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Locating And Estimating Air Emissions From Sources Of Phosgene

U.S. ENVIRONMENTAL PROTECTION AGENCY
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EPA-450/4-84-007i

CONTENTS

	<u>Page</u>
Figures	iv
Tables	v
1. Purpose of Document	1
2. Overview of Document Contents	3
3. Background	5
Properties of phosgene	5
Overview of phosgene production and use	7
Miscellaneous phosgene sources	7
References For Section 3	11
4. Phosgene Emission Sources	12
Phosgene production	12
Isocyanate production	20
Polycarbonate production	25
Herbicides and pesticides production	29
References For Section 4	35
5. Source Test Procedures	37
References for Section 5	39
Appendix	
Phosgene Emissions Data	A-1
References For Appendix	A-14

FIGURES

<u>Number</u>		<u>Page</u>
1	Chemical Use Tree for Phosgene	9
2	Basic Operations in a Phosgene Production Process	14
3a	Flow Diagram of a Phosgene Emission Control System for Merchant Phosgene Operations	16
3b	Flow Diagram of a Phosgene Emission Control System for Phosgene Production and Onsite Consumption	17
4	Basic Operations Used in the Production of Diamino Toluenes	21
5	Basic Operations Used in the Production of Toluene Diisocyanate	22
6	Flow Diagram of a Phosgene Emission Control System	24
7	Basic Operations Used in the Production of Polycarbonates	27
8	Control System for Polycarbonate Production	28
9	Basic Operations Used in the Production of Phenyl Ureas	31
10	Emission Control System for Phenyl Urea Production	32
11	Sampling Train for the Measurement of Phosgene	38

TABLES

<u>Number</u>		<u>Page</u>
1	Some Physical Properties of Phosgene	6
2	Companies That Produce Phosgene	8
3	Estimated Phosgene Emissions From a Hypothetical Phosgene Plant	20
4	Estimated Phosgene Emissions From a Hypothetical Toluene Diisocyanate Plant Using Phosgene Produced on Site	25
5	Estimated Phosgene Emissions From a Hypothetical Polycarbonate Plant Using Phosgene Produced on Site	29
6	Estimated Phosgene Emissions From a Hypothetical Herbicide and Pesticide Plant Using Phosgene Produced on Site	34
A-1	Summary of Estimated Phosgene Emissions from Hypothetical Phosgene and Phosgene Derivative Production Facilities	A-3
A-2	Estimated Fugitive Phosgene Emissions From a Hypothetical Phosgene Plant Producing 200 Million Pounds of Phosgene Per Year	A-8
A-3	Estimated Fugitive Phosgene Emissions From a Hypothetical Toluene Diisocyanate Production Facility	A-9
A-4	Estimated Fugitive Phosgene Emissions From a Hypothetical Polycarbonate Production Facility	A-10
A-5	Estimated Fugitive Phosgene Emissions From a Hypothetical Herbicide and Pesticide Production Facility	A-11
A-6	Process Fugitive Emission Factors for Plants	A-12

SECTION 1

PURPOSE OF DOCUMENT

The U.S. Environmental Protection Agency (EPA), States, 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, EPA is preparing a series of documents that compile available information on the sources and emissions of these substances. This document specifically deals with phosgene. Its intended audience includes Federal, State, and local air pollution personnel and others who are interested in locating potential emitters of phosgene and making gross estimates of air emissions therefrom.

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

The reader is strongly cautioned against using the emissions information contained in this document in any attempt to develop an exact assessment of emissions from any particular facility. Because of insufficient data, 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 orders-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 phosgene 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.

SECTION 2

OVERVIEW OF DOCUMENT CONTENTS

As noted in Section 1, 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 phosgene and making gross estimates of air emissions therefrom. Because of the limited background data available, 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 of this document provides a summary of the physical and chemical characteristics of phosgene and an overview of its production and uses. A chemical use tree summarizes the quantities of phosgene consumed in various end use categories in the United States. This background section presents a general perspective on the nature of the substance and where it is manufactured and consumed.

Section 4 of this document focuses on major industrial source categories that may discharge phosgene air emissions. The production of phosgene is discussed, along with the use of phosgene as an intermediate in the production of isocyanates, polycarbonates, carbamates, chloroformates, and other esters of carbonic acid. Example process descriptions and flow diagrams are provided and potential emission points are identified for each of the major industrial source categories discussed. Where the limited data allow, emission estimates are presented that show the potential for phosgene emissions before and after industry-applied controls. Individual companies reported to be involved with either the production or use of phosgene are named.

Section 5 summarizes available procedures for source sampling and analysis of phosgene. Details are not presented, and the EPA neither gives nor

implies any endorsement of these sampling and analysis procedures. Because the EPA has not yet made a general evaluation of these methods, this document merely provides an overview of applicable source sampling procedures and references for the use of those interested in conducting source tests.

Companies that produce or use phosgene, state air control agencies, and other authorities were contacted in an effort to locate data representing measured phosgene emissions. Only one known direct measurement has been made of phosgene emissions from industries that produce or use phosgene. Aside from this single measurement, the only emission data found were company engineering estimates. These estimated emission levels are included in this report even though the companies provided no bases for them.

Other information was used to obtain phosgene emission estimates. For example, health effects and air monitoring programs are discussed, but only to the extent that they were used to estimate phosgene emissions. References are cited and the methodology is discussed in sufficient detail to allow the reader to assess the probable limitations of these estimates. Additional background information is included in the appendix to assist the reader in understanding the basis for all of the estimates presented in the report.

Comments on the contents or usefulness of this document are welcomed, as is any information on process descriptions, operating practices, control measures, and emission information that would enable EPA to improve its contents. All comments should be sent to:

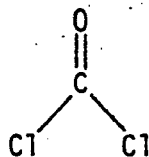
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SECTION 3

BACKGROUND

3.1 PROPERTIES OF PHOSGENE

Phosgene is a highly toxic, colorless gas that condenses at 0°C to a fuming liquid. Impurities can discolor liquid phosgene and cause it to turn a pale yellow to green color.¹ The human nose can detect its characteristic odor only briefly at the time of initial exposure. At a concentration of about 0.5 ppm in the air, this odor has been described as similar to that of new-mown hay or cut green corn. At higher concentrations, the odor may be strong, stifling, and unpleasant. A common decomposition product of chlorinated compounds, phosgene is noncombustible. Its molecular formula is COCl_2 , and it has the following planar structure.



The physical properties of phosgene (also known as carbonyl chloride, carbon oxychloride, carbonic acid dichloride, chloroformyl chloride, and combat gas²) are presented in Table 1.

Phosgene is soluble in aromatic and aliphatic hydrocarbons, chlorinated hydrocarbons, carbon tetrachloride, organic acids, and esters, and it is only slightly soluble in water.¹ It is removed easily from solvents by heating or air blowing. Because the density of phosgene is more than three times that of air, concentrated emission plumes tend to settle to the ground and collect in low areas.³

Phosgene decomposes to hydrogen chloride and carbon dioxide if contaminated with water. Hence, wet phosgene is very corrosive and poses an additional hazard from pressure buildup in closed containers.³

TABLE 1. SOME PHYSICAL PROPERTIES OF PHOSGENE¹

Properties and characteristics	Value
Molecular weight	98.92
Melting point, °C	-127.84
Boiling point (at 101.3 kPa = 1 atm), °C	7.48
Density at 20°C, g/cm ³	1.387
Vapor pressure at 20°C, kPa ^a	161.68
Vapor density (air = 1.0)	3.4
Critical temperature, °C	182.0
Density at critical point, g/cm ³	0.52
Critical pressure, MPa ^b	5.68
Latent heat of vaporization (at 7.5°C), J/g ^c	243
Molar heat capacity of liquid (at 7.5°C), J/K ^c	100.8
Molar heat of formation, kJ ^c	
from elements	218
from CO and Cl ₂	108

^aTo convert kPa to psi, multiply by 0.145.

^bTo convert MPa to psi, multiply by 145.

^cTo convert J to cal, divide by 4.184.

Phosgene reacts with many inorganic and organic reagents.¹ The reaction of oxides and sulfides of metals with phosgene at elevated temperatures yields very pure chlorides. Phosphates and silicates of metals react with phosgene at elevated temperatures and yield metal chloride, phosphorus oxychloride, or silicon dioxide. Anhydrous aluminum chloride forms a variety of complexes with phosgene: Al₂Cl₆·5COCl₂ at low temperatures, Al₂Cl₆·3COCl₂ at 30°C, and Al₂Cl₆·COCl₂ at above 55°C. Ammonia reacts vigorously with phosgene in solution; the products are urea, biuret, ammelide (a polymer of urea), cyanuric acid, and, sometimes, cyamelide (a polymer of cyanic acid).

Phosgene also reacts with a multitude of nitrogen, oxygen, sulfur, and carbon compounds.¹ Reaction with primary alkyl and aryl amines yields carbamoyl chlorides, which can be dehydrohalogenated readily to isocyanate (an intermediate in the manufacture of polyurethane resins). Secondary amines also form carbamyl chlorides when reacted with phosgene. The reaction of phosgene with amino acids has been used to isolate and purify chloroformate derivatives. Hydrazine reacts with phosgene to yield carbohydrazine. The

reaction of phosgene with alcohols, which yields esters, is commercially important because it serves as a basis of widely used polymer systems (polycarbonates).

3.2 OVERVIEW OF PHOSGENE PRODUCTION AND USE

Phosgene is used as a chemical intermediate (i.e., feedstock) in the production of various commercial products. Most commercially produced phosgene is used captively at the production sites in the manufacture of other chemicals. Less than 2 percent of the phosgene produced reaches the marketplace.³ Phosgene is currently produced in the United States by 14 companies at 17 manufacturing facilities (see Table 2). As of January 1983 the annual estimated production capacity was about one million tons.⁴

The chemical use tree in Figure 1 shows the current uses of phosgene. The manufacture of isocyanates consumes about 85 percent of the world's phosgene production.^{3,5} The primary use of phosgene is in the production of toluene diisocyanate (TDI),³ a precursor of the polyurethane resins used to make foams, elastomers, and coatings. A rapidly growing use of phosgene is in the manufacture of polymethylene polyphenylisocyanate (PMPPPI), which is used in the production of rigid polyurethane foams.³ The polycarbonate resins used in appliance and electrical tool housings, electronic parts, and break-resistant glazing are also phosgene-based. About 6 percent of the phosgene production is consumed in the polycarbonate industry.⁵ The remaining 7 to 9 percent is used in the manufacture of herbicides, pesticides, dyes, pharmaceuticals, and other specialty chemicals. The latter include acyl chlorides, chloroformate esters (intermediates in the production of ore-flotation agents and perfumes), diethyl carbonate, and dimethyl carbamyl chloride.⁵

3.3 MISCELLANEOUS PHOSGENE SOURCES

3.3.1 Atmospheric Photooxidation of Chlorinated Hydrocarbons

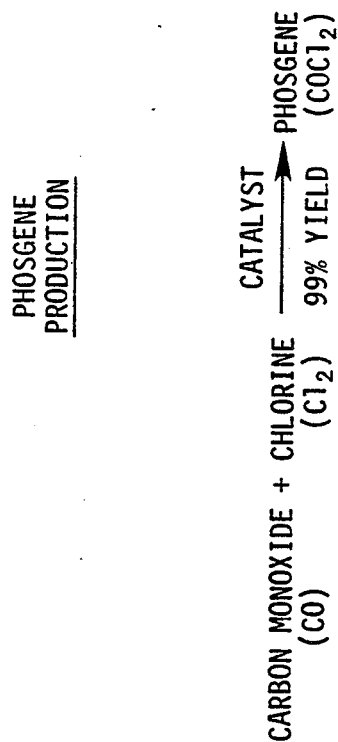
Under laboratory conditions, phosgene has been shown to form when chloroform, methylene chloride, perchloroethylene, and trichloroethylene are irradiated with ultraviolet light. Ambient phosgene measured in urban and nonurban air samples in California appears to confirm the possibility of photochemical phosgene formation in the troposphere.^{6,7}

TABLE 2. COMPANIES THAT PRODUCE PHOSGENE⁴

Company	Location	End Product
BASF Wyandotte Corp.	Geismar, La.	Isocyanates
Dow Chemical Co.	Freeport, Tex.	Isocyanates
E. I. duPont de Nemours & Co., Inc.	Deepwater Point, N.J.	Isocyanates, carbamates
Essex Chemical Co.	Baltimore, Md.	Pesticides
General Electric Co.	Mount Vernon, Ind.	Polycarbonate
ICI Americas	Geismar, La.	Isocyanates
Laurel Industries	La Porte, Tex.	Merchant phosgene, chloroformates
Mobay Chemical Co.	Cedar Bayou, Tex.	Isocyanates
	New Martinsville, W. Va.	Isocyanates
Olin Corp.	Lake Charles, La.	Isocyanates
	Moundsville, W. Va.	Isocyanates
PPG Industries	Barberton, Ohio	Pesticides
Stauffer Chemical Co.	Cold Creek, Ala.	Pesticides
	St. Gabriel, La.	Pesticides
Upjohn Co.	La Porte, Tex.	Isocyanates
Union Carbide Corp.	Institute, W. Va.	Isocyanates
Van De Mark Chemical Co., Inc.	Lockport, N.Y.	Merchant phosgene

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of phosgene emissions from any given facility is a function of variables such as capacity, throughput, and control measures. It should be determined through direct contacts with plant personnel.

It is difficult, however, to assess the amount of phosgene formed in the atmosphere. Although phosgene is evidently one of the photolysis products of a number of high-volume chlorinated hydrocarbon solvents, the role and significance of each solvent, the half-life of phosgene in the air, and the atmospheric fate of phosgene are not well understood. The quantities of phosgene produced by photolysis, however, may be much higher than those emitted by the chemical industry.⁷



<u>REACTANT</u>	<u>END PRODUCT</u>	<u>PERCENT^a</u>
+ AMINE	→ ISOCYANATES	85
+ ALCOHOLS	→ POLYCARBONATES	6
+ AMINES	→ CARBAMATES, THIOCARBAMATES AND PHENYL UREAS	6
+ AMINO ACIDS	→ CHLOROFORMATES AND CHLOROCARBONATES	3
+ METAL ALKYL CARBONATES	→ CARBONATES	<1 100

^aPercent of phosgene production that is used to produce each end product.

Figure 1. Chemical use tree for phosgene.^{3,5}

3.3.2 Thermal and Ultraviolet Decomposition of Chlorinated Hydrocarbons

Phosgene can be produced from the heating and resulting decomposition of many chlorinated hydrocarbons, including methylene chloride, monochlorobenzene, and dichlorobenzene (used as solvents in polymerization reactions involving phosgene), carbon tetrachloride, chloroform, ethyl chloride, polyvinyl chloride, and various fluorocarbons (Freons).^{3,8} When heated, chlorinated hydrocarbon vapors react with oxygen or water to form chlorine, hydrogen chloride, phosgene, and other toxic substances; therefore, incineration used for the control of volatile organic compound emissions can become an inadvertent source of phosgene emissions. A properly operated caustic scrubber can reduce phosgene emissions in exhaust gases from the incineration of chlorocarbons.

The potential for phosgene generation by chlorocarbon decomposition exists at chlorocarbon producing facilities, metallurgical operations, dry-cleaning and degreasing facilities, certain types of industrial fires, and wherever solvents contact heat or ultraviolet light.

REFERENCES FOR SECTION 3

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8. Bjerre, A. Mathematical Modelling in the Hazard Assessment of Substances Forming Toxic Decomposition Products. The Example of Carbon Tetrachloride. Annals of Occupational Hygiene, 24(2):175-183, 1981. Pergamon Press, Ltd., Great Britain.

SECTION 4

PHOSGENE EMISSION SOURCES

This section describes industrial processes that are sources of phosgene emissions, including direct phosgene production and the use of phosgene as an intermediate in the production of isocyanates, polycarbonates, carbamates, thiocarbamates, and phenyl ureas. Included are process descriptions and emission estimates for hypothetical facilities involved in the making or use of phosgene. Because the production of chloroformates and chlorocarbonates represents a minor end use of phosgene, this is not described. The processes and the phosgene emissions and controls associated with the production of these chemicals, however, are similar to those described for polycarbonate production (Section 4.3).

Most phosgene is produced for onsite consumption, with merchant phosgene accounting for less than 2 percent of total production.¹ Hence, phosgene production operations will generally be found at facilities engaged in the manufacture of isocyanates, polycarbonates, carbonates, etc. The production of phosgene is discussed in Section 4.1, and the use of phosgene as a chemical intermediate, in the following sections. For economy, the discussion of phosgene production is not repeated in each of the sections in which its intermediate uses are discussed. Instead, the reader should refer back to Section 4.1.

4.1 PHOSGENE PRODUCTION

4.1.1 Process Description

Phosgene is produced by the reaction of carbon monoxide and chlorine over a highly absorptive activated charcoal catalyst at 200°C and 14 to 28 kPa (2 to 4 psig):



The reaction is rapid and exothermic. Because phosgene decomposes at temperatures above 300°C, a water-cooled reactor is used to remove the excess heat. Figure 2 presents a flow diagram of the production of phosgene from carbon monoxide and chlorine.

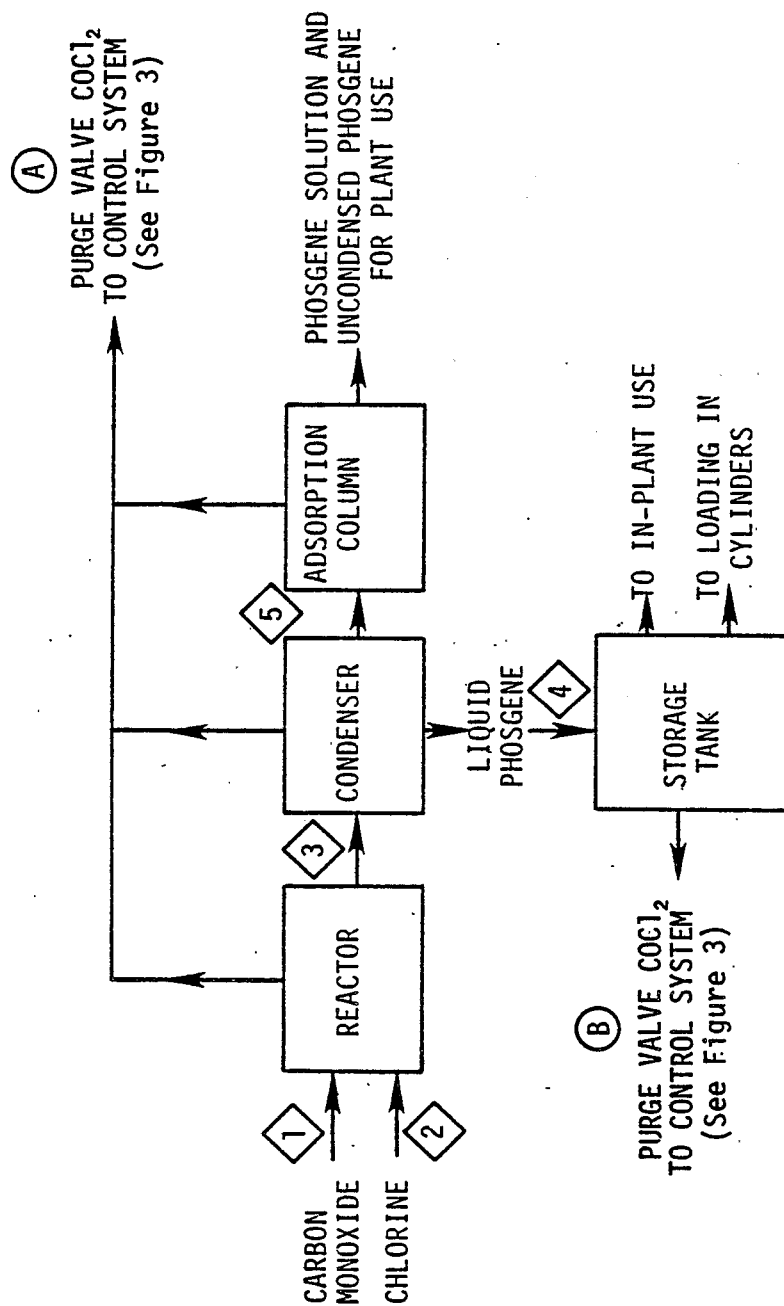
Phosgene production is continuous and highly automated and proceeds as follows:¹

- ° Preparation and purification of carbon monoxide
- ° Preparation and purification of chlorine
- ° Metering and mixing of reactants
- ° Purification and condensation of phosgene
- ° Control of phosgene emissions to assure worker and environmental safety

Carbon monoxide may be manufactured either by the reduction of carbon dioxide over coal or carbon or by the controlled oxidation of hydrocarbon fuels. Chlorine is usually purchased from manufacturers who use the electrolysis of sodium chloride brines (caustic chlorine process). These reactants must be pure. Objectionable impurities include water (which can produce hydrogen chloride, hydrocarbons, and hydrogen that may trigger a reaction between chlorine and steel and destroy the equipment), sulfides (which can produce undesirable sulfur chlorides), and other impurities (which could deactivate the catalyst).

As shown in Figure 2, carbon monoxide (Stream 1) and chlorine (Stream 2) are mixed either in equimolar proportions or with a small excess of carbon monoxide to ensure complete conversion of the chlorine. The product gases (Stream 3) are condensed, the liquid phosgene (Stream 4) is sent to storage, and the remaining gases (Stream 5) are scrubbed with a hydrocarbon solvent to remove residual phosgene. Uncondensed phosgene and the solvent that is used in the scrubber may be used for subsequent processing (e.g., in the production of isocyanate).

The liquid phosgene is stored in pressurized steel tanks. A typical precautionary measure is to store the material in two tanks, neither of which is filled to more than half of its capacity.² This allows the transfer of the phosgene to either tank in case a leak develops in one of the tanks or its piping system.



NOTE: The numbers in this figure refer to the process streams as discussed in the text, and the letters designate the process vents. Process vent gases are always sent to a control system.

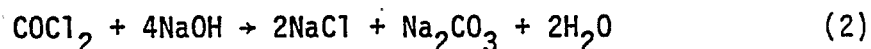
Figure 2. Basic operations in a phosgene production process.

4.1.2 Emissions and Controls

Phosgene emissions fall into three categories--process emissions (including storage tank vents which are exhausted to the control system), fugitive emissions, and emissions that occur during process upsets. Each type is discussed, estimates are presented, and controls are explained. The development of emission estimates is discussed further in the appendix.

Process Emissions--

All process emissions from phosgene production and utilization are typically routed to a caustic scrubber. The caustic scrubber is the control of choice because phosgene is rapidly and completely destroyed by aqueous sodium hydroxide, as shown in the following reaction:



The sodium hydroxide concentration should be maintained at between 3 and 8 weight percent, and the sodium chloride and sodium carbonate must not precipitate and clog the reactor. It should be noted that the solubility of these components is appreciably lower in caustic solution than in water.³ These requirements are met by continually replacing the solution in the scrubber with fresh caustic solution. Data generated by the U.S. Army indicate that a two-stage scrubber can reduce phosgene emissions to below 0.5 ppm by volume.³ This study demonstrated that phosgene control is severely reduced if 1) the phosgene flow to the scrubber exceeds the design capacity of the scrubber, or 2) the caustic concentration in the scrubber is not maintained between 3 and 8 weight percent. The design of the scrubber therefore must be such that it can accommodate any phosgene surge. It is estimated that a phosgene plant producing 200 million pounds per year would emit 300 pounds per year after scrubbing.

Figures 3a and 3b present flow diagrams for phosgene emission control systems. Figure 3a shows a possible control system for a plant that produces phosgene for sale without any subsequent onsite processing. Control can be achieved with a single caustic scrubber. Figure 3b shows an emission control system for a plant that produces phosgene and then processes it on site to produce other products. These subsequent operations generate additional emissions that must be controlled.

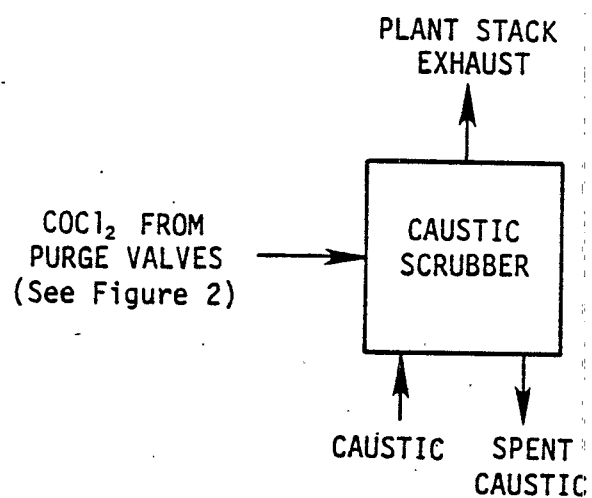


Figure 3a. Flow diagram of a phosgene emission control system for merchant phosgene operations.

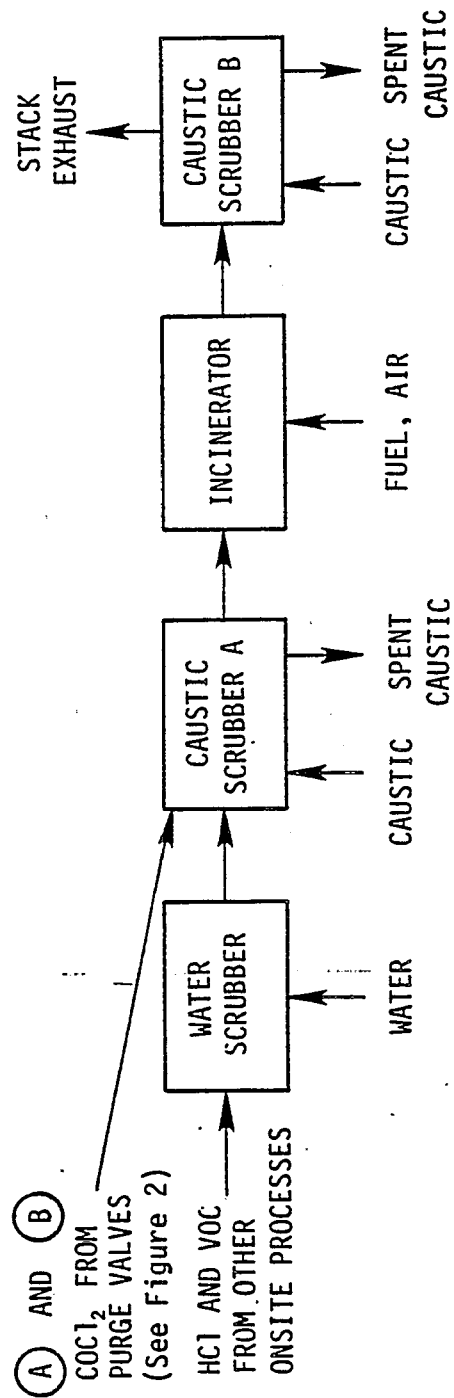


Figure 3b. Flow diagram of a phosgene emission control system for phosgene production and onsite consumption.

In all commercial phosgene processes, the chlorine atoms react with active hydrogen atoms to produce hydrogen chloride (HCl). Hydrogen chloride is an acid gas, and like phosgene, it can be controlled with a caustic scrubber; however, it is usually desirable for a water scrubber to precede the caustic scrubber. This not only permits HCl to be recovered as a byproduct, but also reduces the loadings to the caustic scrubber. The production of toluene diisocyanate includes a nitration step that generates acidic nitrogen and sulfur oxide emissions, which would be routed to a caustic scrubber. These reactions take place in an organic solvent medium, and the solvent is a source of volatile organic compound (VOC) emissions. Solvents include chlorinated compounds such as methylene chloride, monochlorobenzene, and ortho-dichlorobenzene, as well as pyridine, xylene, methanol, and aliphatic hydrocarbons. Whereas VOC can be controlled by incineration, the incineration of chlorinated VOC can produce hydrogen chloride, chlorine, and phosgene emissions. Therefore, a second caustic scrubber is required in series with the incinerator.

Fugitive Emissions--

Pumps and valves are the major sources of fugitive phosgene emissions at facilities where phosgene is produced or used. No compressors are used on phosgene process flows, and emissions from flanges and drains are considered negligible. Because phosgene is known to be very toxic, industry typically takes measures to minimize fugitive emissions. These measures include:⁴

1. Welding pipe joints and monitoring of the quality of all welds.
2. Enclosing the reactor and condenser in a negative-pressure building, and venting the exhaust to the caustic scrubber.
3. Employing special construction materials and techniques for all piping and valves handling hazardous or corrosive substances. Installing plugs or caps on all open-ended lines and plug valves to minimize stem leakage.
4. Enclosing pump couplings and drivers on all pumps handling phosgene. Using special mechanical seals on other pumps (dual seals with barrier fluids) and closed purge sampling systems.
5. Continuous area and individual monitoring and the installation of phosgene-release alarms.
6. Establishing procedures and training for prompt response to phosgene leaks and releases.

7. Practicing intensive preventive maintenance during plant shutdowns and turnarounds. (A turnaround is a planned shutdown to allow equipment to be used to make a different product.)

All plants that produce and use phosgene have individual and/or area monitors to detect excessive phosgene levels in plant air.⁵⁻⁹ Based on the sensitivity of these alarm systems, the fugitive phosgene emissions from a phosgene plant producing 200 million lb/yr are estimated to be 120 lb/yr or 0.6 lb/million lb of phosgene.

Alternatively, this emission rate can be estimated by counting the valves, pumps, and flanges at a typical plant and applying the fugitive leak rates and control efficiencies developed by the Environmental Protection Agency for the synthetic organic chemicals manufacturing industry (SOCMI).¹⁰ This approach yields an estimated fugitive emission rate of 6600 lb/yr, or 33 lb/million lb of phosgene produced. Fugitive emission estimates by both the monitoring approach and the equipment count/emission factor approach are presented hereafter as a range for each plant. It is observed, however, that fugitive controls used in phosgene production are actually much more stringent than those reported in Reference 10.

In phosgene plants where the reactor and condenser are enclosed in a negative-pressure building and the exhaust is vented through the caustic scrubber, 99 percent of the fugitive phosgene emissions are destroyed in the caustic scrubber, and phosgene emissions are further reduced to an estimated 1 to 66 lb/yr (0.005 to 0.3 lb/million lb phosgene produced). Fugitive emission estimates are derived in the appendix.

Process Upsets--

Some phosgene emissions result from process upsets, e.g., pump failures and inadvertent opening of the wrong valve. Based on 15 process upset reports during a recent 6-year period, three Texas plants released a total of 900 pounds of phosgene. Phosgene releases in the 15 episodes ranged from 1 to 220 pounds. The stated amount released in each case usually represented an estimate, and it often was not clear what part of the process was involved. For example, one upset was reported as a ruptured line. Based on the size of these three plants, the total phosgene release, and the number of releases of phosgene (and assuming all releases were reported), it is estimated that a plant producing 200 millions pounds per year of phosgene will

average one process upset per year during which 50 pounds of phosgene is released (0.0005 lb/ton phosgene produced).

Total Phosgene Emissions--

Total phosgene emissions for a plant that produces 200 million pounds of phosgene a year is estimated to be 470 to 7000 pounds, comprising 300 pounds from the process vents, 120 to 6600 pounds in the form of fugitive emissions, and 50 pounds as a result of process upsets. This is equivalent to 2.35 to 34.8 lb phosgene emissions per million pounds of phosgene produced. Table 3 presents a summary of phosgene emissions from phosgene production.

TABLE 3. ESTIMATED PHOSGENE EMISSIONS FROM A HYPOTHETICAL PHOSGENE PLANT^a
(lb/yr)

Process vent emissions ^b	Fugitive emissions ^c	Emissions due to upsets	Total emissions	Emission factor, lb per million lb processed
300	120 to 6600	50	470 to 6950	2.35 to 34.8

^aBased on facilities with a hypothetical rate of 200 million pounds of phosgene production per year.

^bIncinerator and scrubber exhausts.

^cEstimated fugitive emissions would be reduced by a factor of 100 if reactor and condenser are enclosed in a negative-pressure building and vented through a caustic scrubber.

4.2 ISOCYANATE PRODUCTION^{11,12}

4.2.1 Process Description

The commercial production of aromatic and aliphatic isocyanates is accomplished through the reaction of amines and phosgene. Aromatic isocyanates are more important commercially than aliphatic isocyanates. In 1978, the estimated world production of the two principal aromatic isocyanates was 635,000 metric tons of toluene diisocyanate (TDI) and 454,000 metric tons of diphenylmethane-4,4'-diisocyanate (MDI).

Aromatic Diisocyanate Production--

Figures 4 and 5 show the reaction sequences for the production of the major aromatic diisocyanates. Toluene (Stream 1) is the starting material for

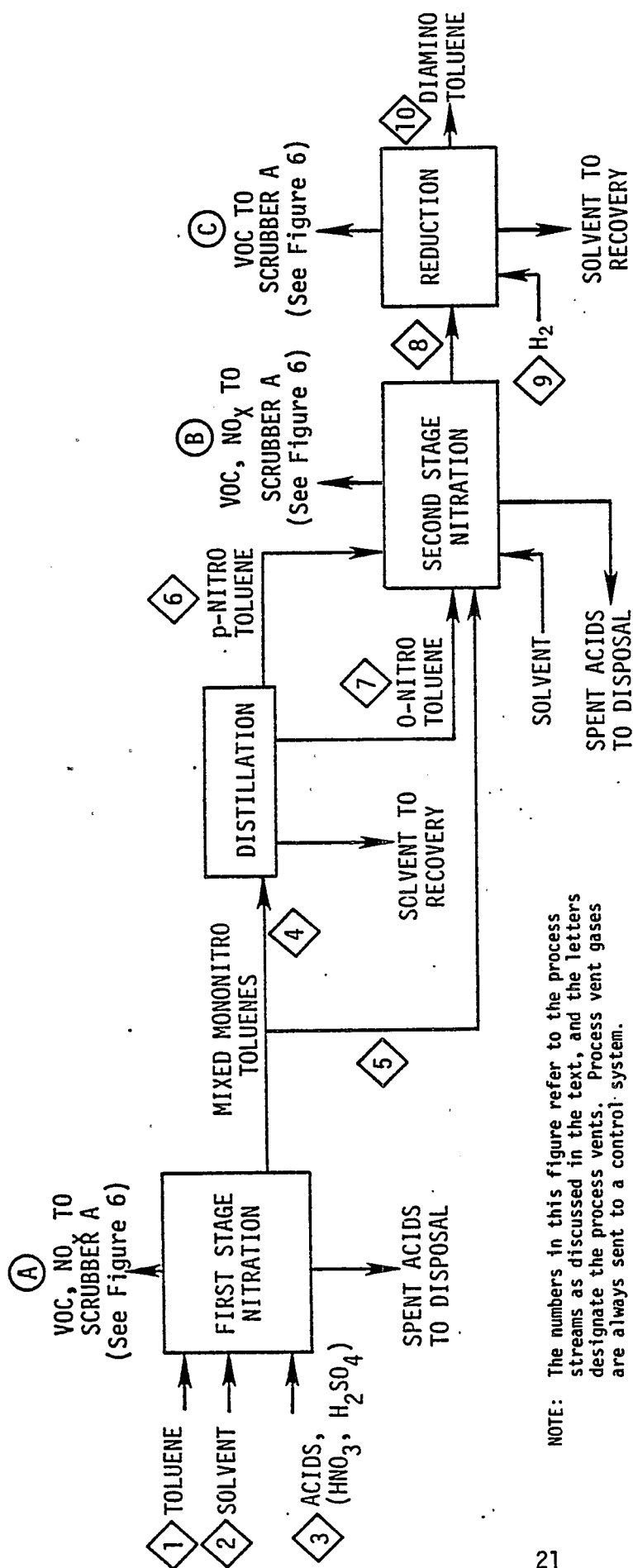
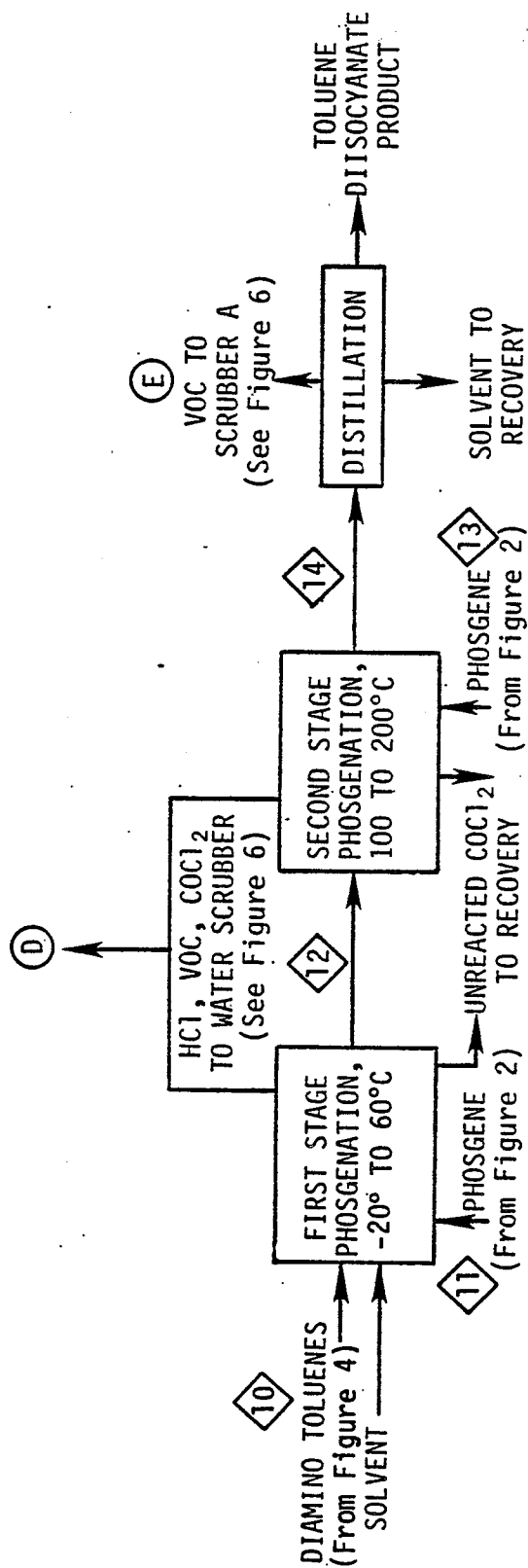


Figure 4. Basic operations used in the production of diamino toluenes.
(This part of the process does not use or emit phosgene.)



NOTE: The numbers in this figure refer to the process streams as discussed in the text, and the letters designate the process vents. Process vent gases are always sent to a control system.

Figure 5. Basic operations used in the production of toluene diisocyanate.
(This part of the process uses phosgene.)

the production of TDI and 3,3'-dimethyldiphenylmethane 4,4'-diisocyanate. Toluene is converted to dinitrotoluene with a mixture of solvent (Stream 2) and sulfuric and nitric acids (Stream 3). (The sulfuric acid ties up water formed in the reaction.) The proportions of dinitrotoluene isomers prepared can differ depending upon operating conditions. Varying the mixture of isomers allows flexibility in the properties of the diisocyanate polymers:

- When dinitrotoluene is made without separating the mononitrotoluene isomers (Stream 5), the resulting mixture is 80 percent 2,4-isomer and 20 percent 2,6-isomer.
- The nitration reaction can be interrupted after the formation of the mononitrotoluenes (Stream 4), and the ortho- and paramononitrotoluenes (Streams 6 and 7) can be separated by distillation. Nitration of paranitrotoluene yields 100 percent 2,4-dinitrotoluene.
- Nitration of orthonitrotoluene yields a mixture of 65 percent 2,4-dinitrotoluene and 35 percent 2,6-dinitrotoluene (Stream 8). Alternatively, orthonitrotoluene can be reduced to orthoaminotoluene (not shown in Figures 4 and 5) and form benzidine through the benzidine rearrangement. Benzidine can then be phosgenated to form 3,3'-tolidene 4,4'-diisocyanate.

The nitrotoluenes (Stream 8) are reduced to the amines with hydrogen (Stream 9). The aminotoluenes (Stream 10) react with phosgene (Streams 11 and 13) to form the isocyanates in a two-step phosgenation process shown in Figure 5. Phosgene is first added at a temperature range of -20° to 60°C and again at 100° to 200°C. Polymerization takes place immediately, but some monomers remain. The product (Stream 14) is then distilled to remove and recover solvent and unreacted monomer.

Aliphatic Diisocyanate Production--

Diphenylmethane-4,4'-diisocyanate, an aliphatic diisocyanate, is produced by reacting two moles of aniline with one mole of formaldehyde, followed by phosgenation of the diamine and polymerization of the resulting diisocyanate. The reaction and process conditions are similar to those for the formation of TDI.

The phosgenation and polymerization reactions are carried out in a solvent medium. Although the role of the solvent is unknown, the choice of solvent influences the rate and extent of the reaction.¹² The solvent must dissolve the amines, phosgene, isocyanate monomers, and at least the lower

molecular weight polymers. Typical solvents are aromatic compounds such as xylene, monochlorobenzene, and o-dichlorobenzene. Aliphatic solvents such as methanol or hydrocarbons may be added to precipitate the polymer from solution.

Process economics require that the solvents be recovered and recycled. All phosgene used in the process reacts with active hydrogen atoms to form hydrogen chloride, which is recovered and either sold or decomposed by electrolysis to yield chlorine (used in the production of phosgene) and hydrogen (used to reduce nitro compounds to amines).

4.2.2 Emissions and Controls

Potential process emissions from the production of isocyanate include phosgene, hydrogen chloride, aromatic and aliphatic solvents, aromatic amines, aromatic nitro compounds, isocyanates, nitrogen oxides, and sulfur oxides. Because these emissions include a number of toxic and corrosive chemicals, controls are necessary. A typical control system (as shown in Figure 6) would include:

1. A water scrubber to remove and recover hydrogen chloride.
2. A caustic scrubber to provide removal of VOC and COCl_2 from the water scrubber as well as to remove VOC from the nitration and distillation processes.
3. An incinerator for volatile organic compounds.
4. A second caustic scrubber for treatment of the incinerator exhaust to remove residues from the combustion of chlorinated hydrocarbons.

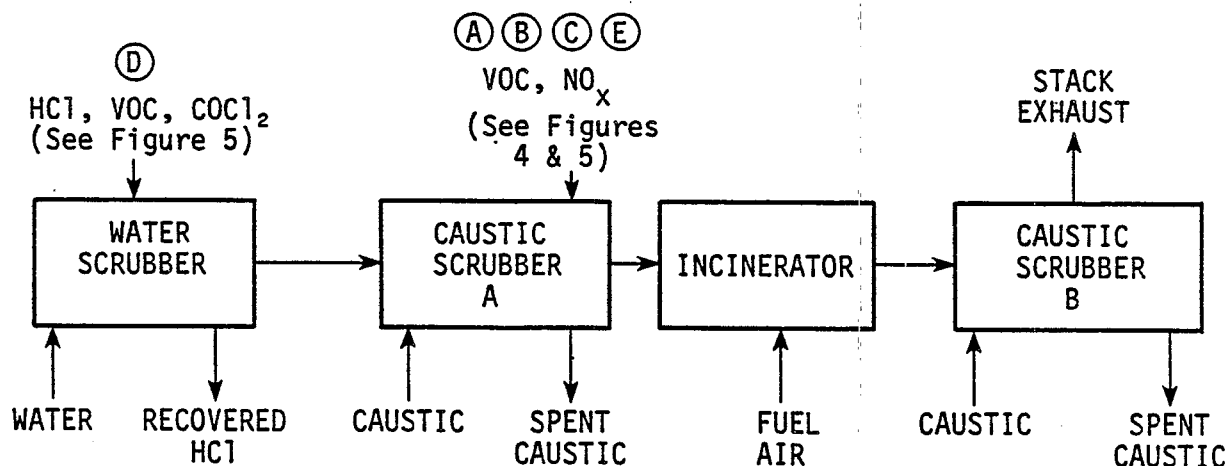


Figure 6. Flow diagram of a phosgene emission control system.

As shown in Table 4, total annual phosgene emissions, after controls, are estimated to be 705 to 9760 pounds for a plant producing 200 million pounds of phosgene and using it on site in the production of TDI. This estimate includes emissions from phosgene production, which were developed in the preceding section and are not reported here. Almost always, phosgene is produced at the same plant where phosgene derivatives, such as isocyanates, are produced.

TABLE 4. ESTIMATED PHOSGENE EMISSIONS FROM A HYPOTHETICAL TOLUENE DIISOCYANATE PLANT USING PHOSGENE PRODUCED ON SITE^a
(lb/yr except as noted)

	Process vent ^b emissions	Fugitive ^c emissions	Emissions due to upsets	Total emissions	Emission factor, lb per million lb phosgene produced
Phosgene production	300	120 to 6600	50	470 to 6950	2.35 to 34.8
Toluene diisocyanate production	150	60 to 2640	25	235 to 2820	1.18 to 14.1
Total plant	450	180 to 9240	75	705 to 9760	3.53 to 48.9

^aBased on facilities with a hypothetical rate of 200 million pounds of phosgene production per year.

^bIncinerator and scrubber exhausts.

^cEstimated fugitive emissions would be reduced by a factor of 100 if reactor and condenser are enclosed in a negative-pressure building and vented through a caustic scrubber.

Derivation of phosgene emissions from TDI production is documented in the appendix.

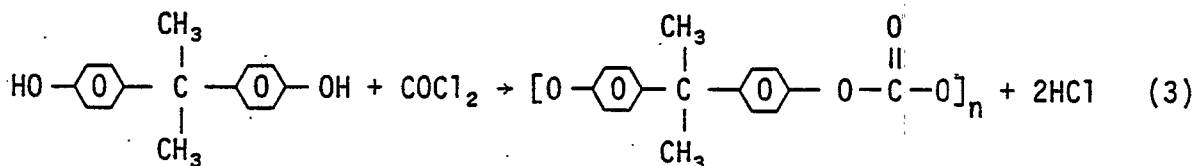
4.3 POLYCARBONATE PRODUCTION^{14,15}

4.3.1 Process Description

In general, polycarbonates are formed by the reaction of a diol (a molecule with two alcohol groups) and a carbonic acid derivative (phosgene is the

chloride of carbonic acid). Because most commercial polycarbonates are derived from the reaction of bisphenol A [2,2 bis(4-hydroxyphenyl) propane] and phosgene, this process is discussed here. Polycarbonates can also be formed by the reaction of other aromatic or aliphatic diols (dihydroxy alcohols) and phosgene.

The sequence of reactions for producing polycarbonate from bisphenol A and phosgene is presented in Figure 7. The basic reaction is:



Bisphenol A and 1 to 3 mole percent monofunctional phenol (to control the molecular weight of the carbonate polymer) are dissolved or slurried in aqueous sodium hydroxide (Stream 1). A solvent and a tertiary amine catalyst (such as pyridine) are added, phosgene gas is bubbled in (Stream 2), and the resulting mixture is vigorously stirred. Additional caustic is added as needed to keep the mixture basic. As the polymer is formed, it is filtrated in the solvent layer. When the reaction is completed, the aqueous phase (Stream 3) contains sodium chloride, sodium carbonate (formed by a side reaction of phosgene and caustic), and possibly traces of phenols. The organic phase (Stream 4) is a polymer solution containing polycarbonate, residual catalyst, and solvent. This polymer solution is washed with water, extracted with acid to remove residual catalyst (Stream 5), and washed again (Stream 6) with water until neutral (Stream 7). The solvent is then stripped from the polymer by evaporation (Streams 8 and 9). These reactions take place at or about room temperature. The reaction may also be carried out in a solvent medium in which a large quantity of pyridine is used to tie up the hydrogen chloride formed by the reaction of phosgene and bisphenol A.

Possible solvents (Stream 1) include methylene chloride, aromatic liquids, chlorinated aromatic liquids, and aliphatic chlorohydrocarbons. Process economics require the recovery and recycling of all organic solvents.

Most of the processing conditions (including reaction conditions) are closely guarded secrets, particularly with regard to processes for isolating

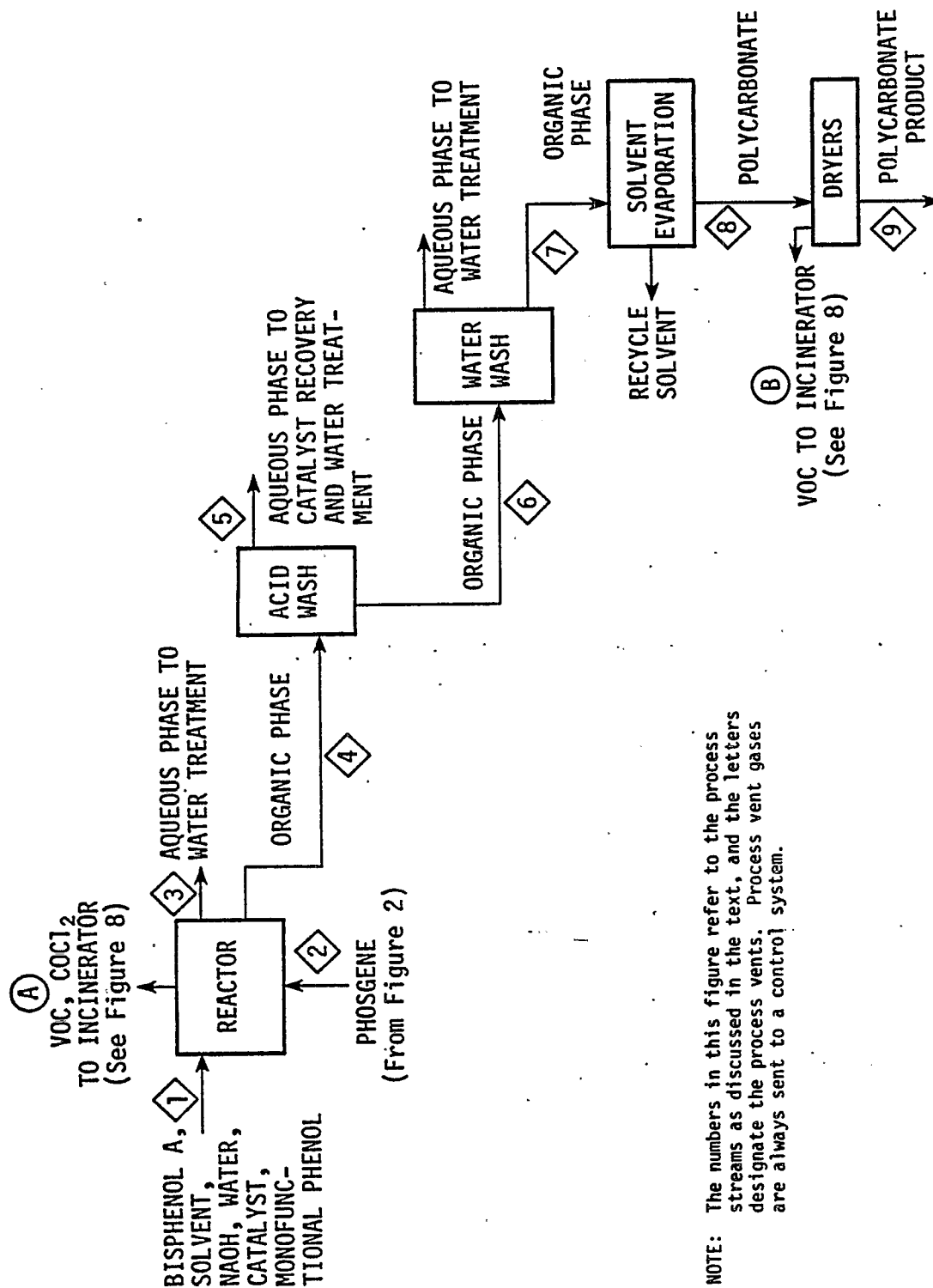


Figure 7. Hypothetical flow diagram for production of polycarbonates. 5

the polymer from the solvents. Possible procedures for separating polymers and solvent include nonsolvent precipitation, spray-drying, multistep total solvent evaporation, and partial or complete solvent removal in boiling water followed by oven-drying. Total solvent evaporation is effected by the use of wiped-film evaporators and multiport vacuum-vented extruders. The total removal of a low-boiling chlorinated hydrocarbon (such as methylene chloride) from a very high-viscosity, high-melting polymer is complicated by two factors: 1) foam formation at low temperatures impedes heat and mass transfer, and 2) the solvent can react with water or thermally decompose and cause product contamination.

4.3.2 Emissions and Controls

Potential emissions from phosgene and polycarbonate production include phosgene, hydrogen chloride, aromatic and aliphatic hydrocarbons (some of which are chlorinated and could produce phosgene on incineration), and phenols. Emission controls for the reactors and solvent recovery systems include incinerators and caustic scrubbers. These controls are similar to those used for isocyanate production. Figure 8 is a flow diagram of a control system.

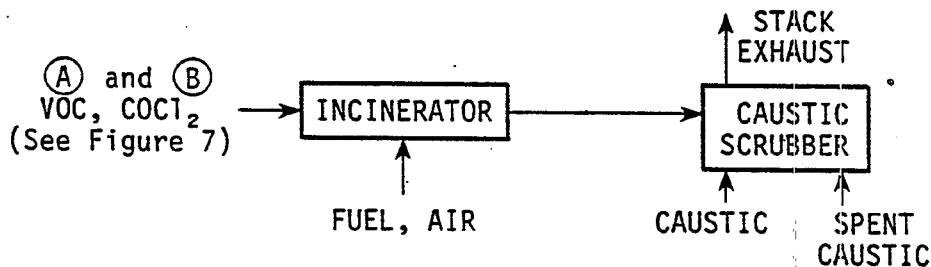


Figure 8. Control system for polycarbonate production.

The wastewater from the reactor, acid wash, and water wash (see Figure 7) is acidic and may contain small amounts of organic compounds. These compounds would probably have high molecular weights, have low water solubility, be non-volatile, and thus would not be a significant source of air emissions.

As shown in Table 5, total annual phosgene emissions are estimated to be 580 to 8190 pounds for a plant producing 200 million pounds of phosgene and using it on site to produce polycarbonates. Derivation of these emission estimates is documented in the appendix.

TABLE 5. ESTIMATED PHOSGENE EMISSIONS FROM A
HYPOTHETICAL POLYCARBONATE PLANT USING PHOSGENE PRODUCED ON SITE^a
(lb/yr)

	Process vent emissions ^b	Fugitive emissions ^c	Emissions due to upsets	Total emissions	Emission factor, lb per million lb phosgene produced
Phosgene production	300	120 to 6600	50	470 to 6950	2.35 to 34.8
Polycarbonate production	70	30 to 1160	10	110 to 1240	0.55 to 6.2
Total plant	370	150 to 7760	60	580 to 8190	2.90 to 41.0

^aBased on facilities with a hypothetical rate of 200 million pounds of phosgene production per year.

^bIncinerator and scrubber exhausts.

^cEstimated fugitive emissions would be reduced by a factor of 100 if reactor and condenser are enclosed in a negative-pressure building and vented through a caustic scrubber.

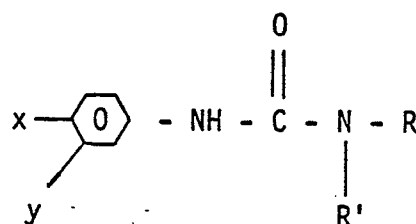
4.4 HERBICIDES AND PESTICIDES PRODUCTION¹⁴

Phosgene is used in the synthesis of some pesticides and herbicides. The active chlorine atoms of phosgene react with hydrogen to produce hydrogen chloride, and the carbonyl group (C=O) is added to the reacting molecule. The three general classes of chemicals comprising herbicides and pesticides are phenyl ureas, carbamates, and thiocarbamates. Sections 4.4.1 through 4.4.3 discuss the production of each of these classes of herbicides and pesticides. The phosgene emissions from the production of each of these are similar. (Phosgene emission estimates for herbicide and pesticide production are presented in Section 4.4.4.)

4.4.1 Production of Substituted Phenyl Ureas

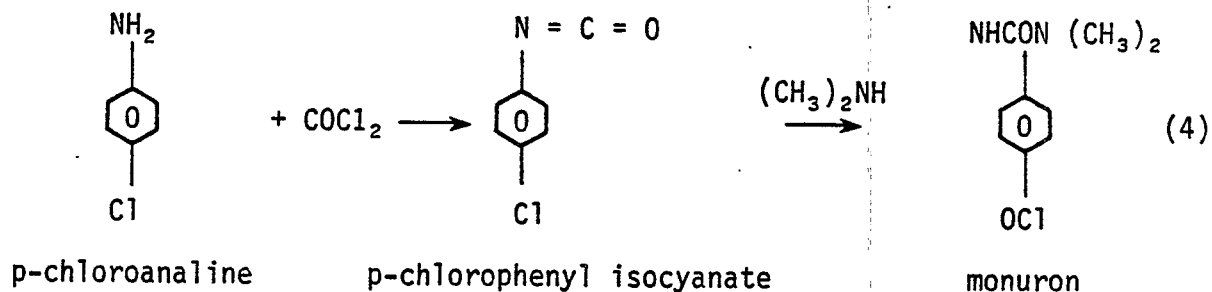
The herbicidal activity of substituted phenyl ureas was discovered in the late 1940's. There are currently 20 to 25 phenyl ureas on the commercial market. Although initially developed as industrial herbicides, they also have been used in selective agricultural applications.

A general reaction for the substituted phenyl ureas (e.g., monuron) can be written as follows:



For monuron, x is hydrogen, y is -OCl, and R and R' are CH₃. Other substituted phenyl ureas have been prepared and are in use with different substituents for x, y, R, and R'.

Figure 9 presents the basic operations used in substituted phenyl urea production, and Figure 10 presents a flow diagram of a control system for such a process. The synthesis of monuron [3-(p-chlorophenyl)-1,1-dimethyl-urea] is typical of the general commercial method used for the production of substituted phenyl ureas. For this synthesis, the p-chloroaniline in dioxane or some other inert solvent (Streams 1 and 2) reacts with anhydrous hydrogen chloride and phosgene at 70° to 75°C (Stream 3) to form p-chlorophenyl isocyanate (Stream 4). This aromatic isocyanate further reacts with dimethylamine at 25°C to give monuron (Stream 5), which is then separated from the solvent by precipitation and evaporation. (See Reaction 4.)



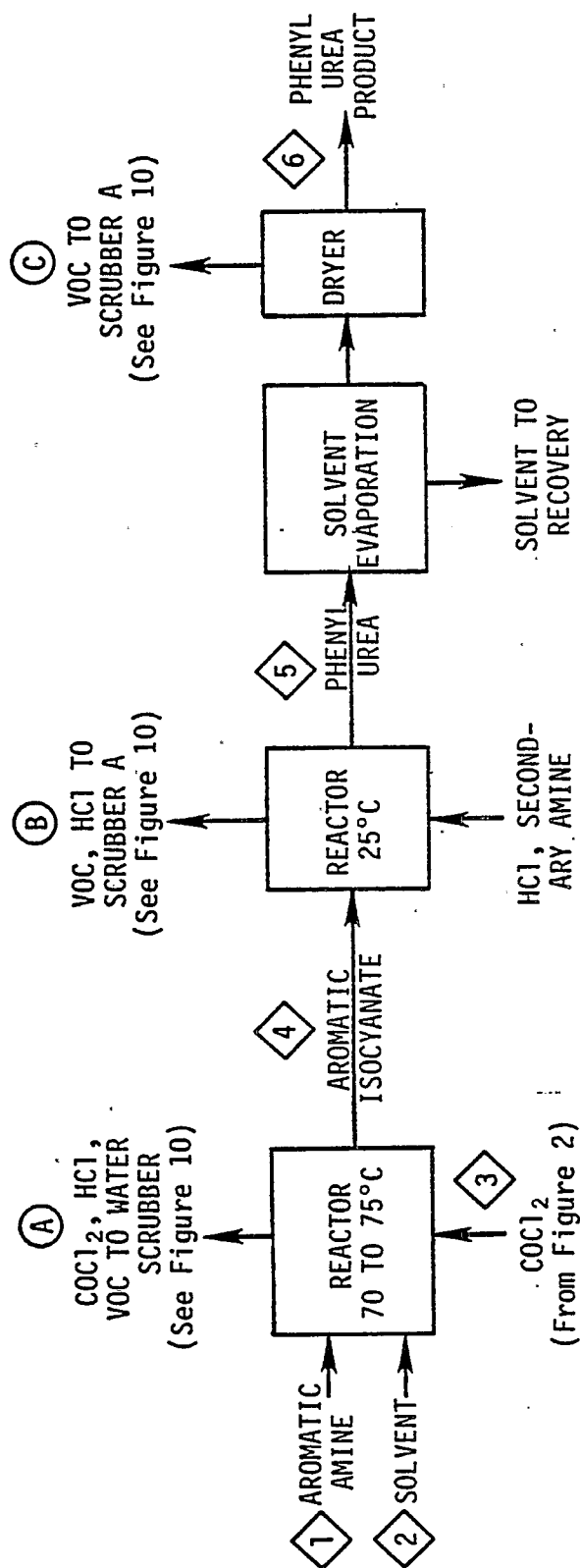


Figure 9. Basic operations used in the production of phenyl ureas.¹³

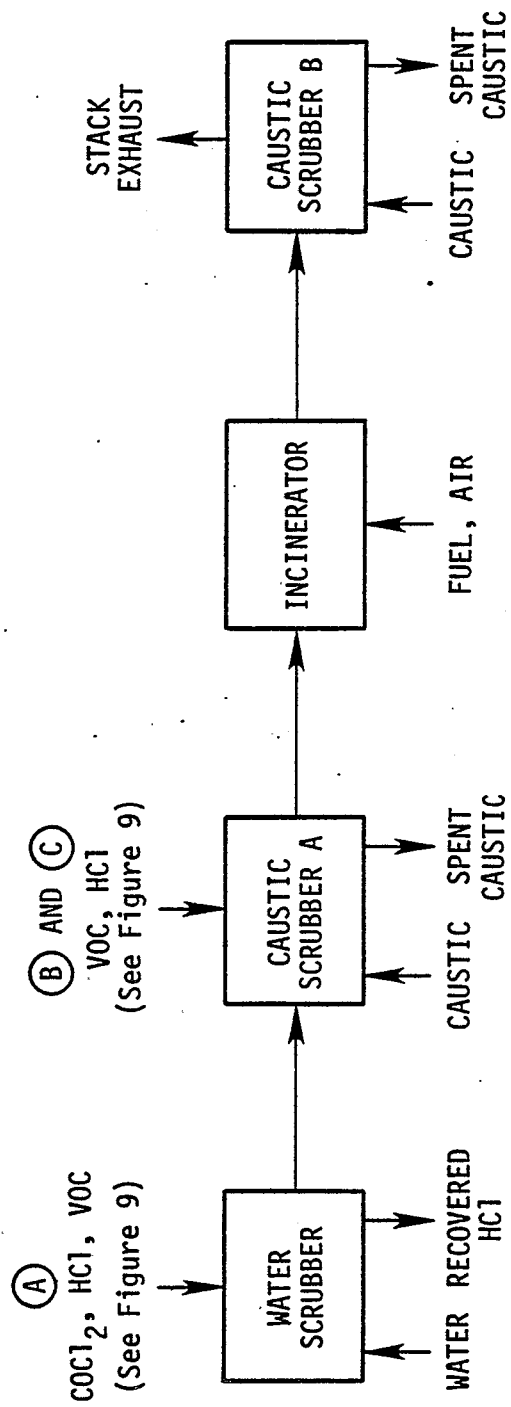
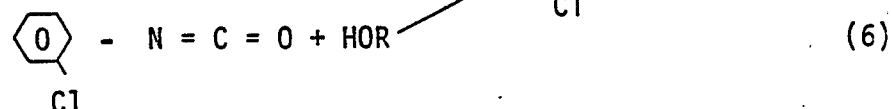


Figure 10. Emission control system for phenyl urea production.

4.4.2 Carbamates Process

Carbamates are used as herbicides, insecticides, and medicinals, and for the control of nematodes, mites, and mollusks. They are obtained either by the reaction of a substituted aniline with a chloroformate ester or the reaction of an isocyanate with an alcohol. The chloroformate ester is made by reacting phosgene with an alcohol ($\text{ROH} + \text{COCl}_2 \rightarrow \text{ClCOOR} + \text{HCl}$), and the isocyanate is made by reacting phosgene with an amine (as described in Section 4.2). The basic reactions are:



Different R groups and substitutions on the benzene ring yield a variety of useful products.

4.4.3 Thiocarbamates Process

Thiocarbamates are used primarily as herbicides, but some have value as fungicides. The phosgene reaction is the same as in the other processes: the chlorine atoms react with hydrogen to form hydrogen chloride, and the carbonyl group is added to the molecule.

Thiocarbamates are formed in a two-stage reaction. The first stage is the reaction of phosgene and a secondary amine to yield a carbamyl chloride:



followed by reaction with a thiol to yield a carbamate:



Alternatively, the secondary amine can react with an alkyl chlorothiol formate in the presence of a proton acceptor to tie up the HCl formed in the reaction:



Varying the R, R', and R'' groups will produce different thiocarbamates.

4.4.4 Emissions and Controls

Generalized flow diagrams for herbicide and pesticide production and emission controls are shown in Figures 9 and 10, respectively. State-of-the-art controls include incineration (to control VOC emissions) and caustic scrubbers (to control phosgene and HCl produced either by reactions involving phosgene or by incineration of the VOCs).

As shown in Table 6, total annual phosgene emissions are estimated to be 580 to 8220 pounds for a plant producing 200 million pounds of phosgene on site and using it to produce herbicides and pesticides. Derivation of this emission estimate is documented in the appendix.

TABLE 6. ESTIMATED PHOSGENE EMISSIONS FROM A HYPOTHETICAL HERBICIDE AND PESTICIDE PLANT USING PHOSGENE PRODUCED ON SITE^a
(lb/yr)

	Process vent emissions ^b	Fugitive emissions ^c	Emissions due to upsets	Total emissions	Emission factor, lb per million lb phosgene produced
Phosgene production	300	120 to 6600	50	470 to 6950	2.35 to 34.8
Herbicide and pesticide production	70	30 to 1190	10	110 to 1270	0.55 to 6.4
Total plant	370	150 to 7790	60	580 to 8220	2.90 to 41.1

^aBased on facilities with a hypothetical rate of 200 million pounds of phosgene production per year.

^bIncinerator and scrubber exhausts.

^cEstimated fugitive emissions would be reduced by a factor of 100 if reactor and condenser are enclosed in a negative-pressure building and vented through a caustic scrubber.

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SECTION 5

SOURCE TEST PROCEDURES

No EPA Reference Method has been established for measuring phosgene; however, the NIOSH Manual of Analytical Methods contains a proposed method for the collection and analysis of phosgene in air.¹ This method involves the reaction of phosgene with a solution of 4,4'-nitrobenzyl pyridine in diethyl phthalate to produce a red color. The color reaction is measured in a photometer.

In the NIOSH method, exhaust or air containing phosgene is passed through midjet impingers (Figure 11) containing a color reagent made up of 2.5 g 4,4'-nitrobenzyl pyridine, 5 g N-phenylbenzylamine, and 992.5 g diethyl phthalate. Fifty liters are drawn through the impingers if the phosgene level is in the range of 0.04 to 1 ppm, whereas a volume of 25 liters is drawn for phosgene levels above 1 ppm. The phosgene reacts with the reagent to form a red color. The N-phenylbenzylamine in the solution stabilizes the color and increases the sensitivity. The resulting red color should be measured with a photometer within 9 hours of sampling. Sampling efficiency is 99 percent or better.

Interfering compounds are acid chlorides, alkyl and aryl derivatives (which are substituted by active halogen atoms), and sulfate esters. If necessary, most of these interfering compounds can be removed in a prescrubber containing an inert solvent, such as Freon-113, that has been cooled by an ice bath. This method has not been validated by EPA.²

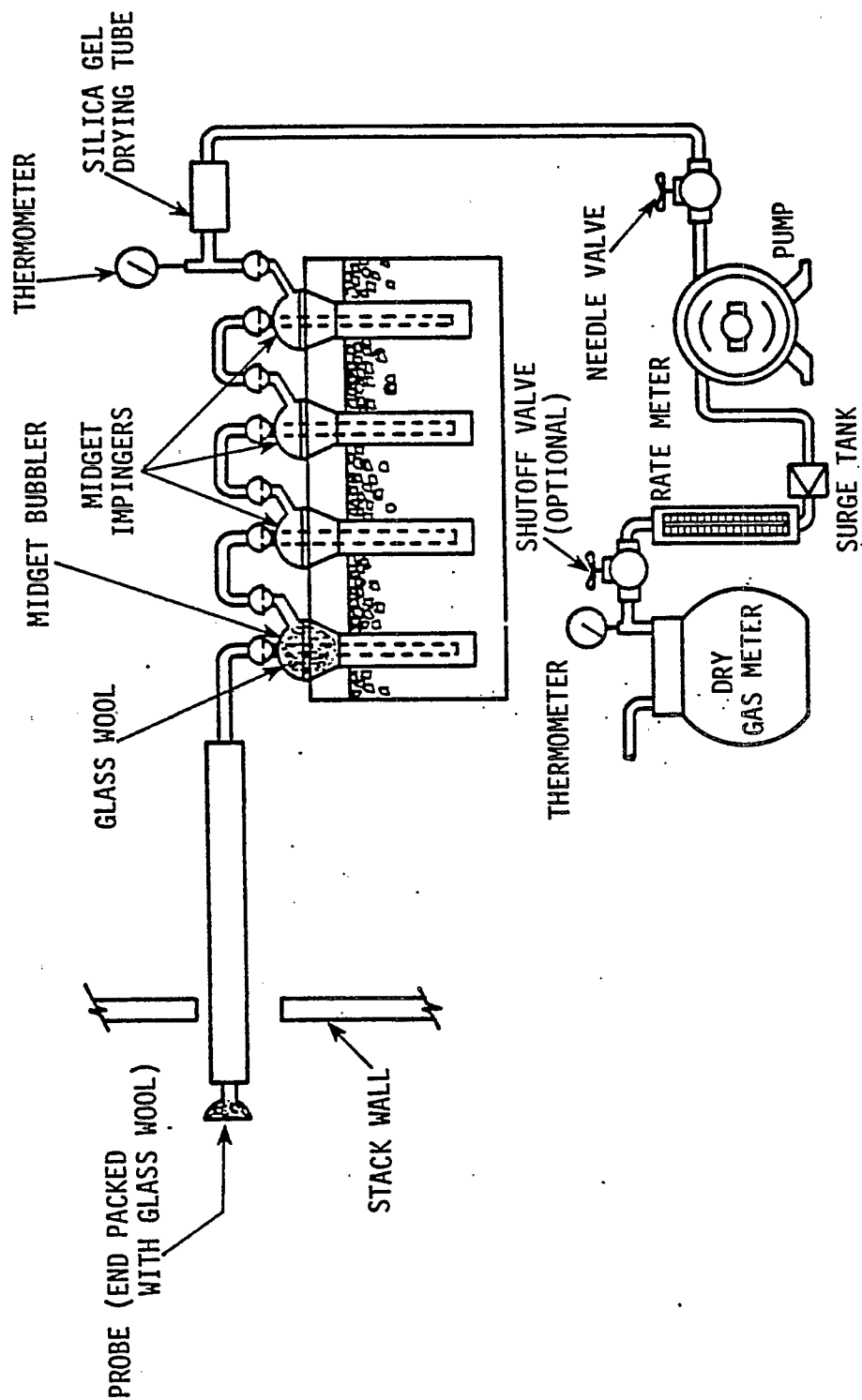


Figure 11. Sampling train for the measurement of phosgene.¹

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APPENDIX

PHOSGENE EMISSIONS DATA

About 89 percent of the phosgene production capacity in the United States is located in West Virginia, Louisiana, and Texas.¹ In an effort to obtain phosgene emissions data, several plants and their respective air control agencies in these States were contacted. Plants in two other states were also contacted. The Texas Air Control Board (TACB) files were also reviewed for information on the Texas plants. Only one direct measurement of phosgene emissions was found, but the companies had made conservative calculations of phosgene emissions. In one case, emission calculations were based on the sensitivity of in-place monitors; no phosgene was actually detected.

Engineering estimates submitted to state air control agencies by eight phosgene producers range from 0 to 7.0 tons of phosgene per year. These estimates contained no breakout of emissions due to phosgene production, storage, use, etc., and the manufacturers did not indicate any basis for the estimates.

Compounds other than phosgene that must be controlled include process solvents, reactants, intermediate products, chlorine, carbon monoxide, and hydrogen chloride (the latter is included unless phosgenation is carried out in an alkaline medium). Most of these compounds are subject to Occupational Safety and Health Administration (OSHA) regulations. A typical plant's emission control system will include the following:

1. A water scrubber to remove and recover hydrogen chloride for sale or reuse.
2. A caustic scrubber to control acidic gases, hydrogen chloride, and phosgene. A backup scrubber, installed as a spare, is used if the primary scrubber malfunctions.
3. An incinerator to control volatile organic compounds (some may contain chlorine) and carbon monoxide. If both caustic scrubbers malfunction, the phosgene will be routed directly to the incinerator for destruction.

4. An additional caustic scrubber that treats the incinerator exhaust to remove residues from the combustion of chlorinated hydrocarbons. In some plants where only one caustic scrubber is used, it is located downstream of the incinerator.
5. For fugitive emissions, plugs or caps on open-ended lines, closed purge sample systems, dual seals with barrier fluids on pumps, and vent systems and rupture disks on safety relief valves. Phosgene plants are also typically enclosed in negative-pressure buildings, which may be vented to caustic scrubbers.

The following three types of emissions are found within a phosgene plant:

1. Process vent emissions--These are emissions from reactors, other processing equipment (including storage tanks), and emission control equipment, including incinerator and scrubber exhausts.
2. Process upsets emissions--These emissions represent inadvertent releases due to equipment failures and human error.
3. Fugitive emissions--These emissions represent releases due to leaks in pumps, valves, and other phosgene handling equipment.

Phosgene Emission Estimates

Estimates of total phosgene emissions from plants producing 200 million pounds of phosgene per year (a capacity chosen to represent production from a large plant) are as follows:

1. From a plant producing phosgene for sale, 470 to 6950 lb/yr.
2. From a plant producing phosgene and converting it to toluene diisocyanates, 705 to 9760 lb/yr.
3. From a plant producing phosgene and converting it to polycarbonates, 580 to 8190 lb/yr.
4. From a plant producing phosgene and converting it to herbicides, 580 to 8220 lb/yr.

The emission factors on which these estimates are based (in terms of pounds of phosgene emitted per million pounds of phosgene processed) are presented in Table A-1.

Phosgene emissions from processes that consume phosgene (TDI, polycarbonate, herbicide, and pesticide production) have been estimated by comparing the processes used to produce these chemicals with the process for phosgene

TABLE A-1. SUMMARY OF ESTIMATED PHOSGENE EMISSIONS FROM
HYPOTHETICAL PHOSGENE AND PHOSGENE DERIVATIVE PRODUCTION FACILITIES^a

	Process vents, ^b lb/yr	Upsets, lb/yr	Fugitive emissions, lb/yr ^c	Total emissions, lb/yr	Emissions, lb/million lb phosgene produced
1. Phosgene production at a merchant phosgene plant	300	50	120 to 6600	470 to 6950	2.35 to 34.8
2. Toluene diisocyanate production	150	25	60 to 2640	235 to 2820	1.18 to 14.1
3. Polycarbonate production	70	10	30 to 1160	110 to 1240	0.55 to 6.2
4. Herbicide and pesticide production	70	10	30 to 1190	110 to 1270	0.55 to 6.4
5. Total for TDI plant (1 + 2) ^d	450	75	180 to 9240	705 to 9760	3.53 to 48.8
6. Total for polycarbonate plant (1 + 3) ^d	370	60	150 to 7760	580 to 8190	2.90 to 41.0
7. Total for herbicide plant (1 + 4) ^d	370	60	150 to 7790	580 to 8220	2.90 to 41.1

^a Based on facilities with a production rate of 200 million pounds of phosgene per year.

^b Incinerator and scrubber exhaust.

^c Fugitive emissions would be reduced by a factor of 100 if process reactor and condenser are enclosed in negative-pressure buildings and vented through the caustic scrubber.

^d Emissions from intermediate production are added to those from the phosgene production operations to estimate total plant emissions.

production and then using engineering judgment to estimate the emissions relative to those for phosgene production. The processes were compared with respect to operations where phosgene might still be present and potential emission sources. For example, emissions due to TDI production were estimated to be one-half of those due to phosgene production, and those for polycarbonate production and herbicide and pesticide production were estimated to be about 25 percent of those due to phosgene production. The TDI estimates are higher because two phosgenation stages are required (Section 4.2) as compared with one phosgene reaction step for polycarbonate (Section 4.3) and herbicide and pesticide production (Section 4.4).

Phosgene emissions from phosgene consuming processes would be expected to be significantly lower than those from the phosgene production process. Phosgene is only used early in the process and is almost completely consumed. No provisions for phosgene recovery and storage after production are needed. Therefore, it is reasonable to expect phosgene production to be the major source of phosgene emissions.

Basis For Emission Estimates

The emission estimates in Table A-1 are approximations based on limited information, derived as shown below:

Process Emissions--

Process emission estimates were based on the following:

1. An assumed phosgene concentration of 0.5 ppm in the caustic scrubber effluent, based on a U.S. Army study.² This study indicates that actual phosgene concentrations in scrubber exhausts could be either significantly higher or lower, depending on whether the scrubber is properly designed and operated. The range was 0.015 to 10.3 ppm. A scrubber would need to have the capacity to handle phosgene surges.
2. Stack flow rates calculated from stack and exhaust velocity data submitted to the Texas Air Control Board by the four Texas phosgene producers.
3. Assumed plant operations of 24 hours a day, 330 days a year (90 percent availability).

Based on this information, phosgene emissions of 19 to 600 pounds per year were calculated for each of these plants. Thus, phosgene emissions from a plant producing 200 million pounds of phosgene per year are estimated to be 300 pounds per year.

Fugitive Emissions (Based on Ambient Exposures)--

Individual and area monitors of phosgene exposures yield the best available information about actual phosgene levels in plants. As standard equipment at plants producing and handling phosgene, these monitors allow upper limit estimations of ambient phosgene concentrations and emissions.

Phosgene exposures are measured in ppm-minutes (the product of the phosgene concentration in parts per million and the time of exposure in minutes). The maximum phosgene concentration that OSHA allows is 0.1 ppm for an 8-hour day, or 48 ppm-minutes. Area monitors can respond to phosgene levels as low as 0.05 ppm. Film badges are worn by all employees in phosgene areas. An exposure of 5 ppm-minutes can be detected by a visible color change, and as low as 2 ppm-minutes can be detected photoelectrically. Based on reported data, photoelectrically detected color changes were infrequent--only five occurrences over an 18-month period in a single plant.³ Other plants contacted indicated that positive monitor responses were also infrequent. Because the badges would detect exposures of 2 ppm-minutes, a steady-state phosgene concentration of 1.2 ppm-minutes for an 8-hour shift was assumed.

Other assumptions included an indoor work area measuring 200 feet by 100 feet by 30 feet, 40 air changes per hour,⁴ and operated 24 hours a day, 330 days a year.

$$\begin{aligned} \text{Process fugitive emissions} &= \frac{1.2 \text{ ppm-min} \times 10^{-6} / \text{ppm}}{8 \text{ h} \times 60 \text{ min/h}} \\ &\times \frac{330 \text{ days/yr} \times 24 \text{ h/day} \times 40 \text{ changes/h} \times 6 \times 10^5 \text{ ft}^3 / \text{change} \times 98.92 \text{ lb/lb-mole}}{380 \text{ ft}^3 / \text{lb-mole}} \\ &= 120 \text{ lb/yr} \end{aligned}$$

This calculation yields a controlled process fugitive phosgene emission of 120 pounds per year. This is a conservative estimate because the steady-state phosgene exposure is assumed to be constantly high throughout the building for every working day during the year.

Fugitive Emissions (Based on Equipment Counts and Emission Factors)--

An alternative method can be used to estimate fugitive emissions; one which applies emission factors to each valve, pump, etc., based on the phosgene content of each process stream. The following steps were followed in this approach:

1. Develop a process flow diagram (see Figures 2, 5, 7, and 9 in text).
2. Identify all process streams containing phosgene.
3. Determine the phosgene content of each stream and whether phosgene is present as liquid or vapor.
4. Identify and estimate the total number of fugitive emission points (valves, pumps, and relief devices).
5. Estimate phosgene emission rates based on the probable degree of control, assuming very stringent inspection and maintenance programs and typical phosgene plant control measures for valves, open-ended pipes, pump seals, and vents.⁵

Fugitive emissions of phosgene and other volatile organics result from leaks in process valves, pumps, compressors, and pressure-relief devices. For the four processes discussed (phosgene production, isocyanate production, polycarbonate production, and herbicides and pesticides production) the phosgene emission rates are based on process flow diagrams, process operation data, fugitive source inventories for hypothetical plants, and emission factors for process fugitive sources.

The first step in estimating fugitive emissions of phosgene entailed listing the process streams in the hypothetical plants and then estimating their compositions. For a reactor product stream, the estimated composition was based on reaction completion data for the reactor and on the plant product mix. For a stream from a distillation column or other separator, the estimated composition was based on the composition of the input stream to the unit, the unit description, and the general description of the stream of interest (i.e., overheads, bottoms, or sidedraw).

After the process streams were characterized, the number of valves per stream was estimated (based on the type of process). Pumps were assigned to each liquid process stream, and relief devices were assumed on all reactors,

columns, and other separators. No compressors are used on phosgene process flows.

Emissions were then calculated for pumps, valves in liquid and gas line service, and relief devices. Welded pipe joints are used in lieu of flanges, and emissions from pipe joints are negligible.⁴ Fugitive emissions from a particular source were assumed to have the same composition as the process fluid to which the source is exposed. For example, phosgene emissions from valves in liquid service were determined by taking the product of 1) the total number of liquid valves in phosgene service, 2) the average phosgene content of the streams passing through these valves, and 3) the average fugitive emission rate per valve per unit time. Emissions from valves in gas service and pumps were calculated in the same manner. For relief devices, the composition of fugitive emissions was assumed to be the same as that of the overhead stream from the reactor or column served by the relief device. Emissions from the various fugitive types of sources were summed to obtain total process fugitive emissions of phosgene.

Emissions from process fugitive sources depend on the number of sources rather than their size; therefore, plant capacity does not affect total process fugitive emissions. For this reason, overall emissions are expressed in terms of kilograms per hour of operation.

The estimates of fugitive phosgene emissions are presented in Tables A-2 through A-5. The emission factors used in these estimates are summarized in Table A-6. At a hypothetical phosgene plant producing 200 million pounds of phosgene per year, the process fugitive emission rate is 0.38 kg/h or 3000 kg/yr (3.3 tons/yr), assuming the plant operates 24 hours per day, 330 days per year. For toluene diisocyanate production, estimated process fugitive emissions are 0.15 kg/h or 1,200 kg/yr (1.3 tons/yr); for polycarbonate production, 0.067 kg/h or 530 kg/yr (0.58 tons/yr); and for herbicide and pesticide production, 0.068 kg/h or 540 kg/yr (0.59 tons/yr), in addition to the emission rate (determined above) associated with captive phosgene production, if carried out at these facilities.

Reference 5, the basis for the emission factors and control efficiencies in this analysis, does not consider fugitive emission controls as stringent as those encountered in phosgene plants. For example, the most stringent level level of control for valves cited in this report only involves monthly

TABLE A-2. ESTIMATED FUGITIVE PHOSGENE
EMISSIONS FROM A HYPOTHETICAL PHOSGENE PLANT
PRODUCING 200 MILLION POUNDS OF PHOSGENE PER YEAR^a

Emission source	Number	Uncon- trolled emission, factor, ^b kg/h	Control efficiency, ^{b,c} %	Avg. COCl ₂ content, %	Emissions, kg/h
Valves					
Liquid	150	0.0071/ valve	59	68	0.30
Gas	100	0.0056/ valve	73	50	0.08
Pumps	2	0.0494/ pump	100	68	0
Relief valves on:					
COCl ₂ reactor	2	0.104	100	65	0
Condenser	2	0.104	100	100	0
Adsorption column	2	0.104	100	35	0
Storage tanks	4	0.104	100	100	0
All sources					0.38

^a Process streams and their composition at hypothetical plant:

Process streams	Phase	% phosgene
Reactor to condenser	Gas	65
Condenser to storage	Liquid	100
Condenser to absorber	Gas	35
Liquid phosgene to plant or shipment	Liquid	100
Phosgene solution to plant	Liquid	5

^b Reference 5.

^c The control efficiencies are based on the use of plugs or caps on open-ended lines, double seals with barrier fluids on pumps, vent systems and rupture disks on safety relief valves, and a monitoring interval of at least monthly for valves.

TABLE A-3. ESTIMATED FUGITIVE PHOSGENE EMISSIONS
FROM A HYPOTHETICAL TOLUENE DIISOCYANATE PRODUCTION FACILITY^a

Emission source	Number	Uncontrolled emission factor, ^b kg/h	Control efficiency, ^{b,c} %	Avg. COCl ₂ content, %	Emissions, kg/h
Valves					
Liquid	100	0.0071/ valve	59	5	0.01
Gas	200	0.0056/ valve	73	45	0.14
Pumps	2	0.0494/ pump	100	5	0
Relief valves on: Phosgene line to first-stage phosgenator	2	0.104	100	85	0
Phosgene line to second-stage phosgenator	2	0.104	100	85	0
Unreacted phos- gene to recycle line	2	0.104	100	5	0
First-stage phosgenation	2	0.104	100	5	0
Second-stage phosgenation	2	0.104	100	1	0
Distillation column	2	0.104	100	1	0
All sources					0.15

^a Process streams and their composition at the hypothetical plant:

Process streams	Phase	% phosgene
Phosgene to first-stage phosgenation	Gas	85
Phosgene to second-stage phosgenation	Gas	85
Unreacted phosgene to recycle	Gas	5
Monoisocyanate to second-stage phosgenation	Liquid	5
Diisocyanate to distillation	Liquid	5
Waste phosgene to scrubber	Gas	5

^b Reference 5.

^c The control efficiencies are based on the use of plugs or caps on open-ended lines, double seals with barrier fluids on pumps, vent systems and rupture disks on safety relief valves, and a monitoring interval of at least monthly for valves.

TABLE A-4. ESTIMATED FUGITIVE PHOSGENE EMISSIONS
FROM A HYPOTHETICAL POLYCARBONATE PRODUCTION FACILITY^a

Emission source	Number	Uncontrolled emission factor, kg/h ^b	Control efficiency, ^{b,c} %	Avg. COCl ₂ content, %	Emissions, kg/h
Valves Gas	100	0.0056/ valve	73	44	0.067
Pumps	0	0	0	0	0
Relief valves on: Phosgene line to reactor	2	0.104	100	85	0
Unreacted phos- gene to inciner- ator	2	0.104	100	85	0
All sources					0.067

^a Process streams and their composition at the hypothetical plant:

<u>Process streams</u>	<u>Phase</u>	<u>% phosgene</u>
Phosgene to reactor	Gas	85
Unreacted phosgene to incinerator	Gas	2

^b Reference 5.

^c The control efficiencies are based on the use of plugs or caps on open-ended lines, double seals with barrier fluids on pumps, vent systems and rupture disks on safety relief valves, and a monitoring interval of at least monthly for valves.

TABLE A-5. ESTIMATED FUGITIVE PHOSGENE EMISSIONS FROM A
HYPOTHETICAL HERBICIDE AND PESTICIDE PRODUCTION FACILITY^a

Emission source	Number	Uncontrolled emission factor, kg/h ^b	Control efficiency, ^{b,c} %	Avg. COCl ₂ content, %	Emissions, kg/h
Valves					
Gas	100	0.0056/ valve	73	44	0.067
Liquid	50	0.0071/ valve	59	1	0.001
Pumps	1	0.0494/ pump	100	1	0
Relief valves on: Phosgene line to reactor	2	0.104	100	85	0
Unreacted phos- gene to scrubber	2	0.104	100	2	0
All sources					0.068

^a Process streams and their composition at the hypothetical plant:

<u>Process streams</u>	<u>Phase</u>	<u>% phosgene</u>
Phosgene to reactor	Gas	85
Unreacted phosgene to incinerator	Gas	2
Aromatic isocyanate to second- stage reactor	Liquid	1

^b Reference 5.

^c The control efficiencies are based on the use of plugs or caps on open-ended lines, double seals with barrier fluids on pumps, vent systems and rupture disks on safety relief valves, and a monitoring interval of at least monthly for valves.

TABLE A-6. PROCESS FUGITIVE
EMISSION FACTORS FOR PLANTS

Facility	Emission source	Emission factor, kg/h
Marketable phosgene producer	Phosgene production	0.38
Toluene diisocyanate producer	Phosgene production	0.38
	TDI production	<u>0.15</u>
		0.53
Polycarbonate producer	Phosgene production	0.38
	Polycarbonate production	<u>0.067</u>
		0.45
Herbicide and pesticide production	Phosgene production	0.38
	Herbicide and pesticide production	<u>0.0068</u>
		0.39

inspection and maintenance. This program provides 73 percent leak control for valves handling gases, and 59 percent leak control for valves handling light liquids. A control efficiency of 100 percent, however, was estimated for plugs and caps on open-ended lines, dual seals with barrier fluids on pumps, and vent systems and rupture disks on safety relief valves. These efficiencies were used to estimate fugitive phosgene emissions from valves, pumps, and relief valves.

The emission factors from Reference 5 are based on "leaking" and "non-leaking" sources. Leaking is defined as "screening at or above 10,000 ppm with a portable VOC monitor." Nonleaking is defined as "screening below 10,000 ppm." These data do not allow extrapolation to the actual level of control most likely in phosgene plants. A 10,000 ppm phosgene concentration could not be tolerated because the average lethal exposure is 400 to 500 ppm-minutes (concentration in ppm multiplied by exposure in minutes). The current OSHA standard is 0.1 ppm. Phosgene plant monitoring equipment typically responds to concentrations of 0.02 to 0.2 ppm.⁶⁻⁸ Film badges typically respond to exposures of 2 ppm-min.

The estimated fugitive phosgene emission rate of 120 lb/yr based on the monitoring approach from a facility with a capacity of 200 million pounds

corresponds to 99.3 percent control of valve emissions. Considering that phosgene concentrations of 0.02 to 0.2 ppm⁶⁻⁸ produce immediate responses from monitoring equipment, this level of control seems achievable. Both estimates of fugitive phosgene emissions, however, are presented in the report to provide a range of fugitive phosgene emissions.

In plants where the reactor, condenser, and associated valves, pumps, etc. are enclosed in negative-pressure buildings and the exhausts are vented through a caustic scrubber, phosgene fugitive emissions will be reduced by a factor of 100 from the above estimates.

Process Upsets--

As discussed earlier, a search of the Texas Air Control Board files yielded process upset reports for three producers of phosgene. Based on the 15 process upset reports during a recent 6-year period, the three plants had a total phosgene release of 900 pounds. Phosgene releases in the 15 episodes ranged from 1 to 220 pounds. The stated amount released in each case usually represented an estimate. All releases may not have been reported. One letter in the file responding to a Notice of Violation stated that the company was not obligated to report the release because none of the released material (not phosgene) had left the company property. One of the 15 releases led to a fatality, and two other releases were responsible for lost-time accidents. Based on the size of the plants, the total phosgene release, and the number of releases of phosgene, it is estimated that a plant producing 200 million pounds of phosgene per year will have one process upset per year during which 50 pounds of phosgene is released.

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16. ABSTRACT <p>To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this to compile available information on sources and emissions of these substances. This document deals specifically with phosgene. Its intended audience includes Federal, State and local air pollution personnel and others interested in locating potential emitters of phosgene in making gross estimates of air emissions therefrom.</p> <p>This document presents information on 1) the types of sources that may emit phosgene, 2) process variations and release points that may be expected within these sources, and 3) available emissions information indicating the potential for phosgene release into the air from each operation.</p>		
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