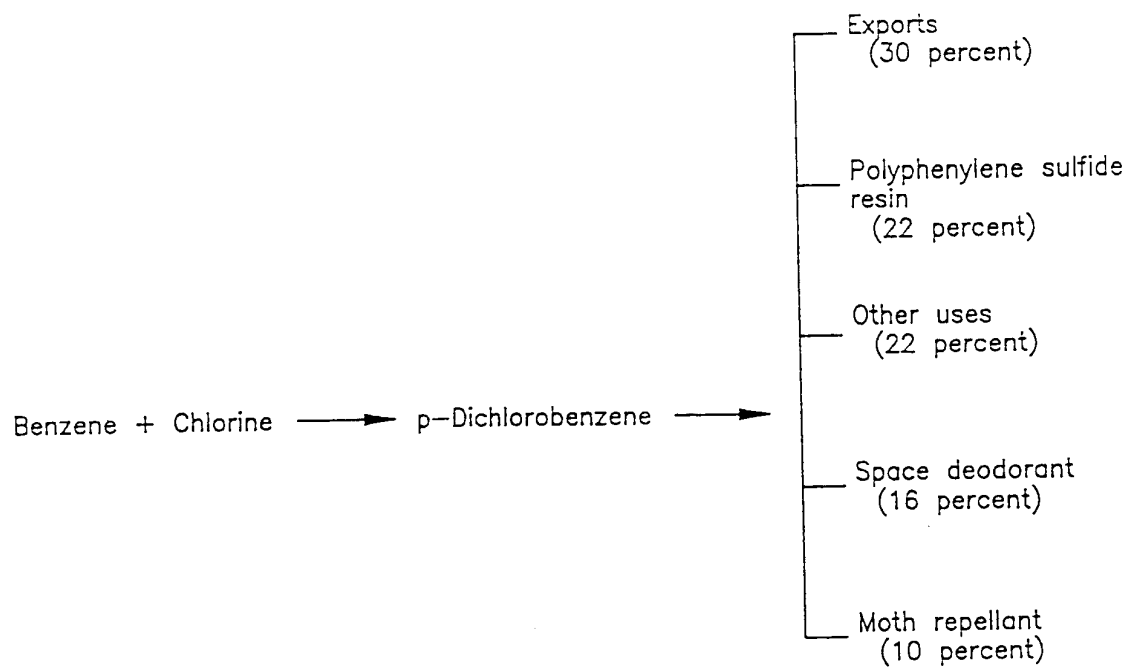


Figure 3-3. End uses of p-dichlorobenzene¹²

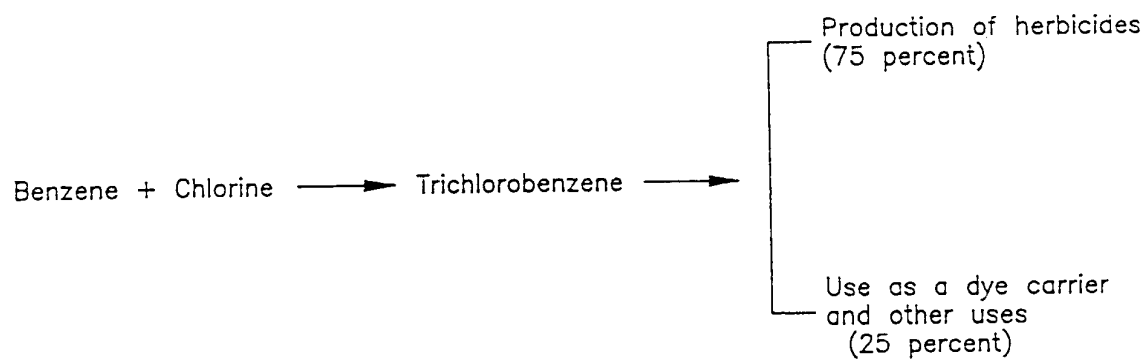


Figure 3-4. End uses of trichlorobenzene¹²

**TABLE 3-3.
END USES OF CHLOROBENZENES**

Chlorobenzene Isomer and Use	End Use
Monochlorobenzene	
Nitrochlorobenzenes	Used as intermediates in the manufacture of rubber chemicals, agricultural chemicals, antioxidants, dyes and pigments
Solvents	Used as a solvent in processes to produce rubber products, pesticides, pharmaceuticals, and resins
Diphenol ether and phenylphenols	Used as an intermediate for dyes, optional bleaches, ultraviolet stabilizers for plastics, pharmaceuticals and pesticides
Sulfone polymers	Used in engineering plastics
Dichlorobenzenes	
p-Dichlorobenzene	
Deodorant	Used as a space and sanitary deodorant
Moth repellent	Used as moth repellent
Resins	Used as an intermediate in polyphenylene sulfide resins for high performance plastics
o-Dichlorobenzene	
Chemical manufacture	Used as an intermediate for the production of pesticides
Solvents	Used in formulated paint strippers and cleaners and as a heat transfer agent
Trichlorobenzenes	
Chemical manufacture	Used as an intermediate for the production of dyes, pesticides and dielectric fluids
Dye carrier	Used as a dye carrier in the textile fabric dyeing industry

Source: References 10-12.

3.3 REFERENCES FOR SECTION 3.0

1. U.S. Environmental Protection Agency, *Investigation of Selected Potential Environmental Contaminants: Halogenated Benzenes*, EPA-560/2-77-004, Office of Toxic Substances, Washington DC, July 1977, pp. 6-43.
2. U.S. Environmental Protection Agency, *Health Assessment Document for Chlorinated Benzenes*, EPA-600/8-84-015a, Office of Research and Development, Cincinnati, Ohio, April 1984, pp. 3-6.
3. Sax, N.I. and R.J. Lewis, *Dangerous Properties of Industrial Materials, Seventh Edition, Volumes I & II*, Van Nostrand Reinhold, New York, NY, 1989.
4. *Handbook of Environmental Fate and Exposure Data for Organic Chemicals, Volume I*, Lewis Publishers, Inc., Chelsea, Michigan, 1990.
5. Reid, R.C., Prausnitz, J.M., and T.K. Sherwood, *The Properties of Gases and Liquids, Third Edition*, McGraw-Hill Book Company, New York, NY, 1977, p. 184.
6. Windholz, M. (ed.), *The Merck Index, Tenth Edition*, Merck and Company, Rahway, NJ, 1984. pp. 298, 444, 677, 1377.
7. Weast, R.C. (ed.), *CRC Handbook of Chemistry and Physics, 59th Edition*, CRC Press Inc., West Palm Beach, FL, 1978, pp. C-153, 157, 171.
8. *Kirk-Othmer Encyclopedia of Chemical Technology, Volume 5, Third Edition*, Wiley-Interscience Publication, New York, NY, 1980, pp. 797-808.
9. *1990 Directory of Chemical Producers, United States of America*, SRI International, Menlo Park, CA, 1990.
10. "Chemical Profile: Monochlorobenzene," *Chemical Products Synopsis*, Mannsville Chemical Products Corporation, Ashbury Park, NJ, July 1990.
11. "Chemical Profile: Dichlorobenzenes," *Chemical Products Synopsis*, Mannsville Chemical Products Corporation, Asbury Park, NJ, March 1983.
12. *SRI Chemical and Economics Handbook*, "Chlorobenzene Production," Menlo Park, CA, 1989.
13. Brooks, G.W. and G.E. Hunt, *Source Assessment for Hexachlorobenzene*, Final Report, U.S. Environmental Protection Agency, Pollutant Assessment Branch, Research Triangle Park, NC, 1984, pp. 9-18.

SECTION 4.0

EMISSIONS FROM CHLOROBENZENES PRODUCTION

Production of chlorobenzenes and the associated air emissions are described in this section. Process flow diagrams are included as appropriate, with specific streams or vents labeled to correspond with the discussion in the text. Emission factors for the production processes are presented when available and control technologies are described. Subsection 4.1 presents potential problems and solutions in determining fugitive emissions from equipment leaks. Subsections 4.2 through 4.4 detail production processes by which monochlorobenzene (MCB), m-, o-, and p-dichlorobenzenes (DCB), isomers of trichlorobenzenes (TCB), and hexachlorobenzene are isolated and processed. The reader should contact the specific facility to verify the nature of the process used, production volume, and controls that are in place before applying any of the emission factors presented.

Chlorobenzenes are currently produced by three companies at three locations in the United States. In 1989, production capacity for monochlorobenzene was 168 million kilograms (371 million pounds), for o-dichlorobenzene it was 36.7 million kilograms (80.9 million pounds), and for p-dichlorobenzene, 60 million kilograms (132 million pounds).¹

4.1 EQUIPMENT LEAK EMISSIONS

Although the production of chlorobenzenes and other chemicals (discussed in Section 5) involves varied processes, all of these processes are known to release fugitive emissions. For this reason, equipment leak emissions are discussed before detailed specific process descriptions; are referenced in these descriptions; and, where applicable, are referenced in the discussion of end uses of chlorobenzenes in Section 5.

Emission factors for fugitive emissions are presented in some of the following subsections and in Section 5. However, these emission factors should be used cautiously and are only recommended for obtaining very crude emission estimates. They do not take into account the actual number of various leaking and nonleaking components within a facility, but are only a

general estimate based on a hypothetical plant. The discussion below presents a more credible approach to determining fugitive emissions.

Emissions occur from process equipment components whenever the liquid or gas streams leak from the equipment. Equipment leaks can occur from the following components: pump seals, process valves, compressor seals and safety relief valves, flanges, open-ended lines, and sampling connections. Emission estimates can be calculated in the five ways described in the EPA publication *Protocols for Generating Unit-Specific Emission Estimates for VOC and VHAP* (EPA-450/3-88-010).² The methods differ in complexity; however, greater complexity usually yields more accurate emission estimates.

The simplest methodology requires the following input data: number of each component type, chlorobenzenes percent weight of the stream, and the number of hours per year the component is in service. These data are then multiplied by EPA's average emission factors for the Synthetic Organic Chemical Manufacturing Industries (SOCMI) shown in Table 4-1. This method should be used only if no other emissions data are available, as it may result in overestimating equipment leak emissions. Emissions can be estimated by using the formula shown below.²

$$\left[\begin{array}{c} \text{No. of} \\ \text{equipment components} \end{array} \right] \times \left[\begin{array}{c} \text{Weight percent} \\ \text{Chlorobenzene in the stream} \end{array} \right] \times \left[\begin{array}{c} \text{Component-specific} \\ \text{emission factor} \end{array} \right] \times \left[\begin{array}{c} \text{No. hrs/yr in} \\ \text{Chlorobenzene service} \end{array} \right]$$

One of the more complex methodologies may be used to obtain more accurate equipment leak emission estimates. However, these methodologies require that some level of emission measurements be made for the facility's process equipment components. These methodologies are briefly described here, and the reader is referred to *Fugitive Emission Sources of Organic Compounds--Additional Information on Emissions, Emission Reductions, and Costs* for calculation details.³

**TABLE 4-1.
AVERAGE EMISSION FACTORS FOR FUGITIVE EQUIPMENT
LEAK EMISSIONS**

Equipment	Service	Emission Factor (kg/hr/source)	Emission Factor (lb/hr/source)	Emission Factor Quality Rating^a
Valves	Gas	0.0056	0.0123	U
	Light Liquid	0.0071	0.0157	
	Heavy Liquid	0.00023	0.00051	
Pump Seals	Light Liquid	0.0494	0.1089	U
	Heavy Liquid	0.0214	0.0472	
Compressor Seals	Gas/Vapor	0.228	0.5027	U
Pressure Relief Seals	Gas/Vapor	0.104	0.2293	U
Flanges	All	0.00083	0.0018	U
Open-Ended Lines	All	0.0017	0.0037	U
Sampling Connections	All	0.0150	0.0331	U

^aBased on engineering judgement.
Source: Reference 2.

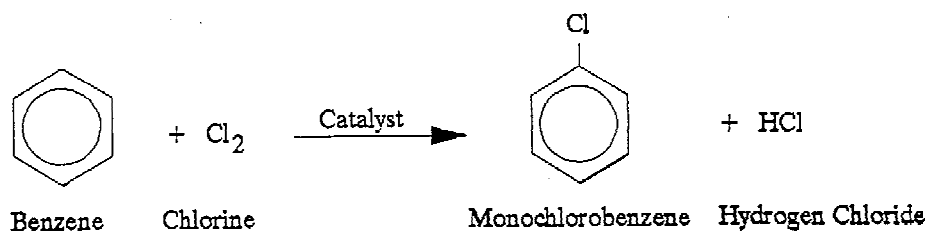
The first methodology is referred to as the leak/no leak approach. It is based on a determination of the number of leaking and nonleaking components. These values are then multiplied by two separate sets of EPA-derived emission factors (for leaking and nonleaking). The second methodology groups screening results of process equipment components into three ranges: 0 - 1,000 ppmv; 1,000 - 10,000 ppmv; and greater than 10,000 ppmv. The number of each component falling in a particular range is then multiplied by the component-specific emission factor for that range. The third methodology uses screening data in correlation equations derived by EPA. Finally, the fourth methodology gives each facility an option to develop its own correlation equations, but requires more rigorous testing, bagging, and analysis of equipment leaks to determine mass emission rates.³

Although no specific information on emissions controls used by the industry was identified, equipment components in chlorobenzene service typically have some type of control. Generally, control of fugitive emissions requires the use of sealless or double mechanical seal pumps, an inspection and maintenance program, and routine replacement of leaking valves and fittings. Typical controls for equipment leaks are listed in Table 4-2.³ In addition, other leakless process equipment is available such as leakless valves and sealless pumps.

4.2 MONOCHLOROBENZENE PRODUCTION

4.2.1 Process Description

In general, the most widely used process by which benzene is chlorinated to form MCB is by passing dry chlorine into benzene gas in the presence of a catalyst in the following reaction:



The catalyst most often used is ferric chloride (FeCl_3); catalysts employed to a lesser extent are anhydrous aluminum chloride, stannic chloride, molybdenum chloride, Fuller's earth, and metallic iron or aluminum filings.⁴ Specific processes, including the continuous, batch, and Raschig methods of benzene chlorination, are most often used in the production of MCB. A purification process is then used to further separate the crude MCB from other chlorobenzene forms and impurities. Prior to the reaction for all of the above methods, benzene gas is dried either by azeotropic distillation or with silica gel, caustic soda, or alumina. Chlorine gas is prepared by scrubbing with concentrated sulfuric acid to remove moisture and impurities.⁵ The chlorination then proceeds by one of the above-mentioned methods.

**TABLE 4-2.
CONTROL TECHNIQUES AND EFFICIENCIES APPLICABLE TO EQUIPMENT LEAK
EMISSIONS**

Equipment Component (Emission Source)	Control Technique	Percent Reduction	
Pump Seals Packed and Mechanical	Seal area enclosure vented to a combustion device	100	
	Monthly LDAR ^a	61	
	Quarterly LDAR	32	
	Semiannual LDAR	0	
	Annual LDAR	0	
Double Mechanical ^b	N/A ^c	--	
Compressors	Vent degassing reservoir to combustion device	100	
Flanges	None available	0	
Valves Gas	Monthly LDAR	73	
	Quarterly LDAR	64	
	Semiannual LDAR	50	
	Annual LDAR	24	
	Liquid	Monthly LDAR	59
		Quarterly LDAR	44
		Semiannual LDAR	22
		Annual LDAR	0
Pressure Relief Devices Gas	Monthly LDAR	50	
	Quarterly LDAR	44	
	Rupture Disk	100	
Sample Connections	Closed-purge sampling	100	
Open-ended Lines	Caps on open ends	100	

^a LDAR (Leak detection and repair).

^b Assumes the seal barrier fluid is maintained at a pressure above the pump stuffing box pressure and the system is equipped with a sensor that detects failure of the seal and/or barrier fluid system.

^c N/A (Not applicable). There are no VOC emissions from this component.

Source: Reference 3.

The continuous process is most often used because it produces high yields containing up to 95 percent MCB and small amounts of DCB isomers. It is not possible by selecting catalyst conditions or by modifying process parameters to prevent the formation of DCBs. Basic operations that may be used in the continuous production of MCB are shown in Figure 4-1. The process begins with a series of small, externally cooled cast iron or steel vessels containing the catalyst (which may consist of Rashig rings of iron or iron wire). Chlorine is supplied into each vessel through suitably positioned inlets to maintain a large benzene-to-chlorine reaction at all points along the reaction stream. The temperature is held between 20°C to 40°C (68°F to 104°F) to minimize the production of DCBs which form at higher temperatures. Dry benzene (Stream 1) and dried recycled benzene (Stream 2) are introduced into the reactor, which produces an overhead gas (Stream 3). The gas stream (containing HCl, unreacted chlorine, inert gases from the chlorine feed, benzene, and other VOCs) is sent to an organic absorber where benzene and other VOCs are removed. The bottoms from the organic absorber (Stream 6) flow to the HCl stripper for recovery of HCl.⁶ The overhead gas (Stream 5) is sent to HCl absorption. Byproduct hydrogen chloride is then removed in the HCl absorber where it is saturated by washing with a refrigerated solvent (*e.g.*, *o*-dichlorobenzene) or low vapor pressure oil, and then recovered in wash towers as commercially usable hydrochloric acid.^{6,7}

Crude reaction liquid product (Stream 4) enters the crude chlorobenzene distillation column which produces overheads (Stream 7) containing most of the chlorobenzenes, unreacted benzene, and some HCl, and a bottom stream from which catalyst and other byproducts are separated (Stream 8) and processed for reuse. The overheads (Stream 7) pass through an HCl stripper and into a benzene recovery column (Stream 9). Part of the subsequent benzene-free stream (Stream 10) is returned to the organic absorber while the remainder (Stream 11) enters the MCB distillation column. The overhead MCB distillation product (Stream 12) is then stored while the bottom stream containing DCB and TCB isomers is processed.⁶ Although in most cases, isomer separation processing is conducted simultaneously with MCB production, it is discussed separately in subsequent sections of this document.

In the batch process, benzene is contained in a deep, iron or mild steel vessel lined with lead cooling coils. The catalyst, usually sublimed FeCl₃, is added in a benzene solution.

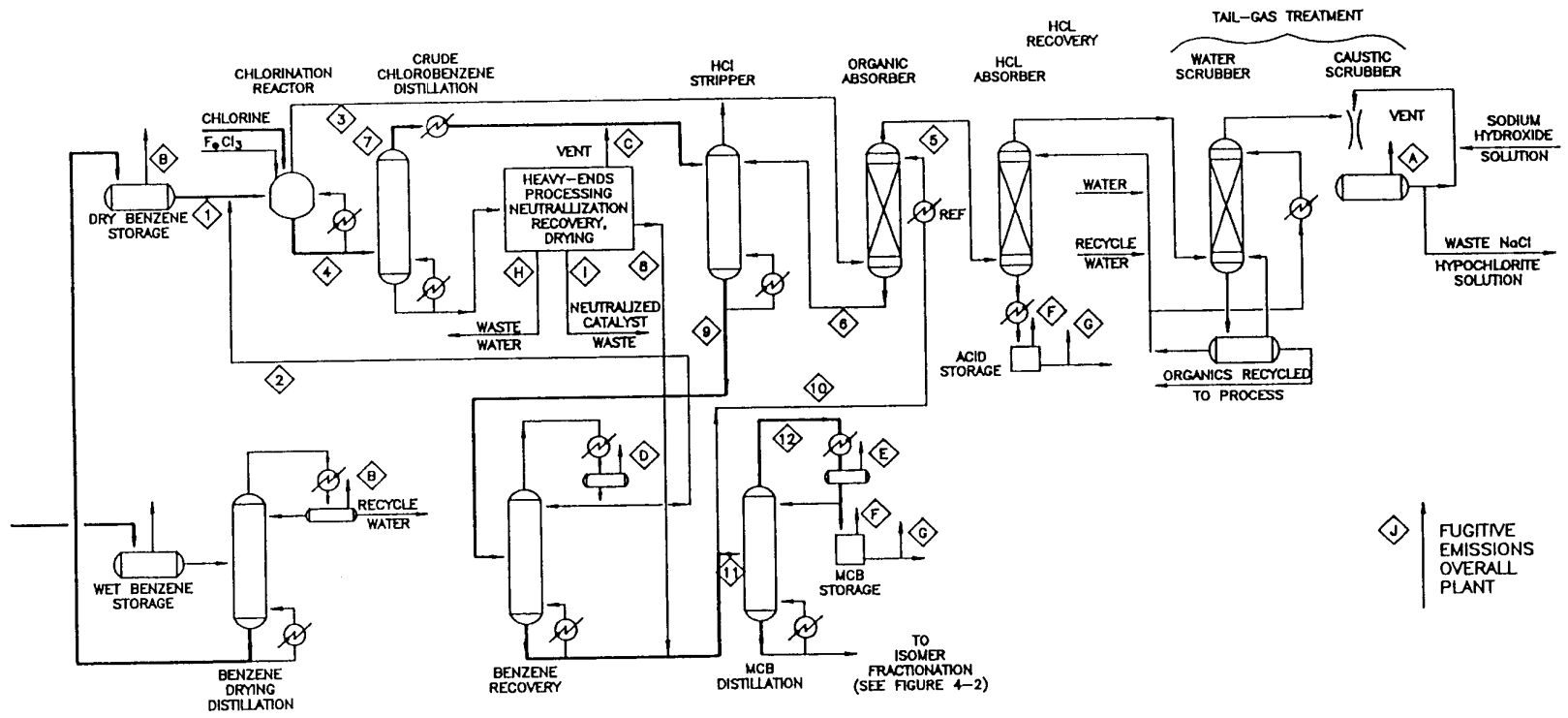


Figure 4-1. Monochlorobenzene continuous production process diagram.⁶

Chlorine is fed into the bottom of the chlorinator through a lead covered pipe at a rate that maintains the temperature below 45°C (113°F) in order to minimize production of DCBs.⁵ The crude chlorobenzene stream and HCl waste stream are collected and treated as in the purification and recovery processes described previously.

Faith, Keyes, and Clark's Industrial Chemicals describe a higher temperature batch process where chlorine is bubbled into a cast iron or steel tank containing dry benzene with one percent of its own weight of iron filings. Temperature is maintained at 40°C to 60°C (104°F to 140°F) until density studies indicate that all benzene is chlorinated. The temperature is then raised to between 55°C and 60°C (131°F to 140°F) for six hours until the density raises to 1.280 g/cm³ (79.91 lb/ft³). The same methods of chlorobenzene purification and HCl recovery in batch form are then employed. At 100 percent chlorination, the products are 80 percent monochlorobenzene, 15 percent p-dichlorobenzene, and 5 percent o-dichlorobenzene.⁷

Another method of MCB production is the vapor phase chlorination of benzene by the Raschig process. Chlorine produced by the catalytic oxidation of hydrogen chloride is introduced into a preheated mixture of benzene vapor, air and steam. The mixture is then contacted at 220°C to 260°C (428° to 500°F) with a mixed catalyst of copper oxide and oxides of Group III and VIII metals on a silica gel. To control the temperature, the catalyst is packed in small diameter tubes. To reduce DCB formation, only 10 percent of the benzene is reacted at a time. Purification and recovery proceed as indicated previously.⁵

In 1989, three facilities had the capacity to produce an annual total of 168 million kilograms (371 million pounds).^{1,8} These three major producers of monochlorobenzene are listed in Table 4-3. Plant-specific production processes from the producers of MCB were not available. The facilities producing monochlorobenzene are subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contact with plant personnel.

TABLE 4-3.
CHEMICAL PRODUCERS OF MONOCHLOROBENZENE - 1989

Facility	Location	Capacity Million kg/yr (Million lbs/yr)
Monsanto Company Monsanto Industrial Chemicals Company	Sauget, Illinois	80 (176)
PPG Industries, Inc. Chemicals Group Industrial Chemical Division	Natrium, West Virginia	20.4 (45)
Standard Chlorine Chemical Company, Inc.	Delaware City, Delaware	68 (150)
Total		168.4 (371)

Source: References 1, 8.

4.2.2 Emissions

Figure 4-1 is labeled to show potential emission release points. The primary emissions from the production of MCB result from the tailgas treatment vent (A), where inert gases originally contained in the chlorine feed are vented. The vent stream also contains benzene and chlorobenzenes. Other sources of chlorobenzene emissions include: benzene drying (B); heavy-ends processing (C); benzene recovery (D); MCB distillation (E); emissions due to storage (F) and handling (G); volatilization of MCB from waste water (H); fugitive emissions during solid waste handling (I); and fugitive emissions from valves, flanges, seals, etc. (J).⁶

Emission factors for the production of monochlorobenzene are given in Table 4-4. The emission factors in Table 4-4 are only general estimates derived from site visit measurements. No specific information was available on particular emission points included in each of the emission categories, on the type of production processes used (batch or continuous), or on specific control technologies employed, if any.

TABLE 4-4.
EMISSION FACTORS FOR A HYPOTHETICAL
MONOCHLOROBENZENE PRODUCTION PLANT^a

Emission Category	kg MCB Emitted Per Mg MCB Produced	lb MCB Emitted Per Ton MCB Produced	Emission Factor Quality Rating
Process	2.06	4.12	E
Storage	0.45	0.90	E
Fugitive	0.69	1.38	E
TOTAL	3.20	6.40	

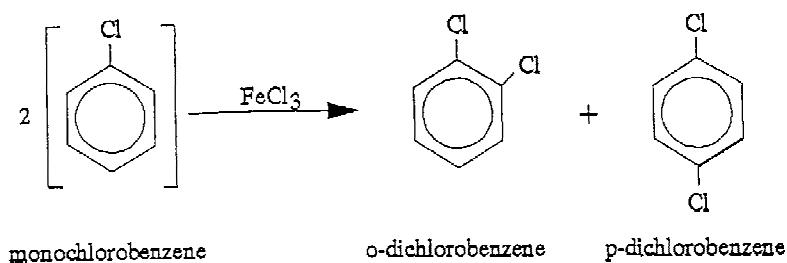
^a1981 data.

Source: Reference 9.

Any given monochlorobenzene production plant may be different from this hypothetical facility in configuration and level of control. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions.

4.3 DICHLOROBENZENES PRODUCTION

Mixtures of dichlorobenzenes can be produced at facilities formulating MCB by chlorinating MCB or benzene at 150°C to 190°C (302° to 374°F) in the presence of ferric chloride, as shown below.



4.3.1 Ortho- and Para-Dichlorobenzene

The residue from distillation of crude chlorobenzene, consisting mainly of o- and p-DCB, is the principal source of these isomers. Figure 4-2 presents basic operations that may be used to produce o- and p-DCB and TCB. In a continuation of the production of MCB, o- and p-DCB can be separated by fractional distillation. Isomer fractionation yields p-DCB (with traces of o-DCB and m-DCB) which enters the overhead (Stream 1) while the o-DCB enters the bottoms (Stream 2). The o-DCB bottoms (Stream 2) undergoes fractional distillation and produces an o-DCB overhead (Stream 3), which is sent to storage, and bottoms (Stream 4), which is further processed to yield TCBs.⁶

The crude p-DCB with other trace isomers (Stream 5) is purified by batch crystallization. Part of the purified p-DCB (Stream 6) is sent to liquid storage while the remainder (Stream 7) undergoes freezing, crushing, screening, and packing of p-DCB crystals. The mother liquor from crystallization (Stream 8) is sent to DCB solvent grade fractionalization where it is separated into solvent grade o-DCB (Stream 9) and p-DCB (Stream 10) and stored.⁶

Currently, three facilities have the capacity to produce both o- and p-dichlorobenzene. Annual capacity of o-dichlorobenzene is 36.7 million kilograms (80.9 million pounds). The annual capacity of p-dichlorobenzene is 60 million kilograms (132 million pounds). The three major producers of o- and p-dichlorobenzene are listed in Table 4-5.^{1,8} The major producers of dichlorobenzenes are subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contact with plant personnel.

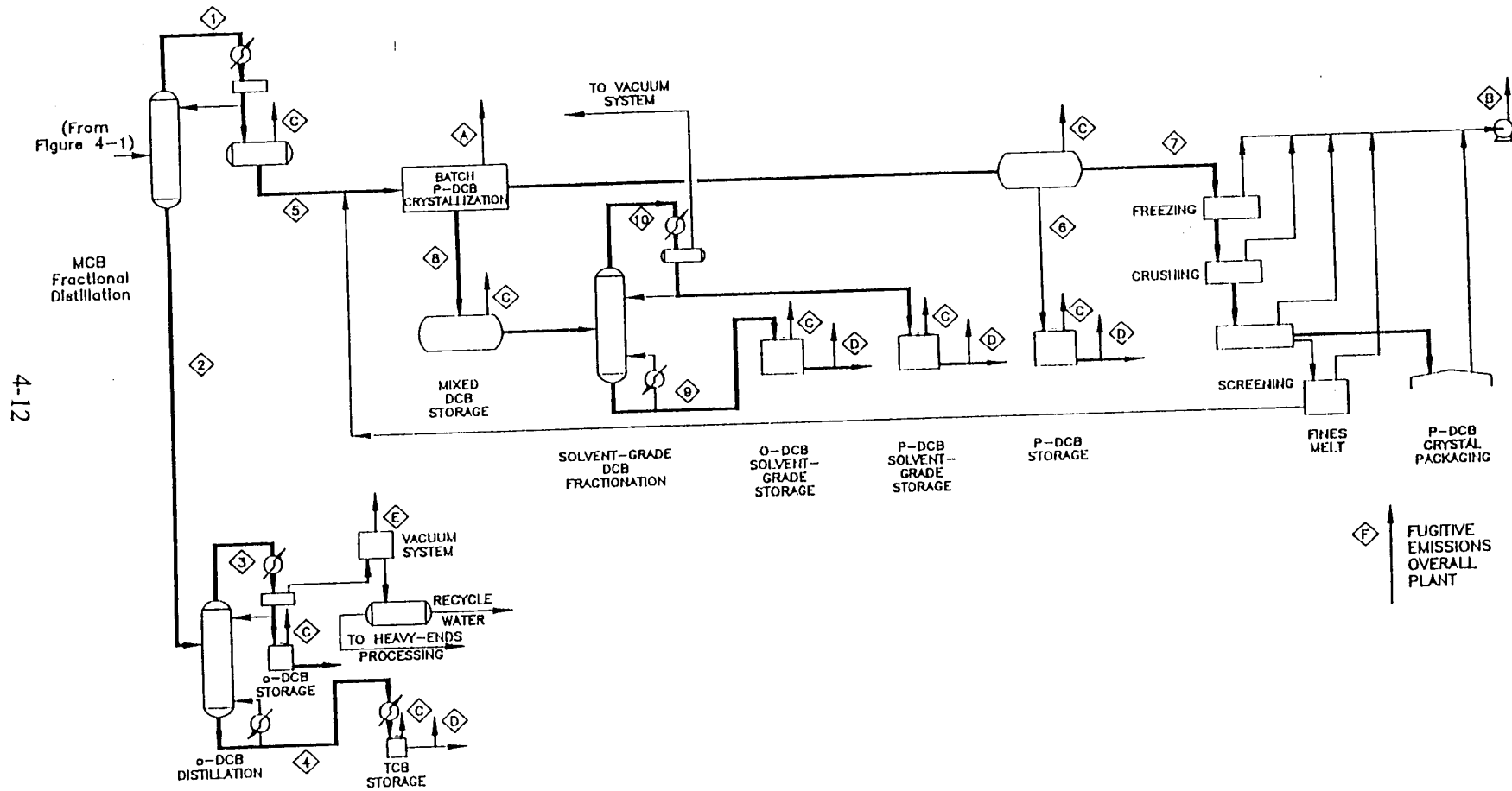


Figure 4-2. Dichlorobenzene and trichlorobenzene continuous production diagram.⁶

**TABLE 4-5.
CHEMICAL PRODUCERS OF o-DICHLOROBENZENE AND
p-DICHLOROBENZENE, 1989**

Facility	Location	Capacity Million kg/yr (Million lbs/yr)	
		o-DCB	p-DCB
Monsanto Company Monsanto Industrial Chemicals Company	Sauget, Illinois	4.5 (9.9)	11.3 (24.9)
PPG Industries, Inc. Chemicals Group Industrial Chemical Division	Natrium, West Virginia	9 (19.8)	13.6 (30)
Standard Chlorine Chemical Company, Inc.	Delaware City, Delaware	22.7 (50)	34 (75)
Total		36.7 (80.9)	59.6 (131.4)

Source: References 1, 8.

4.3.2 Meta-Dichlorobenzene

The isolation of m-dichlorobenzene from mixed dichlorobenzene streams is not economical, since it usually occurs at a level of one (1) percent or less. Meta-dichlorobenzene is sold with other isomers as mixed chlorobenzenes.¹⁰

It should be noted that discussions in this chapter have principally described the manufacture of selected chlorobenzene isomers from non-chlorobenzene materials. Numerous manufacturers also purchase select chlorobenzene isomers from original manufacturers for repackaging. Other manufacturers purchase mixed chlorobenzenes and isolate selected isomers for resale.¹⁰

4.3.3 Emissions

The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel. Emissions from the continuous process (Figure 4-2) are primarily from the batch p-DCB crystallization vent (A). An exhaust fan (B) releases sublimation losses from freezing, crushing, and the p-DCB crystal packaging hoods to the atmosphere. Some emissions are also expected from liquid product storage (C), handling (D), and the vacuum system (E) which services the vacuum stills. Fugitive emissions may be expected from certain valves, pumps, etc. (F).⁶ Data are not available to estimate emissions from the production of m-DCB. Emission factors for o- and p-DCBs are shown in Tables 4-6 and 4-7, respectively. The emission factors are only general estimates derived from site visit measurements. No specific information was available on particular emission points included in each of the emission categories or on the type of production processes used (batch or continuous) or on only specific control technologies employed.

Any actual o-DCB and p-DCB production plant may vary in configuration and level of control from the hypothetical facilities. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

4.4 TRICHLOROBENZENES PRODUCTION

The most common process by which trichlorobenzenes are formed is the catalytic chlorination of o- and p-DCB at 20°C to 30°C (68°F to 86°F) in the presence of ferric chloride. The reaction is allowed to proceed until a density of 1.4 g/mL at 15°C (59°F) is obtained, at which time the acid is neutralized and the products are fractionally distilled to yield 1,2,4- and 1,2,3-isomers.¹²

**TABLE 4-6.
EMISSION FACTORS FOR A HYPOTHETICAL
o-DICHLOROBENZENE PRODUCTION PLANT^a**

Emission Category	kg o-DCB Emitted Per Mg o-DCB Produced	lb o-DCB Emitted Per Ton o-DCB Produced	Emission Factor Quality Rating^b
Process	2.32	4.64	U
Storage	0.47	0.94	U
Fugitive	0.76	1.52	U
TOTAL	3.55	7.10	

^a1980 data.

^bNot enough information available to assign a quality rating.

Source: Reference 11.

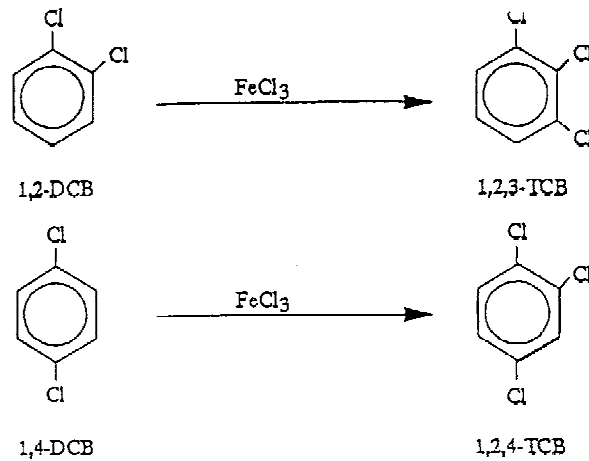
**TABLE 4-7.
EMISSION FACTORS FOR A HYPOTHETICAL
p-DICHLOROBENZENE PRODUCTION PLANT^a**

Emission Category	kg p-DCB Emitted Per Mg p-DCB Produced	lb p-DCB Emitted Per Ton p-DCB Produced	Emission Factor Quality Rating^b
Process	5.81	11.62	U
Storage	0.41	0.82	U
Fugitive	1.02	2.04	U
TOTAL	7.24	14.48	

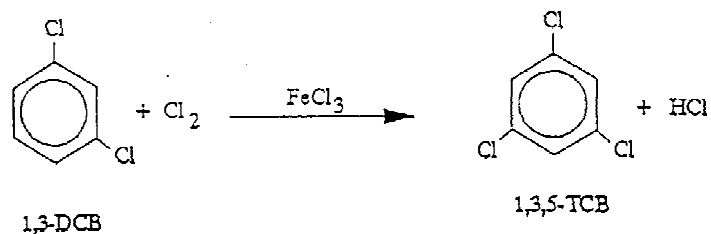
^a1980 data.

^bNot enough information available to assign a quality rating.

Source: Reference 11.



Similarly, 1,3,5-TCB can be obtained by the chlorination of m-DCB.



Most TCBs are produced at the same location as the lower chlorinated benzenes. At these facilities the TCBs are fractionally separated from DCBs.⁵ It is assumed that most TCBs are produced by the batch method due to the low volume of domestic production.¹²

Other trichlorobenzene production processes mentioned in the literature include: (1) the reaction of α , β , or γ -benzene hexachloride with alcoholic potash at 100°C (212°F) to produce all three TCB isomers; (2) the dehalogenation of α -benzene hexachloride with pyridine to form all three TCB isomers; and (3) the reaction of α -benzene hexachloride with calcium hydroxide to form primarily 1,2,4-TCB.⁶ Further process details are not available. Contact should be made with specific plants to determine manufacturing processes used on site. Currently, the Standard Chlorine Chemical Company, Incorporated, of Delaware City, Delaware is the only known producer of trichlorobenzenes.⁸ The facility's production capacity is unknown. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of

variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

Trichlorobenzene emissions released during the continuous product process (Figure 4-2) result from storage (C) and handling (D) of trichlorobenzene products. Fugitive emissions of TCBs may also occur when leaks develop in valves, pump seals, and major equipment (F). Secondary emissions from MCB production (Figure 4-1) are also possible from volatilization of TCB from the wastewater stream (H) containing dissolved benzene and other VOC, and the catalyst waste stream (I).⁶ No information was available concerning identification of specific TCB isomers at the time this report was prepared.

4.5 REFERENCES FOR SECTION 4.0

1. *1990 Directory of Chemical Producers, United States of America*, SRI International, Menlo Park, CA, 1990.
2. U.S. Environmental Protection Agency, *Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP*, EPA-450/3-88-010, Office of Air Quality Planning and Standards, Research Triangle Park, NC, 1988.
3. U.S. Environmental Protection Agency, *Fugitive Emission Sources of Organic Compounds--Additional Information on Emissions, Emission Reductions, and Costs*, EPA-450/3-82-010, Office of Air Quality Planning and Standards, Research Triangle Park, NC, April 1982.
4. Liepins, R. and F. Nixon, *Industrial Process Profiles for Environmental Use: Chapter 6. The Industrial Organic Chemicals Industry*, EPA-600/2-77-023f, U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Cincinnati, OH, February 1977, pp. 6-55 to 6-56.
5. *Kirk-Othmer Encyclopedia of Chemical Technology, Volume 5*, Third Edition, Wiley-Interscience Publication, New York, NY, 1980. pp. 797-808.
6. U.S. Environmental Protection Agency, *Organic Chemical Manufacturing, Volume 6: Selected Processes*, EPA-450/3-80-028a, Office of Air Quality Planning and Standards, Research Triangle Park, NC, December 1980.
7. Lowenheim, F.A. and M.K. Moran, *Faith, Keyes, and Clark's Industrial Chemicals*, Fourth Edition, John Wiley and Sons, New York, NY, 1975.
8. *SRI Chemical and Economics Handbook*, "Chlorobenzene Production," Menlo Park, CA, 1989.
9. U.S. Environmental Protection Agency, *Human Exposure to Atmospheric Concentrations of Selected Chemicals, Volume II: A Summary of Data on Chlorobenzenes*, Office of Air Quality Planning and Standards, Research Triangle Park, NC, PB83-265249, February 1982. pp. 7-16.
10. Opatick, Richard, Chlorobenzene Producers Association. Memorandum to Michael Ling, TRC Environmental Corporation, August 4, 1993.
11. U.S. Environmental Protection Agency, *An Exposure and Risk Assessment for Dichlorobenzenes*, Final Draft, Office of Water Regulations and Standards, Washington, DC, 1981, p. A-1.

12. U.S. Environmental Protection Agency, *Investigation of Selected Potential Environmental Contaminants: Halogenated Benzenes*, EPA-560/2-77-004, Office of Toxic Substances, Washington DC, July 1977.

SECTION 5.0

EMISSIONS FROM MAJOR USES OF CHLOROBENZENES

Chlorobenzenes are used as a solvent and/or feedstock in the manufacture of many products, as discussed in Section 3. Additionally, chlorobenzenes are used as a dye carrier in the textile industry and as an additive in functional fluids. This section discusses the emissions of chlorobenzenes from processes that use chlorobenzenes as feedstocks in the manufacture of another product or as a solvent. Emissions of chlorobenzenes as residual components of a product containing chlorobenzenes are discussed separately in Section 6. Emissions of chlorobenzenes as byproducts of the manufacture of another product, or through combustion of fossil fuels or wood are discussed in Section 7.

5.1 MANUFACTURE OF NITROCHLOROBENZENES FROM MONOCHLOROBENZENE

The largest consumption of monochlorobenzene in the United States is in the production of nitrochlorobenzenes. In 1988, nitrochlorobenzenes production consumed 42 percent of all the monochlorobenzene produced in the United States. Nitrochlorobenzene is used as a chemical intermediate in the manufacture of rubber chemicals, antioxidants, and dyes and pigments. It is also used in the manufacture of pharmaceutical products.¹

Twenty-three percent of the nitrochlorobenzenes produced in 1983 were used in dye and pigment production. Nitrochlorobenzenes are used as starting materials and to produce dye intermediates, including nitroaniline and phenylenediamine.²

Nitrochlorobenzenes are also used in the manufacture of agricultural chemicals to produce intermediate forms including p-chloroaniline and p-nitrophenol. p-Nitrophenol is necessary in the manufacture of the organophosphate pesticides, parathion, and methylparathion.¹ Reduction of p-nitrophenol yields p-aminophenyl, which is further processed to make acetaminophen (analgesic/antipyretic).^{1,2}

5.1.1 Process Description

Nitrochlorobenzenes are manufactured by the nitration of monochlorobenzene using a mixed acid solution of nitric acid and sulfuric acid at 40°C to 70°C (104°F to 158°F) for 12 hours. Input materials to produce 1 metric ton of combined nitrochlorobenzenes include 4536 kilograms (10,000 pounds) of MCB and 9570 kilograms (21,098 pounds) of combined 30 to 35 percent nitric acid and 52 to 55 percent sulfuric acid. The product mixture at the end of 12 hours is comprised of (34 percent) ortho- and (65 percent) para-nitrochlorobenzenes.³ This step is illustrated in the following reaction.

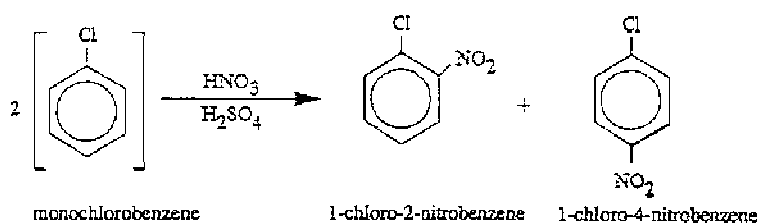


Table 5-1 lists producers of o- and p-nitrochlorobenzene in the United States. In 1989, 66.2 million kilograms (146 million pounds) of nitrochlorobenzenes were produced and 50 million kilograms (110 million pounds) of monochlorobenzene were consumed for the production of nitrochlorobenzene.¹ The manufacturers are subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves.

5.1.2 Emissions

The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel. Facilities manufacturing nitrochlorobenzene have a potential to emit monochlorobenzene from process equipment vents, open process equipment, equipment leaks, storage tank vents, secondary sources, and transfer and handling operations. No specific emissions data are currently available on the use of MCB in the production of

**TABLE 5-1.
CHEMICAL PRODUCERS OF o- AND
p-NITROCHLOROBENZENES - 1989**

Facility	Location	Capacity Millions kg (Millions lbs)
E.I. duPont de Nemours & Company, Inc. Chemicals and Pigments Department	Deepwater, New Jersey	27.5 (60.6)
Monsanto Company Monsanto industrial Chemicals Company	Sauget, Illinois	38.7 (85.3)
TOTAL		66.2 (146)

Source: Reference 4.

nitrochlorobenzenes. The discussion in Section 4.1 on fugitive emissions should be referred to for more detail. The reader is advised to contact plant personnel to identify control technology and emissions for a specific plant process.

5.2 MANUFACTURE OF DIPHENYL OXIDE FROM MONOCHLOROBENZENE

Monochlorobenzene is used in the manufacture of diphenyl oxide. Diphenyl oxide (also known as diphenyl ether) finds its major use in the manufacture of heat transfer fluids, such as Therminol[®] VP-1, a product manufactured by Monsanto Company, and Dowtherm[®], a product manufactured by Dow Chemical. Another use for diphenyl oxide is as a chemical intermediate for brominated fire retardants. The primary producers of fire retardants are Dow, Ethyl, and Great Lakes Chemical Companies. Diphenyl oxide is also used as an intermediate for specialty surfactants. Dowfax[®], which is manufactured by Dow Chemical, is the leading surfactant produced using the intermediate diphenyl oxide. Diphenyl oxide is also used as a perfume in soaps.¹

5.2.1 Process Description

Diphenyl oxide is typically produced in a continuous flow tubular reaction system. Chlorobenzene is reacted with aqueous sodium hydroxide (NaOH) and recycled products (containing phenol and sodium phenoxide). These reactants are heated to between 275°C and 300°C (527°F and 572°F) by passing through a nickel-lined heat exchanger. The reaction temperature of 400°C (752°F) is achieved electrically and the reactants are allowed to flow through the system for 10 to 30 minutes. The reaction must be maintained at sufficient pressure [> 26.2 MPa (2586 atm)] to prevent vaporization, which would allow NaCl, NaOH, or phenoxide to be deposited on the tube walls causing hot spots and excessive corrosion. The resulting two layers from the reaction are aqueous phenoxide and an oily layer consisting mainly of diphenyl oxide and unreacted chlorobenzene. Diphenyl oxide is recovered by distillation of this oily layer.³

Dow Chemical, U.S.A. of Midland, Michigan is the only known facility producing diphenyl oxide as reported in the *SRI Chemical and Economics Handbook*.¹ This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves.

5.2.2 Emissions

The level of chlorobenzenes emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel. Although quantitative estimates are unavailable, only small quantities of MCB are believed to be emitted during the diphenyl oxide manufacturing process. The reader is advised to contact plant personnel for information concerning emissions and control technology employed for specific processes.

5.3 MANUFACTURE OF PHENYLPHENOLS FROM MONOCHLOROBENZENE

Monochlorobenzene is used in the manufacture of o-phenylphenol and p-phenylphenol. Ortho-phenylphenol is primarily used in hard surface disinfectants, such as Lysol®. Para-phenylphenol is used in combination with formaldehyde to make a resin used in carbonless paper. It is also used in resins found in marine varnishes.¹

In 1988, 20.4 million kilograms (45 million pounds) of monochlorobenzene were consumed during the manufacture of diphenyl oxide, o-, and p-phenylphenol. Currently, Dow Chemical of Midland, Michigan is the only known producer of o- and p-phenylphenol.¹ The manufacturers are subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. Specific process information used in the manufacture of phenylphenols was not identified during the writing of this report.

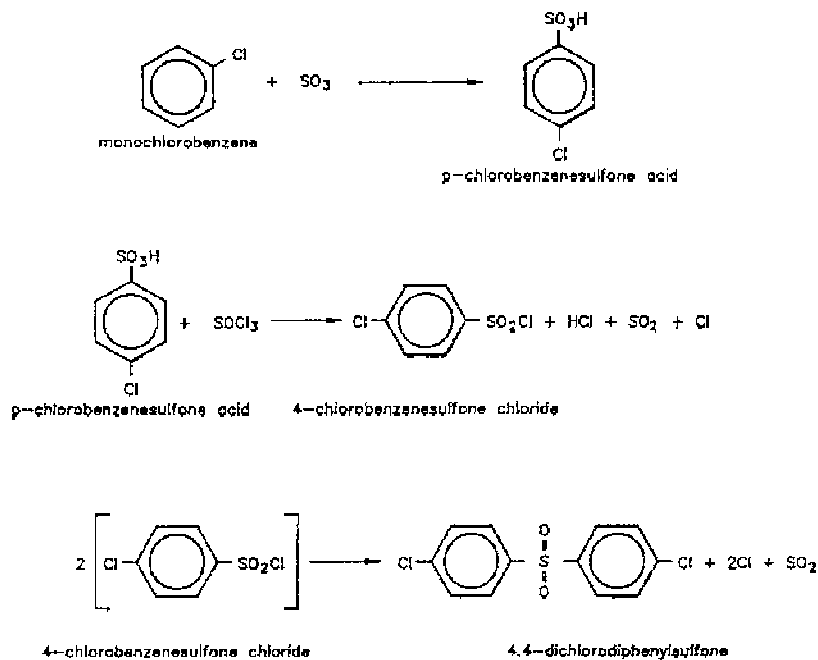
No emissions data are available on the use of MCB in the production of phenylphenols. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel. The reader is advised to contact plant personnel to identify control technology and emissions for a specific plant process.

5.4 MANUFACTURE OF 4,4'-DICHLORODIPHENYLSULFONE FROM MONOCHLOROBENZENE

Monochlorobenzene is used in the production of the sulfone-containing monomer, 4,4'-dichlorodiphenylsulfone (4,4'-DCDPS), which is used in the manufacture of all polysulfone engineering plastics. Sulfone polymers find major applications in the electrical/electronic components, medical equipment and supplies, and food related industries.¹

5.4.1 Process Description

Specific process information used in the manufacture of 4,4'-DCDPS was not identified during the writing of this report. However, 4,4'-dichlorodiphenylsulfone is formed by the following reactions:



4,4'-Dichlorodiphenylsulfone is manufactured for captive use by Amoco Corporation of Marietta, Ohio and ICI American Holdings Company of Fayetteville, North Carolina. In 1988, approximately 6.8 million kilograms (15 million pounds) of sulfone were produced. During the 1988 production year, approximately 5.4 million kilograms (12 million pounds) of monochlorobenzene were consumed.¹ The manufacturers are subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves.

5.4.2 Emissions

No emissions data are available on the use of MCB in the production of 4,4'-dichlorodiphenylsulfone. The level of chlorobenzene emissions from any given facility is a

function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel. The reader is advised to contact plant personnel to identify control technology and emissions for a specific plant process.

5.5 MANUFACTURE OF 3,4-DICHLOROANILINE FROM ORTHO-DICHLOROBENZENE

An important compound derived from o-dichlorobenzene (o-DCB) is 3,4-dichloroaniline. In 1988, the manufacture of 3,4-dichloroaniline consumed 31 percent of all the o-dichlorobenzene produced in the United States. 3,4-Dichloroaniline is used as an intermediate in the production of an anilide pesticide (propanil), and two substituted urea pesticides (diuron and linuron).¹ Pesticides and production locations from the *Farm Chemicals Handbook* are listed in Table 5-2.⁵ Dow Chemical also cited usage of 3,4-dichloroaniline as an intermediate for polyethers and as a cross-linkage agent in epoxy tar products.⁶ A small volume of 3,4-dichloroaniline is used for the production of 3,4,4'-trichlorocarbanilide (also known as TCC and triclocarbon).¹ 3,4,4'-trichlorocarbanilide is used as a bacteriostat and antiseptic in soaps and other cleaning compositions.⁷

5.5.1 Process Description

Commercially, 3,4-dichloroaniline is prepared by the nitration of o-DCB followed by reduction of the resulting 3,4-dichloronitrobenzene. In many cases, the nitration operation produces two immiscible layers. For safety reasons and ease of operation, temperatures from 0°C to 120°C (32°F to 248°F) and atmospheric pressure are used. At higher temperatures, competing oxidation reactions become important. Reaction residence times for nitration range from 1 to 60 minutes.³ The nitration reaction may be written as:

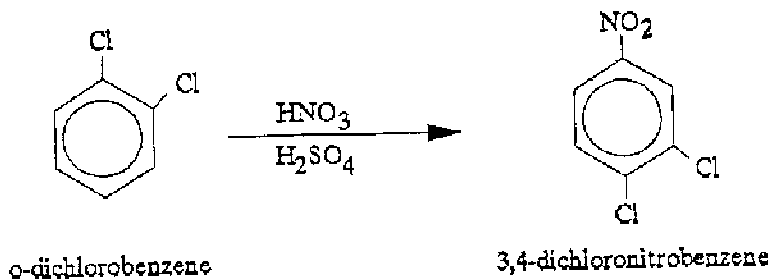
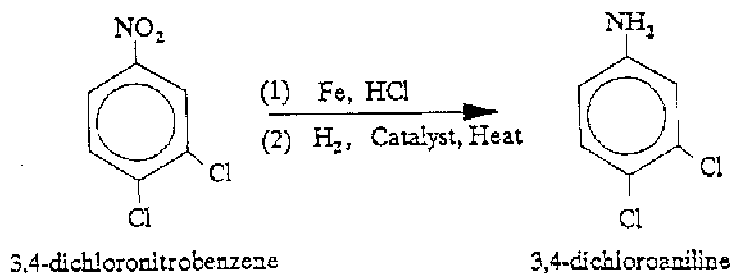


TABLE 5-2.
PESTICIDES USING 3,4-DICHLOROANILINE
AS AN INTERMEDIATE - 1989

Pesticide Class	Scientific Name	Common/Registered Brand Name	Producers	Location(s)
Anilide Pesticide	3,4-Dichloropropionanilide	<u>Propanil</u> Stamm® and Stampede®	Rohm and Hass Company	Philadelphia, PA
		Cedar Propanil® 4 and Wham EZ®	Cedar Chemical Corp.	Memphis, TN Vicksburg, MS
		Chem Rice®	Tifa Ltd.	Millington, NJ
Substituted Urea Pesticide	3-[3,4-Dichlorophenyl]-1,1-dimethylurea	<u>Diuron</u> Crisuron®	Crystal Chemical Inter-America	Houston, TX
		Diumate®	Drexel Chemical Company	Memphis, TN
	3-[3,4-Dichlorophenyl]-1-methoxy-1-methylurea	Karmex® and Krovar®	E.I. du Pont de Nemours & Company, Inc. Agricultural Products Department	LaPorte, TX
		Direx® 4L	Griffin Corporation Agricultural Chemicals Group	Valdosta, GA
		<u>Linuron</u> Lorox®	E.I. du Pont de Nemours & Company, Inc. Agricultural Products Department	LaPort, TX
		Linurex®	Griffin Corporation Agricultural Chemicals Group	Valdosta, GA

Source: Reference 5.

The reduction of 3,4-dichloronitrobenzene may be achieved in two ways: (1) by employing iron and HCl; and (2) by using hydrogen and a catalyst with some heating. Other operating parameters could not be found at the writing of this report.³ The reduction reaction may be written as:



The Deep Waters, New Jersey plant of the E.I. duPont de Nemours & Company, Inc. is the only known producer of 3,4-dichloroaniline.^{4,8} Producers of 3,4-dichloroaniline and their locations for 1989 are given in Table 5-3. Production estimates of 3,4-dichloroaniline are not available; however, in 1988, the production of 3,4-dichloroaniline consumed 11.3 million kilograms (25 million pounds) of o-DCB.¹

TABLE 5-3.
CHEMICAL PRODUCERS OF 3,4-DICHLOROANILINE - 1989

Facility	Location
E.I. duPont de Nemours & Company, Inc. Chemicals and Pigments Department	Deep Water, New Jersey

Source: Reference 4,8.

5.5.2 Emissions

Table 5-4 lists general process, storage, and fugitive emission factors, with no specific controls, for the production of 3,4-dichloroaniline. The emission factors were derived from various detections of o-DCB in industrial wastewater streams. The discussion in Section 4.1 on

TABLE 5-4.
EMISSION FACTORS FOR THE PRODUCTION OF
3,4-DICHLOROANILINE^a

Emission Category	kg o-DCB emitted per Mg o-DCB used	lbs o-DCB emitted per ton of o-DCB used	Emission Factor Quality Rating^b
Process	1.05	2.10	U
Storage	0.15	0.30	U
Fugitive	0.30	0.60	U
TOTAL	1.50	3.0	

^a1980 data.

^bNot enough information available to assign a quality rating.

Source: Reference 9.

fugitive emissions should be referred to for more detail. The reader is encouraged to contact plant personnel for information regarding actual emissions and control technologies employed at specific locations.

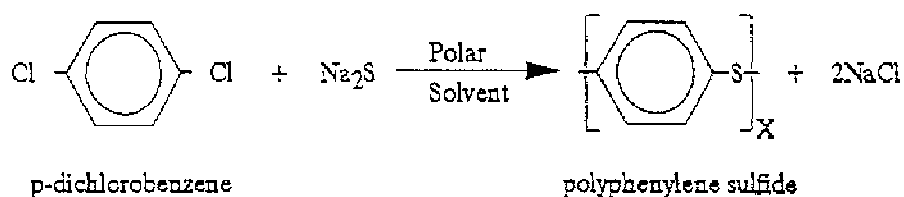
5.6 USE OF PARA-DICHLOROBENZENE IN THE PRODUCTION OF POLYPHENYLENE SULFIDE

Para-dichlorobenzene is used in the production of polyphenylene sulfide: it is the single largest product manufactured from p-DCB. Polyphenylene is a commercial polymer known as Ryton[®], having many industrial applications.¹ Characteristics of polyphenyl sulfide (PPS), also named polythio-1,4-phenylene, include good thermal stability, retention of mechanical properties at elevated temperatures, excellent chemical resistance, and an affinity for a variety of fillers.¹⁰ Polyphenylene sulfide is used in electrical applications for its insulating, dielectric, and chemical/heat resistant properties.¹ Polyphenylene sulfide may also be used to replace fabricated steel parts in mechanical, appliance, and automotive equipment such as molded parts including

nonlubricated bearings, seals, pistons, impellers, pump vanes and electronic components. It can also be used as a coating to metals and ceramics as a protective and corrosion resistant medium, which is useful for equipment in the chemical and petroleum industries. When mixed with small amounts of polytetrafluoroethylene, the mixture provides a non-stick surface in cookware and other industrial applications, such as Teflon[®] and Silverstone.^{1,10}

5.6.1 Process Description

Polyphenylene sulfide is formed by the following reaction of p-DCB and sodium sulfide in a polar solvent.



Steps involved in the manufacture of PPS shown in Figure 5-1 are as follows: (1) preparation of sodium sulfide from aqueous caustic and aqueous sodium hydrosulfide in a polar solvent; (2) dehydration by distillation of the above feedstock; (3) polymer formation from the reaction of the sodium sulfide stream and p-DCB at an elevated temperature in a polar solvent; (4) polymer recovery; (5) removal of byproduct sodium chloride by washing, (6) drying and (7) packaging. PPS produced by this process can be used in coating applications by slurry-coating procedures; however, it is most often used as a feedstock in the production of molding-grade resins.¹¹

Molding-grade resins are produced by a curing process in which the virgin polymer is exposed to a small amount of air at a high temperature. At this point, a higher molecular weight resin is produced while lower molecular weight polymers are volatilized. Residence time, reaction temperature, and melt viscosity are important in the formation of various grades of PPS.

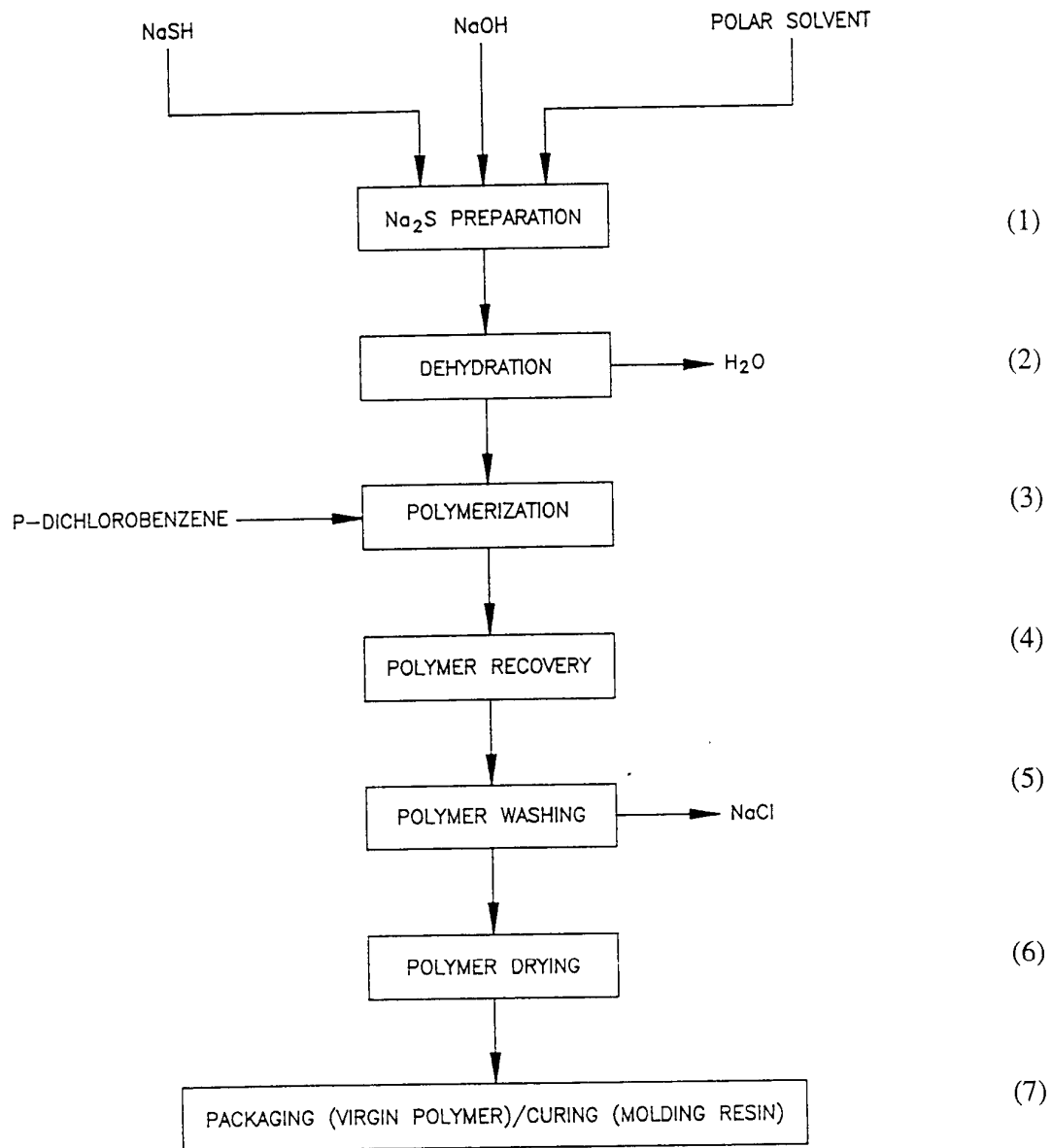


Figure 5-1. Process flow diagram of polyphenylene sulfide manufacture.¹¹

The cured polymer is cooled, combined with fillers (such as glass fibers, if desired), pelletized, and then packaged.¹¹

Polyphenylene sulfide is produced by Phillips Petroleum Company in Borger, Texas. This manufacturing facility had production capacities of 5.4 million kilograms (12 million pounds) and 7.3 million kilograms (16 million pounds) in 1988 and 1989, respectively. In 1988, polyphenylene sulfide production consumed 22 percent of all the p-DCB produced.¹ Consumption of PPS has continued to grow since the early 1980s. This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves.

5.6.2 Emissions

Facilities manufacturing polyphenylene sulfide have a potential to emit p-dichlorobenzene from process equipment vents, open process equipment, equipment leaks, storage tank vents, transfer and handling operations, and polymer washing and drying operations. No specific emissions data are available for the production of polyphenylene sulfide. The discussion in Section 4.1 on fugitive emissions should be referred to for more detail. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. To determine actual emissions from particular processes, specific plants should be contacted.

5.7 USE OF CHLOROBENZENES IN THE MANUFACTURE OF TOLUENE DIISOCYANATE

Ortho-dichlorobenzene and MCB are used in the manufacture of 2,4-toluene diisocyanate (TDI). Toluene diisocyanates are industrial intermediates used in the production of polyurethane foams, paints, varnishes, elastomers, and coatings. Rigid polyurethane foams, accounting for

about five percent of TDI demand, are used as insulation in refrigeration equipment.¹² Flexible polyurethane foams, used in furniture cushioning, transportation (*e.g.*, automotive seating), bedding, packaging, and carpet underlay, account for approximately 90 percent of the use of toluene diisocyanates.¹³ Little or no growth in production of TDI is expected for several reasons. Methyl diphenyl diisocyanate (MDI) is replacing TDI in many polyurethane foam applications. TDI can react violently with compounds containing an active hydrogen atom.¹³ In the TDI manufacturing process described below, *o*-DCB is used as an inert process solvent.

5.7.1 Process Description

The manufacture of commercial toluene diisocyanates is based on the phosgenation of primary amines. Most commercial TDI plants also produce the intermediates dinitrotoluene (DNT), toluene diamine (TDA) and phosgene.¹⁴

TDI is produced by the following chemical reactions:

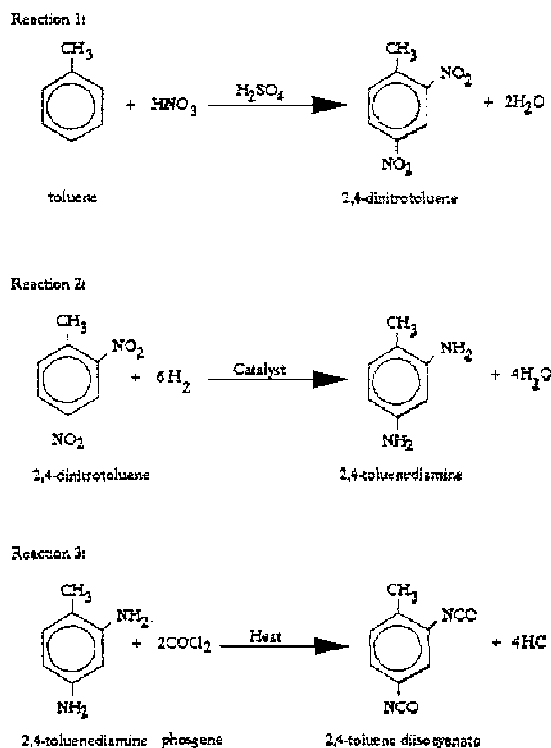


Figure 5-2 illustrates the basic operations that may be used in toluene diisocyanate production. The first step in the manufacture of TDI is the nitration of toluene (Step 1). Nitration grade toluene is reacted with nitric acid to form DNT, as shown in Reaction 1. The reaction takes place at 65°C to 80°C (149°F to 176°F) in a well-agitated reactor equipped with cooling coils using sulfuric acid (60 to 70 percent) as the catalyzing agent.¹⁵ The spent sulfuric acid is separated from the DNT reaction mixture, concentrated in a direct contact evaporator, and recycled to the nitration reactor (Step 2).¹⁴

The DNT is washed in a wash tank (Step 3) and then reacted with hydrogen in catalytic reduction reactors (Step 4), using precious metal, nickel, or carbon catalysts, to form crude TDA (Reaction 2). The hydrogenation of DNT normally occurs in an inert diluent (*e.g.*, an alcohol) to avoid explosion hazards and to control the heat resulting from the exothermic process. The crude TDA is purified by filtration and distillation (Step 5).^{14,15}

TDA is reacted with phosgene in a solvent, usually *o*-dichlorobenzene or monochlorobenzene, to form crude TDI and hydrogen chloride (HCl), as shown in Reaction 3 (Step 6). Phosgene is condensed out of the HCl byproduct and recycled to the reactor. The overhead HCl stream from the condenser may contain trace amounts of phosgene and is therefore sent to the phosgene absorber. Crude TDI is sent to a distillation column for the removal of residual phosgene (Step 7). After a series of distillation and condensation steps, the phosgene (from the crude TDI) is recycled to the phosgenation reactor. The phosgene overhead (Step 7) from this distillation column and the HCl and trace-phosgene stream from the reactor condenser are combined and sent to a column that absorbs phosgene with the *o*-DCB solvent. The solvent is then stripped of phosgene in a distillation column and recycled to the absorber.

The crude TDI still contains some of the chlorobenzenes solvent in which it was reacted. This mixture (TDI and solvent) is transferred to a vacuum distillation column where the solvent is recovered and recycled (Step 8). The remaining crude TDI is vaporized by vacuum flash distillation to separate TDI from any polymeric isocyanates that may have formed (Step 9). The TDI is then condensed and sent to a vacuum distillation column from which purified TDI is

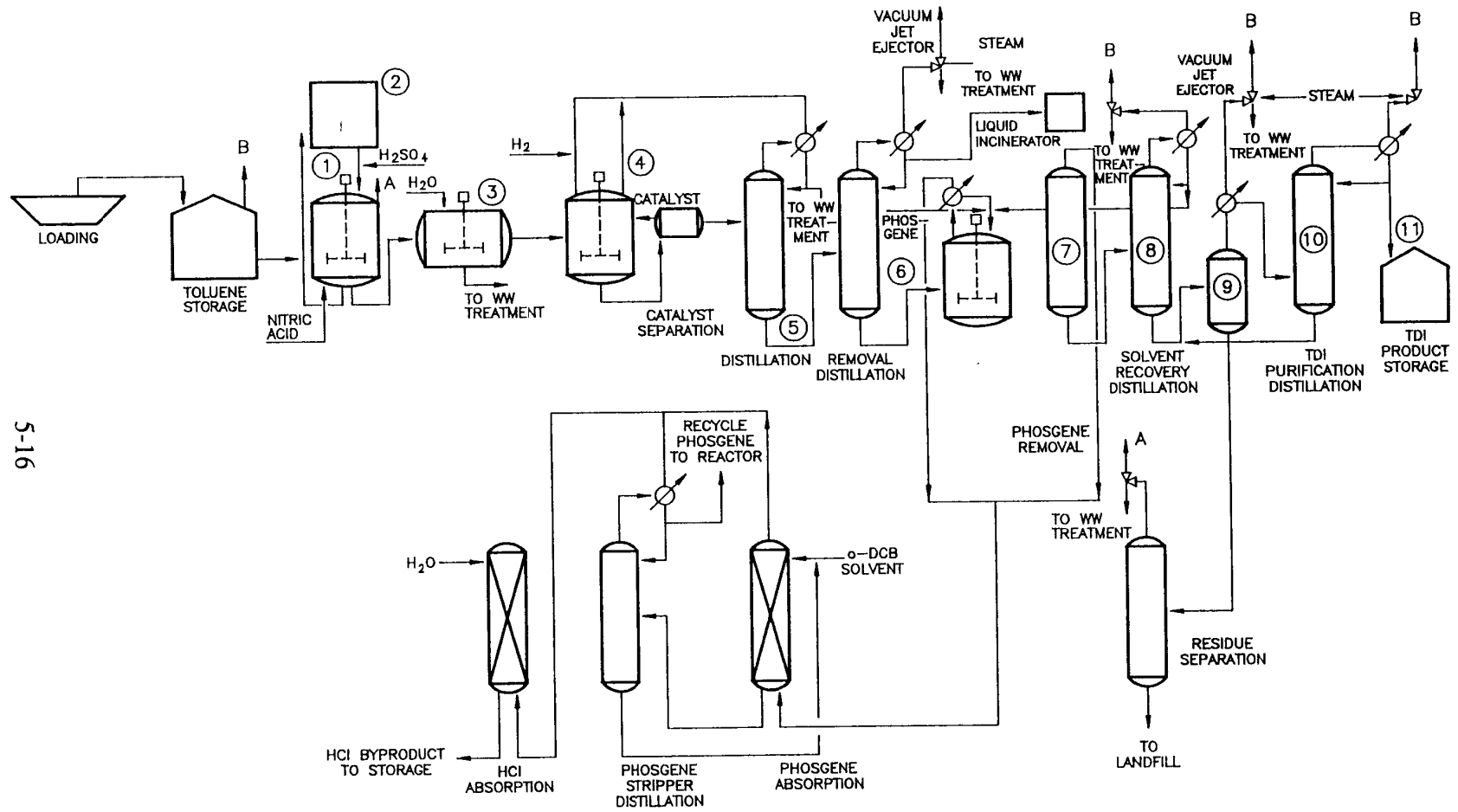


Figure 5-2. Basic operations that may be used in toluene diisocyanate production.¹⁴

removed (Step 10). The purified TDI stream undergoes a final condensation step before being transferred to product storage (Step 11).^{14,15}

Toluene diisocyanate is currently produced by five companies at six facilities in three States. These facilities and their 1989 production capacities are listed in Table 5-5. This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves.

5.7.2 Emissions

Potential o-DCB emissions may occur at the residue separation vacuum jet vent (A) and the vacuum jet vents (B) associated with solvent recovery distillation, TDI flash distillation, and TDI purification distillation.¹⁴ It is estimated that only a small fraction of o-DCB utilized is released into the atmosphere.¹⁶ However, no emission factors could be found nor developed for this process. The level of chlorobenzenes emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

5.8 USE OF CHLOROBENZENES IN THE PRODUCTION OF DYES AND PIGMENTS

The uses of chlorobenzenes in the dye and pigment industry are two-fold: (1) to synthesize other intermediates which are subsequently utilized in the formation of specific dyes and pigments; and (2) as inert process solvents in dye and pigment manufacturing. The use of chlorobenzenes in each of these applications is described here. The Ecological and Toxicological Association of Dyestuffs Manufacturing Industry indicated in 1985 that the process information mentioned below is outdated; however, no new information was available.¹⁷

**TABLE 5-5.
TOLUENE DIISOCYANATE PRODUCTION LOCATIONS AND
CAPACITIES**

Producers	Location	Capacity Millions of kilograms (Millions of pounds)
BASF Corporation	Geismar, Louisiana	73 (161)
Dow Chemical	Freeport, Texas	63 (139)
ICI Americas	Geismar, Louisiana	32 (71)
Mobay Chemical Corporation	New Martinsville, West Virginia	45 (99)
Mobay Chemical Corporation	Baytown, Texas	61 (134)
Olin Chemicals Corporation	Lake Charles, Louisiana	88 (194)

Source: Reference 4.

5.8.1 Use of Chlorobenzenes in the Synthesis of Intermediates

The chlorobenzene group is one of many classes of compounds used to synthesize intermediates in the dye and pigment industry. Chlorobenzenes are normally purchased outside

of the industry, converted into more complex intermediates and ultimately into dyes and pigments. Some more complex intermediates may be dyes themselves, making the distinction between them and dyes and pigments somewhat arbitrary.

Process Description - -

In the dye and pigment industry, reactions for the production of intermediate dyes are generally carried out in kettles made from cast iron; stainless steel; or steel lined with rubber, glass (enamel), brick, or carbon blocks. The kettles have capacities of 2,200 to 44,000 liters (581 to 11,625 gallons) and are equipped with mechanical agitators, thermometers or temperature recorders, condensers, pH probes, etc., depending on the nature of operation. Jackets or coils heat by circulation of high-boiling fluids (hot oil, Dowtherm[®]), steam or hot water. The kettles may be cooled with chilled brine. Unjacketed kettles are often used for aqueous reactions where heating is effected by direct introduction of steam and cooling is effected by addition of ice or by the use of heat exchangers.¹⁸

Products are transferred from one piece of equipment to another by gravity flow, pumping, or by blowing with air or inert gas. Solids are separated by centrifuges, filter boxes, continuous belt filters, or either plate-and-frame or recessed plate filter presses.

When possible, intermediates are taken for subsequent manufacture without drying. When drying is required, air or vacuum ovens, rotary dryers, or spray dryers are used. Drum dryers (flakers) may also be used, although less commonly. Dyestuffs which require wet grinding, especially disperse dryers, are often spray dried with solid diluents to achieve standardization.¹⁸

Because the dye industries' use of small amounts of numerous intermediates has made continuous processes impractical, batch processes remain the rule. However, progress in computer and electronic technologies has led to growing use of automatic process control.¹⁸

Emissions - -

Possible sources of chlorobenzenes emissions from the synthesis of intermediates include kettles, separation processes, equipment leaks, drying processes, and transfer and handling operations. No emissions data are available for the synthesis of intermediates using chlorobenzenes. The discussion in Section 4.1 on fugitive emissions should be referred to for more detail. To determine actual emissions from particular processes, specific plants should be contacted.

5.8.2 Use of Chlorobenzenes as Process Solvent

Chlorobenzenes are used as inert process solvents in the production of a number of dyes and pigments. In Table 5-6, dyes and pigments which use specific chlorinated benzenes as solvents are categorized into dye and pigment classes according to the nature of their chemical structure. Table 5-7 presents common names and manufacturers for those generic dyes and pigments shown in Table 5-6. Individual dyes and pigments within a class are produced by the same processes described here.

Process Description Using Monochlorobenzene - -

Monochlorobenzene is used as a process solvent in the manufacture of three indigoid dyes and pigments. All the pigments and dyes are thioindigoid colors. Due to the corrosive nature of the reactants involved in these processes, glass-lined vessels and efficient stirring are required.²⁰

The manufacture of the thioindigoid colors involves two process steps, one of which is a diazotization. Temperature conditions range from 0° to 70°C (32° to 158°F).²⁰ Because low temperatures are required, ice is used in substantial quantities. Information regarding these processes is somewhat limited.

**TABLE 5-6.
DYES AND PIGMENTS UTILIZING
CHLOROBENZENE SOLVENTS**

Solvent	Dye or Pigment Class	Color Index (C.I.)	Generic Dye or Pigment Name
Monochlorobenzene	Thioindigoid	73312	Pigment Red 88
	Thioindigoid	73360	Vat Red 1, Pigment Red 181, D+C Red 30
	Thioindigoid	73385	Vat Violet 2
o-Dichlorobenzene	Oxazine	51300	Direct Blue 106
	Oxazine	51319	Pigment Violet 23
	Pyranthrone	69700	Vat Orange 9
	Anthraquinone (oxazine)	67000	Vat Red 10
1,2,4-Trichlorobenzene	Benzanthrone	59825	Vat Green 1

Source: Reference 19.

Process Description Using ortho-Dichlorobenzene - -

Ortho-dichlorobenzene is used as a process solvent in the production of two oxazine pigments, one pyranthrone dye, and one anthraquinone dye. In addition, these dyes may be used to produce other related dyes and pigments by halogenation.

The manufacture of the oxazine pigments involves the condensation of substituted aniline compounds with a substituted phenolic compound (or a phenol ether), followed by an oxidative

**TABLE 5-7.
DYE AND PIGMENT NAMES AND MANUFACTURERS**

Color Index	Generic Name	Common Name	Manufacturer(s)
73312	Pigment Red 88	Microlith Bordeaux R-K Microlith Bordeaux R-N Thiofast Red MV-6606 Thiofast Red MV-6613 Thiofast Red MV-6655 Thiofast Red Presscake MV-6613	Ciba-Geigy Corp., ^a Hawthorne, NJ Ciba-Geigy Corp., ^a Greensboro, NC Mobay Corporation, Union, NJ
73360	Vat Red 1, Pigment Red 181, D+C Red 30	Calcophyl Pink FF D&C Red No. 30 Fast Pink Y Hostavat Brilliant Pink RD Thiovat Pink FF Oracet Pink RF ^b	American Cyanamid Co., Marietta, OH H. Kohnstamm & Co., New York, NY Johnson Matthey, Inc., Irvington, NJ American Hoechst Corp., Charlotte, NC Atlantic Industries, Nutley, NJ Ciba-Geigy Corp., ^c Hawthorne, NJ Ciba-Geigy Corp., ^c Greensboro, NC
73385	Vat Violet 2	Thiovat Violet 2	Atlantic Industries, Nutley, NJ
51300	Direct Blue 106	Intralite Brilliant Blue 2GLL Patcolite Blue N2LL Solophenyl Blue BL Tertrodirect Light Brilliant Blue 2GLN	Crompton and Knowles, Reading, PA C.H. Patrick, Greenville, SC Ciba-Geigy Corp., ^d Hawthorne, NJ Ciba-Geigy Corp., ^d Greensboro, NC Crompton and Knowles, Reading, PA

(continued)

TABLE 5-7.
DYE AND PIGMENT NAMES AND MANUFACTURERS (continued)

Color Index	Generic Name	Common Name	Manufacturer(s)
51319	Pigment Violet 23	Acramin Violet FFR Hostatone Violet RL Indofast Violet B-4005 Indofast Violet B-4018 Indofast Violet B-4044 Indofast Violet B-4019 Microlith Violet RL-WA Monolite Violet RN Roma Violet RL Sunfast Carbozole Violet	Mobay Corporation, Rock Hill, SC American Hoechst Corp., Charlotte, NC Mobay Corporation, Union, NJ Ciba-Geigy Corp., ^a Hawthorne, NJ Ciba-Geigy Corp., ^a Greensboro, NC ICI Americas, Wilmington, DE Roma Color, Inc., Fall River, MA Sun Chemical Corp., Cincinnati, OH
69700	Vat Orange 9	Anthravat Golden Orange GD	Atlantic Industries, Nutley, NJ
67000	Vat Red 10	Anthravat Red FBB Cibanone Red 2B Patcovat Red FBB	Atlantic Industries, Nutley, NJ Ciba-Geigy Corp., ^f Hawthorne, NJ Ciba-Geigy Corp., ^f Greensboro, NC C.H. Patrick, Greenville, SC
59825	Vat Green 1	Anthravat Jade Green Cibanone Brilliant Green BF Cibanone Brilliant Green BFD Intravat Brilliant Green BFD Patcovat Jade Green Solanthrene Green XBN	Atlantic Industries, Nutley, NJ Ciba-Geigy Corp., ^e Hawthorne, NJ Ciba-Geigy Corp., ^e Greensboro, NC Crompton and Knowles, Reading, PA C.H. Patrick, Greenville, SC ICI Americas, Wilmington, DE

Source: Reference 19.

^a Both are producers of Microlith Bordeaux R-K and R-N.

^b Represents the common name for Pigment Red 181.

^c Both are producers of Oracet Pink RF.

^d Both are producers of Solophenyl Blue BL.

^e Both are producers of Microlith Violet RN.

^f Both are producers of Cibanone Red 2B.

^g Both are producers of Cibanone Brilliant Green BF and BFD.

reaction which forms the oxazine ring system.²⁰ Stirred batch reactors with glass linings are required for most of the reactions involved in making these products. The oxazine pigment (C.I. 51319) is produced by condensing chloranil with 3-amino-9-ethylcarbazole using sodium acetate as a catalyst. Ortho-dichlorobenzene is used as the process solvent in the reaction which requires 7 hours at 60° to 115°C (140° to 239°F). The condensation product is cyclized (refers to ring formation) to the pigment with benzenesulfonyl chloride at 180°C (356°F). The crude pigment is subsequently washed and filtered.¹⁹ Ortho-dichlorobenzene is also used as a process solvent in the manufacture of another oxazine pigment (C.I. 51300); however, no specific process information was available at the time this report was prepared.

Pyranthrone dye (C.I. 59700) can be made from either 1-chloro-2-methylantraquinone or pyrene as the principal organic starting material. Glass-lined, stirred reaction vessels are required due to the corrosive nature of the reactants. Ortho-dichlorobenzene is used as a process solvent in this process. The dimerization of the 1-chloro-2-methyl-anthraquinone takes place at 150° to 160°C (302° to 320°F) in 6 hours, while cyclization to the dye requires an additional 3 hours at the same temperature.²⁰

The anthraquinone dye which uses o-DCB as a process solvent is an oxazole compound (C.I. 67000) and is made from 2-amino-3-hydroxyanthraquinone. Batch-type reactions made of iron and with good stirrers are typically used. In addition, the reactor must have a cooling coil to remove heat generated by the moderately exothermic first reaction between the aminoanthraquinone and the acid chloride. The cyclization of the resulting amide to the desired oxazole is carried out in o-DCB at 140°C (284°F) in 5 hours.²⁰

Description of Process Using Trichlorobenzenes - -

Trichlorobenzene is used as a process solvent in the production of a benzanthrone dye, commonly called Vat Green 1 (C.I. 59825). The manufacture of benzanthrone dyes depends on the modification of the primary intermediate, benzanthrone. In order to make Vat Green 1, three process steps are required. The alkali treatment of benzanthrone to make dibenzanthronyl takes

place at 112°C (234°F) for 1 to 4 hours. The dibenzanthronyl is then oxidized to the diketo-compound at 25° to 30°C (77° to 86°F) for 4 hours. The methylation of the dihydroxy-compound is achieved by reducing the diketo-compound with boiling sodium bisulfite at 210°C (410°F) for 4 hours.²⁰

Table 5-8 lists dye and pigment manufacturers from *Ward's Business Directory* which may utilize chlorobenzenes in certain processes.²¹ The list of manufacturers is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves.

Emissions - -

Emission factors for the use of o-DCB in dye synthesis appear in Table 5-9. The emission factors are only general estimates. No information was found on specific emission points included in each emission category, the type of production processes used, or specific control technologies employed, if any. Emission factors for monochlorobenzene and trichlorobenzenes were not available. The discussion in Section 4.1 on fugitive emissions should be referred to for more detail. Any given dye synthesis plant may vary in configuration and level of control from this hypothetical facility. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. Literature information does not distinguish between emissions resulting from the synthesis of intermediates or process solvent usage. Information regarding the nature and quantities of air emissions of other chlorobenzenes produced during dye and pigment manufacture was not available. The reader is advised to seek emissions data through contact with specific plant personnel.

**TABLE 5-8.
DYE AND PIGMENT MANUFACTURING COMPANIES**

State	Facilities	
Alabama		
	McWane Inc. Empire Coke-By-Products Tuscaloosa, Alabama	
California		
	Davis Colors Rockwood Industries Inc. Los Angeles, California	Hurst Graphics Inc. Los Angeles, California
	LM Scofield Company Los Angeles, California	
Connecticut		
	Crompton & Knowles Corporation Stamford, Connecticut	Carey Industries Inc. Danbury, Connecticut
Florida		
	Southern Mill Creek Products Company, Inc. Tampa, Florida	
Georgia		
	ABC Compounding Company Inc. Morrow, Georgia	Colloids Inc. Lyndal Division Dalton, Georgia
	Kemira Inc. Savannah, Georgia	New Riverside Ochre Co., Inc. Cartersville, Georgia
Illinois		
	Apollo Colors Inc. Northbrook, Illinois	Chi-Vit Corporation Downers Grove, Illinois
	Chroma Corporation St. McHenry, Illinois	Color Communications Inc. Chicago, Illinois
	Industrial Color Corporation Inc. Joliet, Illinois	
Indiana		
	Western Tar Products Corporation Terre Haute, Indiana	
Louisiana		
	Omnitech International Inc. Thibodaux, Louisiana	
Maryland		
	Mineral Pigments Corporation Rockwood Industries Inc. Beltsville, Maryland	Mobay Corporation Pemco Products Baltimore, Maryland

(continued)

**TABLE 5-8.
DYE AND PIGMENT MANUFACTURING COMPANIES (continued)**

State	Facilities	
	SCM Chemicals Inc. Baltimore, Maryland	
Massachusetts		
	Roma Color Inc. Fall River, Massachusetts	
Minnesota		
	GNB Inc. Metal Division St. Paul, Minnesota	Spectrum Colors Minneapolis, Minnesota
Mississippi		
	First Chemical Corporation First Mississippi Corporation Pascagoula, Mississippi	First Mississippi Corporation Jackson, Mississippi
Missouri		
	Warner-Jekinson Company St. Louis, Missouri	
New Jersey		
	Buffalo Color Corporation Parsippany, New Jersey	Colorco Inc. Linden, New Jersey
	Dye Color Pope Inc. Clifton, New Jersey	H Kohnstamm & Company Inc. Color Division Camden, New Jersey
	H Kohnstamm & Company Inc. South Plainfield, New Jersey	Indol Color Company Inc. Magruder Color Inc. Carteret, New Jersey
	International Dyestuffs Company Clifton, New Jersey	MA Hanna Company PMS Consolidated Division Somerset, New Jersey
	Mallinckrodt Inc. Van Dyk & Co. Belleville, New Jersey	Max Marx Color Company Irvington, New Jersey
	Magruder Color Company Inc. Elizabeth, New Jersey	Pfister Chemicals Inc. Ridgefield, New Jersey
	Pigment Dispersions Inc. Edison, New Jersey	PMS Consolidated Somerset, New Jersey
	RBH Dispersions Inc. Bound Brook, New Jersey	Repeat-O-Type Manufacturing Corporation Wayne, New Jersey

(continued)

**TABLE 5-8.
DYE AND PIGMENT MANUFACTURING COMPANIES (continued)**

State	Facilities	
	Rheox Inc. NL Industries Inc. Hightstown, New Jersey	Standard Chlorine Chemical Company Kearny, New Jersey
	Whittaker Clark & Daniels South Plainfield, New Jersey	
New York		
	EM Industries Inc. Hawthorne, New York	Mealr Corporation Ossining, New York
	Pennwalt Corporation Lucidol Division Buffalo, New York	R & A Specialty Chemicals Company Inc. Brooklyn, New York
North Carolina		
	Sandoz Chemicals Corporation Charlotte, North Carolina	
Ohio		
	Accurate Color Inc Lodi, Ohio	Americhem Inc. Cuyahoga Falls, Ohio
	Flint Ink Corporation Ridgway Color Company Cincinnati, Ohio	Sun Chemical Corporation Pigments Division Cincinnati, Ohio
Pennsylvania		
	Indespec Chemical Corporation Pittsburgh, Pennsylvania	Mobay Corporation Dyes Pigments & Organic Division Pittsburgh, Pennsylvania
	Rutgers-Jenkinson Company State College, Pennsylvania	Siberline Manufacturing Company Inc. Tamaqua, Pennsylvania
	Zinc Corporation of America Monaca, Pennsylvania	
South Carolina		
	Pat-Chem Inc. Greenville, South Carolina	Synalloy Corporation Blackman Uhler Chemical Division Spartanburg, South Carolina
Tennessee		
	Avecor Inc. Vonore, Tennessee	

(continued)

**TABLE 5-8.
DYE AND PIGMENT MANUFACTURING COMPANIES (continued)**

State	Facilities	
Texas		
	Allco Chemical Corporation Dallas, Texas	American Chrome & Chemical Inc. Corpus Christie, Texas
	Hitox Corporation of America Corpus Christi, Texas	NL Industries Inc. Valhi Inc. Houston, Texas
	Valhi Inc. Dallas, Texas	
Virginia		
	Fred Whitaker Company Roanoke, Virginia	Hoechst Celanese Corporation Performance Products Division Portsmouth, Virginia
	Hoover Color Corporation Hiwassee, Virginia	

Source: Reference 21.

**TABLE 5-9.
EMISSION FACTORS FOR o-DICHLOROBENZENE IN DYE
SYNTHESIS^a**

Emission Category	kg o-DCB emitted per Mg o-DCB used	lb o-DCB emitted per ton o-DCB used	Emission Factor Quality Rating ^b
Process	0.40	0.80	U
Storage	0.05	0.10	U
Fugitive	0.05	0.10	U
TOTAL	0.5	1.0	

^a1980 data.

^bNot enough information available to assign a quality rating.

Source: Reference 9.

5.9 USE OF MONOCHLOROBENZENE AND ORTHO-DICHLOROBENZENE AS DYE CARRIERS IN TEXTILE DYEING

Monochlorobenzene (MCB) and o-dichlorobenzene (o-DCB) are effective dye carriers in the coloring of textile products.^{18,22} Dye carriers or dyeing accelerants are used to promote dye migration and transfer to produce even and satisfactory dyeings. They may be used on cellulose triacetate fibers, but are typically used on polyester.

Carrier selection is governed primarily by the carrier's boiling point, which must be high enough to prevent evaporation or steam distillation of the carrier from occurring at the dyeing temperatures, and low enough to be removed from the fabric under plant drying conditions. Since dye carriers have little or no solubility in water, emulsifiers are needed to disperse the carrier in the dye bath. Many carriers are available in the pre-emulsified form. As a general rule, stronger carriers, including phenolic and chlorinated aromatic compounds, are used in open equipment, at a boil, while weaker carriers are used in high temperature dyeing.

The Standard Industrial Classification (SIC) codes for establishments engaged in the dyeing of fibers are listed below.

- Broadwoven fabric mills, wool - 2231
- Knitting mills - 225
- Finishers of broadwoven fabrics of man-made fibers and silk - 2262
- Finishers of textiles, not elsewhere classified - 2269

In 1987, 106 wool, broadwoven fabric mills, 245 plants producing broadwoven fabrics of man-made fibers and finishing silk, and 176 finishing plants for man-made fibers and silk were in operation in the United States.²³

Knitting mills varied greatly in numbers depending on the type of product. In 1987, over 800 facilities were estimated to have produced knit outerwear (SIC 2253), while only 58 were

estimated to have produced knit underwear (SIC 2254). The number of weft knit fabric mills (SIC 2257) was estimated at 304 in 1987. SICs 2251 and 2252, which include women's hosiery (except socks and hosiery, not elsewhere classified), respectively, had a combined 514 facilities.²³

Ward's Business Directory lists 31 fabric finishing facilities (SIC 2262) in the United States with sales greater than \$1,000,000.²¹ *Ward's* also lists 55 finishing facilities for SIC 2269, 38 fabric mills for SIC 231, and 436 knitting mills for SIC 225. These lists are provided in Appendix B, Tables B-1, B-2, B-3 and B-4, respectively.

Potential emission sources of o-DCB in the textile dyeing industry include process equipment vents, open process equipment, equipment leaks, drying operations, and transfer and handling operations. The discussion in Section 4.1 on fugitive emissions should be referred to for more detail. No quantitative emissions data for the textile dyeing industry are available. The reader is encouraged to contact plant personnel to confirm the existence of emissions and control technology to estimate emissions for a specific source.

5.10 USE OF 1,2,4-TRICHLOROBENZENE AS A DYE CARRIER IN THE TEXTILE DYEING INDUSTRY

Textile mill operations which use 1,2,4-TCB include wool scouring, woven fabric finishing (simple and complex processing with desizing), and knit fabric finishing. In most cases, 1,2,4-TCB dye carrier is used only when specific (usually darker) hues are required in man-made fibers.²⁴

When used as a dye carrier, 1,2,4-TCB is combined with a disperse dye and a leveling agent, and then applied to the material at 100°C (212°F) for several hours. Typically, the amount of TCB contained in the dye carrier formulation ranges from 10 percent to 90 percent of the total formulation or from less than 2 percent to 10 percent by weight, once added to the bath. At this point, excess carrier is removed by either alkaline scour at 70° to 80°C (158° to 176°F) with sulfated fatty alcohol, or rinsing the material followed by heating to 190°C (374°F) for one

minute.²⁴ General processes and equipment for use of dye carriers are described in Section 5.8 of this report.

A listing of the plants involved in the finishing of textile products is included in Appendix B. The Standard Industrial Classification (SIC) codes for these establishments are listed below.

- Finishers of broadwoven fabrics of man-made fibers and silk - 2262
- Finishers of textiles, not elsewhere classified - 2269

Potential emission sources of 1,2,4-TCB in the textile dyeing industry include process equipment vents, open process equipment, equipment leaks, drying operations, and transfer and handling operations. The discussion in Section 4.1 on fugitive emissions should be referred to for more detail. No quantitative emissions data for the textile dyeing industry are available. The reader is encouraged to contact plant personnel to confirm the existence of emissions and control technology to estimate emissions for a specific source.

5.11 USE OF PARA-DICHLOROBENZENE AS A PESTICIDE

Para-dichlorobenzene has historically been used in a variety of agricultural applications including use in tobacco seed beds for blue mold control and in peach trees for borer control.^{5,8} However, current federal manufacturing use registrations support only indoor use, including primarily moth control.⁸

The pesticide Paracide[®] is produced at PPG Industries, Inc. of Pittsburgh, Pennsylvania. In 1988, the consumption of p-DCB (para-dichlorobenzene) as a pesticide was 4.5 million kilograms (10 million pounds).¹ Para-dichlorobenzene is typically used in its solid form at nominally 100 percent purity.⁸ The manufacturers are subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of

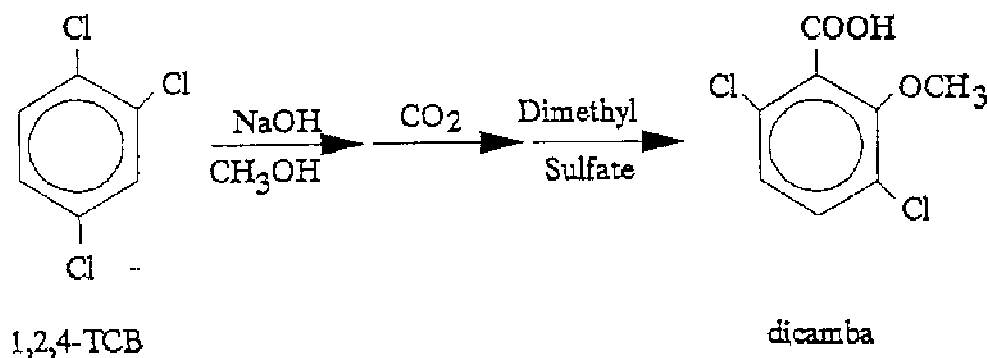
chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

5.12 USE OF 1,2,4-TRICHLOROBENZENE IN THE MANUFACTURE OF THE HERBICIDE BANVEL®

Trichlorobenzene is used in the formulation of the herbicide Banvel®. The common name of Banvel® is dimethylamine salt of dicamba (CAS number 2300-66-5). Banvel® is used as a herbicide to control weeds in crops such as asparagus, corn, grain sorghum, and sugarcane. Banvel® is also used in noncropland areas such as rangeland and pastures to control brush and vines.⁵

5.12.1 Process Descriptions

1,2,4-Trichlorobenzene is used to produce dicamba (Banvel®, 3,6-dichloro-o-anisic acid, 3,6-dichloro-2-methoxybenzoic acid) by what is known as the dicamba process.



In the process, TCB and sodium hydroxide are dissolved in methanol in the presence of carbon dioxide and dimethyl sulfate and heated to 190°C (374°F) for 4 hours in a bomb. The resultant mixture is cooled, filtered, dried, and further processed to make Banvel®.²⁴

In 1988, the production of Banvel® consumed 6.4 to 7.3 million kilograms (14 to 16 million pounds) of trichlorobenzene.¹ In 1991, Sandoz Crop Protection Corporation of Beaumont, Texas was the only facility to produce Banvel®.^{1,5} Capacity and/or production estimates were not available from this facility. The manufacturer is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. Due to the limited number of production facilities, information was not available for the formulation process or specific application procedures of Banvel®.

5.12.2 Emissions

An estimated 33 percent of the total quantity of the TCB used by the pesticide industry was converted or consumed during the manufacturing process. Furthermore, based on process descriptions, approximately one percent of the TCB used was released into the environment, of which two-thirds was discharged to air.²⁴

In the first step of Banvel® manufacture, 90 percent of 1,2,4-TCB is consumed in production of 2,5-dichlorophenyl.⁵ The remaining 10 percent is assumed to be released into the environment, most of which is probably converted to other compounds by side reactions. Less than 1 percent used for dicamba (Banvel®) production was released to the air in the form of fugitive and handling emissions.²⁴

5.13 USE OF ORTHO-DICHLOROBENZENE AS A SOLVENT IN PHARMACEUTICAL MANUFACTURING

Ortho-dichlorobenzene is used as a solvent in the manufacturing of pharmaceutical products by chemical synthesis. Current consumption estimates of o-DCB in pharmaceutical preparations were not available.

5.13.1 Process Description

Synthetic pharmaceuticals are normally manufactured in batch operations, many of which involve the use of solvents.²⁵ Figure 5-3 presents basic operations that may be used in a batch synthesis process. To begin a production cycle, the reactor is washed with water and dried with a solvent. Air or nitrogen is usually used to purge the tank after it is cleaned. Solid reactants and solvent are then charged to the reactor (Step 1). After the reaction is complete, remaining unreacted volatile compounds and solvents may be distilled off, typically using a water cooled condenser. The pharmaceutical product is then transferred to a holding tank (Step 2). In the holding tank, the product may be washed three to four times with water or solvent to remove any remaining reactants and byproducts. The solvent used in washing is generally distilled from the reaction product (Step 3). The crude product may then be dissolved in another solvent and transferred to a crystallizer for purification (Step 4). After crystallization, the solid material is separated from the remaining solvent by centrifuging (Step 5). While in the centrifuge, the product cake may be washed several times with water or solvent. Tray, rotary, or fluid-bed dryers are employed for final product finishing (Step 6).²⁵

The Standard Industrial Classification (SIC) code for pharmaceutical preparations is 2834. There are approximately 732 pharmaceutical plants producing drugs in the United States and its territories. Fifty percent of the plants are small and have fewer than 20 employees. Fifty-three percent of the plants are located in 6 states: 13 percent in New York, 13 percent in California, 12 percent in New Jersey, and 5 percent in Pennsylvania, Illinois and Texas.²³ These states also

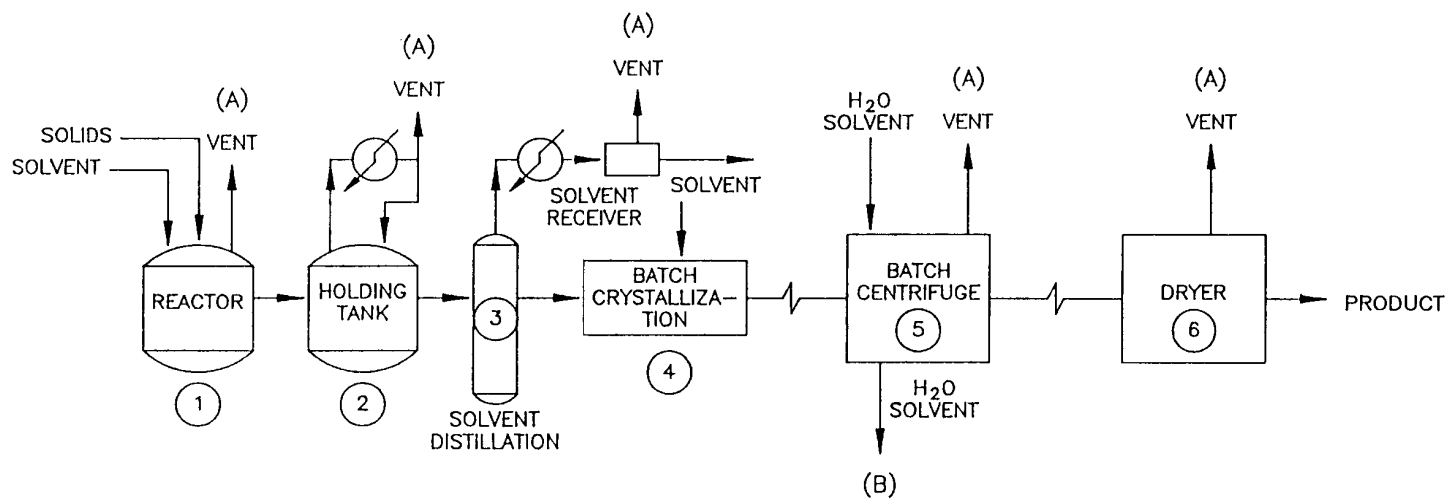


Figure 5-3. Basic operations that may be used in pharmaceutical manufacturing.²⁵

contain the largest plants in the industry. Puerto Rico has had the largest increase in number of operational plants in recent years.

5.13.2 Emissions

Each step of the manufacturing process of a pharmaceutical product may be a source of o-DCB emissions. The magnitude of emissions varies widely within and among operations; therefore, it is impossible to cite typical emission rates for various operations. Figure 5-3 identifies process vents (A) or solvent waste streams (B) from which potential emissions are possible.

The following is an approximate ranking of emission sources that has been established in order of decreasing emission significance. The first four sources typically account for the majority of emissions from a plant.²⁵

- Dryers
- Reactors
- Distillation units
- Storage and transfer
- Filters
- Extractors
- Centrifuges
- Crystallizers

Another potential emission source is equipment leaks. The discussion in Section 4.1 on fugitive emissions should be referred to for more detail.

Condensers, scrubbers, and carbon adsorbers can be used to control emissions from all of the above emission sources. Storage and transfer emissions can also be controlled by the use

of vapor return lines, conservation vents, vent scrubbers, pressurized storage tanks, and floating roof storage tanks.

5.14 MISCELLANEOUS USES OF CHLOROBENZENES

This section discusses miscellaneous production uses of chlorobenzenes for which no detailed process information was available.

Use of Trichlorobenzenes - -

1,2,4-Trichlorobenzene is used in formulations of functional fluids such as dielectric liquids and transformer oils. 1,2,4-TCB is also used as a solvent for crystallization of high melting point products, in termite control, septic tank and drain cleaner preparations, and as a lubricant. Further information on these uses was not available at the time of report preparation. Emissions occur during production and use of secondary products.²²

1,3,5-Trichlorobenzene is used as a solvent for high temperature melting point products in addition to uses as coolants in electrical installations and glass tempering, heat transfer mediums, lubricants, and synthetic transformer oils. It is used in termite preparations and polyester dyeing. Emissions of 1,3,5-trichlorobenzene are expected during the production and use of these products.^{18,24}

1,2,3-Trichlorobenzene is used as an organic intermediate and in synthetic transformer oil. Emissions are expected from general laboratory usage and from its use as a transformer oil.⁹ Historically, 1,2,3-trichlorobenzene was also used as a termite control agent but is not currently used for that purpose.⁸

5.15 REFERENCES FOR SECTION 5.0

1. *SRI Chemical and Economics Handbook*, "Chlorobenzene Production," Menlo Park, CA, 1989.
2. *Nitrochlorobenzene Chemical Product Synopsis*, Mannsville Chemical Products Corporation, Asbury Park, NJ, September 1983.
3. Liepins, R. and F. Nixon, *Industrial Process Profiles for Environmental Use: Chapter 6. The Industrial Organic Chemicals Industry*, EPA-600/2-77-023f, U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Cincinnati, OH, February 1977.
4. *1990 Directory of Chemical Producers, United States of America*, SRI International, Menlo Park, CA, 1990.
5. *Farm Chemicals Handbook, 1991*, Meister Publishing Company, Willoughby, OH, 1991.
6. U.S. Environmental Protection Agency, *Investigation of Selected Potential Environmental Contaminants: Halogenated Benzenes*, EPA-560/2-77-004, Office of Toxic Substances, Washington, DC, July 1977.
7. *The Merck Index, Tenth Edition*, Merck and Company, Rahway, NJ, 1984.
8. Opatick, Richard, Chlorobenzene Producers Association. Memorandum to Michael Ling, TRC Environmental Corporation, August 4, 1993.
9. U.S. Environmental Protection Agency, *An Exposure and Risk Assessment for Dichlorobenzenes*, Final Draft, Office of Water Regulations and Standards, Washington DC, 1981.
10. Boscato, J.F. et al., *Synthesis of Polyphenylene Sulfur*, Polymer Bulletin (Berlin) 4(7):357-359, 1981.
11. *Kirk-Othmer Encyclopedia of Chemical Technology, Volume 18*, John Wiley and Sons, New York, NY, 1982.
12. *Toluene Diisocyanate Chemical Products Synopsis*, Mannsville Chemical Products Corp., Asbury Park, NJ, October 1990.
13. International Programme on Chemical Safety, *Environmental Health Criteria 75: Toluene Diisocyanates*, World Health Organization, Geneva, 1987.

14. U.S. Environmental Protection Agency, *Organic Chemical Manufacturing, Volume 7: Selected Processes, Report 4: Toluene Diisocyanate*, EPA-450/3-80-028b, Office of Air Quality Planning and Standards, Research Triangle Park, NC, December 1980.
15. Hancock, E.G. (ed.), *Toluene, the Xylenes and their Industrial Derivatives*, Elsevier Scientific Publishing Company, New York, NY, 1982.
16. Rosensteel, R.E., U.S. Environmental Protection Agency, Chemicals Manufacturing Section. Memorandum to T. Lahre, including review comments by D. Beck, U.S. Environmental Protection Agency, Air Management Technology Branch, Research Triangle Park, NC, November 16, 1984.
17. Clarke, Eric A., *Ecological and Toxicological Association of Dyestuffs Manufacturing Industry*, Scarsdale, New York. Letter to Tom Lahre, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Durham, NC, March 13, 1985.
18. *Kirk-Othmer Encyclopedia of Chemical Technology, Volume 8, Third Edition*, John Wiley and Sons, New York, NY, 1979.
19. *Color Index International, Third Edition*, The Society of Dyers and Colourists, London, England. 1987.
20. Steadman, T.R., et al. *Industrial Process Profiles for Environmental Use: Chapter 7, Organic Dyes and Pigments Industry*, EPA-600/2-77-023g, U.S. Environmental Protection Agency, Cincinnati, OH, February 1977.
21. Gale Research Inc., *Ward's Business Directory of U.S. Private and Public Companies-1991, Volume 4*, Detroit, MI. 1991.
22. Slimak, K. et al., *Materials Balance for Chlorobenzenes*, EPA-560/13-80-001, U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC, January 1980.
23. *1987 Census of Manufacturers*, U.S. Department of Commerce, Bureau of Census.
24. McNamara, P.W. et al., *An Exposure and Risk Assessment for 1,2,4-Trichlorobenzene Final Draft*, U.S. Environmental Protection Agency, Office of Water Regulations and Standards, Washington, DC, June 1981.
25. *Control of Volatile Organic Emissions from Manufacture of Synthesized Pharmaceuticals Products*, EPA-450/2-78-029, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC, December 1978.

SECTION 6.0

EMISSIONS FROM THE USE OF MATERIALS CONTAINING CHLOROBENZENES

Chlorobenzenes are an ingredient in the manufacture of a number of products and materials. This section discusses air emissions from these products containing chlorobenzenes. Potential emissions sources are identified and available emission factors are presented where available. The reader is advised to contact the specific sources in question to verify the nature of the process, production volume, and control techniques used before applying any of the emission factors presented in this section.

6.1 USE OF PARA-DICHLOROBENZENE IN MOTH CONTROL

Para-dichlorobenzene is used in consumer, commercial, and industrial sectors for moth control. Cakes, blocks, and balls formulated by p-DCB contain greater than 99 percent p-DCB.¹ In 1988, ten percent of p-DCB production in the United States, equalling 4.5 million kilograms (10 million pounds), was consumed as a moth control substance.² Information on the manufacture of these products was not available at the time of report preparation.

Commercial applications of moth control products include preservation of glycerin treated dried flowers during storage and handling and moth proofing of textiles during production.¹ Para-dichlorobenzene is applied to the textiles during the dyeing operation and may be fixed in the fibers by chemical reactions with protein.³ It may also be combined and sprayed with a volatile solvent onto fabric.

A study performed in 1987 tested fourteen combinations of several variables affecting the rate of p-DCB emissions from crystal moth control cakes.⁴ These tests were conducted in environmental test chambers with temperature, humidity, and air exchange rate controls. The measured emission rate was compared with a model emission rate equation and found to be within ten percent in all cases. The emission rate equation is presented below.

$$E = (C) \times (F/A)$$

where:

E = emission rate ($\mu\text{g}/\text{cm}^2\text{-hr}$)

C = concentration of p-DCB ($\mu\text{g}/\text{cm}^3$)

F = flow rate through chamber ($10^6 \text{ cm}^3/\text{hr}$)

A = area of sample (cm^2)

All of the p-DCB used in moth control products and applications is expected to be emitted to the atmosphere by sublimation during production or use.¹ In general, the use of moth control agents are too widespread to categorize. Manufacturers of moth control agents containing p-DCB were not identifiable due to limited information.

6.2 USE OF PARA-DICHLOROBENZENE AS A SPACE DEODORANT

Sixteen percent of p-DCB produced in the United States has a non-intermediate dispersive use in space, toilet bowl, and garbage deodorants. Due to its volatility, density, pleasant odor, and solid nature at room temperature, it is used alone or in combination with disinfectant substances to produce deodorants in a variety of continuous evaporation forms, most commonly solid air deodorizers and toilet blocks.

6.2.1 Process Description

Para-dichlorobenzene-derived deodorant products contain up to 100 percent p-DCB with a perfume added in some cases. Limited information was available detailing the processes by which the deodorant types are manufactured. However, most solid block deodorants are formed by combining the active ingredients such as p-DCB with a carrier substance. The most common carrier for all types of deodorants is water; however, other carriers such as process oils, solvents, and various petroleum products are also employed depending on the form of the deodorant. In solid and semisolid products, active ingredients are incorporated into sublimable water based gels,

waxy solids, or powder form.⁵ The process by which active substances are incorporated into toilet blocks is assumed to be similar in nature.

In 1988, 16 percent of p-DCB production in the United States, equalling 6.8 million kilograms (15 million pounds), was consumed in the manufacture of space deodorants.² Information concerning specific manufacturers was not available. Users of p-DCB-based deodorant products include the industrial, commercial, and consumer sectors.

6.2.2 Emissions

It is estimated that all p-DCB incorporated into solid space and garbage deodorants will enter the atmosphere by sublimation during production or use. It is estimated that approximately 90 percent of the p-DCB used for this purpose is released to the air; the remaining 10 percent is released to either land or water, depending upon whether it is used as a garbage deodorant or toilet deodorant, respectively.¹

6.3 USE OF CHLOROBENZENES AS SOLVENTS IN ORGANIC SOLVENT CLEANING OPERATIONS

Surface cleaning or degreasing includes the solvent cleaning or conditioning of metal surfaces and parts, fabricated plastics, electronic and electrical components, and other nonporous substrates. These cleaning processes are designed to remove foreign materials such as grease, oils, waxes, carbon deposits, and moisture, usually in preparation for further treatment such as painting, electroplating, galvanizing, anodizing, or applying conversion coatings.

Chlorobenzenes are employed as cleaning and degreasing agents in solvent cleaning operations to remove water-insoluble soils from metal, plastic, fiberglass or other surfaces. Ortho-DCB is contained in automobile engine cleaners; carburetor cleaners; in formulations to remove paints, inks, varnishes, lacquers, resins, gums, waxes, heavy greases, acetylcellulose, sulfur and organic sulfur compounds, and tarry substances in stills and processing equipment;

shoe polish; metal polish; rust preventatives; and other cleaning/polishing formulations.¹ 1,2,4-Trichlorobenzene is used in degreasing formulations for electronic wafer stripping in the electronic components industry and engine cleaning.⁶

Data on the current use of chlorobenzenes in solvent cleaning operations are scarce.⁷ This section describes general processes, emissions sources, and available emissions data from degreasing operations.

6.3.1 Process Description

The three most commonly used types of organic solvent cleaners are open top vapor cleaners (OTVCs), in-line cleaners, and cold cleaners. OTVCs are primarily used in metalworking operations and other manufacturing operations.⁸ The vapor cleaning process is one in which solvent vapors rise to the level of the condensing coils and form a controlled vapor zone that prevents vapors from escaping the tank. Parts are immersed into this zone where solvent vapors condense and dissolve foreign materials on the parts.⁷

In-line cleaners (also called conveyORIZED cleaners) employ a continuous feed of soiled parts into the cleaning unit. The majority of in-line cleaners operate in the vapor phase, however, they may also operate in the non-vapor phase. In-line cleaners are typically used in large-scale operations and are normally enclosed except for parts inlet and exit openings.⁸ With these exceptions, the cleaning techniques are the same as those used in vapor or cold cleaning.

Cold cleaning is a batch process operation in which solvents are applied at room temperature or slightly above room temperature, but always below the solvent's boiling point. The mechanical or industrial parts or tools to be cleaned are placed in a basket inside the cold cleaner and immersed in the solvent. Parts too large for immersion may be sprayed or brushed. The solvent tank is often agitated to enhance its cleaning action. After cleaning, the parts are removed from the tank and allowed to dry.

Cold cleaners are usually the simplest and least expensive to operate of the three types of solvent cleaners. The two basic types of cold cleaners are maintenance cold cleaners and manufacturing cold cleaners. The primary cold cleaning application is cleaning of tools or metal parts at service and automotive repair stations and manufacturing facilities. Cold cleaners may incorporate covers and freeboards to limit the evaporative loss of solvents. Freeboard is the distance between the solvent level and the top edge of the unit.⁹

No further information could be gathered on the actual quantities of chlorobenzenes used or specific processes or equipment which are employed for the uses of chlorobenzenes as cleaning solvents.

6.3.2 Emissions

Types of emissions produced by cold cleaning include those generated by bath evaporation to surrounding air, solvent carry-out of cleaned parts, agitation, waste solvent evaporation, and spray evaporation. Emissions associated with conveyORIZED degreasers result from the same processes but are reduced because of the nearly complete enclosure of the conveyORIZED system. Some emissions are also expected from evaporation of blended cleaning solvents during mixing and handling.¹⁰

Uncontrolled emissions from degreasers can be approximated by material balance by assuming that the quantity of makeup solvent is equal to the amount of solvent evaporated from the process over the long term. To estimate emissions after controls by material balance, the quantity of solvent collected or destroyed in control devices, and not recycled to the process, must be subtracted from the quantity of makeup solvent.

Although chlorobenzenes are expected to contribute to degreaser emissions, it should be noted that significant use of chlorobenzenes as primary degreasing solvents has not been documented. Chlorobenzenes, by themselves, are not used as solvents, but probably occur only in solvent mixtures. Moreover, the quantities of chlorobenzenes used in solvent mixtures are not

likely to be very large.¹¹ The reader is encouraged to contact local plant personnel for information on specific processes, solvent formulations emissions, and control technologies.

6.4 USE OF TRICHLOROBENZENES IN WOOD PRESERVATIVES

Trichlorobenzene is used as a soil treatment to repel or poison termites around the foundation of buildings.¹² The trichlorobenzene products are applied on surfaces or injected into standing wood buildings.⁶ The technical product of trichlorobenzene is a mixture of the 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene isomer.¹² No information was available on the formulation process or application practices.

The formulations and users of wood preservatives and products containing trichlorobenzene could not be identified from the literature. Approximately one percent of 1,2,4-TCB is estimated to be emitted to the atmosphere during application and handling, with the balance remaining in the wood.⁶ Emissions factors for 1,2,3-TCB have not been reported.

6.5 REFERENCES FOR SECTION 6.0

1. U.S. Environmental Protection Agency, *An Exposure and Risk Assessment for Dichlorobenzenes*, Final Draft, Office of Water Regulations and Standards, Washington, DC, 1981. p. A-1.
2. *SRI Chemical and Economics Handbook, "Chlorobenzene,"* Menlo Park, CA, October 1989.
3. *Kirk-Othmer Encyclopedia of Chemical Technology, Volume 13*, John Wiley and Sons, New York, NY, 1981.
4. Nelms, L. M. et. al., *Determination of Emission Rates and Concentration Levels of p-Dichlorobenzene from Moth Repellant*, EPA-600/D-87/165, Research Triangle Park, NC, May 1987.
5. *Kirk-Othmer Encyclopedia of Chemical Technology, Volume 16*, John Wiley and Sons, New York, NY, 1982. pp. 297-306.
6. McNamara, P.W., et al., *An Exposure and Risk Assessment for 1,2,4-Trichlorobenzene, Final Draft*, U.S. Environmental Protection Agency, Office of Water Regulations and Standards, Washington, DC, June 1981.
7. Crume, R.V. and M.B. Turner, *Air Pollution Engineering Manual, "Organic Solvent Cleaning (Degreasing),"* Air & Waste Management Association, Van Nostrand Reinhold, New York, NY, 1992.
8. U.S. Environmental Protection Agency, *Alternative Control Technology Document - Halogenated Solvent Cleaners*, EPA-450/3-89-030, Office of Air Quality Planning and Standards, Research Triangle Park, NC, August 1989.
9. U.S. Environmental Protection Agency, *Organic Solvent Cleaners - Background Information of Proposed Standards*, EPA-450/2-78-045a, 1979.
10. U.S. Environmental Protection Agency, *Guidelines for Control of Trichloroethylene, Perchloroethylene, 1,1,1-Trichloroethane, Methylene Chloride, and Trichlorofluoroethane from Existing Organic Cleaners, Working Group Draft*, Office of Air Quality and Planning Standards, Research Triangle Park, NC, July 1981.
11. Rosensteel, R.E., U.S. Environmental Protection Agency, Chemicals Manufacturing Section. Memorandum to T. Lahre, including review comments by D. Beck, U.S. Environmental Protection Agency, Air Management Technology Branch, Research Triangle Park, NC, November 16, 1984.

12. *Ullmann's Encyclopedia of Industrial Chemistry, Fifth Edition, Volume A14, "Insect Control,"* VCH Publishers, New York, NY, 1989.

SECTION 7.0

BYPRODUCT EMISSIONS -- PROCESSES UNRELATED TO PRODUCTION OR USE OF CHLOROBENZENES

Chlorobenzenes and many other pollutants can be emitted to the atmosphere as the result of product manufacturing or from the burning of fossil fuels. Processes that release chlorobenzenes as a byproduct are described in this section. These processes include waste treatment processes, waste oil combustion, and chlorinated solvent production.

7.1 VOLATILIZATION OF CHLOROBENZENES FROM WASTEWATER TREATMENT OPERATIONS

Chlorobenzenes may be emitted when wastes containing chlorobenzenes are present in surface impoundments for treatment and storage of wastewater or in open treatment and storage tanks. Treatment and storage facilities may be located at the site of generation of the waste, or at a separate commercial waste treatment plant. In addition, publicly owned treatment works (POTWs) may emit chlorobenzenes if they receive wastewater from plants producing chlorobenzenes either as a main product or as a byproduct, or from plants using chlorobenzenes as an intermediate. For example, at one 42 million gallon per day (MGD) POTW, 93, 61 and 100 percent, of the influent contributions of 1,2,4-TCB, m-DCB, and p-DCB, respectively, were found to have originated as byproducts of industrial processes. Moreover, at this plant, approximately 54 percent of the volatile organics (including MCB) were attributed to industrial origins.¹

A typical secondary treatment facility sequence utilized by many existing wastewater treatment facilities consists of screening, grit removal, primary clarification, use of conventional activated sludge with aeration, and chlorination. Due to the volatile nature of chlorobenzenes, air emissions are expected mainly from clarification and aeration processes. Measurements of the concentrations of chlorobenzenes in the effluent of the 42 MGD POTW discussed above suggest that the overall treatment process removes 40 to 90 percent of the incoming chlorobenzenes, primarily during activated sludge aeration. Partitioning of 1,2,4-TCB, m-DCB,

and p-DCB to the primary clarifier sludge and activated sludge indicates that some fraction of these pollutants may accumulate onto settleable or floatable solids. However, the remainder is expected to be removed by either air stripping or by biodegradation.¹ Air stripping would result in air emissions of chlorobenzenes.

A study conducted at two Chicago-area wastewater treatment facilities estimated that approximately 95 percent of the chlorobenzenes in the influent waters biodegraded in activated sludge systems while only 2 percent volatilized. However, if all of the influent chlorobenzenes at the two facilities were to volatilize, it would account for 7 kilograms (15.4 pounds) per year.² Another study conducted in California on statewide municipal wastewater treatment plants identified chlorobenzenes as one category of 16 VOC compounds being emitted.³ The study did not elaborate on the amount of chlorobenzenes emitted because the compounds had been detected in fewer than 25 percent of the plants. No other information was available on emissions from this study.

Testing of the aeration basins at a small municipal treatment plant (handling 40 percent industrial and 60 percent municipal sewage) resulted in the measurement of emissions of o-DCB and m-DCB ranging from levels of 148 to 478 grams/hour and 155 to 609 grams/hour, respectively.⁴ Monochlorobenzene was measured only at trace quantities. No data were collected for other chlorobenzenes. Too little data are available to extrapolate these test results to other wastewater treatment plants.

A study developed for emissions modeling from a typical POTW facility identified that chlorobenzenes were present. The emission factors from the model POTW plant are presented in Table 7-1, and represent emissions from the POTW overall. *[Further information was not available due to the inability to locate the document from which the emission factors were presented. The following reference is likely to have information on the emission factors located in the table: White, T.S. Volatile Organic Compound Emissions From Hazardous Waste Treatment Facilities at Downstream POTW (Final Report). Radian Corporation. Prepared under EPA Contract No. 68-02-4378. U.S. Environmental Protection Agency, Research Triangle Park, NC, 1987.]*

**TABLE 7-1.
EMISSION FACTORS FOR WASTEWATER TREATMENT
OPERATIONS**

Pollutant	Emission Factor^a	Emission Factor Quality Rating
p-DCB	0.39 Mg/Mg p-DCB in influent (780 lb/ton p-DCB in influent)	E
o-DCB	0.41 Mg/Mg o-DCB in influent (820 lb/ton o-DCB in influent)	E
m-DCB	0.50 Mg/Mg m-DCB in influent (1000 lb/ton m-DCB in influent)	E
Chlorobenzenes	0.52 Mg/Mg chlorobenzenes in influent (1040 lb/ton chlorobenzenes in influent)	E

^aBased on emission modeling for hypothetical POTW. Represents average POTW that treat industrial wastewater.

Source: Reference 5.

Specific locations of POTWs that treat wastewater containing chlorobenzenes were not identified, therefore the reader should contact particular facilities to determine if such wastes are treated.

7.2 HAZARDOUS AND SOLID WASTE INCINERATION

The majority of atmospheric emissions of pollutants from municipal waste combustion comes from incineration. In addition to particulate matter, other pollutants, such as volatile organic compounds (including chlorobenzenes) and carbon monoxide are often emitted as a result of incomplete combustion of the waste due to improper combustion design or poor operating conditions.

Several methods are used to incinerate municipal waste. These include mass burn excess air combustion, starved air or modular combustion, and refuse-derived fuel combustion. Approximately 70 percent of the total municipal solid waste is incinerated in mass burn units. More information on the methods of municipal waste combustion can be found in the document, *Characterization of the Municipal Waste Combustion Industry*.⁶ Similarly, hazardous waste can be incinerated by several methods including thermal, catalytic and regenerative incineration.

Several chlorobenzenes emission factors have been identified for municipal waste combustion and are presented in Table 7-2. The emission factors include all isomers of chlorobenzenes. These emission factors were derived from tests on five facilities which were using electrostatic precipitators (ESPs) or dry alkaline scrubbers in combination with fabric filters as control devices. The emission factors were determined by calculating the average emission rate for all facilities of a given type.⁷ Therefore, the emission factors are given a rating of "D".

Open-air burning presents a particularly unique source of atmospheric emissions of pollutants. This method of solid waste incineration allows for exposure to many variables including wind, ambient temperatures, and other environmental parameters such as rain and humidity, degree of compactness of the refuse, and composition and moisture of the refuse. In general, lower temperatures are achieved in open-air burning than in closed combustion. Therefore, this allows for increased emissions of particulate matter, carbon monoxide, and volatile organic compounds (including chlorobenzenes) with decreased emissions of nitrogen oxides. Other important regulating factors for open-air burning are fuel loading (how much refuse material is burned per unit of land area) and arrangement of the refuse (in rows, piles, or spread out).⁹ Emission factors for chlorobenzenes have not been identified.

7.3 BURNING OF WASTE OIL

Monochlorobenzene and o-dichlorobenzene have been identified as contaminants of potential concern in waste crankcase oils used as fuel. Approximately 1.2 billion gallons of used automotive and industrial oils are generated annually, of which 35 percent is collected and used as fuel.¹⁰ Studies of waste oil composition show that waste industrial oils are contaminated with

**TABLE 7-2.
EMISSION FACTORS FOR MUNICIPAL WASTE COMBUSTION**

Emission Category	Combined Chlorobenzenes Emission Factor (g/Mg of waste combusted)	Comment	Emission Quality Factor Rating
Existing mass burn heat recovery facility ⁷	0.32	Controlled by ESP, based on source test	E
Mass burn nonheat recovery facility ⁷	0.32	Controlled by ESP, based on source test	E
Refuse-derived fuel facility ⁷	0.14	Controlled by ESP, based on source test	E
Modular facility ⁷	0.018	Controlled by ESP, based on source test	E
Existing mass burn heat recovery facility ⁸	0.02	Controlled by dry alkaline scrubber and fabric filter, assumes 95% control efficiency	E
Mass burn nonheat recovery facility ⁸	0.02	Controlled by dry alkaline scrubber and fabric filter, assumes 95% control efficiency	E
Refuse-derived fuel facility ⁸	0.009	Controlled by dry alkaline scrubber and fabric filter, assumes 95% control efficiency	E
Modular facility ⁸	0.001	Controlled by dry alkaline scrubber and fabric filter, assumes 95% control efficiency	E

Source: References 7, 8.

chlorinated solvents. It has also been suggested that chlorinated hydrocarbons in the oils are formed chemically during oil use or may result from contamination by solvents in holding tanks. Observed concentration ranges for MCB and o-DCB in waste oils are 4 to 500 µg/l and 60 to 160 µg/l, respectively.¹⁰

Locations of boilers which use waste oils for fuel have not been identified in the literature. It is uncertain how much MCB and o-DCB are released into the atmosphere during the burning of waste oil as fuel. Emissions are related to initial concentrations of chlorobenzenes in the waste oil as well as boiler operating parameters and control devices. No information was available concerning actual emission rates.

7.4 HEXACHLOROBENZENE GENERATION DURING CHLORINATED SOLVENT PRODUCTION

Approximately 60 percent of the total national HCB waste load is attributable to chlorinated solvent production, primarily from the production of carbon tetrachloride, trichloroethylene, and perchloroethylene. Of these, perchloroethylene production is expected to produce the greatest quantity. The production of several other chlorinated solvents, such as ethylene dichloride and 1,1,1-trichloroethane, also has the potential to produce HCB at trace levels.¹¹

7.4.1 Process Description

During the production of carbon tetrachloride, trichloroethylene, and perchloroethylene, HCB is formed as a reaction byproduct from chlorination, oxychlorination, and cracking operations. Flow diagrams illustrating the main processes from producing carbon tetrachloride, trichloroethylene, and perchloroethylene are presented in Figures 7-1, 7-2, and 7-3, respectively. Potential HCB-containing waste streams are indicated in these figures. Hexachlorobenzene is usually found as a residue in the heavy ends of still bottoms during distillation of the purification process. The heavy, tarry residue also contains other chlorinated hydrocarbons in addition to

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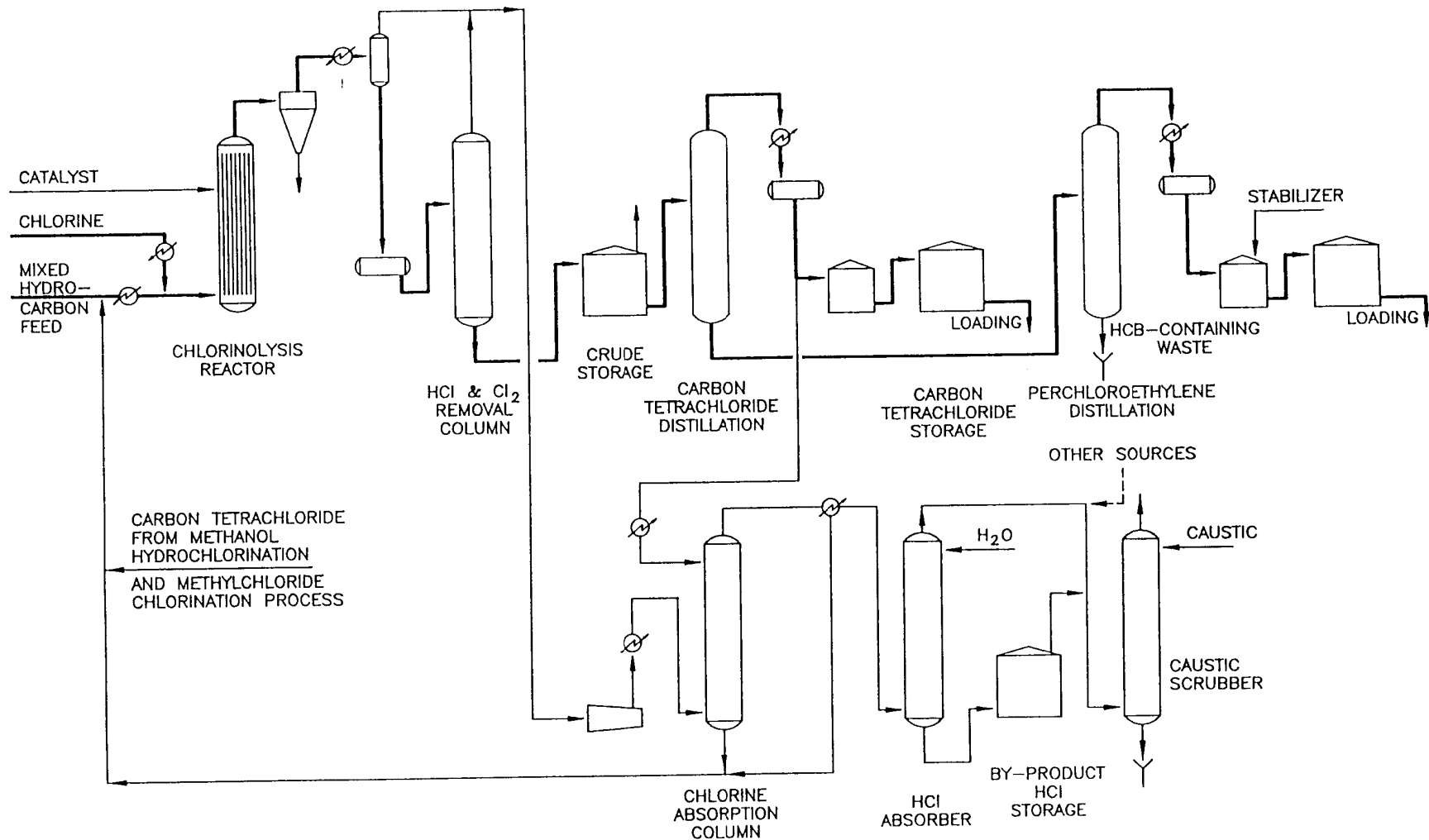


Figure 7-1. Process flow for the production of carbon tetrachloride and perchloroethylene by hydrocarbon chlorinolysis.¹¹

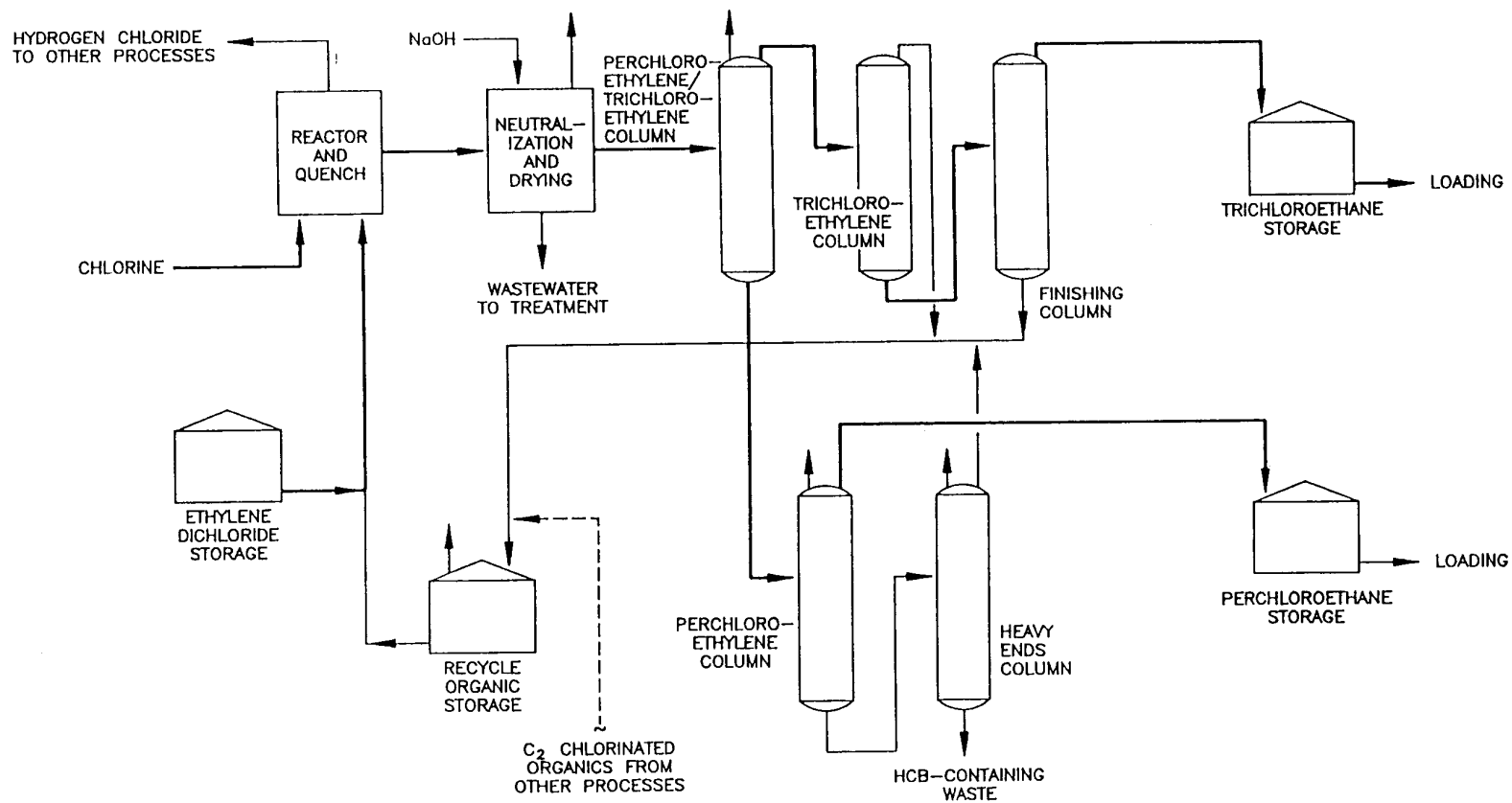


Figure 7-2. Process flow diagram for the production of perchloroethylene and trichloroethylene by chlorination.¹¹

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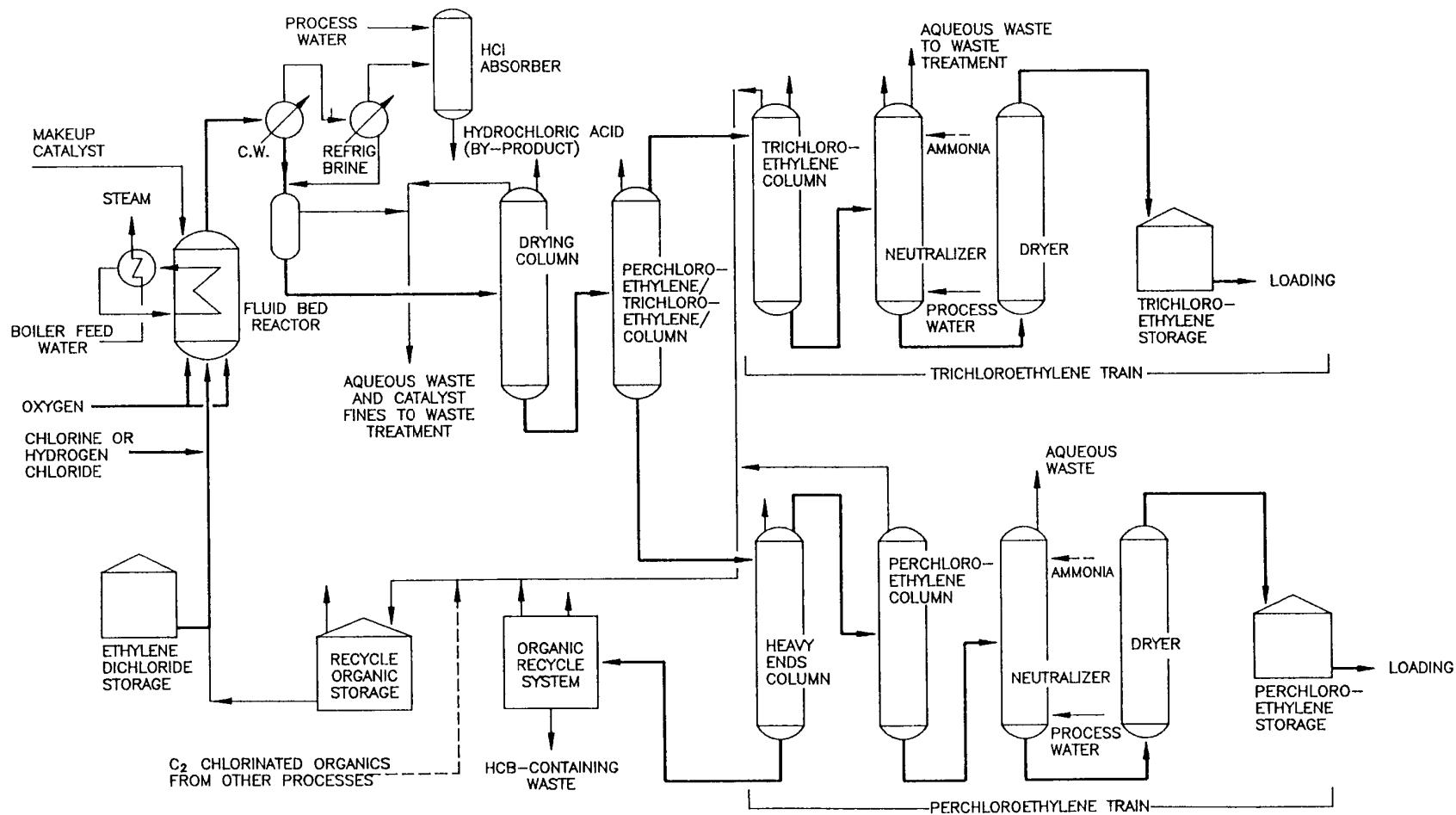


Figure 7-3. Process flow diagram for the production of perchloroethylene and trichloroethylene by oxychlorination.¹¹

HCB. Generally, these wastes are removed and stored in containers prior to their ultimate disposal by incineration.¹¹

The HCB levels in production wastes vary greatly by chemical and by plant. This variability in the HCB concentration is related to the processes and feedstock materials used. Wastes generated by trichloroethylene production appear to contain the lowest levels of HCB. In general, it is difficult to quantify a typical HCB concentration in the process wastes.¹¹

Currently, known producers of carbon tetrachloride, trichloroethylene, and perchloroethylene and their methods of production are shown in Tables 7-3, 7-4, and 7-5, respectively. Most of the listed facilities reported HCB-containing wastes on their Resource Conservation and Recovery Act (RCRA) Part A applications on file with the EPA and state hazardous waste agencies.¹¹

TABLE 7-3.
CHEMICAL PRODUCERS OF TRICHLOROETHYLENE - 1989

Company Location	Capacity Millions kg/yr (Millions lbs/yr)	Method of Production
Dow Chemical U.S.A. Freeport, Texas	54.4 (120)	Chlorination of ethylene dichloride
PPG Industries, Inc. Lake Charles, Louisiana	90.7 (200)	Oxychlorination of ethylene dichloride

Source: Reference 12.

7.4.2 Emissions

The HCB generated by the production of the chlorinated solvents occurs as bottoms from distillation processes. When the HCB-containing waste is removed from the distillation unit, the HCB portion is essentially solid. Considering its physical state and the low vapor pressure of HCB at ambient temperatures (*i.e.*, 20°C or 68°F), the potential for fugitive HCB volatilization

TABLE 7-4.
CHEMICAL PRODUCERS OF CARBON TETRACHLORIDE -
1989

Company Location	Capacity Millions kg/yr (Millions lbs/yr)	Method of Production
Akzo Chemicals Inc. Akzo America Inc. Chemical Division Le Moyne, Alabama	118 (260)	Not available
Dow Chemical U.S.A. Pittsburg, California	36.3 (80)	Methane chlorination and chlorinolysis of mixed hydrocarbons with perchloroethylene co-product
Plaquemine, Louisiana	56.7 (125)	Chlorinolysis of mixed hydrocarbons with perchloroethylene co-product
Hanlin Group, Inc. LCP Chemicals Division Moundsville, West Virginia	3.6 (8)	Not available
Occidental Petroleum Corporation Occidental Chemical Corp., subsidiary Electrochemical & Specialty Products Group Electrochemicals Division Belle, West Virginia	negligible	Not available
Vulcan Materials Company Vulcan Chemicals Division Geismar, Louisiana	40.8 (90)	Chlorinolysis of mixed hydrocarbons with perchloroethylene co-product
Wichita, Kansas	27.2 (60)	Methyl chloride chlorination and methane chlorination, chlorinolysis of mixed hydrocarbons with perchloroethylene co-product

Source: Reference 12.

during waste generation and waste handling operations is minimal. Actual tests at a perchloroethylene plant have indicated that HCB waste handling operations are not a source of

**TABLE 7-5.
CHEMICAL PRODUCERS OF PERCHLOROETHYLENE - 1989**

Company Location	Capacity Millions kg/yr (Millions lbs/yr)	Method of Production
Dow Chemical U.S.A. Pittsburg, California	22.7 (50)	Chlorinolysis of mixed hydrocarbons producing carbon tetrachloride as a co-product
Plaquemine, Louisiana	40.8 (90)	Chlorinolysis of mixed hydrocarbons producing carbon tetrachloride as a co-product
Occidental Petroleum Corporation Occidental Chemical Corp., subsidiary Electrochemical & Specialty Products Group Electrochemicals Division Deer Park, Texas	81.6 (180)	Not available
PPG Industries, Inc. Chemicals Group Lake Charles, Louisiana	90.7 (200)	Chlorination of ethylene dichloride
Vulcan Materials Company Vulcan Chemicals Division Geismar, Louisiana	68 (150)	Chlorinolysis of mixed hydrocarbons producing carbon tetrachloride as a co-product
Wichita, Kansas	22.7 (50)	Chlorinolysis of mixed hydrocarbons producing carbon tetrachloride as a co-product

Source: Reference 12.

HCB air emissions. In these tests, neither uncontrolled air emissions associated with handling HCB-containing waste nor air emissions from waste storage tanks were found to contain HCB.¹¹

In the past, waste storage piles at plants indirectly generating HCB may have released fugitive HCB emission due to slow evaporative losses. However, the recent advent of the management and control of hazardous wastes under the Resource Conservation and Recovery Act (RCRA), has greatly reduced the use of waste storage piles because of the stringent site contaminant and monitoring requirements in place for open piles. Most HCB waste generators currently store their wastes in containers prior to final disposal in incinerators or landfills.¹¹

The majority of chlorinated solvent plants known to generate HCB wastes use incineration as a means of ultimate disposal, while a few utilize offsite landfill facilities. The offsite incinerator must meet the same RCRA requirements to be allowed to burn HCB. The ultimate HCB emission point from incinerating these wastes will not necessarily be the incinerator stack, but will probably be the stack on the caustic wet scrubber used to control hydrochloric acid emissions from the incinerator.¹¹

7.5 REFERENCES FOR SECTION 7.0

1. U.S. Environmental Protection Agency, *Fate of Priority Toxic Pollutants in POTW's - 30-Day Study*, EPA-440/1-82-302, Effluent Guidelines Division, August 1982, pp. 1-65.
2. Rittman, B.E. and N. Eun, "Estimating Volatile Organic Compound Emissions from Publicly Owned Treatment Works," *Journal of the Water Pollution Control Federation*, 59(7):670-678, July 1987.
3. Corsi, Richard L, "Emissions of Volatile and Potentially Toxic Organic Compounds from Municipal Wastewater Treatment Plants," Presented at the 80th Annual Meeting of APCA, New York, NY, June 21-26, 1987.
4. Pellizzari, E.D, *Volatile Organics in Aeration Gases of Municipal Treatment Plants: Project Summary*, EPA-600/52-82-056, U.S. Environmental Protection Agency, Office of Research and Development, Municipal Environmental Research Laboratory, Cincinnati, OH, August 1982.
5. White, T.S., *Volatile Organic Compounds Emissions From Hazardous Waste Treatment Facilities at Downstream POTW (Final Report)*. Radian Corporation. Prepared under EPA contract No. 68-02-4378. U.S. Environmental Protection Agency, Research Triangle Park, NC, 1987.
6. Radian Corporation, *Characterization of the Municipal Waste Combustion Industry, Appendix A*, Research Triangle Park, NC, October 1986.
7. U.S. Environmental Protection Agency, *Municipal Waste Combustion Study: Assessment of Health Risks Associated with Municipal Waste Combustion Emissions*, EPA/530-SW-87-021g, Standards and Air Strategies Division, Research Triangle Park, NC, 1987.
8. U.S. Environmental Protection Agency, *Emission Data Base for Municipal Waste Combustors*, EPA/530-SW-87-021b, Standards and Air Strategies Division, Research Triangle Park, NC, 1987.
9. Gerstle, R.W., and D.A. Kemnitz, "Atmospheric Emissions from Open Burning," *Journal of the Air Pollution Control Association*, 12:324-327, May 1967.
10. *Liquid Fuel Sample Analysis*, Eureka Laboratories, Inc., Sacramento, CA, November 10, 1984.
11. Brooks, G.W. and G.E. Hunt, *Source Assessment for Hexachlorobenzene, Final Report*, U.S. Environmental Protection Agency, Pollutant Assessment Branch, Research Triangle Park, NC, 1984.

12. *1990 Directory of Chemical Producers, United States of America*, SRI International, Menlo Park, CA, 1990.

SECTION 8.0

AMBIENT AIR AND STATIONARY SOURCE TEST PROCEDURES

Chlorobenzene emissions can be measured from ambient air and stationary sources utilizing the test methods presented below. If applied to stack sampling, the ambient air monitoring methods may require adaptation or modification. If ambient air methodology is applied to stationary source testing, appropriate precautions must be taken to ensure that the capacity of the methodology is not exceeded so that results will be quantitative. Ambient methods which require the use of sorbents are susceptible to sorbent saturation if high concentration levels exist. If this happens, breakthrough will occur, and quantitative analysis is not possible.

- EPA Method TO-1: Determination of Volatile Organic Compounds in Ambient Air Using Tenax[®] Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS)
- EPA Method TO-14: Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA[®] Passivated Canister Sampling and Gas Chromatographic (GC) Analysis
- EPA Method 0030: Volatile Organic Sampling Train (VOST) with EPA Method 5040: Analysis of Sorbent Cartridges from VOST
- EPA Method 0010: Modified Method 5 Sampling Train with EPA Method 8270: Gas Chromatography/Mass Spectrometry for Semi-volatile Organics: Capillary Column Technique

The following subsections briefly describe the recommended sampling and analytical methods for determining chlorobenzene emissions.

8.1 EPA METHOD TO-1¹

Ambient air concentrations of chlorobenzene can be measured using EPA Method TO-1 from the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*. This method is used to collect and determine volatile nonpolar organics (aromatic hydrocarbons, chlorinated hydrocarbons) that can be captured on Tenax[®] and determined by

thermal desorption techniques. The compounds determined by this method have boiling points in the range of 80°C to 200°C (180°F to 390°F). Figure 8-1 presents a schematic of the sampling system and Figure 8-2 presents a schematic of typical Tenax[®] cartridge designs.

Ambient air is drawn through the cartridge which contains approximately 1-2 grams (0.035 to 0.07 ounces) of Tenax[®]. Chlorobenzene is trapped on the Tenax[®] cartridge which is then capped and sent to the laboratory for analysis utilizing purge-and-trap gas chromatography/mass spectrometry (GC/MS) according to the procedures specified in EPA Method 5040 (see Section 8.4). The recommended GC column is a 50 meter capillary, type SE-30 with an internal diameter of 0.3 mm.

The exact run time, flow rate and volume sampled varies from source to source depending on the expected concentrations and the required detection limit. Typically, 10 to 20 L (0.35 to 0.7 ft³) of ambient air are sampled. Analysis should be conducted within 14 days of sample collection.

8.2 EPA METHOD TO-14¹

Ambient air concentrations of chlorobenzene can also be measured using EPA Method TO-14 from the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*. This method is based on collection of a whole air sample in SUMMA[®] passivated stainless steel canisters and is used to determine semi-volatile and volatile organic compounds. The compounds are separated by gas chromatography and measured by mass-selective detector or multidetector techniques such as FID, electron capture detection (ECD), and photoionization detection (PID). The recommended column for Method TO-14 is an HP OV-1 capillary with 0.32mm I.D. x 0.88 µm cross-linked methyl silicone coating or equivalent. Samples should be analyzed within 14 days of collection.

This method is applicable to specific semi-volatiles and volatile organic compounds that have been tested and determined to be stable when stored in pressurized and subatmospheric pressure canisters. Chlorobenzene can be successfully measured at the parts per billion by

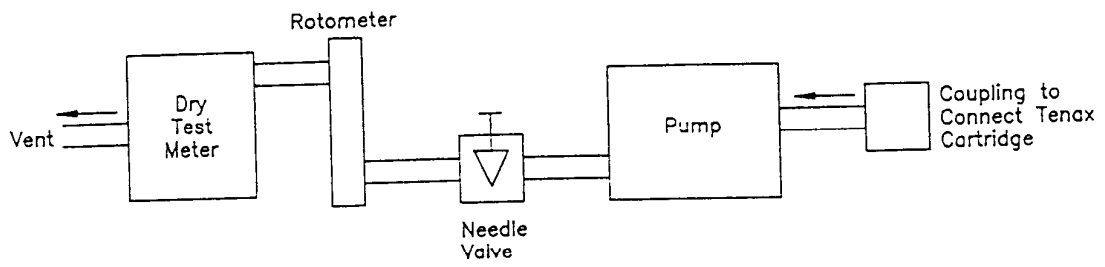
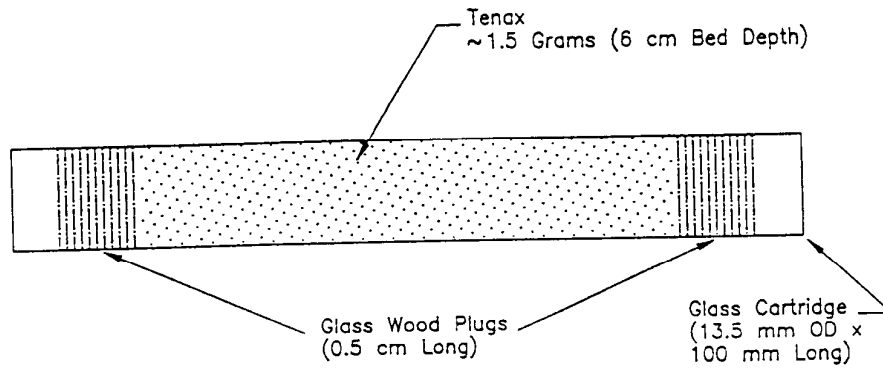


Figure 8-1. EPA Method TO-1 sampling system.¹



(a) Glass Cartridge

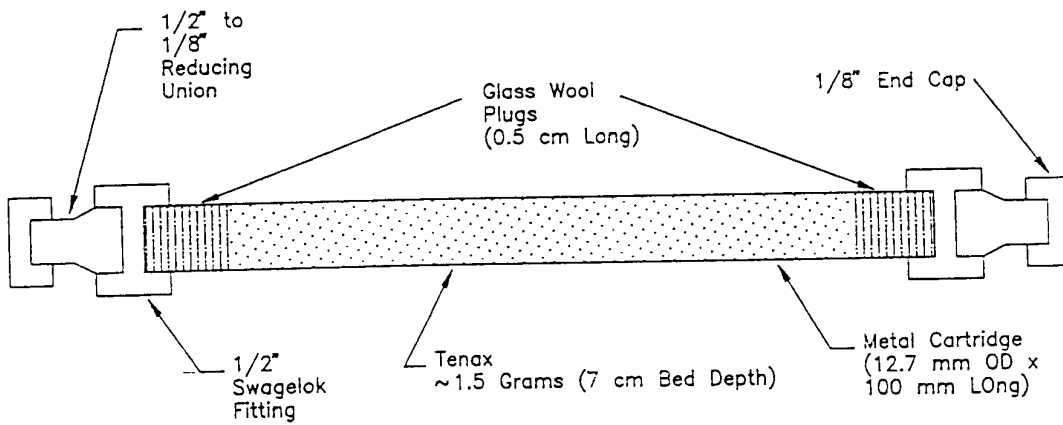


Figure 8-2. Tenax[®] cartridge design.¹

volume (ppbv) level using this method. Figure 8-3 presents a diagram of the canister sampling system.

8.3 EPA METHOD 0030²

The volatile organic sampling train (VOST) from SW-846, (third edition) is designed for the collection of volatile organic compounds from the stack gas effluents of hazardous waste incinerators. The VOST method was designed to collect volatile organics with boiling points in the range of 30°C to 100°C (86°F to 212°F). Many compounds with boiling points above 100°C (212°F) may also be effectively collected using this method. Chlorobenzene concentrations can be measured using this method. Figure 8-4 presents a schematic of the principle components of the VOST.

In most cases, 20 L (0.7 ft³) of effluent stack gas are sampled at an approximate flow rate of 1 L/minute (0.035 ft³/min) using a glass-lined heated probe. The gas stream is cooled to 20°C (68°F) by passage through a water-cooled condenser and the volatile organics are collected on a pair of sorbent resin traps. Liquid condensate is collected in the impinger located between the two resin traps. The first resin trap contains about 1.6 g (0.06 ounce) Tenax[®] and the second trap contains about 1 g (0.04 ounce) each of Tenax[®] and petroleum-based charcoal.

The Tenax[®] cartridges are then thermally desorbed and analyzed by purge-and-trap GC/MS along with the condensate catch as specified in EPA Method 5040. Analysis should be conducted within 14 days of sample collection.

8.4 EPA METHOD 5040²

The contents of the sorbent cartridges (collected via EPA Method 0030) are spiked with an internal standard and thermally desorbed for 10 minutes at 80°C (176°F) with organic-free nitrogen or helium gas (at a flow rate of 40 mL/min (2.4 in³/min)), bubbled through 5 mL (0.3 in³) of organic-free water, and trapped on an analytical adsorbent trap. After the 10 minute desorption, the analytical adsorbent trap is rapidly heated to 180°C (356°), with the carrier gas

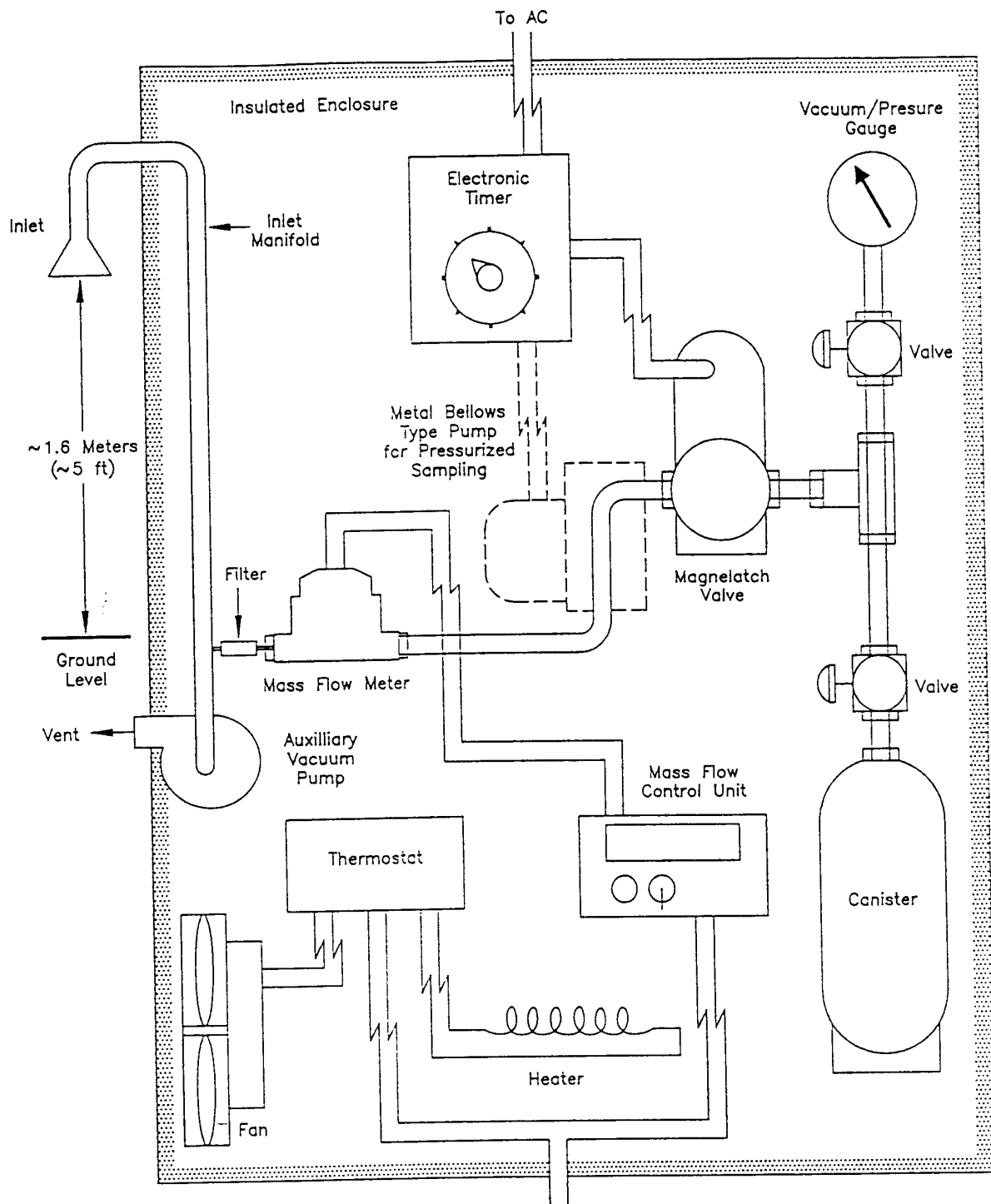


Figure 8-3. Canister sampling system.¹

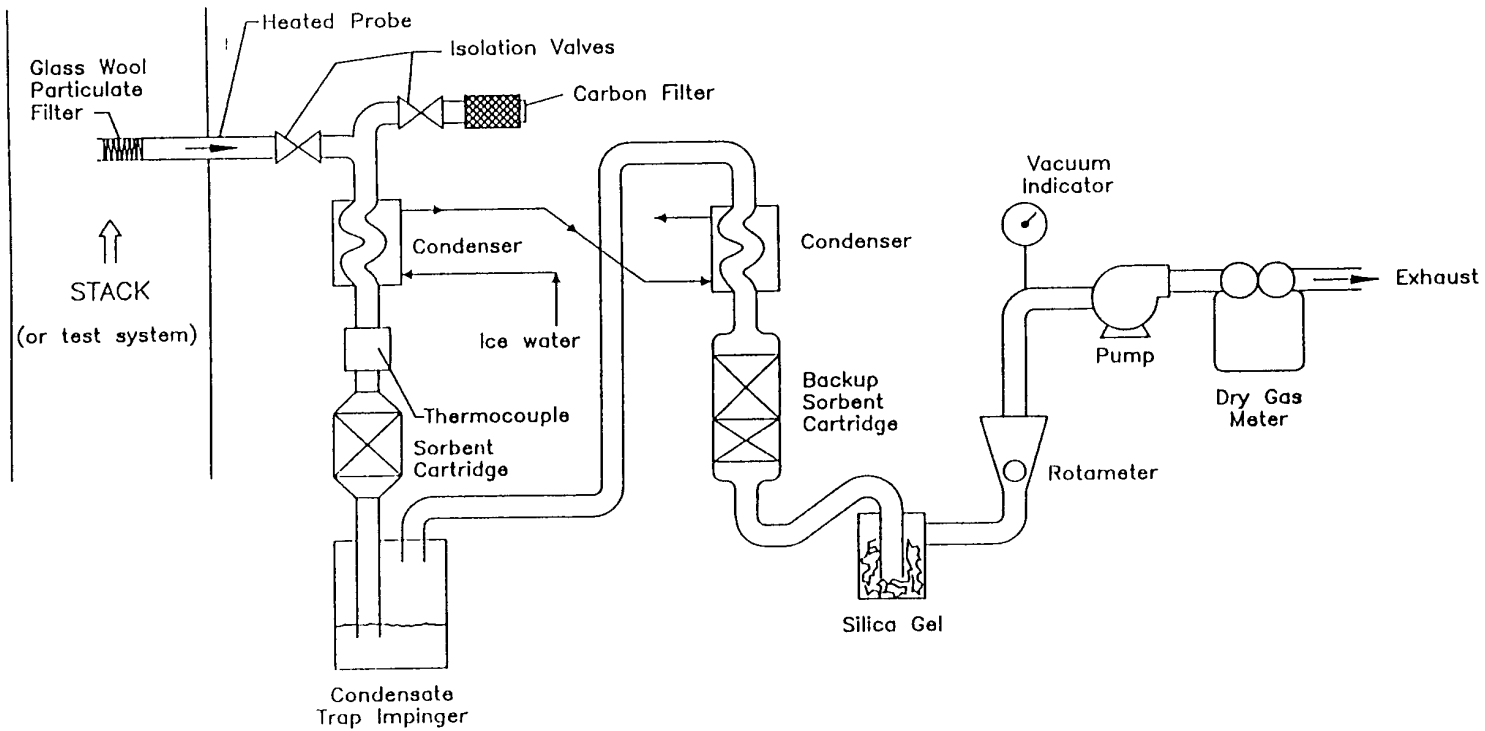


Figure 8-4. Schematic of volatile organic sampling train (VOST).²

flow reversed so that the effluent flow from the analytical trap is directed into the GC/MS. The volatile organics are separated by temperature-programmed gas chromatography and detected by low resolution mass spectrometry. The concentrations of the volatile organics are calculated using the internal standard technique.

EPA Methods 5030 and 8240 may be referenced for specific requirements for the thermal desorption unit, purge-and-trap unit, and GC/MS system.

A diagram of the analytical system is presented in Figure 8-5. The Tenax[®] cartridges should be analyzed within 14 days of collection. The desired detection limit of this method is 0.1 ng/L (20 ng per Tenax[®] cartridge).

8.5 EPA METHOD 0010²

EPA Method 0010 (Modified Method 5 Sampling Train) is used to determine the destruction and removal efficiency of semi-volatile principal organic hazardous constituents (POHCs) from incineration systems. This method may be used for determining chlorobenzene emissions.

Gaseous and particulate pollutants are withdrawn isokinetically from an emission source and collected in a multicomponent sampling train. Figure 8-6 presents a schematic of the sampling system. Principal components of the train include a high-efficiency glass- or quartz-fiber filter and a packed bed of porous polymeric adsorbent resin (typically XAD-2[®] or polyurethane foam for PCBs). The filter is used to collect organic-laden particulate materials and the porous polymeric resin to adsorb semi-volatile organic species (compounds with a boiling point above 100°C (212°F)). Comprehensive chemical analyses, using a variety of applicable analytical methodologies, are conducted to determine the identity and concentration of the organic materials.

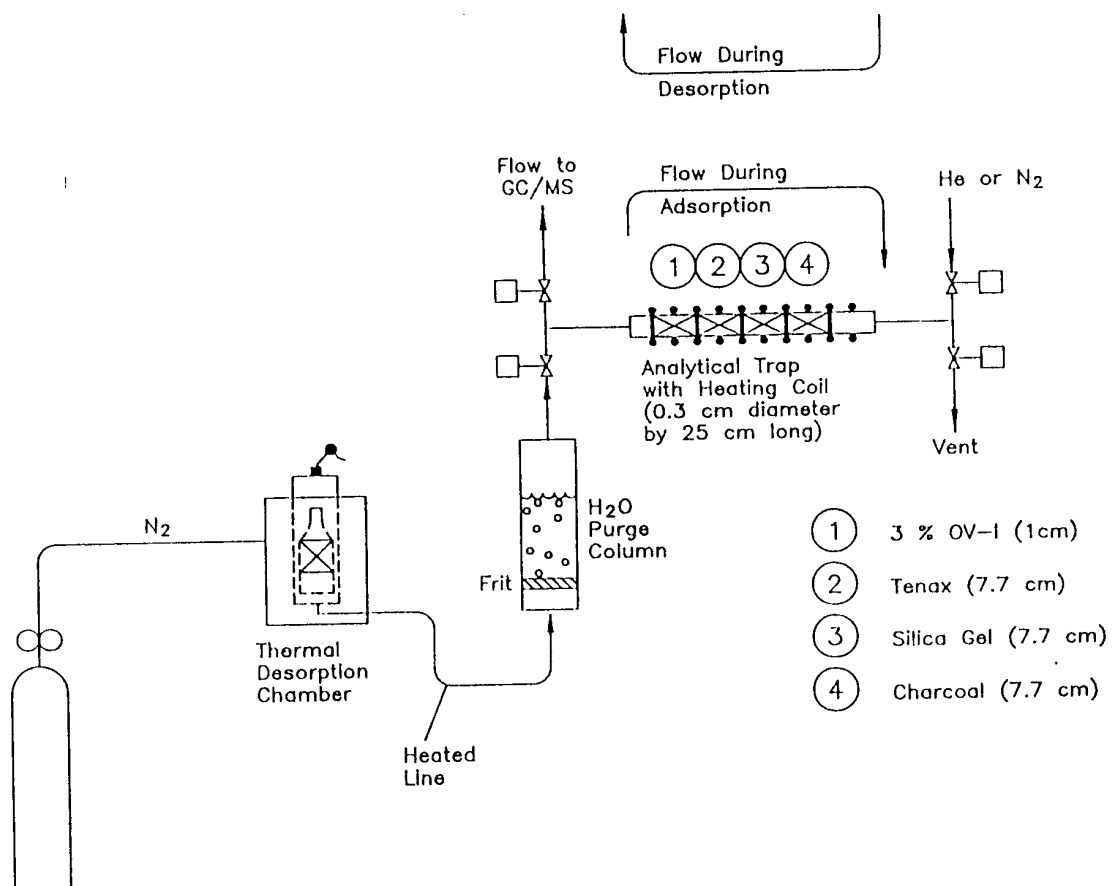


Figure 8-5. Schematic diagram of trap desorption/analysis system.²

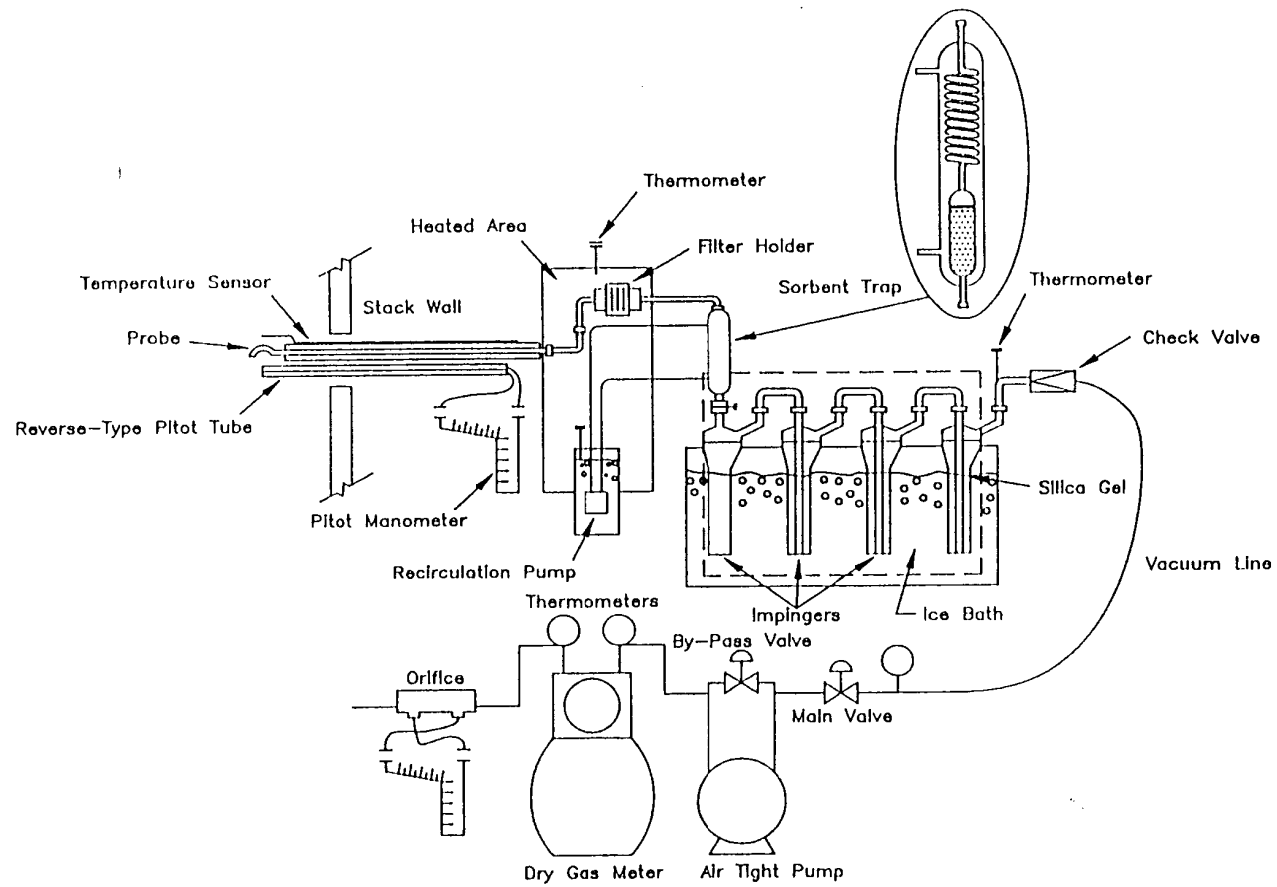


Figure 8-6. Modified Method 5 sampling train.²

8.6 EPA METHOD 8270²

EPA Method 8270 is used to determine the concentration of semi-volatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and ground water. It is also applicable to an extract from sorbent media in conjunction with Method 0010. Direct injection of a sample may be used in limited applications.

Method 8270 can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Chlorobenzenes are within the boiling point range and may be determined using this methodology.

The practical quantitation limit for Method 8270 is approximately 50 µg/mL of extract. The entire sorbent module with filter is typically extracted and concentrated to 1 mL (0.03 in³) [a final volume of 5 mL (0.3 in³) is used to avoid loss of volatile compounds], and this final extract volume represents the entire volume of gas sampled.

8.7 REFERENCES FOR SECTION 8.0

1. U.S. Environmental Protection Agency, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA/600/4-89/017, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, June 1988.
2. U.S. Environmental Protection Agency, *Test Methods for Evaluating Solid Waste, Third Edition, Report No. SW-846*, Office of Solid Waste and Emergency Response, Washington, DC, November 1986.

APPENDIX A

POTENTIAL SOURCE CATEGORIES OF CHLOROBENZENES EMISSIONS

**TABLE A-1.
POTENTIAL SOURCE CATEGORIES OF CHLOROBENZENES
EMISSIONS**

SIC Code	Source Description
1,2,3-TCB (87-61-6)	
3679	Electronic components, nec
5093	Scrap and waste materials
o-DCB (95-50-1)	
0711	Soil preparation services
0721	Crop planting and protecting
1382	Oil and gas exploration services
1400	Mining and quarrying of nonmetallic minerals
1475	Phosphate rock
1499	Asbestos milling
2044	Rice milling
2082	Beer production
2262	Finishing plants, manmade
2269	Finishing plants, nec
2491	Wood preserving
2611	Pulp mills
2621	Paper mills
2791	Typesetting (lead remelting)
2800	Floating roof tanks
2812	Alkalies and chlorine
2813	Industrial gases
2816	Inorganic pigments
2819	Industrial inorganic chemicals, nec

(continued)

**TABLE A-1.
POTENTIAL SOURCE CATEGORIES OF CHLOROBENZENES
EMISSIONS**

SIC Code	Source Description
2821	Plastics materials and resins
2822	Synthetic rubber
2833	Medicinals and botanicals
2834	Pharmaceutical preparations
2841	Soap and other detergents
2842	Polishes and sanitation goods
2844	Toilet preparations
2851	Paints and allied products
2861	Gum and wood chemicals
2865	Cyclic crudes and intermediates
2869	Industrial organic chemicals, nec
2873	Nitrogenous fertilizers
2874	Normal superphosphate
2879	Agricultural chemicals, nec
2899	Chemical preparations, nec
2911	Petroleum refining
3111	Leather tanning and finishing
3241	Cement mfg.: Wet process
3255	Castable refractory
3275	Gypsum mfg
3299	Nonmetallic mineral products, nec
3312	By-product coke manufacturing
3354	Aluminum extruded products

(continued)

**TABLE A-1.
POTENTIAL SOURCE CATEGORIES OF CHLOROBENZENES
EMISSIONS**

SIC Code	Source Description
3400	General processes
3431	Porcelain enamel/ceramic glaze spraying booth
3449	Miscellaneous metal work
3471	Plating and polishing
3544	Special dies, tools, jigs & fixtures
3571	Electronic computers
3572	Computer storage devices
3575	Computer terminals
3577	Computer peripheral equipment, nec
3671	Electron tubes
3674	Semiconductors and related devices
3679	Electronic components, nec
3695	Magnetic and optical recording media
3699	Electrical equipment & supplies, nec
3812	Search and navigation equipment
3861	Photographic equipment and supplies
3900	Miscellaneous industrial processes
3949	Sporting and athletic goods, nec
4011	Railroads, line-haul operating
4013	Switching and terminal services
4491	Bulk materials elevators
4741	Rental of railroad cars

(continued)

**TABLE A-1.
POTENTIAL SOURCE CATEGORIES OF CHLOROBENZENES
EMISSIONS**

SIC Code	Source Description
4953	Refuse systems
5085	Drum cleaning/reclamation
5541	Gasoline service stations
7342	Disinfecting & pest control services
	p-DCB (106-46-7)
0711	Soil preparation services
0721	Crop planting and protecting
1400	Mining and quarrying of nonmetallic minerals
1475	Phosphate rock
1499	Asbestos milling
2044	Rice milling
2082	Beer production
2261	Finishing plants, cotton
2392	House furnishings, nec
2491	Wood preserving
2791	Typesetting (lead remelting)
2800	Floating roof tanks
2812	Alkalies and chlorine
2816	Inorganic pigment
2819	Industrial inorganic chemicals, nec
2821	Plastics materials and resins
2822	Synthetic rubber
2834	Pharmaceutical preparations

(continued)

**TABLE A-1.
POTENTIAL SOURCE CATEGORIES OF CHLOROBENZENES
EMISSIONS**

SIC Code	Source Description
2841	Soap and other detergents
2842	Polishes and sanitation goods
2843	Surface active agents
2861	Gum and wood chemicals
2865	Cyclic crudes and intermediates
2869	Industrial organic chemicals, nec
2873	Nitrogenous fertilizers
2874	Normal superphosphate
2879	Agricultural chemicals, nec
2992	Lubricating oils and greases
3241	Cement mfg.: Wet process
3251	Brick and structural clay tile
3253	Ceramic wall and floor tile
3255	Castable refractory
3275	Gypsum mfg
3291	Abrasive products
3312	By-product coke manufacturing
3400	General processes
3431	Porcelain enamel/ceramic glaze spraying
3471	Electroplating operations
3674	Semiconductors and related devices
3900	Miscellaneous industrial processes
3991	Brooms and brushes

(continued)

**TABLE A-1.
POTENTIAL SOURCE CATEGORIES OF CHLOROBENZENES
EMISSIONS**

SIC Code	Source Description
4491	Bulk materials elevators
4952	Sewerage systems
4953	Refuse systems
5085	Drum cleaning/reclamation
7342	Disinfecting & pest control services
MCB (108-90-7)	
1311	Crude petroleum and natural gas
1321	Natural gas liquids
1382	Oil and gas exploration services
1400	Mining and quarry of nonmetallic minerals
1475	Phosphate rock
1499	Asbestos milling
2044	Rice milling
2082	Beer production
2200	Knit fabric scouring with chlorinated solvent
2262	Finishing plants, manmade
2269	Finishing plants, nec
2295	Coated fabrics, not rubberized
2395	Pleating and stitching
2672	Paper coated and laminated, nec
2791	Typesetting (lead remelting)
2800	Floating roof tanks
2812	Alkalies and chlorine

(continued)

**TABLE A-1.
POTENTIAL SOURCE CATEGORIES OF CHLOROBENZENES
EMISSIONS**

SIC Code	Source Description
2813	Industrial gases
2816	Inorganic pigments
2819	Industrial inorganic chemicals, nec
2821	Plastics materials and resins
2822	Synthetic rubber
2833	Medicinals and botanicals
2834	Pharmaceutical preparations
2842	Polishes and sanitation goods
2851	Paints and allied products
2861	Gum and wood chemicals
2865	Cyclic crudes and intermediates
2869	Industrial organic chemicals, nec
2873	Nitrogenous fertilizers
2874	Normal superphosphate
2879	Agricultural chemicals, nec
2891	Adhesives and sealants
2899	Chemical preparations, nec
2911	Petroleum refining
2951	Asphalt paving mixtures and blocks
2992	Lubricating oils and greases
3053	Gaskets, packing and sealing devices
3069	Fabricated rubber products, nec
3142	House slippers

(continued)

**TABLE A-1.
POTENTIAL SOURCE CATEGORIES OF CHLOROBENZENES
EMISSIONS**

SIC Code	Source Description
3241	Cement, hydraulic
3255	Castable refractory
3275	Gypsum mfg.
3292	Asbestos products
3295	Minerals, ground or treated
3312	By-product coke manufacturing
3364	Nonferrous die-casting exc. aluminum
3366	Copper foundries
3400	General processes
3431	Porcelain enamel/ceramic glaze spraying
3471	Electroplating operations
3555	Printing trades machinery
3674	Semiconductors and related devices
3679	Electronic components, nec
3699	Electrical equipment & supplies, nec
3711	Motor vehicles and car bodies
3714	Motor vehicle parts and accessories
3728	Aircraft parts and equipment, nec
3812	Search and navigation equipment
3861	Photographic equipment and supplies
3900	Miscellaneous industrial processes
3999	Manufacturing industries, nec
4011	Railroads, line-haul operating

(continued)

**TABLE A-1.
POTENTIAL SOURCE CATEGORIES OF CHLOROBENZENES
EMISSIONS**

SIC Code	Source Description
4013	Switching and terminal services
4226	Special warehousing and storage, nec
4491	Bulk materials elevators
4741	Rental of railroad cars
4952	Sewerage systems
4953	Refuse systems
5085	Drum cleaning/reclamation
5171	Petroleum bulk stations & terminals
5541	Gasoline retail operations - Stage I
7389	Business services, nec
9511	Air, water, & solid waste management
HCB (118-74-1)	
0721	Crop planting and protecting
2812	Alkalies and chlorine
2813	Industrial gases
2819	Industrial inorganic chemicals, nec
2821	Plastics materials and resins
2865	Cyclic crudes and intermediates
2869	Industrial organic chemicals, nec
2879	Agricultural chemicals, nec
2892	Explosives
2951	Asphalt paving mixtures and blocks
3822	Environmental controls

(continued)

**TABLE A-1.
POTENTIAL SOURCE CATEGORIES OF CHLOROBENZENES
EMISSIONS**

SIC Code	Source Description
4952	Sewerage systems
4953	Refuse systems
1,2,4-TCB (120-82-1)	
2211	Broadwoven fabric mills, cotton
2221	Broadwoven fabric mills, manmade
2231	Broadwoven fabric mills, wool
2253	Knit outerwear mills
2254	Knit underwear mills
2257	Weft knit fabric mills
2258	Lace & warp knit fabric mills
2261	Finishing plants, cotton
2262	Finishing plants, manmade
2269	Finishing plants, nec
2273	Carpets and rugs
2491	Wood preserving
2812	Alkalies and chlorine
2816	Inorganic pigments
2819	Industrial inorganic chemicals, nec
2841	Soap and other detergents
2842	Polishes and sanitation goods
2843	Surface active agents
2861	Gum and wood chemicals
2865	Cyclic crudes and intermediates

(continued)

**TABLE A-1.
POTENTIAL SOURCE CATEGORIES OF CHLOROBENZENES
EMISSIONS**

SIC Code	Source Description
2869	Industrial organic chemicals, nec
2873	Nitrogenous fertilizers
2879	Agricultural chemicals, nec
2899	Chemical preparations, nec
2992	Lubricating oils and greases
3251	Brick and structural clay tile
3253	Ceramic wall and floor tile
3291	Abrasive products
3357	Nonferrous wiredrawing & insulating
3449	Miscellaneous metal work
3479	Metal coating and allied services
3612	Transformers, except electronic
3621	Motors and generators
3674	Semiconductors and related devices
3679	Electronic components, nec
3699	Electrical equipment & supplies, nec
3812	Search and navigation equipment
3822	Environmental controls
3861	Photographic equipment and supplies
4953	Refuse systems
7342	Disinfecting & pest control services
	m-DCB (541-73-1)
0711	Soil preparation services

(continued)

**TABLE A-1.
POTENTIAL SOURCE CATEGORIES OF CHLOROBENZENES
EMISSIONS**

SIC Code	Source Description
0721	Crop planting and protecting
2131	Chewing and smoking tobacco
2431	Millwork
2499	Wood products, nec
2511	Wood household furniture
2522	Office furniture, except wood
2541	Wood partitions and fixtures
2542	Partitions and fixtures, except wood
2800	Fugitive emissions
2812	Alkalies and chlorine
2819	Industrial inorganic chemicals, nec
2821	Plastics materials and resins
2833	Medicinals and botanicals
2834	Pharmaceutical preparations
2851	Paints and allied products
2861	Charcoal manufacturing
2865	Cyclic crudes and intermediates
2869	Industrial organic chemicals, nec
2873	Nitrogenous fertilizers
2879	Agricultural chemicals, nec
3111	Leather tanning and finishing
3400	General processes
3412	Metal barrels, drums, and pails

(continued)

**TABLE A-1.
POTENTIAL SOURCE CATEGORIES OF CHLOROBENZENES
EMISSIONS**

SIC Code	Source Description
3431	Porcelain enamel/ceramic glaze spraying
3444	Sheet metalwork
3471	Plating and polishing
3479	Metal coating and allied services
3563	Air and gas compressors
3612	Transformers, except electronic
3641	Electric lamps
3671	Electron tubes
3674	Semiconductors and related devices
3679	Electronic components, nec
3695	Magnetic and optical recording media
3699	Electrical equipment & supplies, nec
3713	Truck and bus bodies
3812	Search and navigation equipment
3861	Photographic equipment and supplies
3900	Miscellaneous industrial processes
4953	Refuse systems
5085	Drum cleaning/reclamation
5511	New and used car dealers
7532	Top & body repair & paint shops
7534	Tire retreading and repair shops
8299	Schools & educational services, nec

nec - not elsewhere classified

APPENDIX B
TEXTILE FIBER DYEING FACILITIES WITH ANNUAL SALES
GREATER THAN \$1 MILLION

TABLE B-1.
TEXTILE FIBER DYEING FACILITIES (SIC 2269) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)

Name	Address	Sales in \$ Millions
Willcox and Gibbs Inc.	530 Fifth Ave, New York, NY 10036	568
Hanes Companies Inc.	PO Box 202, Winston-Salem, NC 27102	110
PAXAR Corp.	275 N Middletown Rd, Pearl River, NY 10965	73
Meridian Industries Inc.	100 E. Wisconsin Ave, Milwaukee, WI 53202	70
Covington Fabrics Corp.	267 Fifth Ave, New York, NY 10016	60
Morganton Dyeing and Finishing Corp.	PO Box 1327, Morganton, NC 28655	31*
Valdese Manufacturing Co.	PO Box Drawer 10, Valdese, NC 28690	30
Hanes Dye and Finish Company Inc.	PO Box 202, Winston-Salem, NC 27102	25
Cross Mills Inc.	PO Box 520, Marion, NC 28752	25
Spectrum Fibers Inc.	1450 Broadway, New York, NY 10018	21*
Phoenix Dye Works	4755 W. 150th St, Cleveland, OH 44135	21*
US Label Corp.	PO Box 9378, Greensboro, NC 27429	18
Jaftex Corp. Oxford Printing and Finishing	604 W. Industry Dr, Oxford, NC 27565	16*
SMS Textile Mills Inc., Spantex	132 Franklin St, Norwich CT 06360	16
Brittany Dyeing and Printing Company	1357 E. Rodney French, New Bedford, MA 02744	15*
J and C Dyeing Inc.	PO Box 9000, Shelby, NC 28151	14*
Garment Graphics Inc.	12862 E. Florence Ave, Santa Fe Springs, CA 90670	14*
Duro Industries Inc., Sanford Finishing Co	PO Box 550, Sanford, NC 27330	12
Jefferies Southern Processors Inc.	PO Box 430, Albemarle, NC 28001	12
Southampton Textile Co.	520 Reese St, Emporia, VA 23847	12
Collins and Alkman Corp Home Fabrics	PO Box 427, Concord, NC 28025	11*
CYP Inc.	PO Drawer A, Tryon, NC 28782	11

(continued)

**TABLE B-1.
TEXTILE FIBER DYEING FACILITIES (SIC 2269) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)**

Name	Address	Sales in \$ Millions
Burlington Industries Inc., Burlington Versatech	PO Box 158, Cooleemee, NC 27014	11
Travis Knits Inc.	PO Box 65, Maiden, NC 28065	10
Pharr Yarns Inc.	PO Box 630, Belmont, NC 28012	10
India Ink	2457 E 27th St, Los Angeles, CA 90058	10*
Pisgah Yarn and Dyeing Company Inc.	PO Box 606, Old Fort, NC 28762	10
Fabricut Inc.	5920 S. Triangle Dr, City of Commerce CA 90040	10
Textile Dyeing and Finishing Co., Inc.	2015 City Line Rd, Bethlehem, PA	8
Providence Brald Company Inc.	358 Lowden St, Pawtucket, RI 02860	8
Spinnerin Yarn Company Inc.	30 Wesley St, South Hackensack, NJ	7
Western Piece Dyers	2845 W. 48th Pl, Chicago, IL 60632	7
Jaunty Textile Corp. - Libbie Trading Corp,	15 Poplar St, Scranton PA 18501	7*
Geltman Corp.	PO Box 717, Conover, NC 28613	7*
Aurora Bleachery Inc. - Meridian Industries Inc.	PO Box 70, Aurora, IL 60508	7*
North Hickory Dyeing and Processing Co.	1329 2nd St NE, Hickory, NC 28601	6
Wolfe dye and Bleach Works Inc.	25 Ridge Rd, Shoemakersville, PA 19555	5
Eagle Dyeing and Finishing Co.	PO Box 180, Mount Holly, NJ 08060	5
Royal Carolina Corp.	7305 W. Friendly Ave, Greensboro, NC 27410	5
ITC Manufacturing Group Inc.	1261 Broadway, New York, NY 10001	4
Globe Dye Works Company	4500 Worth St, Philadelphia, PA 19124	4*
Interstate Dyeing and Finishing Co.	35 8th St, Passaic NJ 07055	4*
Elmore-Pisgh Inc.	204 Oak St, Spindale, NC 28160	3

(continued)

TABLE B-1.
TEXTILE FIBER DYEING FACILITIES (SIC 2269) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)

Name	Address	Sales in \$ Millions
Fine Art Pillow and Specialties Corp.	601 W 26th St, New York, NY 10001	3*
Lisbon Textile Prints Inc.	PO Box 278, Jewett City, CT 06351	3*
Renco Finishing Corp.	20-21 Wagaraw Rd, Fair Lawn, NJ 07410	3*
William J Dixon Comp. Inc.	756 Springdale Dr, Exton, PA	3
Luithlen Dye Corp.	Tioga St & J St, Philadelphia, PA 19134	2*
GJ Littlewood and Son	4045-61 Main St, Philadelphia, PA 19127	2
Dyutex Inc.	14 Stevens St, Haverhill, MA 01830	2
Classic Draperies Corp., Lensol Fabric-Seattle Div.	7920 S. Occidental Ave, Seattle, WA 98108	2*
J and M Dyrs Inc.	PO Box 550, Sumter, SC 29150	1
Morgan Dyeing Company Inc.	327 W. 36th St, New York, NY 10018	1*
Classic Draperies Corp., Lensol Fabric-Phoenix Div.	4829 S. 36th St, Phoenix, AZ 85040	1*

* Indicates an estimated financial figure.

Source: Gale Research, Inc. *Ward's Business Directory of U.S. Private and Public Companies-1991*, Volume 4, Detroit, MI, 1991.

TABLE B-2.
TEXTILE FIBER DYEING FACILITIES (SIC 2262) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)

Name	Address	Sales in \$ Millions
Gilbert Frank Corp.	16 E 34th St, New York, NY 10016	60
TSG Inc	1400 Welsh Rd, North Wales, PA 19454	28
Champagne Dye Works Inc.	PO Box 716, Asheboro, NC 27203	25
Kenyon Industries Inc.	PO Box 147, Kenyon, RI 02836	24
Goldtex Inc.	401 Patetown Rd, Goldsboro, NC 27530	22
Marijon Dyeing and Finishing Co.	219 Murray Hill Pkwy, East Rutherford, NJ 07073	21*
Amerbelle Corp.	PO Box 150, Vernon, CT 06066	20
Yates Bleachery Co.	PO Box 150, Flintstone, GA 30725	15
Milliken and Co. Enterprise	512 Pumpkintown Rd, Marietta, SC 29661	14*
Wansona Manufacturing Corp.	1 Wansona Pl, Wadesboro, NC 28170	11
Amatex Corp.	1032 Stanbridge St, Norristown PA 19401	10*
Hampton Print Works Inc.	2212 Buffalo Rd, Johnson City, TN 37604	9*
Oxford Textile Inc.	PO Box 90, Oxford, NJ 07863	9
J and J Flock Products Inc.	1150 Centre St, Easton, PA 18042	8
Craftsmen Fabrics Industries Inc.	PO Box 1329, Concord, NC 28026	7
Duro Industries Inc., Duro Textile Printers Inc.	PO Box 61, Fall River MA 02724	7*
Kent-Bragaline Inc.	27-35 Jackson Ave, Long Island City, NY 11101	7
Deep River Dyeing Company Inc.	PO Box 217, Randleman, NC 27317	6
Hemmerich Industries Inc.	PO Box 286, Denver, PA 17517	6
AS Haight and Co.	PO Box 501, Cartersville, GA 30120	5
Trio Dyeing and Finishing	440 E. 22nd St, Paterson, NJ 07509	5
Decorative Screen Prints Inc.	9 Wisconsin Ave. Norwich, CT 06360	5*
Quip Industries	18th & Jefferson, Carlyle, IL 62231	5
Melville Textile Print Works Inc.	PO Box 5420, Statesville, NC 28677	4
Crown Prince Inc.	PO Box 37, Brookfield WI 53008	4

(continued)

TABLE B-2.
TEXTILE FIBER DYEING FACILITIES (SIC 2262) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)

Name	Address	Sales in \$ Millions
Yarnell Group	48 W. 37th St, New York, NY 10018	3
Apollo Dyeing and Finishing Company, Inc.	PO Box 3072, Paterson, NJ 07509	3
Bronxwood Dyeing Company, Inc.	900 E. 229th St, Bronx, NY 10466	3
American Art Ltd.	95 Morton St, New York, NY 10014	1
Paw Prints of California	3166 Bay Rd, Redwood City, CA 94063	1

* Indicates an estimated financial figure.

Source: Gale Research, Inc. *Ward's Business Directory of U.S. Private and Public Companies-1991*, Volume 4, Detroit, MI, 1991.

TABLE B-3.
TEXTILE FIBER DYEING FACILITIES (SIC 2231) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)

Name	Address	Sales in \$ Millions
Forstmann & Co., Inc	1185 Ave of the Americas, New York, NY 10036	215
Pendleton Woolen Mills Inc.	PO Box 1691, Portland, OR 97207	140*
Asten Group Inc.	PO Box 10700, Charleston, SC 29411	100
Guilford of Maine Inc.	Oak St, Guilford, ME 04443	75
Gilbert Frank Corp.	16 E 34th St 15th Fl, New York, NY 10016	60
American Woolen Co.	7600 NE 69th Ave, Medley, FL 33166	46
Worcester Co	Greystone Ave, Centerdale, RI 02911	38*
Carleton Woolen Mills Inc.	51 Main St, Winthrop, ME 04364	37*
LW Packard & Co. Inc	6 Mill St, Ashland, NH 03217	35
Anglo Fabrics Co Inc	561 7th Ave 16th Fl, New York, NY 10018	32
Eastland Woolen Mills Inc.	Main St, Corinna, ME 04928	27
Dorr Woolen Co.	Main St, Guild, NH 03754	25
Stillwater Inc.	151 W 40th St, New York, NY 10018	20
Westgate Fabrics Inc.	1000 Fountain Pkwy, Grand Prairi, TX 75050	20
Cascade Woolen Mill Inc.	PO Box 157, Oakland, ME 04963	16
Faribault Woolen Mill Co.	PO Box 369, Faribault, MN 55021	16*
Scapa Inc	PO Box 1949, Waycross, GA 31502	15*
Niagara Lockport Industries Inc. Lockport Felt	Hwy 12 W. Starkville, MS 39759	14
JM Voith GmbH Appleton Mills	PO Box 1899, Appleton, WI 54913	13
Robinson Mfg. Co.	PO Box 195, Oxford, ME 04270	12*
Stanley Woolen Co., Inc.	140 Mendon St, Uxbridge, MA 01569	11
Astro-Dye Works, Inc.	PO Box 788, Calhoun, GA 30701	9
Robinson Mfg. Co. Kexar Falls Woolen Co.	Federal Road, Kexar Falls, ME 04047	8
Brooks Woolen Co., Inc.	PO Box 671, Lowell, MA 01853	7*

(continued)

TABLE B-3.
TEXTILE FIBER DYEING FACILITIES (SIC 2231) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)

Name	Address	Sales in \$ Millions
Henry Mali Co., Inc.	257 Pk Ave S, New York, NY 10010	7
Charles W. House and Sons, Inc	PO Box 158, Unionville, CT 06085	6
G Thomas & Sons Inc	PO Box 218, North Grosve, CT 06255	6
Hickory Dyeing & Winding Co, Inc.	PO Box 1975, Hickory, NC 28603	5
Ronitex Jacquard Mills Inc.	22 Spruce St, Paterson, NJ 07501	5
Aetna Felt Corp.	2401 W Emmaus Ave, Allentown, PA 18103	5
Boris Kroll Jacquard Looms	66 Gray St, Paterson, NJ 07501	4
Striar Textile Mill	PO Box 189, Orono, ME 04473	4
Anchor Dye'g & Finish'g Co., Inc	Adams Ave & Leiper St, Philadelphia, PA 19124	3*
Anthra Textile Co., Inc	1400 Chestnut St, Kulpmont PA 17834	3
Louis Krieger Co.	2000 S. Main St, Los Angeles, CA 90007	3
Jacquard Fabrics Inc.	1965 Swathmore Ave, Lakewood, NJ 08701	3
Litchfield Woolen Mill	PO Box 722, Litchfield, MN 55355	2
Ortega's Weaving Shop, Inc.	PO Box 325, Chimayo, NM 87522	1

* Indicates an estimated financial figure.

Source: Gale Research, Inc. *Ward's Business Directory of U.S. Private and Public Companies-1991*, Volume 4, Detroit, MI, 1991.

**TABLE B-4.
TEXTILE FIBER DYEING FACILITIES (SIC 225) WITH ANNUAL
SALES GREATER THAN \$1 MILLION**

Name	Address	Sales in \$ Millions
(SIC 2251) Women's Hosiery Exc Socks		
Sara Lee Corp L'eggs Prdts Inc.	PO Box 2495, Winston-Salem, NC 27102	480
Ithaca Industries Inc.	PO Box 620, Wilkesboro, NC 28697	320
Hanes Hosiery Inc.	PO Box 1413, Winston-Salem, NC 27102	220*
Esmark Apparel Inc.	111 W. 40th St, New York, NY 10018	110
Maro Hosery Corp.	350 5th Ave, New York, NY 10118	78*
Americal Corp.	PO Box 1419, Henderson, NC 27536	75
Danskin Inc., Esmark Apparel Inc.	305 State St, York, PA 17403	50*
Pennaco Hosiery Inc., Esmark Apparel Inc.	111 W. 40th St, New York, NY 10018	50
Alba-Waldensian Inc.	PO Box 100, Valdese, NC 28690	47
US Textile Corp	PO Box 5643, Charlotte, NC 28225	38
Ithaca Industries Inc., Robbins Div.	PO Box 37, Robbins, NC 27325	38
Camp Hosiery	350 5th Ave, New York, NY 10118	35*
Auburn Hosiery Mills Inc.	113 E, Main, Auburn, KY 42206	35
Roane Hosiery Inc.	PO Box 431, Harriman, TN 37748	31*
Kentucky Derby Hosiery Co., Inc.	PO Drawer 550, Hopkinsville, KY 42240	29
Cluett Peabody & Co., Inc., Great Amer Knitting Mills	530 5th Ave. 8th Fl, New York, NY 10036	28*
Jockey Intl Inc., Thorobred Hosiery	2300 60th St, Kenosha, WI 53140	27
Acme-McCrary Corp.	PO Box 1287, Asheboro, NC 27203	25
Hampshire-Designers Inc, Hampshire Hosiery Co.	PO Box 528, Spruce Pine, NC 28777	25
Highland Mills Inc.	PO Box 33775, Charlotte, NC 28233	22
Glendale Hosiery Inc.	PO Box 686, Siler City, NC 27344	20
Holt Hosiery Mills Inc.	PO Box 1757, Burlington, NC 27215	18
Knit Prdts Corp.	PO Box 1126, Belmont, NC 28012	17
Bossong Hosiery Mills	PO Box 789, Asheboro, NC 27203	17
Sara Lee Corp, Rice Hosiery Corp	PO Box 2112, High Point, NC 27261	17*
US Hosiery Corp	PO Box 160, Lincolnton, NC 28092	16

(continued)

TABLE B-4.
TEXTILE FIBER DYEING FACILITIES (SIC 225) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)

Name	Address	Sales in \$ Millions
Chic Hosiery Corp	PO Box 31009, Charlotte, NC 28231	16
Tower Mills Inc.	PO Box 1088, Burlington, NC 27215	15
Arrowood Mills Inc.	350 5th Ave, New York, NY 10118	13
Glen Raven Mills Inc., Consumer Prdts Div.	1831 N. Pk Ave, Altamahaw, NC 27217	13
Niota Textiles Mill Co.	Rte 3 Indus Pk, Fort Payne, AL 35967	13
Harriss & Covington Hosiery Mills	PO Box 1909, High Point, NC 27261	13
No-Nonsense Inc.	534 S. Main, Burlington, NC 27220	12*
Laughlin Hosiery Mills Inc.	PO Box 517, Randleman, NC 27317	12*
Admiration Hosiery Mill Inc.	PO Box 240787, Charlotte, NC 28224	11*
Carolina Hosiery Mills Inc.	PO Drawer 850, Burlington, NC 27216	11*
Hampshire Hosiery Inc.	1412 Broadway 7th Fl, New York, NY 10018	11*
Trimfit Inc., Bonnie Doon	10360 Drummond Rd, Philadelphia, PA 19154	11*
Willard Insus Inc., Holiday Hosiery Mills	666 Main St, Hudson, NC 23683	11*
Willis Hosiery Mills Inc.	PO Box 407, Concord, NC 28025	11*
Willwear Hosiery Mills Inc.	2000 Stuart St, Chattanooga, TN 37406	11
Sidney J Kreiss Inc.	PO Box 718, Lynbrook, NY 11563	10
Amsco-Craftsmen Hosiery Inc.	PO Box 127, Concord, NC 28027	10
Amos Hosiery Cos	PO Box 127, Pilot Mounta, NC 27041	10
Homespun Hosiery Inc., US Hosiery Div.	980 3rd Ave SE, Hickory, NC 28602	9*
Lemco Mills Inc.	PO Box 2098, Burlington, NC 27215	8
Stimpson Hosiery Mills Inc.	PO Box 151, Statesville, NC 28677	6*
Candor Hosiery Mill Inc.	PO Box 738, Biscoe, NC 27209	5
Tennaco Hosiery	PO Box 7435, Memphis, TN 38107	4
Huitt Mills Inc.	136 Sparta Rd, North Wikes, NC 28659	4*
Efland Hosiery Mill Inc.	PO Box 246, Efland, NC 27243	3
Cabot Hosiery Mills Inc.	N Main St, Northfield, VT 05663	3
Keepers Indus Inc., EG Smith Socks	379 5th Ave 4th Fl, New York, NY 10016	3*

(continued)

TABLE B-4.
TEXTILE FIBER DYEING FACILITIES (SIC 225) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)

Name	Address	Sales in \$ Millions
Troydon Hosiery Mills Inc.	PO Box 96, Granite Fall, NC 28630	1*
(SIC 2252) Hosiery Nec		
Adams-Mills Corp	225 N Elm St, High Point, NC 27260	210
Trimfit Inc.	10450 Drummond Rd, Philadelphia, PA 19154	91*
Renfro Corp.	PO Box 908, Mount Airy, NC 27030	85
Chipman-Union Inc.	500 Sibley Ave, Union Point, GA 30669	50
Newville Indus Inc.	200 Madison Ave, New York, NY 10016	50
Durham Hosiery Mills Inc.	PO Drawer 1705, Danville, VA 24541	43
Spalding Knitting Co, Inc.	PO Drawer K, Griffin, GA 30224	43*
Clayson Knitting Co, Inc.	PO Box 39, Star, NC 27356	40
Premiere	PO Box 100, Morganton, NC 28655	37
Cherokee Hosiery Mill	208 NE 35th St, Fort Payne, AL 35967	33
Charleston Hosiery Inc.	Raider Dr, Cleveland, TN 37311	32*
Annedeem Hosiery Mills Inc.	PO Box 1359, Burlington, NC 27216	32
Trimfit Inc, Kayby Mills of North Carolina	208 Carmalt St, Thomasville, NC 27360	31*
Johnson Hosiery Mills Inc	PO Box 89, Fort Payne, AL 35967	30
Brown Wooten Mills Inc.	PO Box 1440, Burlington, NC 27216	27
Adams Millis Corp Silver Knit Indus Div.	401 S Hamilton St, High Point, NC 27261	27*
Slane Hosiery Mills Inc.	PO Box 2486, High Point, NC 27261	27*
Niota Textile Mills Co, Inc.	PO Box 117, Athens, TN 37303	26*
Leroi Princeton Hosiery Mills Inc.	PO Box 589, Princeton, KY 42446	26*
Jean Hosiery Mill Inc.	628 Old Town Rd, Villa Rica, GA 30180	22*
Parker Hosiery Co, Inc.	PO Box 699, Old Fort, NC 28762	21
Ridgeview Inc.	PO Box 8, Newton, NC 28658	20
Cooper Hosiery Mill Inc.	PO Box 909, Fort Payne, AL 35967	20*
Golden City Hosiery Mills	PO Box 939, Villa Rica, GA 30180	20
Rudin & Roth Inc.	350 5th Ave #2609, New York, NY 10118	19*

(continued)

**TABLE B-4.
TEXTILE FIBER DYEING FACILITIES (SIC 225) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)**

Name	Address	Sales in \$ Millions
Ellis Hosiery Mills Inc.	1500 13th SW, Hickory, NC 28602	18
Influential Hosiery Inc.	PO Box 309, High Point, NC 27261	17*
Belmont Hosiery Mills	PO Box 750, Belmont, NC 28012	17
Meywebb Hosiery Mills Inc.	PO Box 266, Meridian, MS 39301	17
Royce Hosiery Mills Inc.	350 5th Ave, New York, NY 10118	17*
Mayo Knitting Mills Inc.	Austin St, Torboro, NC 27886	16
Mauney Hosiery Mills Inc.	PO Box 1279, Kings Mounta, NC 28086	16
Ballston Knitting Co.	Saratoga Ave, Box 30, Ballston Spa, NY 12020	15
Maryon Mill Co.	PO Box 1386, Carrollton, GA 30117	15
Crescent Hosiery Mills Inc.	PO Box 370, Niota, TN 37826	15
Fox River Mills Inc.	PO Box 298, Osage, IA 50461	15
Maro Hosiery Corp Thomasville	PO Box 698, Thomasville, NC 27360	15*
Twin City Knitting Co.	PO Box 1179, Conover, NC 28613	15
Catawba Sox Inc.	PO Box 517, Conover, NC 28613	15
Keppers Indus Inc.	20720 Marilla St, Chatsworth, CA 91311	15
Monarch Hosiery Mills Inc.	PO Box 1205, Burlington, NC 27216	15
Nation Hosiery Mills Inc.	PO Box 3130, Chattanooga, TN 37404	14*
Adams-Millis Corp Drexel Knitting Millis	PO Box 128, Drexel, NC 28619	13
Huffman Finishing Co.	PO Box 170, Granite Fall, NC 28630	13
Wigwam Mills Inc.	PO Box 818, Sheboygan, WI 53081	11
Ithaca Indus Inc, Anderson Hosiery	PO Box 525, Clinton, SC 29325	11*
Thorneburg Hosiery Co.	PO Box 5440, Statesville, NC 28677	11*
Candor Hosiery Mills Inc.	602 E Hwy St, Candor, NC 27229	11
Lea-Wayne Knitting Mills Inc.	PO Box 1026, Morristown, TN 37814	11*
Spalding Knitting Mills Pittsburgh Knitting Mills	212 E 1st St, South Pittsb, TN 37380	11*

(continued)

TABLE B-4.
TEXTILE FIBER DYEING FACILITIES (SIC 225) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)

Name	Address	Sales in \$ Millions
Fred S Kahn Co., Inc.	1720 W End Bldg, Nashville, TN 37203	11
Commonwealth Hosiery Mills	PO Box 545, Randleman, NC 27317	10*
Mebane Hosiery Inc.	PO Box 427, Mebane, NC 27302	10
WY Shugart & Sons Inc.	405 Beason Gap Rd, Fort Payne, AL 35967	10
Johnson Hosiery Mills Inc.	2808 Main Ave NW, Hickory, NC 28601	10
Shogren Indus Inc, Runnymede Mills Div.	PO Box 1239, Tarboro, NC 27886	10*
CM Indus Inc	50 Willow St, Adamstown, PA 19501	10
Trimfit Inc., Lawler Hosiery Mills	PO Box 158, Carrolton, GA 30117	9
Montgomery Hosiery Mill Inc.	PO Box 69, Star, NC 27356	9
Ben Berger & Sons Inc.	417 5th Ave #600, New York, NY 10016	9
Seneca Knitting Mills	PO Box 231, Seneca Falls, NY 13148	8
Robinson Hosiery Mill Inc.	Rte 1 Box 230, Valdese, NC 28690	8
Sanmark-Stardust Inc. Fountain Mfg. Div.	PO Box 6076, Evansville, IN 47712	8*
Furtune Mills Inc.	PO Box 907, La Fayette, GA 30728	8
Chase Hosiery Mills Inc.	7 W 30th St, New York, NY 10001	8
Tennessee Machine & Hosiery	PO Box 1507, Hickory, NC 28601	7
Nelson Knitting Co.	40 3rd St SE, Hickory, NC 28601	7
Handcraft Co., Inc.	PO Drawer 399, Dandridge, TN 37725	7
Kayser-Roth Corp Mens Knitting Div.	909 S. Main St, Rockford, IL 61101	7
Southern Hosiery Mill Inc.	Mechanic St., Princeton, WI 54968	7
Dura-Tred Hosiery Mills	413 Tucker St, Burlington, NC 27215	7*
Gateway Hosiery Mills	PO Box 789, Hickory, NC 28603	6*
Singer Hosiery Mills Inc.	PO Box 2288, Burlington, NC 27215	6
Catawba Valley Finishing Co.	PO Box 3100, Chattanooga, TN 37404	6
H Glaser & Son Inc.	PO Box 758, Thomasville, NC 27360	6
Hole-in-None Hosiery	PO Box 407, Newton, NC 28658	6
Lyerly-Morgan Co Inc.	PO Box 5977, Holliston, MA 01746	6

(continued)

**TABLE B-4.
TEXTILE FIBER DYEING FACILITIES (SIC 225) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)**

Name	Address	Sales in \$ Millions
Bennett Corp.	PO Box 607, Gibsonville, NC 27249	6
Damascus Hosiery Mills Inc.	PO Box 397, Damascus VA 24236	5*
Danridge Textile Inc.	PO Box 119, Dandridge, TN 37725	5*
Lynne Hosiery Mills Inc.	PO Box 987, Mount Airy, NC 27030	5*
Sweetwater Hosiery Mills Inc.	818 N Main St, Sweetwater, TN 37874	5
Bailey Knit Corp.	1606 Sanders Ave N, Fort Payne, AL 35967	5*
Pickett Hosiery Mills	PO Box 877, Burlington, NC 27215	5
Staley Hosiery Mill Inc.	2445 Bellmont, Burlington NC 27215	5*
Cormier Corp.	144 Lexington Dr., Laconia, NH 03246	5
Pine Hosiery Mills Inc.	208 S Main St, Star, NC 27356	5*
Allied Hosiery Mills Inc.	E Main St, Englewood, TN 37329	5
Superior Mills Inc.	PO Box 732, Chilhowie, VA 24319	5*
Elizabeth-Meade hosiery Mills Inc.	PO Box 1029, Burlington, NC 27215	5
Dogwood Hosiery Co., Inc.	PO Box 39, Thomasville, NC 27360	5
Excel Hosiery Mills Inc.	PO Box 607, Union, SC 29379	5
Wrightenberry Hosiery Inc.	PO Box 859, Graham, NC 27253	5
Crowm Hosiery Mills Inc.	PO Box 14010, Archdale, NC 27263	5
Polot Hosiery Mills Inc.	PO Box 608, Pilot Mouna, NC 27041	4
Burnsville Hosiery Mills Inc.	PO Box 278, Burnsville, NC 28714	4
Fort Payne Dekalb Hosiery Mills Inc.	PO Box 318, Fort Payne, AL 35967	3
Walton Knitting Mills Inc.	PO Box 1808, Hickory, NC 28603	3
Arlene Hosiery Mill Inc.	PO Box 4036, Hickory, NC 28603	2*
Bisher Hosiery Mill Inc.	PO Box 68, Denton, NC 27239	2
VI Prewett & Son Inc.	PO Box 258, Fort Payne, AL 35967	2*
Softspun Knitting Mills Inc.	PO Drawer 729, Henderson, NC 27536	2
Daisy Hosiery Mills Inc.	PO Box 5165, High Point, NC 27262	2*
Burke Hosiery Mills Inc.	PO Box 406, Hildebran, NC 28637	2

(continued)

**TABLE B-4.
TEXTILE FIBER DYEING FACILITIES (SIC 225) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)**

Name	Address	Sales in \$ Millions
Cricket Hosiery Inc.	112 W 34th St, New York, NY 10120	1*
(SIC 2253) Knit Outerwear Mills		
Tultex Corp.	PO Box 5191, Martinsville, VA 24115	334
Sara Lee Knit Prdts.	PO Box 3019, Winston-Salem, NC 27102	320*
Chesterfield Mfg Corp.	PO Box 732, Chesterfield, SC 29709	140*
Oneita Indus Inc.	PO Drawer 24, Andrews, SC 29510	123
HL Miller & Son Inc.	PO Box 348, Schuylkill H, PA 17972	80
Hampshire-Designers Inc.	PO Box 2667, Anderson, SC 29622	75
St. John Knit Inc.	17422 Derian Ave, Irvine, CA 92714	74*
American Argo Corp.	Margaretta & Market, Schuylkill H, PA 17972	70
Klear Knit Inc.	PO Box 236, Clover, SC 29710	62
Cross Creek Apparel Inc.	US Hwy 52 S, Mount Airy, NC 27030	57*
Spencers Inc.	PO Box 988, Mount Airy, NC 27030	55
Savoy Indus Inc.	315 E 62nd St, New York, NY 10021	49
Young Stuff Apparel Group Inc.	1411 Broadway 10th Fl, New York, NY 10018	46
Jasper Textiles Inc.	PO Box 472, Lake Forest, IL 60045	43*
Kentucky Textiles Inc.	1 20th St, Paris, KY 40361	40
Greenbrier Indus Inc.	333 Sylvan Ave, Englewood Cliffs, NJ 07632	36
Private Brands Inc.	750 Kent Ave, Brooklyn, NY 11211	35
Brundidge Shirt Corp.	555 S Main St, Brundidge, AL 36010	35*
Warnaco Inc., Warnaco Knitwear Div.	PO Box 1669, Altoona, PA 16603	34*
Somerset Knitting Mills Inc.	700 Spring Garden St, Philadelphia, PA 19123	31*
Garland Corp.	33 Dover St, Brockton, MA 02401	30
Pine State Knitwear Co.	PO Box 631, Mount Airy, NC 27030	30
Albert & Wechsler Inc.	34 W 33rd St, New York, NY 10001	30
Wellmore Inc.	498 7th Ave Fl 15, New York, NY 10018	30
Heritage Sportswear	PO Box 1060, Marion, SC 29571	25*

(continued)

TABLE B-4.
TEXTILE FIBER DYEING FACILITIES (SIC 225) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)

Name	Address	Sales in \$ Millions
East-Tenn Mills Inc.	3112 Indus Dr, Johnson City, TN 37601	25
Russell Corp. Knit Goods	PO Box 45, Sylacauga, AL 35150	24*
Spectex Indus Inc.	505 Carroll St, Brooklyn, NY 11215	24
Winona Knitting Mills Inc.	902 E 2nd St, Winona, MN 55987	23
Albert & Wechsler Inc.	34 W 33rd St, New York, NY 10001	22*
Great American Sweater	1431 Broadway 2nd Fl, New York, NY 10018	20*
Gloray Knitting Mills Inc.	317 E Penn Ave, Robesonia, PA	20
FR Knitting Mills Inc.	PO Box 4360, Fall River, MA 02723	20*
Bangor America Inc.	159 Singleton, Woonsocket, RI 02895	20
Alpha Mills Inc.	122 Margaretta St, Schuylkill H, PA 17972	19
Brinlaw Inc.	PO Box 816, Gastonia, NC 28053	17*
Everite Knitting Mills Inc.	2 E Lehman St, Lebanon, PA 17042	17*
Gelfo Mfg. Co., Inc.	650 Cantigue Rd, Jericho, NY 11753	17*
Gramercy Mills Inc.	39 Plymouth St, Fairfield, NJ 07006	17*
Reliable Knitting Works	233 E Chicago St, Milwaukee, WI 53201	15
School Apparel Inc.	4610 Mission #300, San Francisco, CA 94112	15
AD Everitt Knitting Co.	234 W Florida St, Milwaukee, WI 53204	15
Ruse-Rouge Mfg. Co.	PO Box 749333, Dallas, TX 75374	15
Bryan Mills Inc.	PO Box 5439, Statesville, NC 28677	14
AM Knitwear Inc.	315 Seigel St, Brooklyn, NY 11206	14*
Lion Knitting Mills Co.	12845 NW 45th Ave, Opa-Locka, FL 33054	14*
Ohio Knitting Mills Inc.	230 S Poplar St, Berwick, PA 18603	13
FAB Indus Inc.	3256 W 25th St, Cleveland, OH 44109	13
Kentthoo Inc.	1974 E 61st, Cleveland, OH 44103	13
Charter Apparel Ltd.	Lower Sweeney St, Amsterdam, NY 12010	12
Academy Knitters Inc.	60 Metro Way, Secaucus, NJ 07094	12
Cullman Indus.	PO Box 628, Allentown, PA 18105	12

(continued)

**TABLE B-4.
TEXTILE FIBER DYEING FACILITIES (SIC 225) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)**

Name	Address	Sales in \$ Millions
B & B Accesories	15 W 37th St, New York, NY 10018	11
J & M Knitting Mills Co.	1636 Decatur St, Ridgewood, NY 11385	11
Knitcraft Corp.	4020 W 6th St, Winona, MN 55987	10
Travis Knits Inc.	1515 W Academy St, Cherryville, NC 28201	10
Beth Leon Togs Inc.	120-28 W Union Blvd, Bethlehem, PA 18018	10
Encore Textiles Inc.	PO Box 2004, Monroe, Nc 28110	10
Blue Bird Knitwear Co.	112 W 34th St, New York, NY 10018	10
Lord Jeff Knitting Co, Inc.	10 Maple St, Norwood, NJ 07648	10
Alps Sportswear Mfg. Inc.	5 Franklin St, Lawrence, MA 01840	10
Fortune Knits Inc.	142 W 36th St, New York, NY 10018	10
Calvert Knitwear Inc.	333 Scholes St, Brooklyn, NY 11206	10
Klear-Knit Inc.	1209 E Main St, Rock Hill, SC 29730	10*
Asheville Dyeing & Finishing	Farm School Rd, Swannanoa, NC 28778	9*
A & G Mfg Inc.	183 Loraine St, Brooklyn, NY 11231	9*
Manchester Knitted Fashion	33 S Commercial St, Manchester, NH 03101	9
Drasin Knitting Mills Inc.	1721 Trinity St, Los Angeles, CA 90015	9
Schuessler Knitting Mills Inc.	1523 N fremont, Chicago, IL 60622	9
Genesco Inc., Capital Swimwear	1429 Pk St, Hartford, CT 06106	9*
Scarves by Vera Inc.	417 5th Ave, New York, NY 10016	8
Natalie Knitting Mills Inc.	PO Box 722, Chilhowie, VA 24319	8
Granite Knitwear Inc.	PO Box 498, Granite Quar, NC 28072	8
Briar Knitting Inc.	PO Box 312, Berwick, PA 18603	8
Taren Holdings Inc.	PO Box 578, Tracy City, TN 37387	8*
North American Knitting Co.	490 Dewey Ave, Mansfield, OH 44901	8*
Royal Knitting Mills	2007 S California St, Chicago, IL 60608	8
Kiss Knitting Mills Inc.	2 Horizon Rd #1422, Fort Lee, NJ 07024	8*
Apparel America Inc.	1407 Broadway, New York, NY 10018	7

(continued)

**TABLE B-4.
TEXTILE FIBER DYEING FACILITIES (SIC 225) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)**

Name	Address	Sales in \$ Millions
Holden Mfg. Co.	216 W 2nd, Holden, MO 64040	7
Cornish Knit Goods Mfg. Corp.	121 Ingraham St, Brooklyn, NY 11237	7
Apparel America Inc., Mayfair Industries	41 Noble Ave, Shoemakersville, PA 19555	7
Gould Fabrics Inc.	1457 Broadway, New York, NY 10036	7
Kandel Knitting Mill	4834 N Interstate Ave, Portland, OR 97217	6
Garon Knitting Mills Inc.	1901 Winter St, Superior, WI 54880	6
Windsor Knitting Mill Inc.	202 S 3rd St, Hamburg, PA 19526	6
Cuddle Knit Inc.	681 Grand Blvd, Deer Park, NY 11729	6
Catoosa Knitting Mills Inc.	PO Box 526, Crossville, TN 38557	6
Littlefield Adams & Co., Collegiate-Pacific Co.	PO Box 210, Roanoke, VA 24002	6
Minnesota Knitting Mills Inc.	1450 Medota Heights, St Paul, MN 55120	6
Terry Tuck Inc.	4321 Exchange Ave, Los Angeles, CA 90058	6
Dehen Knitting Co.	404 NW 10th St, Portland, OR 97209	5
Acker Knitting Mills	112 W 34th St, New York, NY 10120	5*
HAB Industries Inc.	PO Box 573, Allentown, PA 18105	5
OB Dyers	45 Noble St, Reading, PA 19611	5*
Oakdale Knitting Mills Inc.	101 Wyckoff Ave, Brooklyn, NY 11237	5*
Ocello Inc.	PO Box 609, Richland, PA 17087	5*
Reilly Co., Inc.	1306 River St, Valatie, NY 12184	5*
Alpha Mills Corp.	201 S Lancaster St, Annville, PA 17003	5
Brig A Knits Inc.	130 Parlin Ln, Watchung, NJ 07060	5
Colonial Textile Mfg. Corp.	PO Box A-2093, New Bedford, MA 02741	5
Eckmil Knitting Inc.	PO Box 389, West New York, NJ 07093	5*
Boutique Knitting Corp.	37-50 57th St, Woodside, NY 11377	4*
Gotthelf Knitting Mills	607 Myrtle Ave, Boonton, NJ 07005	4
Fit-All Sportswear Inc.	PO Box 1428, Pilot Mounta, NC 27041	4
A & R Knitting Mill Corp.	9 Wyckoff Ave, Brooklyn, NY 11237	4

(continued)

**TABLE B-4.
TEXTILE FIBER DYEING FACILITIES (SIC 225) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)**

Name	Address	Sales in \$ Millions
North Carolina Knits Inc.	PO Box 218, Albermarle, NC 28001	4*
Antmart II Inc.	816 Farren St, Portage, PA 15946	4*
Lewis Gallet Inc.	120 Delaware Ave, Uniontown, PA 15401	4*
Kaufman Knitting Co. Inc.	123 N 3rd st, Minneapolis, MN 55401	4*
Happyknit Inc.	42 Central Ave, Farmingdale, NY 11735	4
S & R Knitting Mills Inc.	240 Broadway, Brooklyn, NY 11211	3
Western Sportswear Inc.	467 Troutman St, Brooklyn, NY 11237	3*
Broadway Knitting Mills Inc.	2152 Sacramento St, Los Angeles, CA 90021	3*
Jacques Moret Inc.	1350 Broadway, New York, NY 10018	3
Lanz Inc, Poppy by Lanz	8680 Hayden Pl, Culver City, CA 90232	3*
Andrews Knitting Mills Inc.	3560 Hoffman E, St Paul, MN 55110	3
Crown Globe Inc.	338 Main St, Shoemakersville, PA 19555	3
WF Hofford Inc.	Bridge St & Railroad St, Weissport, PA 18235	2*
West Coast Knitting Mills	420 W 33rd Ave, Los Angeles, CA 90031	2
Amboy Knits Inc.	PO Box 969, Perth Amboy, NJ 08861	2*
Best Knitting Mills Inc.	241 Taaffe Pl, Brooklyn, NY 11205	2*
Wright Mfg. Co. Inc.	114 44th St, Union City, NJ 07087	2*
Worcester Knitting Co., Worcester Spinning Co.	80 Chapel St, Cherry Valley, MA 01611	2*
Hellam Hosiery Co. Inc.	PO Box 6158, Hellam, PA 17406	2
TM Athletics	163 S Jackson St, Seattle, WA 98104	2
Centralia Knitting Mills	PO Box 269, Centralia, WA 98531	2
Wisconsin Knitting Co.	904 E Pearson St, Milwaukee, WI 53202	1
Binghamton Knitting Co.	PO Box 1646, Binghamton, NY 13902	1
Dependable Knits Inc.	PO Box 25, Kings Mountain, NC 28086	1
Stanley Mfg. Co.	PO Box 152, Stanley, VA 22851	1*
Apparel America Inc. Pilgrim Sportswear Inc.	350 5th Ave, New York, NY 10118	1*
Renegade Knitwear Inc.	Rt 14 Box 542, Crossville, TN 38555	1*

(continued)

TABLE B-4.
TEXTILE FIBER DYEING FACILITIES (SIC 225) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)

Name	Address	Sales in \$ Millions
Penn Keystone Knitting Mills Inc.	1410 Broadway Ste 801, New York, NY 10018	1
Pronto Group	PO Box 545, Varnville, SC 29944	1*
(SIC 2254) Knit Underwear Mills		
Sara Lee Knit Prdts.	PO Box 3019, Winston-Salem, NC 27102	320
Jockey Intl Inc.	2300 60th St, Kenosha WI 53140	250*
Spring City Knitting Co. Inc.	PO Box 1109, Cartersville, GA 30120	120
Martin Mills Inc.	PO Box 129, St, Martinville, LA 70582	100
Cinderella Knitting Mills Inc.	120 W 45th St, New York, NY 10036	80
Panola Mills Inc.	PO Box 630, Bateville, MS 38606	63*
Gerber Childrenswear Inc.	400 W Main St, Ephrata, PA 17522	50
JE Morgan Knitting Mill Co.	Rte 54, Tamaqua, PA 18252	40
Medalist Indus Inc.	PO Box 803, Piqua, OH 45356	26
American Mills Inc.	PO Box 209, Griffin, GA 30224	22*
Johnstown Knitting Mill Co.	309 W Montgomery St, Johnstown, NY 12095	20
American Mills Inc.	PO Box 107, Jackson, GA 30233	17*
Rubens & Marble Inc.	2340 N Racine Ave, Chicago, IL 60614	17
Beltex Corp.	PO Box 749, Belmont, NC 28012	12
Fruit of the Loom Inc.	130 Zenker Rd, Lexington, SC 29072	11
Indera Mills Co.	PO Box 10918, Winston-Salem, NC 27108	10
Yocom Knitting Co.	Race & Monroe St, Stowe, PA 19464	10
HH Fessler Knitting Co Inc.	Church & Sherman St, Orwigsburg, PA 17961	8
Union Knitting Mills	PO Box 60, Schuylkill H, PA 17972	7
Jacob Boltz Knitting Mill Inc.	317 N 9th St, Pottsville, PA 19464	5*
Geissler Knitting Mills Inc.	45 E Green St, Hazleton, PA 18201	5*
Gerber Children's Wear Inc.	PO Box 819, Fuquay-Varina, NC 27526	5*
Classtex Knitting Mills Inc.	E Mifflin St, Orwigsburg, PA 17961	5
Swanknit Inc.	PO Box 675, Cohoes, NY 12047	5

(continued)

TABLE B-4.
TEXTILE FIBER DYEING FACILITIES (SIC 225) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)

Name	Address	Sales in \$ Millions
Ashland Knitting Mills Inc.	Front & Chestnut Sts. Ashland, PA 17921	4*
Tru-Health Inc.	38 St Johns Pl, Freeport, NY 11520	4
Linden Knitwear Corp.	Centerport Rd, Nohrville, PA 19541	3
(SIC 2257) Weft Knit Fabric Mills		
West Point-Pepperell Inc., Alamac Knitting Div.	1221 Ave of the Americas, New York, NY 10020	170*
Dyersburg Fabrics Inc.	PO Box 767, Dyersburg, TN 38025	100
Gold Mills Inc.	4925 W Market St, Greensboro, NC 27409	76
Dixie Yarns Inc, Caro-Knit	PO Box 366, Jefferson, SC 29718	52
Cleveland Mills Co.	101 W Main St, Lawndale, NC 28090	40
Stony Creek Knitting Mill	PO Box 2445, Rocky Mount, NC 27802	29
Dixie yarns Inc., Clyde Fabrics	PO Box 760, Newton, NC 28658	26
United Piece Dye Works	111 W 40th St, New York, NY 10018	25
Stevcoknit Fabrics Co.	PO Box 64635, Fayetteville, NC 28306	25*
BTF Corp.	450 Murray Hill Pkwy, East Rutherford, NJ 07073	24
International Paper Co.	335 Athena Industrial Pk, Athens, GA 30601	22*
Edmond Stern Inc.	350 5th Ave, New York, NY 10118	22*
American Fabrics Co.	1069 Connecticut Ave, Bridgeport, CT 06607	20
Gurney Industries Inc.	242 Ct St, Prattville, AL 36067	20
Stevcoknit Fabrics Co.-Holly Plant	601 Wilmington Rd, Wallace, NC 28466	18
Jomac Inc.	683 Easton Rd, Warrington, PA 18976	14
Domestic Mfg Co.	PO Box 3548, Kinston, NC 28502	12
Milliken & Co. Excelsior Mill	108 W Williams St, Union, SC 29379	12
Guilford Mills Inc. Guilknits	PO Box 1645, Lumberton, NC 28358	11*
Celand yarn Dyers Inc.	PO Box 2220, Thomasville, NC 27360	10
Draper Bros, Co., Inc.	28 Draper Ln, Canton, MA 02021	7
Ames Textile Corp.	720 Suffolk St, Lowell, MA 01854	5*
Arc Knitwear Mills Inc.	435 E 79 St #9V, New York, NY 10021	5*

(continued)

**TABLE B-4.
TEXTILE FIBER DYEING FACILITIES (SIC 225) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)**

Name	Address	Sales in \$ Millions
Clover Knit Inc.	PO Box 539, Clover, SC 29710	5*
Montex Corp.	1101 S 6th St, Allentown, PA 18103	5
National Looms Corp.	229 W 36th St, New York, NY 10018	5*
Originit Fabrics Inc.	462 7th Ave, New York, NY 10018	5*
Schuylkill Haven Bleach & Knitting Inc.	PO Box 307, Schuylkill H, PA 17972	5
Chapel Hill Mfg. Co.	1807 Walnut St, Oreland, PA 19075	5
Mi-Jan Fabrics Inc.	Washington St, Denver, PA 17517	4
American Research & Knitting Inc.	PO Box 1004, Cleveland, TN 37364	4*
O & H Mfg. Co., Inc.	332 N Front St, Allentown, PA 18102	3
Knitcraft Inc.	PO Box 825, Belmont, NC 28012	2*
Kings Mountain Knit Fabrics Inc.	Oak & Railroad, Kings Mountain, NC 28086	2
Kenda Knits Inc.	PO Box 276, Clover, SC 29710	2*
Jasco Fabrics Inc.	450 7th Ave, New York, NY 10123	1*
(SIC 2258) Lace & Warp Knit Fabric Mills		
Guilford Mills Inc.	4925 W Market St, Greensboro, NC 27407	620
Stevcoknit Fabrics Co.	PO Box 1500, Greer, SC 29652	189*
Fab Industries Inc.	200 Madison Ave, New York, NY 10016	168
Liberty Fabrics Inc.	295 5th Ave, New York, NY 10016	150
Liberty Fabrics Inc. of Virginia	PO Box 308, Gordonsville, VA 22942	75*
Carisbrook Indus Inc., Native Textiles	16 E 34th St, New York, NY 10016	60
Glenoit Mills Inc.	PO Box 1157, Tarboro, NC 27886	45
Liberty Penn Corp.	PO Box 279, Jamesville, NC 27846	40
Mohican Mills Inc.	PO Box 190, Lincolnton, NC 28092	35
Lida Mfg. Co.	2222 South Blvd, Charlotte, NC 28203	31*
Liberty Fabrics Inc., MainDell Processing	4201 Tonnelle Ave, North Bergen, NJ 07047	29*
Hornwood Inc.	PO Box 799, Wadesboro, NC 28170	25
Klauber Bros. Inc.	114 E 32nd St, New York, NY 10016	25

(continued)

**TABLE B-4.
TEXTILE FIBER DYEING FACILITIES (SIC 225) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)**

Name	Address	Sales in \$ Millions
Andrex Indus Corp.	1430 Broadway, New York, NY 10018	25
Westchester Lace Inc.	3901 Liberty Ave, North Bergen, NJ 07047	23
Furtex Corp.	PO Box 400, Jacksboro, TN 37757	22
Charbert Inc.	Church St, Alton, RI 02894	20
Clinton Mills Inc., Elastic Fabrics of America	PO Box 21986, Greensboro, NC 27420	17*
Pottsville Bleach & Dye	Rte 61, Schuylkill H, PA 17972	14
Contempora Fabrics Inc.	2451 Contempo Dr., Lumberton, NC 28358	13*
Naomi Knitting Mills Inc.	PO Box 889, Zebulon, NC 27597	12
Mohican Mills Inc, Travis Knits	PO Box 65, Maiden, NC 28650	11*
Quaker Lace Inc.	4th & Lehigh Ave, Philadelphia, PA 19133	11
Apex Mills Corp.	168 Doughty Blvd, Inwood, NY 11696	11
Bayeux Fabrics Inc.	PO Box 490, Swepsonville, NC 27359	10
Carolace Embroidery Co. Inc.	501 Broad Ave, Ridgefield, NJ 07657	10
Russ Knits Inc.	PO Box 130, Candor, NC 27229	10
Continental Fabrics Inc.	40 E 34th St, New York, NY 10016	10
Roman Knit Inc.	PO Box 888, Norwood, NC 28128	9
Allura Corp.	6600 Blvd E #1B, West New York, NJ 07093	8*
Campell Mills Inc.	1104 Southerlnd St, Graham, NC 27253	8
Pomona Textile Co. Inc.	1019 S Main St, Los Angeles, CA 90015	8
Angier Knitting Corp.	PO Box 128, Angier, NC 27501	8*
Knox-Trim Inc.	PO Box 50126, Knoxville, TN 37950	7*
Fleisher Finishing Inc.	313 Mill St, Waterbury, CT 06720	7
Scranton Lace Co.	1313 Meylert Ave, Scranton, PA 18501	6
Fablok Mills Inc.	140 Spring St, Murray Hill, NJ 07974	6
Aridyne Corp.	PO Box 62, Graham, NC 27253	6*
Bojud Knitting Mills Inc.	4 Willow St, Amsterdam, NY 12010	5*
Bridgton Knitting Mill	Portland Rd, Bridgton, ME 04009	5*

(continued)

TABLE B-4.
TEXTILE FIBER DYEING FACILITIES (SIC 225) WITH ANNUAL SALES GREATER THAN \$1 MILLION (continued)

Name	Address	Sales in \$ Millions
Joseph Titone & Sons Inc.	1002 Jacksonville Rd, Burlington, NJ 08016	5
Knit-Wear & Fabric Inc.	145 N Cobb St, Burlington, NC 27215	5
RCR Mill Inc.	31 Caterine St, Shillington, PA 19607	5*
International Veiling Corp.	PO Box 108, Clifton, NJ 07011	5*
Beaufab Mills Inc.	1901 W Main St, Stroudsburg, PA 19607	5
Alcor Lace Corp.	108 W 39th St, New York, NY 10018	5
Fairystone Fabrics Inc.	PO Box 689, Burlington, NC 27216	4*
Buckley & Mann Inc.	PO Box 409, Franklin, MA 02038	4
Nanray Inc.	PO Box 1362, Lumberton, NC 28358	4
Mohawk Fabric Co. Inc.	96 Guy Pk Ave, Amsterdam, NY 12010	4
Paris Lace Inc.	1500 Main Ave, Clifton, NJ 07011	4
Rue de France Inc.	78 Thames St, Newport, RI 02840	3
Sterling Lace Inc.	48 W 37th St 12th Fl, New York, NY 10018	3
United Veil Dyeing & Finishing Co.	28 Bostwick Ave, Jersey City, NJ 07305	3
Helmont Mills Inc.	27 Lion Ave, St Johnsville, NY 13452	1*
(SIC 2259) Knitting Mills Nec		
Zwicker Knitting Mills Inc.	PO Vox 1819, Appleton, WI 54913	50
Darlington Fabrics Corp.	1359 Broadway, New York, NY 10018	50
El & El Novelty Co. Inc.	152 W 36th St, New York, NY 10018	41
H Warshow & Sons Inc.	45 W 36th St, New York, NY 10018	40
Beacon Looms Inc.	295 5th Ave, New York, NY 10016	25
Dorothy's Ruffled Originals Inc.	6721 Market St, Wilmington, NC 28405	18
Leading Lady Inc.	24050 Commerce Pk, Beachwood, OH 44122	17
Novelty Textile Mills Inc.	PO Box 498, Wauregan, CT 06387	13
Kleinert's Inc. of Alabama, Scott Mills Div.	PO Box 2189, Gastonia, NC 28053	13
Samax Co.	206 Carroll St, Galax, VA 24333	6
Reeves Bros Inc., Comfy Div.	PO Box 68, Pageland, SC 29728	5*

(continued)

TABLE B-4.
TEXTILE FIBER DYEING FACILITIES (SIC 225) WITH ANNUAL
SALES GREATER THAN \$1 MILLION (continued)

Name	Address	Sales in \$ Millions
Flexlon Fabrics Inc.	PO Box 1058, Burlington, NC 27215	4
Wear-A-Knit Corp.	1306 18th St, Cloquet, MN 55720	1
Sandler Sanitary Wiping Cloth	2229 S Halsted St, Chicago, IL 60608	1

* Indicates an estimated financial figure.

Source: Gale Research, Inc. *Ward's Business Directory of U.S. Private and Public Companies-1991*, Volume 4, Detroit, MI, 1991.

APPENDIX C

SUMMARY OF EMISSION FACTORS LISTED IN THIS DOCUMENT

**TABLE C-1.
SUMMARY OF CHLOROBENZENE EMISSION FACTORS**

SIC	SIC Description	SCC	SCC Description	Emission Factor	Quality Rating	Reference	Note
2865	Cyclic Crudes and Intermediates	301301	Chemical Manufacturing-Chlorobenzene Production	2.06 Kg/MCB/Mg MCB produced	E	4-9	Process Emissions
2865	Cyclic Crudes and Intermediates	30130180	Chemical Manufacturing-Chlorobenzene Production	0.69 Kg/MCB/Mg MCB produced	E	4-9	Fugitive Emissions
2865	Cyclic Crudes and Intermediates	407060	Organic Chemical Storage-Fixed Roof Tanks	0.45 Kg/MCB/Mg MCB produced	E	4-9	Storage of Monochlorobenzene
2865	Cyclic Crudes and Intermediates	301301	Chemical Manufacturing-o-Dichlorobenzene Production	2.32 kg o-DCB/Mg o-DCB produced	U ^a	4-11	Process Emissions
2865	Cyclic Crudes and Intermediates	30130180	Chemical Manufacturing-o-Dichlorobenzene Production	0.76 kg o-DCB/Mg o-DCB produced	U ^a	4-11	Fugitive Emissions
2865	Cyclic Crudes and Intermediates	407060	Organic Chemical Storage-Fixed Roof Tanks	0.47 kg o-DCB/Mg o-DCB produced	U ^a	4-11	Storage of o-Dichlorobenzene
2865	Cyclic Crudes and Intermediates	301301	Chemical Manufacturing-p-Dichlorobenzene Production	5.81 kg p-DCB/Mg p-DCB produced	U ^a	4-11	Process Emissions
2865	Cyclic Crudes and Intermediates	30130180	Chemical Manufacturing-p-Dichlorobenzene Production	1.02 kg p-DCB/Mg p-DCB produced	U ^a	4-11	Fugitive Emissions
2865	Cyclic Crudes and Intermediates	407060	Organic Chemical Storage-Fixed Roof Tanks	0.41 kg p-DCB/Mg p-DCB produced	U ^a	4-11	Storage of p-Dichlorobenzene
2865	Cyclic Crudes and Intermediates	301	Chemical Manufacturing-3,4 Dichloroaniline Production	1.05 kg o-DCB/Mg o-DCB used	U ^a	5-8	Process Emissions
2865	Cyclic Crudes and Intermediates	301	Chemical Manufacturing-3,4 Dichloroaniline Production	0.30 kg o-DCB/Mg o-DCB used	U ^a	5-8	Fugitive Emissions

(Continued)

**TABLE C-1.
SUMMARY OF CHLOROBENZENE EMISSION FACTORS (Continued)**

SIC	SIC Description	SCC	SCC Description	Emission Factor	Quality Rating	Reference	Note
2865	Cyclic Crudes and Intermediates	407060	Organic Chemical Storage-Fixed Roof Tanks	0.15 kg o-DCB/Mg o-DCB used	E	5-8	Storage of 3,4 Dichloroaniline
2865	Cyclic Crudes and Intermediates	301121	Chemical Manufacturing-Organic Dyes/Pigments	0.40 kg o-DCB/Mg o-DCB used	U	5-8	Process Emissions
2865	Cyclic Crudes and Intermediates	301121	Chemical Manufacturing-Organic Dyes/Pigments	0.05 kg o-DCB/Mg o-DCB used	U	5-8	Fugitive Emissions
2865	Cyclic Crudes and Intermediates	407060	Organic Chemical Storage-Fixed Roof Tanks	0.05 kg o-DCB/Mg o-DCB used	U	5-8	Storage of o-dichlorobenzene for dye synthesis
4953	Refuse Systems	50100701	Solid Waste Disposal-Sewage Treatment	0.39 Mg/Mg p-DCB in influent	E	7-5	
4953	Refuse Systems	50100701	Solid Waste Disposal-Sewage Treatment	0.50 Mg/Mg m-DCB in influent	E	7-5	
4953	Refuse Systems	50100701	Solid Waste Disposal-Sewage Treatment	0.41 Mg/Mg o-DCB in influent	E	7-5	
4953	Refuse Systems	50100701	Solid Waste Disposal-Sewage Treatment	0.52 Mg/Mg Chlorobenzene in influent	E	7-5	
4953	Refuse Systems	501001	Solid Waste Disposal-Municipal Incineration	0.001 g/Mg waste combusted	E	7-7 7-8	Modular facility controlled with dry alkaline scrubber and fabric filter
4953	Refuse Systems	501001	Solid Waste Disposal-Municipal Incineration	0.009 g/Mg waste combusted	E	7-7 7-8	Refuse derived fuel facility controlled with dry alkaline scrubber and fabric filter

(Continued)

**TABLE C-1.
SUMMARY OF CHLOROBENZENE EMISSION FACTORS (Continued)**

SIC	SIC Description	SCC	SCC Description	Emission Factor	Quality Rating	Reference	Note
4953	Refuse Systems	501001	Solid Waste Disposal-Municipal Incineration	0.02 g/Mg waste combusted	E	7-7 7-8	Mass burn heat recovery facility controlled with dry alkaline scrubber and fabric filter
4953	Refuse Systems	501001	Solid Waste Disposal-Municipal Incineration	0.02 g/Mg waste combusted	E	7-7 7-8	Mass burn non-heat-recovery facility controlled with dry alkaline scrubber and fabric filter
4953	Refuse Systems	501001	Solid Waste Disposal-Municipal Incineration	0.018 g/Mg waste combusted	E	7-7 7-8	Modular facility controlled with ESP
4953	Refuse Systems	501001	Solid Waste Disposal-Municipal Incineration	0.14 g/Mg waste combusted	E	7-7 7-8	Refuse derived fuel facility controlled with ESP
4953	Refuse Systems	501001	Solid Waste Disposal-Municipal Incineration	0.32 g/Mg waste combusted	E	7-7 7-8	Mass burn heat recovery facility controlled with ESP
4953	Refuse Systems	501001	Solid Waste Disposal-Municipal Incineration	0.32 g/Mg waste combusted	E	7-7 7-8	Mass burn non-heat-recovery facility controlled with ESP

^aNot enough information available to assign a quality rating.

**TABLE C-2.
SUMMARY OF VOC EMISSION FACTORS***

SIC	SIC Description	SCC	SCC Description	Emission Factor	Quality Rating^a	Reference	Note
2869	Industrial Organic Chemicals	30130180	Chlorobenzene Mfg - Fugitives	0.104 kg/hr/source	U	4-2	Fugitives-Gas/vapor pressure relief seals
2869	Industrial Organic Chemicals	30130180	Chlorobenzene Mfg - Fugitives	0.00083 kg/hr/source	U	4-2	Fugitives-Flanges
2869	Industrial Organic Chemicals	30130180	Chlorobenzene Mfg - Fugitives	0.0017 kg/hr/source	U	4-2	Fugitives-Open ended lines
2869	Industrial Organic Chemicals	30130180	Chlorobenzene Mfg - Fugitives	0.015 kg/hr/source	U	4-2	Fugitives-Sampling connections
2869	Industrial Organic Chemicals	30130180	Chlorobenzene Mfg - Fugitives	0.0056 kg/hr/source	U	4-2	Fugitives-Gas valves
2869	Industrial Organic Chemicals	30130180	Chlorobenzene Mfg - Fugitives	0.0071 kg/hr/source	U	4-2	Fugitives-Light liquid valves
2869	Industrial Organic Chemicals	30130180	Chlorobenzene Mfg - Fugitives	0.00023 kg/hr/source	U	4-2	Fugitives-Heavy liquid valves
2869	Industrial Organic Chemicals	30130180	Chlorobenzene Mfg - Fugitives	0.0494 kg/hr/source	U	4-2	Fugitives-Light liquid pump seals
2869	Industrial Organic Chemicals	30130180	Chlorobenzene Mfg - Fugitives	0.0214 kg/hr/source	U	4-2	Fugitives-Heavy liquid pump seals
2869	Industrial Organic Chemicals	30130180	Chlorobenzene Mfg - Fugitives	0.228 kg/hr/source	U	4-2	Fugitives-Gas/vapor compressor seals

*Note: To obtain chlorobenzene leak emission factor for each component, multiply VOC emission factor above by the fraction of chlorobenzene in the stream.

^aBased on engineering judgement.