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Dear Jon:

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Sincerely,



R. Bruce Dickson

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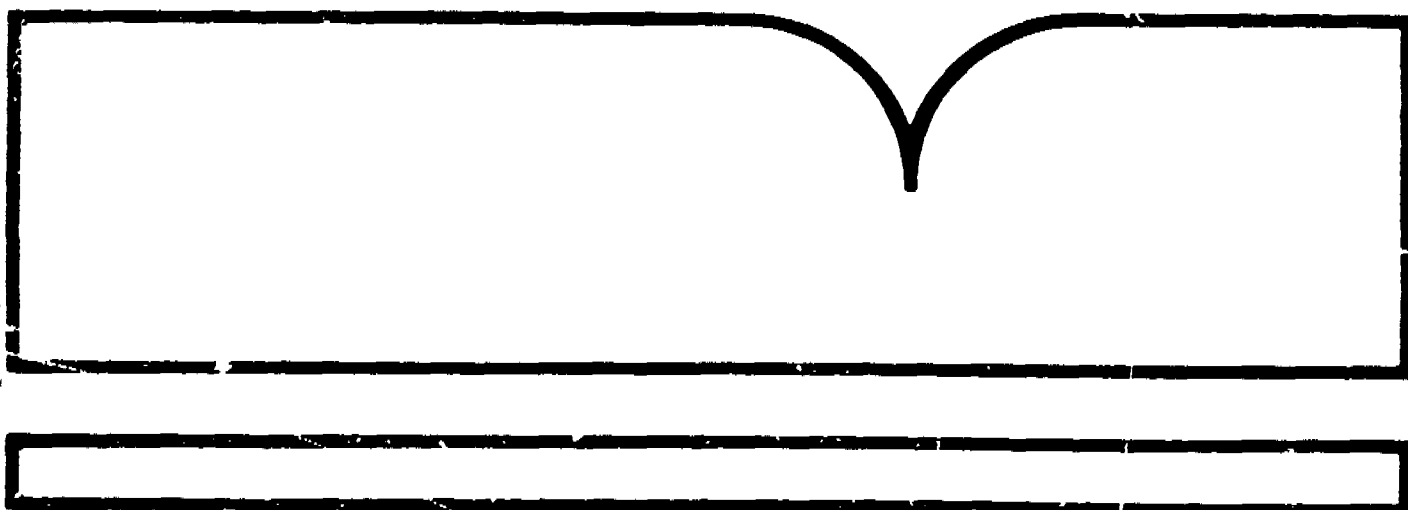
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Locating and Estimating Air
Emissions from Sources of
Vinylidene Chloride

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

Sep 85



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Locating And Estimating Air Emissions From Sources Of Vinylidene Chloride

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Locating And Estimating Air Emissions From Sources Of Vinylidene Chloride

U S ENVIRONMENTAL PROTECTION AGENCY
Office Of Air And Radiation
Office Of Air Quality Planning And Standards
Research Triangle Park, North Carolina 27711

September 1985

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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 as received from the contractor. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, neither does mention of trade names or commercial products constitute endorsement or recommendation for use.

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SECTION 1

PURPOSE OF DOCUMENT

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 such as this that compile available information on sources and emissions of these substances. This document specifically deals with vinylidene chloride. Its intended audience includes Federal, State and local air pollution personnel and others who are interested in locating potential emitters of vinylidene chloride and making preliminary estimates of air emissions therefrom.

Because of the limited amounts of data available on vinylidene chloride emissions, and since 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 vinylidene chloride, 2) process variations and release points that may be expected within these sources, and 3) available emissions information indicating the potential for vinylidene chloride 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. Since 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 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 vinylidene chloride 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.

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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 control agencies and others who are interested in locating potential air emitters of vinylidene chloride and making preliminary 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 provides a brief summary of the physical and chemical characteristics of vinylidene chloride, its commonly occurring forms and an overview of its production and uses. A chemical use tree summarizes the quantities of vinylidene chloride consumed in various end use categories in the United States. This background section may be useful to someone who needs to develop a general perspective on the nature of the substance and where it is manufactured and consumed.

Section 4 focuses on major industrial source categories that may emit vinylidene chloride to the air. This section discusses the production of vinylidene chloride, its use as an industrial feedstock, and processes which produce vinylidene chloride as a byproduct. For each major industrial source category described in Section 4, example process descriptions and flow diagrams are given, potential emission points are identified, and available emission factor estimates are presented that show the potential for vinylidene chloride emissions before and after controls employed by industry. Using trade publications and other sources, individual companies are identified that are reported to be involved with either the production or use of vinylidene chloride.

The final section of this document summarizes available procedures for source sampling and analysis of vinylidene chloride. Details are not prescribed nor is any EPA endorsement given or implied to any of these sampling and analysis procedures. At this time, EPA generally has not evaluated these methods. Consequently, this document merely provides an overview of applicable source sampling procedures, citing references for those interested in conducting source tests.

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

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

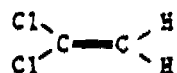
Chief, Source Analysis Section (MD-14)
Air Management Technology Branch
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SECTION 3

BACKGROUND

NATURE OF POLLUTANT

Vinylidene chloride (VDC) is a clear liquid with low viscosity at room temperature. It has a sweet odor similar to other chlorinated hydrocarbons, which can be detected at concentrations of about 500 ppm.¹ The chemical name for vinylidene chloride is 1,1-dichloroethylene; it is also referred to technically as vinylidene dichloride. The structure of VDC is illustrated below:



Vinylidene chloride is practically insoluble in water, but is soluble in most other polar and nonpolar solvents. It is very soluble in chloroform and ether, and is soluble in benzene, acetone, and ethanol. Chemical and physical properties of VDC are summarized in Table 1.1.2

In the presence of air or oxygen, vinylidene chloride can form a peroxide compound that is violently explosive. The peroxide also initiates polymerization of the bulk VDC. Commercial grades of VDC typically contain about 200 ppm of hydroquinone monomethyl ether (MEHQ) inhibitor, which prevents the formation of peroxide and spontaneous polymerization. Other impurities in commercial grade vinylidene chloride include trans-1,2-dichloroethylene (900 ppm), vinyl chloride (850 ppm), 1,1,1-trichloroethane (150 ppm), cis-1,2-dichloroethylene (10 ppm), 1,1-dichloroethane (<10 ppm), ethylene chloride (<10 ppm), and trichloroethylene (<10 ppm).^{1,2}

Vinylidene chloride liquid is very volatile, with a vapor pressure of 660 mm Hg at room temperature. Its vapor burns readily when ignited. The flash point of the liquid is about -15°C, the lower explosive limit of the vapor in air is 7 percent, and the upper explosive limit is 16

TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF VINYLIDENE CHLORIDE²

Synonyms: VDC, 1,1,-dichloroethylene, 1,1-dichloroethene, vinylidene dichloride	
Chemical formula	$\text{Cl}_2\text{C} = \text{CH}_2$
CAS registry number	75-35-4
Molecular weight, g/mole	96.9
Density (20°C liquid), g/cm	1.2137
Boiling point, °C	31.56
Melting point, °C	-122.56
Flash point, °C	
open cup	-16
closed cup	-26
Autoignition temperature in air, °C	513 ^a
Flammable limits in air, volume percent	5.6-16.0
Latent heats, kJ/mole	
vaporization (at boiling point)	26.48
fusion (at freezing point)	6.51
Heat of combustion (25°C liquid), kJ/mole	1095.9
Heat of polymerization (25°C), kJ/mole	-75.3
Heat of formation, kJ/mole	
liquid	-25.1
vapor	1.26
Heat capacity, J/mole-K	
liquid	111.27
vapor (25°C)	67.03
Critical properties	
Temperature, °C	280.8
Pressure, MPa	5.21
Volume, cm ³ /mole	218
Vapor pressure, kPa	
0°C	28.92
10°C	44.54
20°C	66.34
30°C	95.91
Water solubilities at 20°C, g/100g	
Vinylidene chloride in water	0.25
Water in vinylidene chloride	0.035
Dielectric constant (16°C liquid)	4.67
Viscosity (20°C), centipoise	0.33

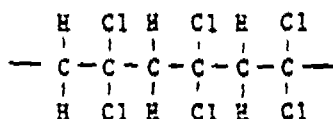
^aVDC stabilized by MEHQ.

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percent. The decomposition products of VDC exposed to oxygen include formaldehyde, phosgene, and hydrogen chloride.^{1,2}

The residence time of vinylidene chloride in the atmosphere is about 23 hours, where residence time is defined as the time required for the concentration to decay to 1/e (37%) of its original value. The major mechanism for destruction of VDC in the atmosphere is reaction with hydroxyl radicals. The principal reaction products are: formic acid, carbon monoxide, chloroacetyl chloride, hydrogen chloride, phosgene, and formaldehyde.^{3,4}

Vinylidene chloride can also be polymerized to produce polyvinylidene chloride (PVDC) polymer chains made up of monomer units joined head to tail:



Vinylidene chloride can also be polymerized with other monomers to produce polyvinylidene chloride copolymers.

OVERVIEW OF PRODUCTION AND USES

Vinylidene chloride was first used in the late 1930's by Dow Chemical Company. VDC is produced commercially by the dehydrochlorination of 1,1,2-trichloroethane with lime or caustic.⁵ It may also be recovered as a byproduct of chlorination and oxychlorination reactions to produce other compounds.⁶ Today, production of VDC in the United States exceeds 90,700 megagrams (Mg) per year.² Exact production figures are not available because the producers of VDC consider these to be proprietary.

Figure 1 gives a chemical use tree summarizing the production and use of VDC.^{2,3,5-7} The main use of VDC is in the production of VDC copolymers. About 68,000 Mg of VDC are consumed annually in the production of polymers containing VDC.² In the United States, the generic term "Saran" is used to refer to high VDC-content polymers. Saran formerly was a trademark of the Dow Chemical Company and is still a Dow trademark in other countries. PVDC homopolymer (Saran A) is difficult to fabricate and for this reason is not used. However, copolymers of

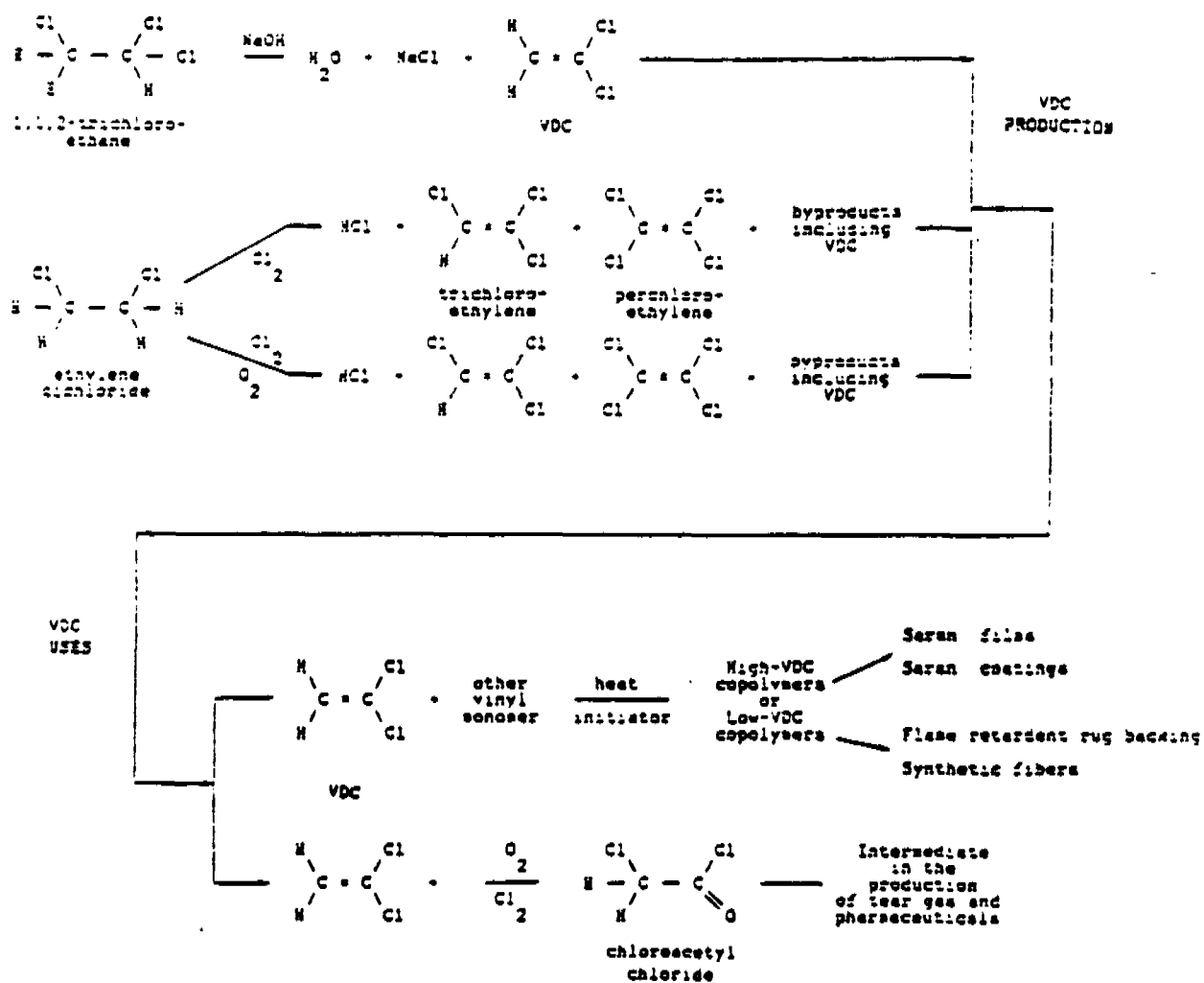


Figure 1. Chemical use tree for vinylidene chloride.2,3,5-7

vinylidene chloride with vinyl chloride (Saran B), alkyl acrylates (Saran C), and acrylonitrile (Saran F) are widely used. Polymers containing VDC are resistant to photodegradation and chemical attack, and because of their high density and crystallinity, they are impermeable to a wide range of gases. The low permeability of VDC copolymers to water and oxygen is the main reason for the commercial importance of vinylidene chloride.^{2,8}

In addition to the production of Saran polymers, VDC is also used as a chemical intermediate in the production of chloroacetyl chloride.⁹ Chloroacetyl chloride is a chemical intermediate in the production of pharmaceutical products and tear gas.⁷ Formerly, a major use of VDC (about 60,000 Mg/yr) was as an intermediate in the production of 1,1,1-trichloroethane. However, the VDC-based process for 1,1,1-trichloroethane was only used at one plant, and was replaced in the late 1970's by a vinyl chloride based process.¹⁰

SECTION 4

VINYLDENE CHLORIDE EMISSION SOURCES

This section discusses vinylidene chloride emissions from processes where the chemical is produced, processes where it is used as a chemical intermediate, and processes where it is produced as a byproduct. Process and emissions data are presented for each source category.

The following industrial processes have been identified as potential sources of VDC emissions:

- vinylidene chloride production,
- perchloroethylene and trichloroethylene production,
- 1,1,1-trichloroethane production,
- VDC polymerization,
- use of VDC in specialty chemical production,
- VDC copolymer fabrication, and
- volatilization from waste treatment, storage, and disposal.

VDC is a byproduct of perchloroethylene and trichloroethylene production and of 1,1,1-trichloroethane production from ethane.

VINYLDENE CHLORIDE PRODUCTION

Vinylidene chloride is produced domestically by the dehydrochlorination of 1,1,2-trichloroethane with sodium hydroxide.^{2,11} Three plants in the U.S. produce VDC; each of these produces a number of other chlorinated hydrocarbons by a variety of processes.¹⁰ The raw material 1,1,2-trichloroethane is produced as coproduct in the chlorination and oxychlorination of ethane, ethylene, and ethylene dichloride (1,2-dichloroethane) to produce chlorinated C₂ species.¹² At the plants using the 1,1,2-trichloroethane dehydrochlorination

process, additional VDC may also be recovered as a byproduct of various chlorination and oxychlorination processes.¹² These processes are discussed in later sections.

Process Description

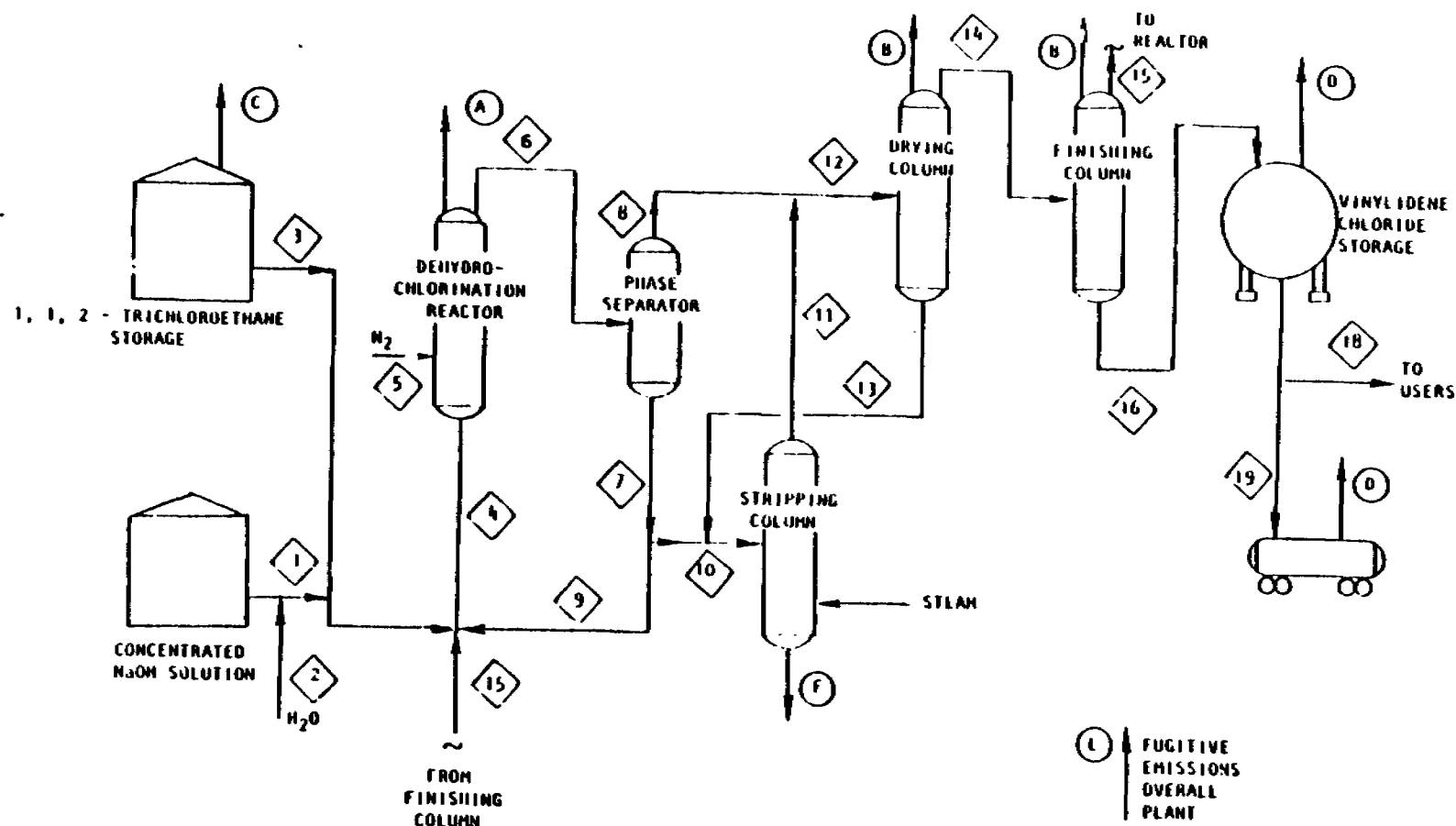
The reaction for the dehydrochlorination of 1,1,2-trichloroethane to produce VDC is as follows:



The reaction is carried out with 2 to 10 percent excess caustic and product yields ranging from 85 to 90 percent.¹¹ Basic operations that may be used in the production of VDC from 1,1,2-trichloroethane are shown in Figure 2. Concentrated sodium hydroxide (Stream 1) is diluted with water (Stream 2) to about 5 to 10 weight percent and is mixed with the 1,1,2-trichloroethane feed (Stream 3) and fed (Stream 4) to the dehydrochlorination reactor. The reaction is carried out in the liquid phase at about 100°C without catalyst. Because the aqueous and organic reactants are not miscible, the reaction is carried out in a liquid dispersion. The dehydrochlorination reactor is continuously purged with nitrogen (Stream 5) to prevent the accumulation of monochloroacetylene impurity in the product VDC. The nitrogen is discharged from Vent A.¹¹

The VDC-containing product from the dehydrochlorination reactor (Stream 6) is separated in a decanter into an aqueous phase (Stream 7) and an organic phase (Stream 8). The aqueous phase, comprising a sodium hydroxide/sodium chloride solution, is divided. One fraction (Stream 9) is recycled (Stream 4) to the hydrochlorination reactor, and the other fraction (Stream 10) is steam stripped to remove organics and discharged to a wastewater treatment system (Discharge F).¹¹

The organics from the aqueous phase (Stream 11) are combined with the organic phase from the decanter (Stream 8). The combined organics (Stream 12) are fed to a drying column, where residual water is removed as a bottoms stream (Stream 13). The water removed from the drying



NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents.

Figure 2. Basic operations that may be used for vinylidene chloride production from 1,1,2-trichloroethane.

column is fed to the steam stripper with the aqueous stream from the product decanter (Stream 10).¹¹

The organic stream from the drying column (Stream 14) is fed to a distillation column, which removes unreacted 1,1,2-trichloroethane as overheads (Stream 15). The unreacted trichloroethane is recycled to the dehydrochlorination reactor. Purified VDC product, removed as bottoms from the finishing column (Stream 16), is used onsite or stored in pressurized tanks before being shipped to users.¹¹

Emissions

Uncontrolled VDC emission factors for VDC production are given in Table 2. The table also lists potentially applicable control techniques and associated controlled emission factors. The emission factors were developed based on published data for individual plants and for general processing techniques. Because of variation in process design, age of equipment, and other process parameters, actual emissions vary for each plant.

Process Vent Emissions--

Process vents which are sources of VDC emissions include the reactor nitrogen purge vent (Vent A, Figure 2) and the distillation column vents (Vents B, Figure 2). Uncontrolled VDC emission factors are estimated at 6.2 kilograms VDC per megagram VDC produced (kg/Mg) for the reactor vent, and 0.7 kg/Mg for the distillation vents.¹³

Emissions from the reactor vent can be controlled by incineration with an efficiency of about 98 percent or higher.^{14,15,39} The major products of VDC incineration are CO₂ and HCl. However, under poor incinerator operating conditions, other products may be formed, including formic acid, carbon monoxide, chloroacetyl chloride, phosgene, and formaldehyde. Incineration destruction efficiency varies with emission stream properties and incinerator operating parameters. The 98 percent efficiency level is a conservative estimate of the control that may be expected at a temperature of at least 870°C and a residence time of at least 0.75 seconds.^{15,39} The emission reduction may be greater than 98 percent for incineration of VDC with these operating parameters,

TABLE 2. ESTIMATED CONTROLLED AND UNCONTROLLED VINYLIDENE CHLORIDE EMISSION FACTORS FOR A HYPOTHETICAL VINYLIDENE CHLORIDE PRODUCTION FACILITY^a

Emission source	Source designation ^b	Uncontrolled VDC emission factor ^c	Potentially applicable controls	Percent reduction	Controlled VDC emission factor
Reactor vent	A	6.2 kg/Mg	Incinerator	98+	≤0.12 kg/Mg
			NA ^d	NA	0.063-0.090 kg/Mg
Distillation vents	B	0.7 kg/Mg	Aqueous scrubber	90	0.070 kg/Mg
			Refrigerated condenser	90	0.070 kg/Mg
			NA	NA	0.18-0.38 kg/Mg
Storage and handling ^e	D	NA	Pressurized tank	NA	NA
			Refrigerated condenser	NA	NA
			NA	NA	0.056 kg/Mg
Fugitive process ^f	E	0.96 kg/hr ^g	Quarterly I/M ^h		0.76 kg/hr
			Monthly I/M	29	0.70 kg/hr
			Monthly I/M; double seals on pumps; and rupture disks on relief valves	88	0.12 kg/hr

^aAny given vinylidene chloride plant may vary in configuration and level of control from this hypothetical facility. 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.

^bLetters refer to vents designated in Figure 2.

^cEmission factors in terms of kg/Mg refer to kilogram of vinylidene chloride emitted per megagram of vinylidene chloride produced. In cases where a particular source designation applies to multiple operations, these factors represent combined emissions for all, not each, of those operations within the hypothetical facility.

^dNot available.

^eHandling refers to loading of barges, trucks, railcars, etc.

^fDerivations of emission rates and potential emission reductions are given in the Appendix. Fugitive emission rate is independent of plant capacity.

^gThis rate represents a relatively uncontrolled facility where no significant leak detection and repair programs are in place to limit fugitive emissions.

^hI/M refers to inspection and maintenance. Industry reports that more stringent I/M programs are practiced than are reflected in the reductions in this table. (See text for discussion.) These more stringent measures result in fugitive emission control efficiencies as high as 90 to 95 percent.^{18,19}

and would also increase at higher temperatures and longer residence times.¹⁵ A 98 percent reduction of reactor vent emissions corresponds to a controlled VDC factor of about 0.12 kg/ Mg VDC produced. Controlled reactor vent emissions reported for specific plants range from 0.063 kg/Mg to 0.090 kg/Mg.¹⁶

VDC emissions from the distillation column vents can be controlled either by aqueous scrubbing or by refrigerated vent condensers with an efficiency of about 90 percent.^{14,17} The distillation column vents can also be combined with reactor emissions and controlled by incineration with a 98 percent or greater control efficiency.³⁹ The control efficiency attainable using these techniques is dependent on operating parameters and emission stream characteristics. A 90 percent reduction of distillation column vent emissions corresponds to a controlled emission factor of about 0.07 kg/Mg VDC produced. Controlled VDC emissions reported for distillation vents at specific plants range from 0.18 kg/Mg to 0.38 kg/Mg.¹⁶

Storage and Handling Emissions--

Vinylidene chloride emissions result from the storage of VDC product and intermediates containing VDC (Source D, Figure 2). VDC emissions also occur where VDC product is loaded to tank cars of trucks. Insufficient data were available to estimate uncontrolled emissions of VDC from storage and handling. Controlled storage and handling emissions of VDC reported for two specific facilities were about 0.056 kg/Mg VDC produced.¹⁶ The types of controls used to attain this emission rate are not known. Controls typically used to reduce storage and handling emissions include pressurized storage tanks and refrigerated vapor condensers.

Process Fugitive Emissions--

Fugitive emissions of VDC, 1,1,2-trichloroethane, and other volatile organic compounds result from leaks in process valves, pumps, compressors, and pressure relief valves (Source D, Figure 2). Fugitive emissions from a typical VDC plant were estimated based on process flow diagrams, process operation data, and emission factors developed by EPA

for typical process emission sources. The techniques used to estimate the numbers of various fugitive emission sources and the total fugitive emission rate are described in detail in the Appendix.

The estimated uncontrolled fugitive emission rate for VDC production from 1,1,2-trichloroethane is about 0.96 kg VDC/hr. Fugitive emission rates differ from plant to plant depending on the number of valves, pumps, flanges, etc., the age of the equipment, and the level of emission control used. Chemical process streams in the production of chlorinated hydrocarbons such as VDC generally contain chlorine and HCl, as well as hydrocarbons. These compounds are extremely corrosive and irritating when exposed to the moisture in ambient air. Thus, it is general practice to control such fugitive emissions in order to prevent corrosion of outside equipment and generation of unpleasant odors.¹⁸

Table 2 gives control efficiencies for preventative maintenance programs, the use of double mechanical seals of pumps, and the use of rupture disks with relief valves. Other controls which may be used include the use of welded pipe in place of flanges, special construction materials for piping and valves, enclosure of pumps, and intensive preventative maintenance during plant shutdown. In addition, inspection and maintenance programs practiced at some plants may be much more intensive than those shown on Table 2, such that most leaks are repaired within as little as 1 day. With these additional controls, industry reports fugitive emission control efficiencies as high as 90 to 95 percent.^{18,19}

Secondary Emissions--

Secondary emissions result from the handling and disposal of process waste streams. In VDC production from 1,1,2-trichloroethane, wastewater from the VDC production reaction (Source F, Figure 2) is a potential source of secondary VDC emissions. Specific data were not available to estimate emissions from the treatment and disposal of this stream. Figure 2 shows that a wastewater stripper typically is incorporated as part of the VDC production process to reduce VDC emissions and for product recovery.¹¹ Emissions from treatment of

contaminated wastewater are discussed in further detail in the section entitled VOLATILIZATION FROM WASTE TREATMENT, STORAGE, AND DISPOSAL

Source Locations

Major vinylidene chloride producers and production locations are listed in Table 3.20

TABLE 3. PRODUCERS OF VINYLIDENE CHLORIDE²⁰

Manufacturer	Location
Dow Chemical U.S.A.	Freeport, TX Plaquemine, LA
PPG Industries, Inc. Chemicals Group Chemical Division	Lake Charles, LA

Note: 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. The level of VDC 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.

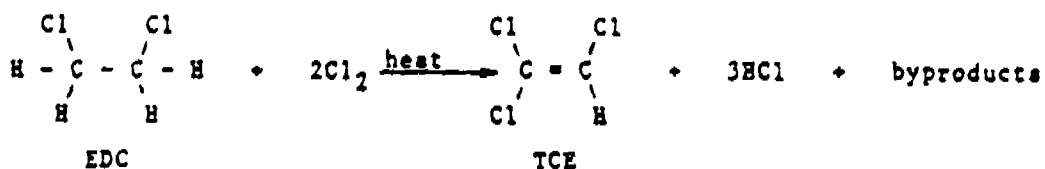
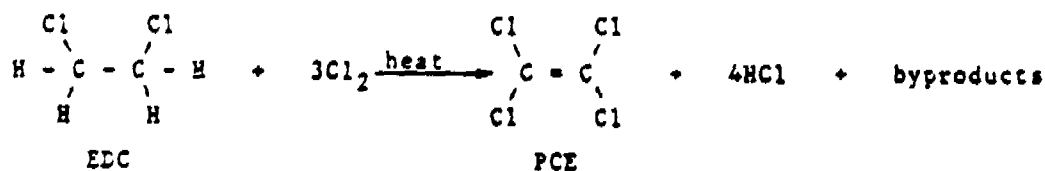
PERCHLOROETHYLENE AND TRICHLOROETHYLENE PRODUCTION

Perchloroethylene (PCE) and trichloroethylene (TCE) are produced separately or as coproducts by either chlorination or oxychlorination of ethylene dichloride (EDC) or other C_2 chlorinated hydrocarbons. A number of byproducts are produced in each of these reactions, including vinylidene chloride (VDC). These byproducts may be isolated and refined, recycled to the process, or discharged in various waste streams. For instance, in a case where VDC is produced from 1,1,2-trichloroethane at a facility which also produces TCE and PCE, the VDC byproduct may be recovered and purified by distillation in the VDC finishing section of the 1,1,2-trichloroethane process.¹² Raw material ratios and reactor conditions determine the relative proportions of PCE, TCE, and any byproducts produced.

Process Descriptions

Ethylene Dichloride Chlorination Process--

The overall reactions for the chlorination of EDC to produce TCE and PCE, are as follows:



VDC is among the byproducts produced in these reactions. Basic operations that may be used in the EDC chlorination process are shown in Figure 3.²¹

Ethylene dichloride (Stream 1) and chlorine (Stream 2) are vaporized and fed to the reactor. Other chlorinated C_2 hydrocarbons or recycled chlorinated hydrocarbon byproducts may also be fed to the

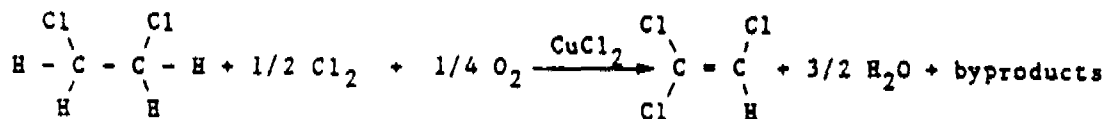
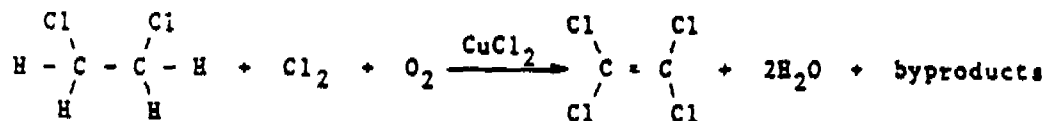
reactor. In the reactor, a chlorination reaction is carried out at 400° to 450°C, slightly above atmospheric pressure. The reaction produces the desired products TCE and PCE, as well as byproducts, including vinylidene chloride and hydrogen chloride. Hydrogen chloride byproduct (Stream 3) is removed as an overhead stream from the chlorinated hydrocarbon mixture (Stream 4) produced in the reactor. The chlorinated hydrocarbon mixture (Stream 4) is neutralized with sodium hydroxide solution (Stream 5) and dried.²¹

The dried crude product (Stream 7) is separated by a distillation column into crude TCE (Stream 8) and crude PCE (Stream 9). The crude TCE (Stream 8) is fed to two columns in series which remove light ends (Stream 10) and heavy ends (Stream 13). TCE (Stream 12) is taken overhead from the heavy ends column and sent to TCE storage; the heavy ends (Stream 13) and the light ends (Stream 10) are combined, stored, and recycled.²¹

The crude (Stream 9) from the PCE/TCE separation column is sent to the PCE column, where PCE (Stream 14) is removed as an overhead stream to PCE storage. Bottoms from this column (Stream 15) are sent to a heavy ends column and separated into heavy ends and tars. Heavy ends (Stream 16) are stored and recycled, and tars are incinerated.²¹

Ethylene Dichloride Oxychlorination Process--

The overall reactions for the production of perchloroethylene and trichloroethylene by EDC oxychlorination are as follows:



The crude product contains 85 to 90 weight percent PCE plus TCE, and 10 to 15 weight percent byproduct organics, including VDC. Essentially all byproduct organics are recovered during purification and are

recycled to the reactor. The process is very flexible, so that the reaction can be directed toward the production of either PCE or TCE in varying proportions. Side reactions produce carbon dioxide, hydrogen chloride, and several chlorinated hydrocarbons. Figure 4 shows basic operations that may be used in oxychlorination.¹⁰

Ethylene dichloride (Stream 1), chlorine or hydrogen chloride (Stream 2), and oxygen (Stream 3) are fed in the gas phase to a fluid bed reactor. The reactor contains a vertical bundle of tubes with boiling liquid outside the tubes which maintains the reaction temperature at about 425°C. The reactor is operated at a pressure slightly above atmospheric, and the catalyst, which contains copper chloride, is continuously added to the tube bundle with the crude product.²¹

The reactor product stream (Stream 4) contains the desired products TCE and PCE, as well as byproducts including VDC. This stream is fed serially to a water cooled condenser, a refrigerated condenser, and a decanter. The noncondensed inert gases (Stream 5), consisting of carbon dioxide, hydrogen chloride, nitrogen, and a small amount of uncondensed chlorinated hydrocarbons, are fed to an absorber, where hydrogen chloride is recovered by absorption in process water to make byproduct hydrochloric acid (Stream 6). The remaining inert gases are purged (Vent A).²¹

In the decanter, the crude product (Stream 7) is separated from the aqueous phase and catalyst fines (Stream 8) and sent to the drying column for removal of dissolved water by azeotropic distillation. The dried crude product (Stream 10) is separated into crude TCE (Stream 11) and crude PCE (Stream 12) in a PCE/TCE column. The aqueous phase from the decanter (Stream 8) and the water from the drying column (Stream 9) are sent to waste treatment.²¹

The crude TCE (Stream 11) is sent to the TCE column, where light ends (Stream 13) are removed to be stored and recycled. The bottoms (Stream 14), containing mainly TCE, are neutralized with ammonia and then dried to produce finished TCE (Stream 15) which is sent to the TCE storage.²¹

The crude PCE (Stream 12) from the PCE/TCE separation column is fed to a heavy ends removal column where PCE and light ends (Stream 16) go

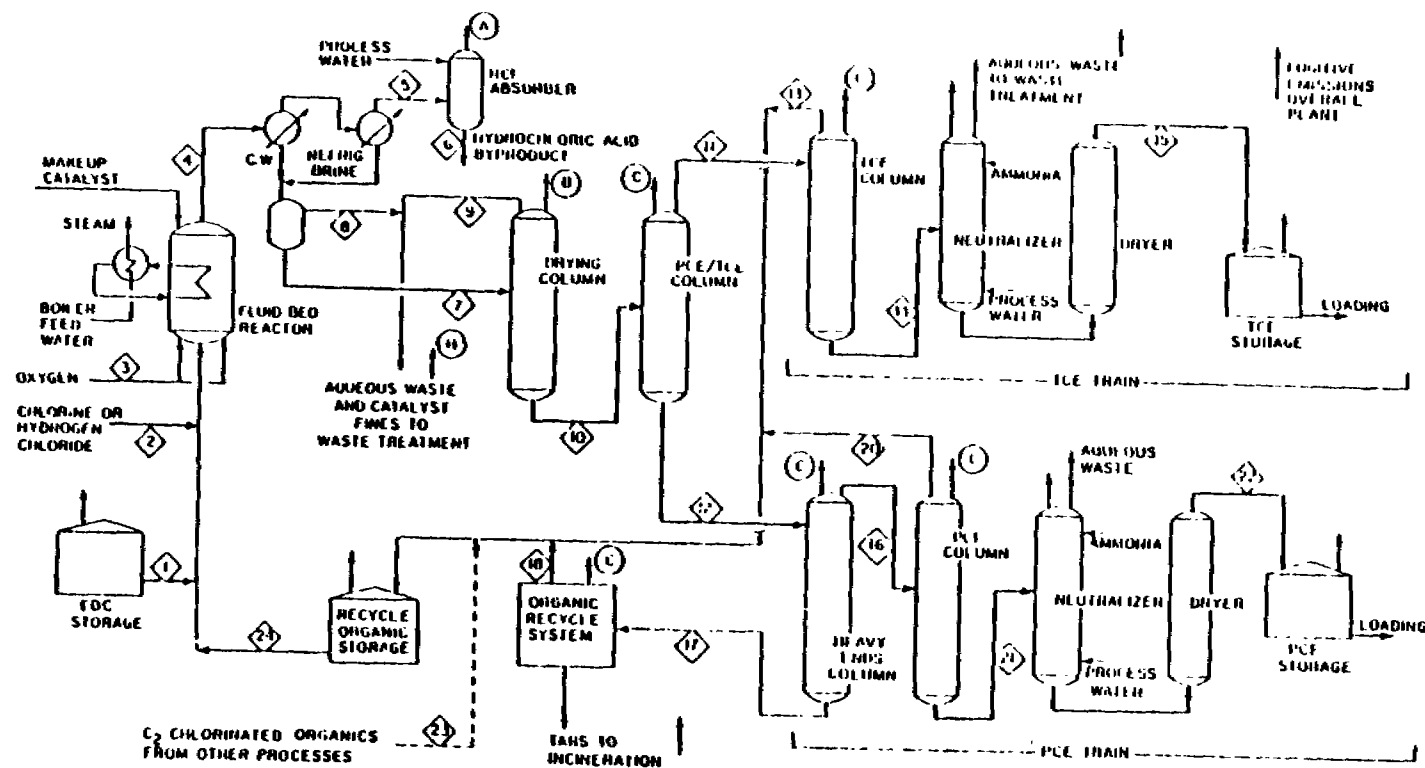


Figure 4. Basic operations that may be used in perchloroethylene and trichloroethylene production by oxychlorination of ethylene dichloride.¹⁰

overhead to a PCE finishing column, and the heavy ends (Stream 17) remaining as the bottoms are sent to the organic recycle system. Here, the organics that can be recycled (Stream 18) are separated from tars and sent to the recycle organic storage. The tars are incinerated. The PCE and light ends (Stream 16) from the heavy ends column are fed to a light ends removal column. Light ends (Stream 20) are removed overhead and are stored and recycled. The PCE bottoms (Stream 21) are neutralized with ammonia and then dried to obtain finished PCE (Stream 22) which is sent to PCE storage.²¹

Emissions

Process Vent Emissions--

Table 4 gives emissions data for process vents in PCE and TCE production processes which may contain VDC. The table lists: uncontrolled VDC emission factors, potentially applicable control techniques, and associated controlled VDC emission factors.²² These emissions data were developed based on published information for general operations used in the production of PCE and TCE. Variations in process design, feed materials, and reaction conditions have a substantial effect on amounts of VDC and other byproducts produced by PCE and TCE production processes. As a result, VDC emissions vary for each plant.

Chlorination process- Vents containing VDC in the EDC chlorination process include the neutralization and drying vent (Vent A, Figure 3), and distillation column vents (Vents B, Figure 3). Uncontrolled VDC emission factors are estimated at 2.5 kilograms per megagram PCE and TCE produced (kg/Mg), for the neutralization and drying vent, and 0.106 kg/Mg PCE and TCE, for the distillation vent.²²

Emissions from both of these sources can be controlled by refrigerated vapor condensers with an efficiency of about 80 percent.¹⁴ The control efficiency attainable using refrigeration is dependent on emission stream characteristics and condenser operating temperatures.

Oxychlorination process - Vent streams containing VDC in the EDC oxychlorination process include the reactor vent (Vent A, Figure 4), the drying column vent (Vent B, Figure 4) and the distillation column vents

TABLE 4. ESTIMATED CONTROLLED AND UNCONTROLLED VINYLIDENE CHLORIDE EMISSION FACTORS FOR
HYPOTHETICAL PERCHLOROETHYLENE/TRICHLOROETHYLENE PRODUCTION PROCESSES^a

Emission source	Source designation ^b	Uncontrolled VDC emission factor (kg/Mg) ^c	Potentially applicable controls	Percent reduction	Controlled VDC emission factor (kg/Mg)
<u>Chlorination</u>					
Neutralization and drying vent	A	2.5	Refrigerated condenser	80	0.50
Distillation vents	B	0.186	Refrigerated condenser	80	0.021
<u>Oxychlorination</u>					
Reactor vent	A	3.8	Thermal oxidation	98+	≤0.076
Drying column vent	B	0.4	Thermal oxidation	98+	≤0.008
Distillation vents	C	0.098	Aqueous scrubbing	90	0.020

^aAny given perchloroethylene/trichloroethylene plant may vary in configuration and level of control from these 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.

^bLetters refer to vents designated in Figure 3 for chlorination and Figure 4 for oxychlorination.

^cEmission factors in terms of kg/Mg refer to kilogram of vinylidene chloride emitted per megagram of perchloroethylene and trichloroethylene produced. In cases where a particular source designation applies to multiple operations, these factors represent combined emissions for all, not each, of these operations within the hypothetical facility.

(Vent C, Figure 4). Uncontrolled VDC emission factors have been estimated at 0.4 kg/Mg PCE and TCE produced, for the drying column vent, and 0.098 kg/Mg PCE and TCE, for the distillation column vent.²²

The uncontrolled emission rate given in Table 4 for the reactor vent was calculated based on a total chlorinated hydrocarbon emission factor for the reactor vent of 21.3 kg chlorinated hydrocarbon emitted per megagram PCE and TCE produced.²² It was assumed that the fraction of the total chlorinated hydrocarbons comprised by VDC in the reactor vent is the same as the fraction of chlorinated hydrocarbons comprised by VDC in the drying column vent. In the drying column vent, VDC comprises about 18 percent of total chlorinated hydrocarbon emissions.²² Thus, VDC emissions from the reactor vent were estimated as follows:

$$(21.3 \text{ kg Cl species/Mg}) \times (0.18 \text{ kg VDC/kg Cl species}) = 3.8 \text{ kg VDC/Mg}$$

Emissions from the reactor and drying column vents can be controlled by incineration with an efficiency of about 98 percent or higher.^{14,15} Emissions from the distillation column vent can be controlled by aqueous scrubbing with an efficiency of about 90 percent.¹⁴

Other Emission Sources--

In addition to process vents, potential VDC emission sources from PCE and TCE production include storage and handling operations, process fugitive sources, and treatment and disposal of process wastes. VDC is expected to be emitted from recycle storage tanks in both the chlorination and oxychlorination processes for PCE and TCE production (Vent C in Figure 3, and Vent D in Figure 4). VDC is also emitted from any pumps, compressors, flanges, and valves which are exposed to streams containing VDC (Source E in Figure 3 and Source I in Figure 4). Insufficient information is available to estimate VDC emissions from these sources.

Source Locations

Major producers of perchloroethylene and/or trichloroethylene are listed in Table 5.²⁰

TABLE 5. FACILITIES PRODUCING PERCHLOROETHYLENE
AND/OR TRICHLOROETHYLENE²⁰

Company	Location	Chemical produced	
		PCE ^a	TCE ^b
Diamond Shamrock Corp.	Deer Park, TX	X	
Dow Chemical U.S.A.	Freeport, TX	X	X
	Pittsburg, CA	X	
	Plaquemine, LA	X	
E.I. duPont de Nemours and Co.	Corpus Christi, TX	X	
PPG Industries, Inc.	Lake Charles, LA	X	X
Strauffer Chemical Co.	Louisville, KY ^c	X	
Vulcan Materials Co.	Geismar, LA	X	
	Wichita, KS	X	

^aPCE = perchloroethylene

^bTCE = trichloroethylene

^cPlant has been on standby since 1981.

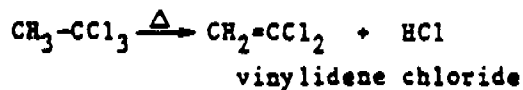
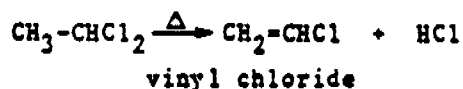
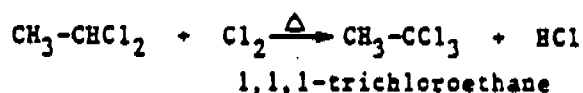
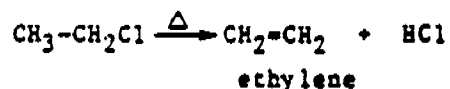
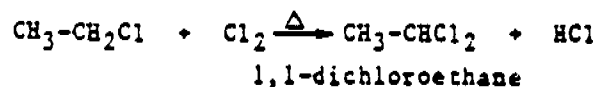
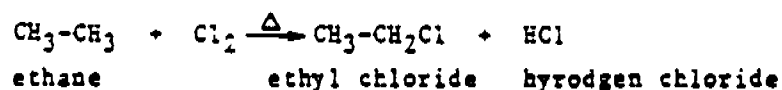
Note: This is a list of major facilities producing perchloroethylene and/or trichloroethylene by any production process. Current information on which of these facilities produce these chemicals by ethylene dichloride chlorination or oxychlorination is not available. This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current listings or the plants themselves. The level of emissions from any given facility is a function of variables, such as operating conditions, product slate, throughput and control measures, and should be determined through direct contacts with plant personnel. Under some operating conditions, byproduct VDC production may be negligible, resulting in negligible or zero VDC emissions. For instance, Dow chemical has indicated that VDC byproduct is only produced in trace quantities at all of its three plants.¹⁹

1,1,1-TRICHLOROETHANE PRODUCTION

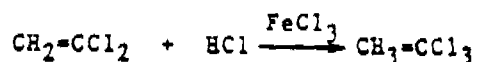
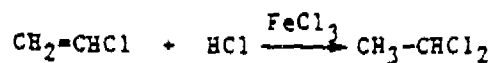
Most 1,1,1-trichloroethane produced in the U.S. is made from vinyl chloride. An ethane-based process currently is used to a lesser extent. Also, a process starting from VDC formerly was used to produce 1,1,1-trichloroethane.^{10,23} This section discusses VDC emissions from the ethane process, which produces VDC as a byproduct. VDC is not produced as a byproduct of the vinyl chloride process.

Process Description

In the ethane process for 1,1,1-trichloroethane production, ethane is chlorinated to produce the product 1,1,1-trichloroethane and a number of byproducts. The main reactions in the chlorination process are as follows:



Minor quantities of 1,2-dichloroethane and 1,1,2-trichloroethane are also produced. Raw material ratios and reactor conditions determine the relative proportions of 1,1,1-trichloroethane and byproducts produced. If 1,1,1-trichloroethane is the only product desired, ethyl chloride and 1,1-dichloroethane can be recycled to the chlorination reactor, and vinyl chloride and VDC can be catalytically hydrochlorinated to yield 1,1-dichloroethane and 1,1,1-trichloroethane, respectively.²³



Basic operations which may be used in the ethane process for 1,1,1-trichloroethane are shown in Figure 5.²³ In this process, byproduct chlorinated species, including VDC, are recycled and converted to 1,1,1-trichloroethane.²³ Chlorine (Stream 1) and ethane (Stream 2) are fed to the chlorination reactor along with recycle streams of 1,1-dichloroethane (Stream 13) and ethyl chloride (Stream 17). The reactor is adiabatic, with a residence time of about 15 seconds, and is maintained at a pressure of about 600 kiloPascals (5.9 atmospheres) and an average temperature of about 400°C. No catalyst is used.

The reactor exit stream (Stream 3) is a gas containing ethane, ethylene, vinyl chloride, ethyl chloride, VDC, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,2-trichloroethane, 1,1,1-trichloroethane, hydrogen chloride, and minor amounts of other chlorinated hydrocarbons. This stream enters a quench column, where it is cooled, and a residue comprising mainly tetrachloroethanes and hexachloroethane is removed (Stream 4).

The overhead stream from the quench column (Stream 5) is fed to a hydrogen chloride column, in which ethane, ethylene, and HCl are removed from chlorinated hydrocarbons. A portion of the overheads (Stream 5) containing HCl is used to provide the HCl requirements for VDC and vinyl chloride hydrochlorination in a later step. The remainder (Stream 7) is purified for use in other processes.

The bottoms from the HCl column (Stream 8), containing chlorinated hydrocarbons, are fed to a heavy ends column, where a bottoms stream (Stream 9), comprising mainly 1,2-dichloroethane and 1,1,2-trichloroethane, is removed for use in other processes. Overheads from the heavy ends column (Stream 10), containing 1,1,1-trichloroethane, vinyl chloride, VDC, ethyl chloride and 1,1-dichloroethane, are fed to the 1,1,1-trichloroethane column, which removes the product as a bottoms stream (Stream 11).

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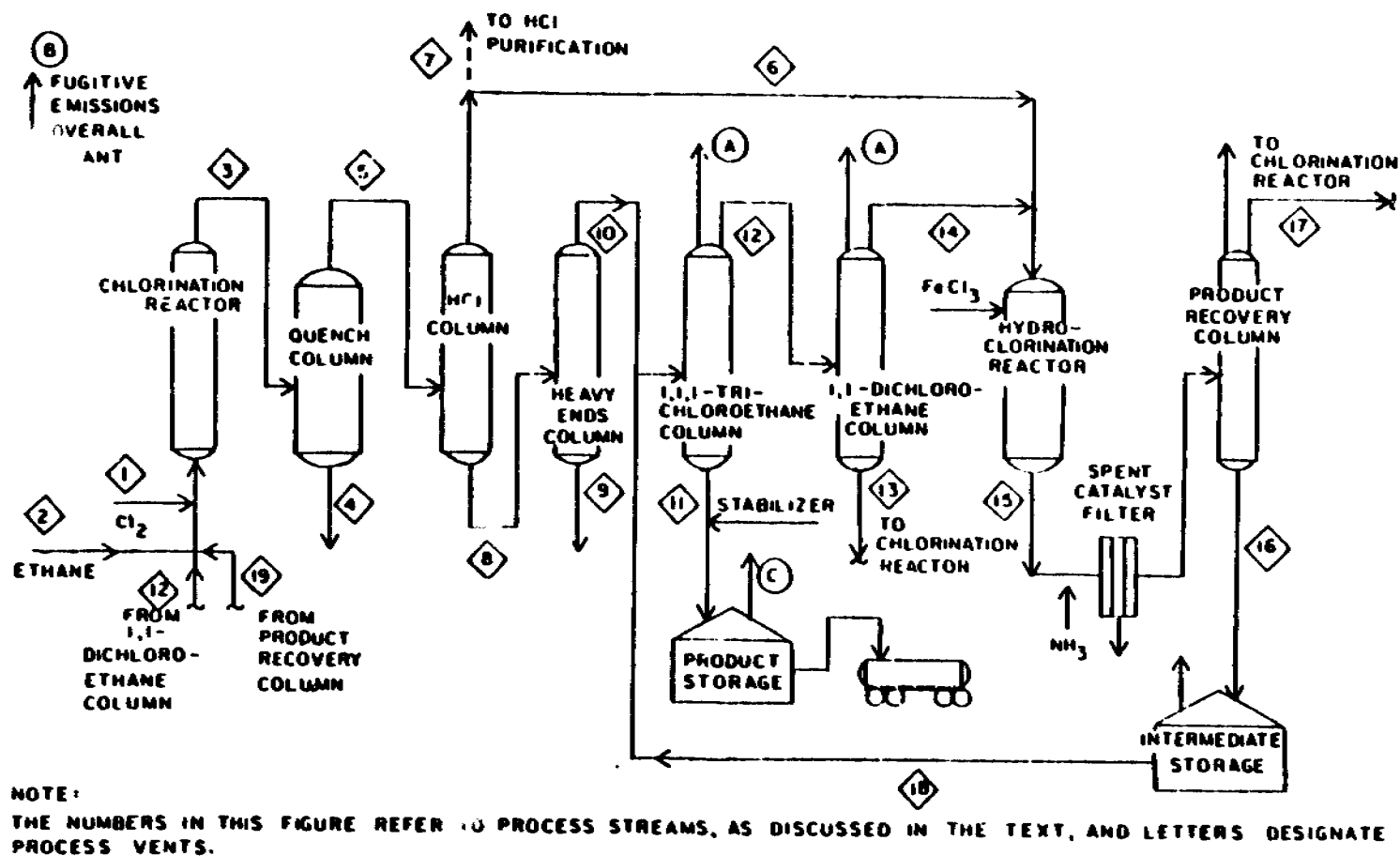


Figure 5. Basic operations that may be used in the production of 1,1,1-trichloroethane from ethane.²⁾

Overheads from the product recovery column (Stream 12) are fed to another column, where 1,1-dichloroethane is removed as bottoms (Stream 13) and recycled to the chlorination reactor. Overheads from this column (Stream 14), containing mainly vinyl chloride, VDC and ethyl chloride, are fed along with the HCl byproduct stream (Stream 6) to a hydrochlorination reactor. This reactor operates at a temperature of about 65°F, a pressure of about 450 kPa, and with ferric chloride catalyst. Alternatively, these byproducts may be used in other processes at the plant.

The hydrochlorination reactor converts vinyl chloride and VDC to 1,1-dichloroethane, and 1,1,1-trichloroethane, respectively. Thus, the reactor product stream (Stream 15) consists of unreacted ethyl chloride and 1,1-dichloroethane and 1,1,1-trichloroethane. This product stream is mixed with ammonia to neutralize residual HCl and catalyst. Spent neutralized catalyst is removed in a filter and the product is then fed to a product recovery column. The bottoms from this column (Stream 16), mostly 1,1,1-trichloroethane, are recycled to the 1,1,1-trichloroethane column. Overheads (Stream 17), composed of ethyl chloride and 1,1-dichloroethane, are recycled to the chlorination reactor.²³

Emissions

Potential VDC emission sources from the ethane process for 1,1,1-trichloroethane include (1) the vents for the 1,1,1-trichloroethane and 1,1-dichloroethane distillation columns (Source A) and (2) process fugitive sources, such as valves, flanges, pumps, relief valves, and drains, located between the chlorination reactor and the hydrochlorination reactor. Data from one plant indicate that the concentration of VDC in the distillation column vents is negligible.²⁴ Data are not available to estimate fugitive emissions of VDC from the ethane process.

Source Locations

Major producers of 1,1,1-trichloroethane are listed in Table 6.^{10,20} Information is not available on which of these plants use the vinyl chloride process and which use the ethane process.

TABLE 6. FACILITIES PRODUCING 1,1,1-TRICHLOROETHANE^{10,20}

Company	Location
Dow Chemical U.S.A.	Freeport, TX
PPG Industries, Inc.	Lake Charles, LA
Vulcan Chemicals	Geismar, LA

Note: This is a list of major facilities producing 1,1,1-trichloroethane by any production process. Current information on which of these facilities produce this chemical from ethane or vinyl chloride is not available. This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current listings or the plants themselves. The level of emissions from any given facility is a function of variables, such as throughput and control measures, and should be determined through direct contacts with plant personnel.

POLYMERIZATION OF VINYLIDENE CHLORIDE

Vinylidene chloride monomer is polymerized with a variety of other monomers to produce copolymers with special properties. VDC copolymers can be divided into high VDC polymers, generally containing 70 to 95 percent VDC, and low VDC polymers, generally containing 10 to 70 percent VDC.

High VDC polymers are unique in their low permeabilities to oxygen, water vapor, and other gases. They also have good clarity and a glossy appearance. High VDC polymers typically are used as vapor barrier coatings on various film substrates, such as paper, polyester, polypropylene, or polyethylene. High VDC polymers are also used to make Saran films which can be used alone or laminated to other plastic films. The comonomers most commonly used to produce high VDC polymers are vinyl chloride, acrylic acid, acrylic esters and acrylonitrile.^{2,25,26}

In low VDC polymers, the VDC monomer generally is added to improve the flame retardant properties of the finished polymer. Low VDC polymers are used as flame resistant coatings, saturants, dipping compounds, and adhesives. They can also be sprayed onto fibers and textiles. Typical comonomers used in these applications include acrylic esters, vinyl acetate, and vinyl chloride. VDC is used with styrene and butadiene monomers to produce a flame retardant styrene-butadiene latex for carpet backing. VDC is also used with acrylonitrile to produce modacrylic synthetic fibers.^{2,25,26}

Emissions from VDC polymerization are discussed in this section. Emissions of residual VDC monomer from the subsequent processing and fabrication of VDC in polymers are discussed in a later section. Copolymer production and fabrication generally are carried out at separate facilities.

Process Description

The reactions involved in the production of vinylidene chloride copolymers are illustrated in Figure 6. The major process used to produce VDC copolymers is emulsion polymerization. This polymerization technique can be used to produce both latex resin and dried resins.²⁵

Suspension polymerization is also used to produce dried resins, and solution polymerization is used to produce copolymers for synthetic fiber production.^{25,26} Table 7 summarizes the types of VDC copolymers produced and identifies production processes, typical comonomers used, VDC contents, and major applications for each resin type.^{25,26}

Emulsion Polymerization--

Basic operations which may be used in emulsion and suspension polymerization of VDC copolymers are shown in Figure 7.1.²⁴ VDC monomer (Stream 1), comonomer (Stream 2), and water (Stream 3) are metered and charged to a batch reactor along with surfactants and initiator (Stream 4). The batch is agitated, resulting in the formation of an emulsion of aqueous and organic phases. After charging, the batch is heated, causing the activation of the initiator. Initiators generally used in emulsion polymerization are water soluble peroxides which dissociate to form free radicals when heated. The initiator radicals, on contacting the organic monomer phase, initiate the polymerization of VDC and the comonomer. The polymerization reaction is exothermic; therefore, after the reaction has commenced, the reactor must be cooled. In emulsion polymerization, the reactor temperature typically is held at about 30°C and the reaction duration is about 7 to 8 hours. Additional monomer and initiator may be fed to the reactor during the course of the reaction. The degree of completion is 95 to 98 percent.^{2,25}

Generally, the polymerized batch (Stream 5) is stripped of unreacted monomers (Stream 6) using steam and vacuum. This can be done either in the reactor itself or in a separate stripping vessel. The unreacted monomer is recycled if possible (Stream 7). For some types of copolymers, contamination of VDC with other comonomers precludes the recycle of VDC. Stripped polymer (Stream 8) is transferred to a holding tank, where it may be mixed with other polymer batches to ensure product uniformity.²⁶

Emulsion polymerization can be used to produce either a latex (Stream 9) or a dry product (Stream 10). A latex is an emulsion of polymer particles in water, which is sold or used undried. If a dried product is desired, water is removed by coagulation and dewatering,

**TABLE 7. VINYLIDENE CHLORIDE COPOLYMERS, PRODUCTION METHODS,
AND APPLICATIONS^{23, 24}**

Polymer description	Production processes	Typical VDC content (percent)	Comonomers used	Applications
High VDC latex	Emulsion	90	Acrylic esters Acrylic acid Acrylonitrile Vinyl chloride	Barrier coatings for packaging films and paper packages
Thermoplastic resin	Emulsion, Suspension	70-85	Vinyl chloride	Packaging film, composite (multilayered) packaging films, monofilaments
Solvent soluble resin	Emulsion	90-95	Vinyl chloride Acrylic esters Acrylic acid	Barrier coating for cellophane
Low VDC latex	Emulsion	40-70	Acrylic esters Vinyl acetate Vinyl chloride Styrene-butadiene	Flame retardant coatings, dips, adhesives, etc., carpet backing
Modacrylic resin	Solution suspension	30	Acrylonitrile	Synthetic fibers

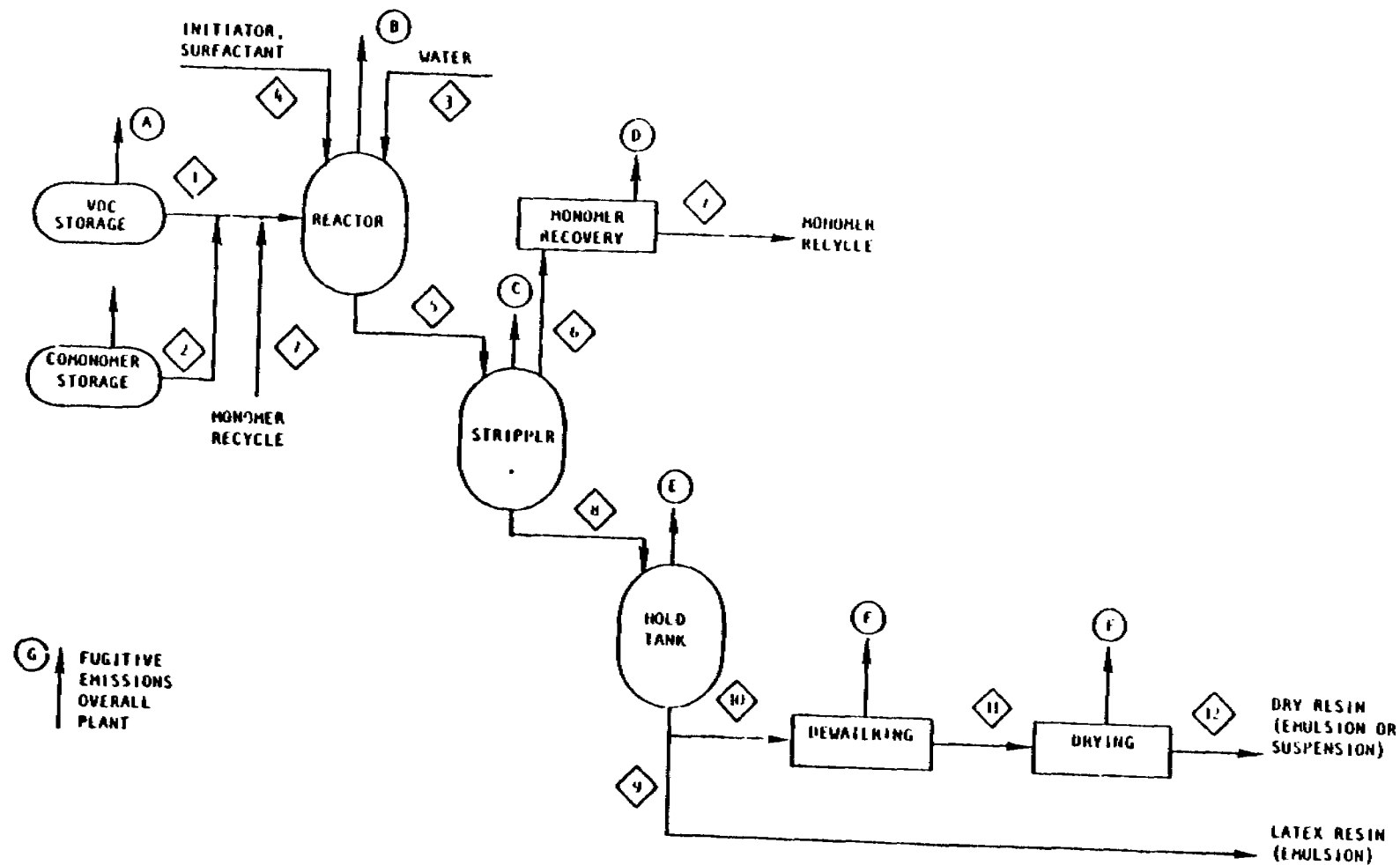


Figure 7. Basic operations that may be used for the production of vinylidene chloride copolymers. 1,24

followed by drying with hot air. The dried product comprises polymer particles. The particle diameter produced by emulsion polymerization is 100 to 150 nanometers.^{2,25}

Suspension Polymerization--

The same basic steps are used in suspension polymerization as in emulsion polymerization (Figure 7).¹ VDC (Stream 1), comonomer (Stream 2), and water (Stream 3) are metered and charged to a batch reactor along with surfactant and initiator (Stream 4). In suspension polymerization, the initiator used is soluble in the organic phase. The batch is agitated to produce a suspension of the organic phase in the water phase. After charging, the batch is heated to activate the initiator, which causes polymerization. The reactor must then be cooled to remove the heat of polymerization.^{2,25}

Suspension polymerization generally is carried out at about 60°C. The duration of the reaction is 30 to 60 hours and the degree of completion is about 85 to 90 percent.² After the polymerization reaction has reached the desired degree of completion, the polymer (Stream 5) generally is stripped of unreacted monomer (Stream 6) by steam and heat, either in the reactor or in a separate vessel. Unreacted monomer is recycled (Stream 7) or vented to a control system. The batch is then transferred to a holding tank (Stream 8) and dried (Stream 11) with hot air to produce dry polymer particles. Typical particle diameters produced by suspension polymerization range from 150 to 590 microns.^{2,25}

Solution Polymerization--

As noted above, solution polymerization is used on the production of vinylidene chloride copolymer synthetic fibers. These fibers typically have a low VDC content.^{2,25,26} Information is not available on the specific steps used in the solution polymerization of VDC copolymers; however, the general reaction steps are expected to be similar to those used in the solution polymerization of other resins.

In a solution polymerization process, the polymerization reaction is carried out in a solvent which dissolves both the monomers and the

finished polymer. Monomers, initiators, and solvents are charged to a polymerization reactor where the reaction typically is carried out under elevated temperature and pressure. The process can be carried out either in a batch process or a continuous process. In either case, the product is a homogeneous mixture of solvent, polymer, and unreacted monomers. Unreacted monomer may be stripped from the polymer/solvent mixture by the use of steam and heat. In a batch process, the stripping step may be carried out either in the reaction vessel or in a separate stripping vessel. In a continuous process, a separate stripping vessel is required.^{27,28}

The resulting polymer solution is used in a "spinning" process to produce the product synthetic fiber. In this step, polymer fibers are extruded into a zone of hot vapor or water, where the fibers are solidified and solvent and residual monomer are removed. This step is discussed in the subsequent section on the fabrication of VDC copolymer products.^{26,27,28}

Emissions

Potential VDC emissions sources at VDC polymerization plants include:

- VDC unloading and storage;
- opening and cleaning of mixing, weighing, holding, and reaction vessels;
- relief valve discharges;
- stripper and monomer recovery system vents;
- evaporation of residual VDC from the finished copolymer; and
- process fugitive sources, including valves, flanges, pumps, compressors, relief valves, and process drains.

Data are not available to estimate uncontrolled VDC emissions from these sources. However, in response to previous EPA surveys, several polymerization plants have reported total controlled emissions of vinylidene chloride and controlled emissions from a number of individual sources.^{16,25} Controlled VDC emission rates reported for VDC polymerization are given in Table 8.

Emission factors given in Table 8 for reactor emissions, monomer recovery emissions, storage and transportation emissions, and total

TABLE 8. ESTIMATED CONTROLLED VINYLIDENE CHLORIDE EMISSION FACTORS
FOR A HYPOTHETICAL VINYLIDENE CHLORIDE POLYMERIZATION PLANT^a

Emission source	Source designation ^b	Controlled VDC emission factor ^c
Reactor	B	3.5 kg/Mg ^d
Monomer recovery	D	0.33 kg/Mg ^d
Unloading/storage	A	2.1 kg/Mg ^d
Process fugitive	G	2.8-11 kg/Mg ^e
Total		1.4-7.0 kg/Mg ^d

^aAny given plant may vary in configuration and level of control from this hypothetical facility. 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.

^bLetters refer to vents designated in Figure 7.

^cEmission factors in terms of kg/Mg refer to kilogram of vinylidene chloride emitted per megagram of vinylidene chloride polymerized. In cases where a particular source designation applies to multiple operations, these factors represent combined emissions for all, not each, of these operations within the hypothetical facility. The types of controls employed were not reported.

^dBased on industry estimates.

^eBased on EPA projections of monomer emissions from small and medium sized generic polymerization plants with quarterly inspection and maintenances of valves, pumps, compressors, flanges, relief valves, and process drains.²⁹ Industry reports that more stringent inspection and maintenance programs are practiced than are reflected in the factors cited in this table. (See text for discussion.) These more stringent measures result in fugitive emission control efficiencies as high as 90 to 95 percent from an uncontrolled situation where no significant measures are taken for leak detection and repair.^{18,19}

plant emissions are based on industry estimates in response to EPA surveys.^{16,25} Data are not available on the specific controls used to attain the reported emission rates. Techniques which can be used to control process and storage emissions of monomers from polymerization plants are identified in Table 9.³⁰

The emission rates given in Table 8 for process fugitive sources are based on EPA estimates of emissions from typical small to medium sized generic polymerization facilities using monthly inspection and maintenance of fugitive sources.²⁷ The control efficiency of monthly inspection and maintenance for fugitive emissions is about 30 percent. Additional controls which might be used include double mechanical seals on pumps, enclosure of pumps, rupture disks on relief valves, use of welded pipe instead of flanges, special construction materials for piping and valves, and intensive preventative maintenance during plant shutdown. In addition, intensive inspection and maintenance programs practiced at some plants can insure repair of most leaks within 1 day instead of 1 month. With these additional controls, many plants have achieved fugitive emission control efficiencies as high as 90 to 95 percent.^{18,19}

Source Locations

Table 10 lists producers of VDC copolymers. The table also gives plant location and identifies the types of VDC copolymer produced at each facility.^{25,26,31}

TABLE 9. POTENTIAL EMISSION CONTROLS FOR POLYMER PLANTS³⁰

Process step	Potential emission points	Source designation ^a	Control technology
VDC unloading and storage	Loading lines, VC storage tank, mixing, weighing and holding tank vents	A	Purged to monomer recovery system, incineration, solvent absorption or carbon adsorption
Polymerization	Polymerization reactor opening loss	B	Solvent cleaning, steam piston, water piston, reactor purge air blower, steam purge, etc., used before opening Vented to atmosphere or monomer recovery system
	Polymerization reactor relief valve discharges	B	Shutstop, containment, instrumentation, improved operator training, etc.
Stripping	Stripping vessel vent	C	Vented to monomer recovery system followed by incineration, solvent absorption or carbon adsorption
Monomer recovery system	Recovery system exhaust vents and knock-out pot	D	Casholders used in some instances to collect all recovery vents and/or refrigeration to condense VDC followed by incineration, solvent absorption or carbon adsorption.
Polymer holding tanks, mixing	Tank vents	E	Stripping
Devulcanizing, drying	Centrifuge vents, dryer vent stacks	F	Stripping

^aLetters refer to sources designated in Figure 7. Note that these measures do not cover fugitive emissions from valves, pumps, flanges, etc.

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/ TABLE 10. FACILITIES PRODUCING POLYVINYLIDENE CHLORIDE^{18, 20, 25, 26, 31}

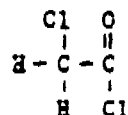
Manufacturer	Location	Products ^a
American Cyanamid Co.	Pace, FL	synthetic fibers
Borden Chemical Div.	Campton, CA Illioopolis, IL	
Dow Chemical Co.	Dalton, GA Midland, MI	low VDC latex high VDC latex, low VDC latex, thermoplastic resin
E.I. DuPont de Nemours and Co.	Circleville, OH	high VDC latex, thermoplastic resin
W.R. Grace and Co. Devey and Almy Chemical Div.	Owensboro, KY	high VDC latex
Monsanto Co.	Decatur, AL	synthetic fibers
Morton Chemical Co.	Ringwood, IL	high VDC latex
National Starch and Chem. Co.	Meredonia, IL	low VDC latex
Olin Corp.	Pisgah Forest, NC	high VDC latex
Reichhold Polymers, Inc.	Cheswold, DE	low VDC latex
Rohm and Haas, Inc.	Bristol, PA Knoxville, TN	low VDC latex low VDC latex
A.E. Staley Manufacturing Co.	Lemont, IL	high VDC latex

^aPolyvinylidene chloride copolymer formulations and uses are summarized in Table 6.

Note: 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. The level of VDC 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.

USE OF VINYLIDENE CHLORIDE IN SPECIALTY CHEMICAL PRODUCTION

Vinylidene chloride is used as a chemical intermediate in the production of chloroacetyl chloride. This use of VDC is minor in comparison with its use in production of VDC copolymers. The structure of chloroacetyl chloride is as follows:



Its main use is in the manufacture of chloroacetophenone, the principal ingredient in tear gas. It is also used in the manufacture of pharmaceuticals.^{7,9}

Process Description and Emissions

Information on the process used to produce chloroacetyl chloride from VDC is not available, nor are data available to estimate VDC emissions from the process. Dow Chemical reports no losses of VDC to the environment from the process used in chloroacetyl chloride production.⁹

Source Locations

The VDC process for chloroacetyl chloride is used by the Dow Chemical U.S.A., of Midland, Michigan.⁹ Production facilities are located at Dow Chemical's Michigan Division plant at Midland.¹⁸

VINYLDENE CHLORIDE COPOLYMER FABRICATION

When VDC is polymerized to produce VDC copolymers, some residual VDC monomer remains in the polymer. During subsequent fabrication, when the polymer is heated, dissolved, or otherwise treated, some of this residual monomer evaporates, resulting in VDC emissions. The level of VDC residue in the polymer, and hence the magnitude of VDC emissions, is dependent on the type of polymer, the comonomer used, and whether stripping technology is used at the polymerization plant.

As noted in the previous section entitled POLYMERIZATION OF VINYLDENE CHLORIDE, VDC copolymers can be divided into two groups: high-VDC copolymers (79 to 90 percent) used to form moisture and vapor barrier coatings and films; and low-VDC copolymers (10 to 70 percent), where VDC is added mainly to improve the flame retardant properties of the finished polymer. VDC copolymers are also produced in a number of forms: dried suspension resin, dried emulsion resin, latex, and polymer solution. The types of VDC copolymers produced, production methods used, and applications of the different types were summarized in Table 7 in the section entitled POLYMERIZATION OF VINYLDENE CHLORIDE. Generally, copolymer fabrication and copolymer production are carried out at separate facilities.

Process Descriptions

Process descriptions are presented below for three methods of fabricating high-VDC resins: coating of cellophane with copolymer solution, coating of paper or plastic film with latex, and extrusion of dried emulsion or suspension resin. Information was not available on the specific methods used to fabricate low-VDC resins.

Cellophane Coating with Copolymer Solutions--

Basic operations that may be used in the coating of cellophane with VDC copolymer are shown in Figure 8.³² The inputs to this process are a dried, high-VDC copolymer and pretreated cellophane film. The VDC polymer is first dissolved in a solvent mixture in a closed tank. The solvent mixture includes methyl ethyl ketone and tetrahydrofuran as the

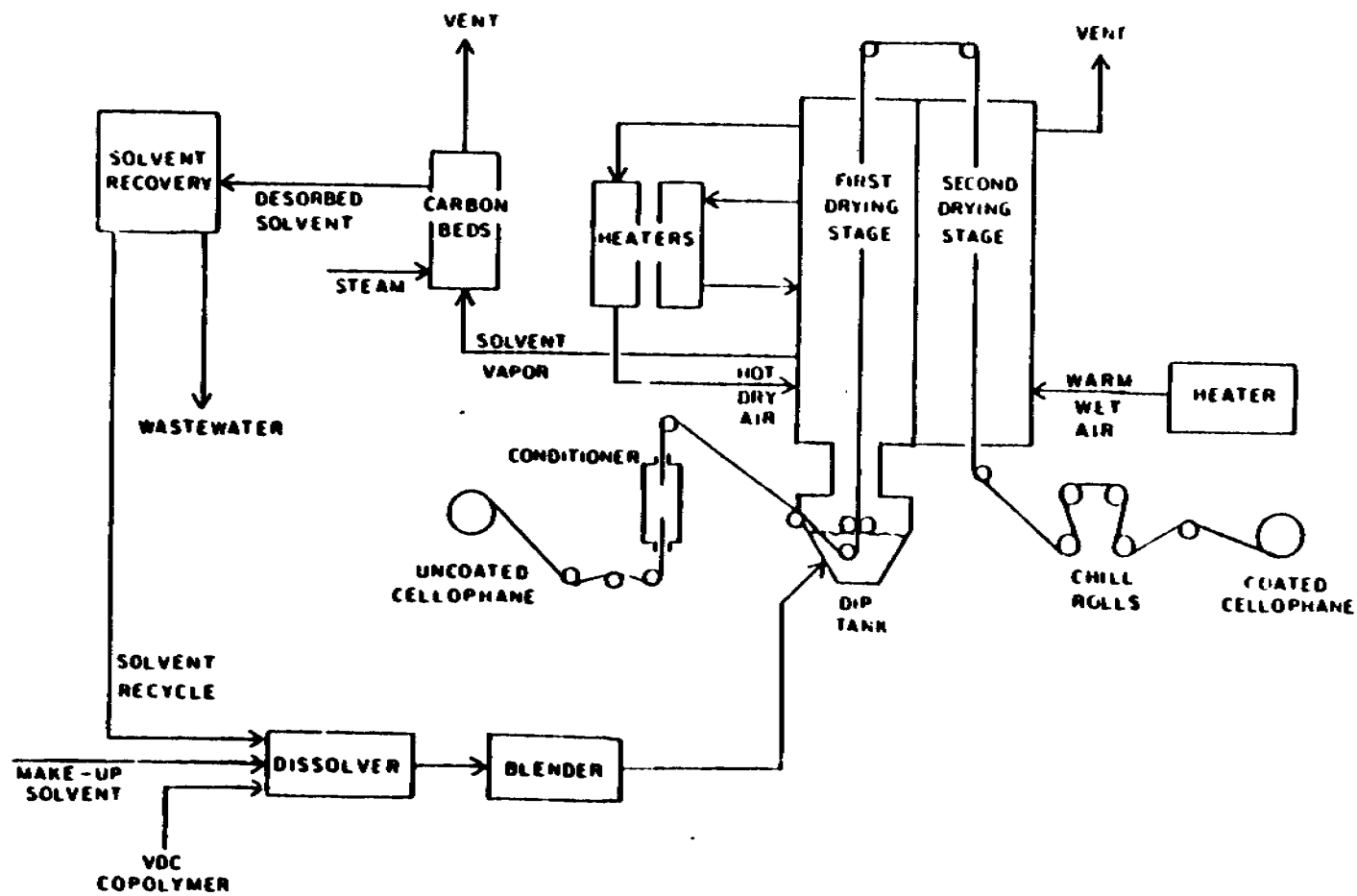


Figure 8. Basic operations that may be used in the coating of cellophane with high-VDC copolymer.¹²

primary solvents and toluene as a diluent. Following the dissolution step, additives such as wax, talc and silica are added in a closed blender. The polymer solution is then fed to a dip tank, through which a cellophane film strip is drawn.

After passing through the dip tank, the cellophane, now coated with VDC copolymer solution, is run through a dryer consisting of two chambers. In the first, dry air at 90 to 140°C is passed over the film, resulting in removal of the solvent.³² In the second chamber, the film is conditioned in warm humid air.

Solvent laden vapor is collected from the drying chamber and ducted to carbon absorption beds. Solvent stripped from the beds is purified by distillation and recycled to the process. Heating air from the second drying chamber is vented to the atmosphere.

Coating with Latex Copolymer--

As noted in the earlier section of POLYMERIZATION OF VINYLIDENE CHLORIDE, a latex is a polymer emulsion in water. Materials typically coated with high-VDC latex include paper products and plastic films.³²

The latex may first be blended with additives, such as wax or pigments, or diluted with additional water in a vented mixing tank. The latex is pumped from the mixing tank to a holding tank and then to the dip tank. The holding tank allows reduction of any foam that may form during mixing. The material to be coated is rolled through the dip tank and then to a drying oven. In the drying oven, water is removed from the latex and the latex forms a barrier film. Both the dip tank and the drying oven are vented to the atmosphere.³²

Extrusion of Thermoplastic Copolymer--

The raw material for extrusion is dried emulsion or suspension resin in the form of a powder or small granules. The polymer is mixed with additives such as plasticizer in a high-intensity blender. Mechanical energy dissipated in the blender heats the resin to about 170°C.³² The blender is vented through a hood, usually to a roof stack. From the high-intensity blender, the resin is fed to a ribbon blender, where it is homogenized further and cooled. The blended resin may be

stored prior to extrusion, or may be extruded immediately after blending.³²

The extrusion process used on high-VDC copolymers is a blown-film process. The resin compound is fed to an extruder, and is extruded through a die in the form of a tube, becoming molten in the extrusion process. The end of the tube is then pinched off, and air is blown into the tube, expanding it into a bubble. The bubble is then cooled by another blast of air and flattened before undergoing further processing to form a film.³²

Emissions

Emission sources from VDC copolymer fabrication include: polymer storage vents, polymer mixing and blending vents, and finished polymer drying. Emissions from individual sources have not been quantified. However, total VDC emissions from copolymer fabrication can be estimated by mass balance from the concentrations of residual VDC monomer in the polymer entering and leaving the process.³²

$$EF = C_i - C_o$$

where EF = the overall uncontrolled emission factor for the fabrication process, g VDC/Mg copolymer processed,

C_i = the concentration of residual VDC monomer in the copolymer entering the dissolver (Figure 8) ppmw, and

C_o = the concentration of residual VDC monomer in the copolymer leaving the dryer (Figure 8), ppmw.

Table 11 summarizes data on residual VDC levels in raw and fabricated high-VDC copolymers, and presents estimates of uncontrolled VDC emission factors for high-VDC copolymer fabrication processes. Data are not available on the residual VDC levels in low-VDC copolymers.

It should be noted that the mass balance technique of estimating emissions involves the assumption that the only removal mechanism for VDC from the copolymer is by emissions to the atmosphere. Thus, emissions estimates developed by the mass balance technique would be worst case estimates. In high temperature fabrication processes and drying processes, some of the residual VDC may be polymerized.

TABLE 11. ESTIMATES OF UNCONTROLLED EMISSION FACTORS FROM HIGH-VDC COPOLYMER FABRICATION PROCESSES

Process	Copolymer VDC concentrations (ppmw) ^a		Estimated uncontrolled emission factor (g/Mg) ^d
	Raw resin ^b (c _i)	Processed resin ^c (c _o)	
Cellophane coating	10-120	neg ^e	10-120
Latex coating	50-2000	0-500	50-1500
Extrusion	2-25	neg ^e	2-25

^aReference 32.

^bResin entering the dissolver (Figure 8).

^cResin leaving the dryer (Figure 8).

^dCalculated from residual VDC levels. Emissions are expressed in terms of grams of VDC per Mg of copolymer processed.

^eneg = negligible.

VDC emissions from copolymer fabrication generally are uncontrolled. In the first stage of the drying operation for cellophane coating, emissions containing solvent are captured and ducted to a carbon adsorption system. The solvent is then desorbed and recycled to the polymer dissolving operation. Some of the VDC vaporizing in the drying process would be captured on the adsorbers. However, unless some process is used to separate the captured VDC from the solvent, the VDC would be recycled to the process and eventually emitted from the second stage of the drying process, from the adsorber vent, or from another vent.

Source Locations

Table 12 gives a list of plants fabricating high-VDC copolymers, along with plant locations.^{31,32} The list includes plants that produce PVDC-coated cellophane, plants that apply PVDC barrier-coated to paper and plastics, and plants that extrude VDC copolymer.

Information is not available on the locations of fabrications of low-VDC polymers. Such plants would be classified under Standard Industrial Classification (SIC) code 282.

TABLE 12. FACILITIES FABRICATING HIGH VINYLIDENE CHLORIDE
COPOLYMERS^{31,32}

Company	Plant Location	Processes		Resin extrusion
		Cellophane coating	Barrier coating	
Allied Chemical Corp.	Pittsville, PA		X	
American Bag and Paper	Philadelphia, PA		X	
American Can Co.	Neenah, WI		X	X
Amtech, Inc.	Odenton, MD			X
Consolidated Paper	Wisconsin Falls, WI		X	
Crown Zellerbach	Portland, OR			
Cryovac Div. of W. R. Grace	Iowa Park, TX Simpsonville, SC		X	X
Curwood Div. of Bemis	New London, WI		X	
Daniels	Rhineland, WI		X	
Diversa-Pak	St. Petersburg, FL		X	
Dow Chemical	Midland, MI			X
E.I. duPont de Nemours	Richmond, VA	X		
	Circleville, OH		X	
	Clinton, LA	X		
	Tecumseh, KS	X		
FMC Corp.	Fredericksburg, VA	X		
	Marcus Hook, PA	X		
Gordon Cartons	Baltimore, MD		X	
Green Bay Packaging	Green Bay, WI		X	
Hercules	Covington, VA		X	
Interstate Folding Box	Middletown, OH		X	

Continued

TABLE 12. (Cont'd.) FACILITIES FABRICATING HIGH VINYLIDENE CHLORIDE COPOLYMERS^{31,32}

Company	Plant Location	<u>Processes</u>		Resin extrusion
		Cellophane coating	Barrier coating	
Michigan Carton Co.	Battle Creek, MI		X	
Milprint	Milwaukee, WI		X	
Minnesota Mining and Manufacturing	Decatur, AL		X	
Olin Corp.	Pisgah Forest, NC	X	X	
	Covington, IN	X		
Olinkraft	West Monroe, LA		X	
Oscar Mayer	Chicago, IL			X
	Davenport, IA			X
	Los Angeles, CA			X
	Madison, WI			X
	Nashville, TN			X
	Philadelphia, PA			X
Rexham	Memphis, TN		X	
Rhineland Div. of St. Regis	Rhineland, WI		X	
Sealed Air Corp.	Fairlawn, NJ		X	
Standard Packaging	Clifton, NJ		X	
Thilmany	Kaukauna, WI		X	
Union Carbide Corp.	Centerville, IA			X
Zumbril	Cincinnati, OH		X	

Note: 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. The level of VDC 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.

VOLATILIZATION FROM WASTE TREATMENT, STORAGE, AND DISPOSAL

Considerable potential exists for emissions of volatile substances, including VDC, from waste treatment, storage, and disposal facilities. VDC is expected to be present in the following wastes: still bottoms and wastewater from VDC production, perchloroethylene and trichloroethylene production, and trichloroethane production; wastewater and off-specification polymer from VDC polymerization; and still bottoms and wastewater from specialty chemical production processes where VDC is used as a feedstock. (See separate sections on emissions from these processes.) In addition, VDC may be present in wastes from other processes.

Potential Sources

VDC may be emitted when waste containing VDC is present in surface impoundments for treatment and storage of wastewater, open treatment and storage tanks, and land-treatment areas for solid wastes and sludges. The above 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 VDC if they receive wastewater from plants producing VDC either as a main product or as a byproduct, or from plants using VDC as an intermediate. Volatile compounds also may be emitted from solid wastes during and even after disposal in a covered landfill. Reference 33 summarizes general theoretical models for estimating volatile substance emissions from generic waste treatment, storage, and disposal operations, including surface impoundments, landfills, land treatment (landfarming), wastewater treatment, and drum handling and storage operations. If facilities of the above types are known to handle wastes containing VDC, the potential for air emissions should be considered.

Emissions³⁴

A pilot-scale study was conducted by EPA to evaluate the partitioning of several volatile organic pollutants, including VDC, in conventional wastewater treatment processes. The tested wastewater treatment system

consisted of a sequence of primary clarifier, aeration basin, and secondary aeration basin. Wastewater influent contained an average of 10.7 parts per billion (ppb) VDC. Over 98 percent of the VDC entering the pilot treatment system was found to evaporate, with about 65 percent evaporating from the primary clarifier and 33 percent from the aeration basin. The 98 percent evaporation rate corresponds to an emission factor of 0.98 grams VDC per gram VDC in the wastewater feed. It should be noted that these tests were conducted at low VDC concentrations (about 10 ppb); the emission factor may change at higher concentrations.

SECTION 5

SOURCE TEST PROCEDURES

Vinylidene chloride emissions can be measured using EPA Reference Method 23, which was proposed in the Federal Register on June 11, 1980.³⁵ The method has not been validated by EPA for vinylidene chloride, but a similar analytical procedure has been used to measure occupational exposures to VDC.^{36,37}

In Method 23, a sample of the exhaust gas to be analyzed is drawn into a Tedlar or aluminized Mylar bag as shown in Figure 9. Tedlar is considered a more reliable bag material than Mylar for VDC.³⁸ The bag is placed inside a rigid leak proof container and evacuated. The bag is then connected by a Teflon[®] sampling line to a sampling probe (stainless steel, Pyrex glass, or Teflon[®]) at the center of the stack. The sample is drawn into the bag by pumping air out of the rigid container.

The sample is then analyzed by gas chromatography (GC) coupled with flame ionization detection (FID). Analysis should be conducted within one day of sample collection. The recommended GC column is 3.05 m by 3.2 mm stainless steel, filled with 20 percent SP-2100/0.1 percent Carbowax 1500 on 100/120 Supelcoport. This column normally provides an adequate resolution of halogenated organics. (Where resolution interferences are encountered, the GC operator should select the column best suited to the analysis.) The column temperature should be set at 100°C. Zero helium or nitrogen should be used as the carrier gas at a flow rate of approximately 20 ml/min.

The peak area corresponding to the retention time of vinylidene chloride is measured and compared to peak areas for a set of standard gas mixtures to determine the VDC concentration. The range of the method is 0.1 to 200 ppm; however the upper limit can be extended by extending the calibration range or diluting the sample. To avoid absorption of VDC by the Tedlar bag, the sample should be analyzed as

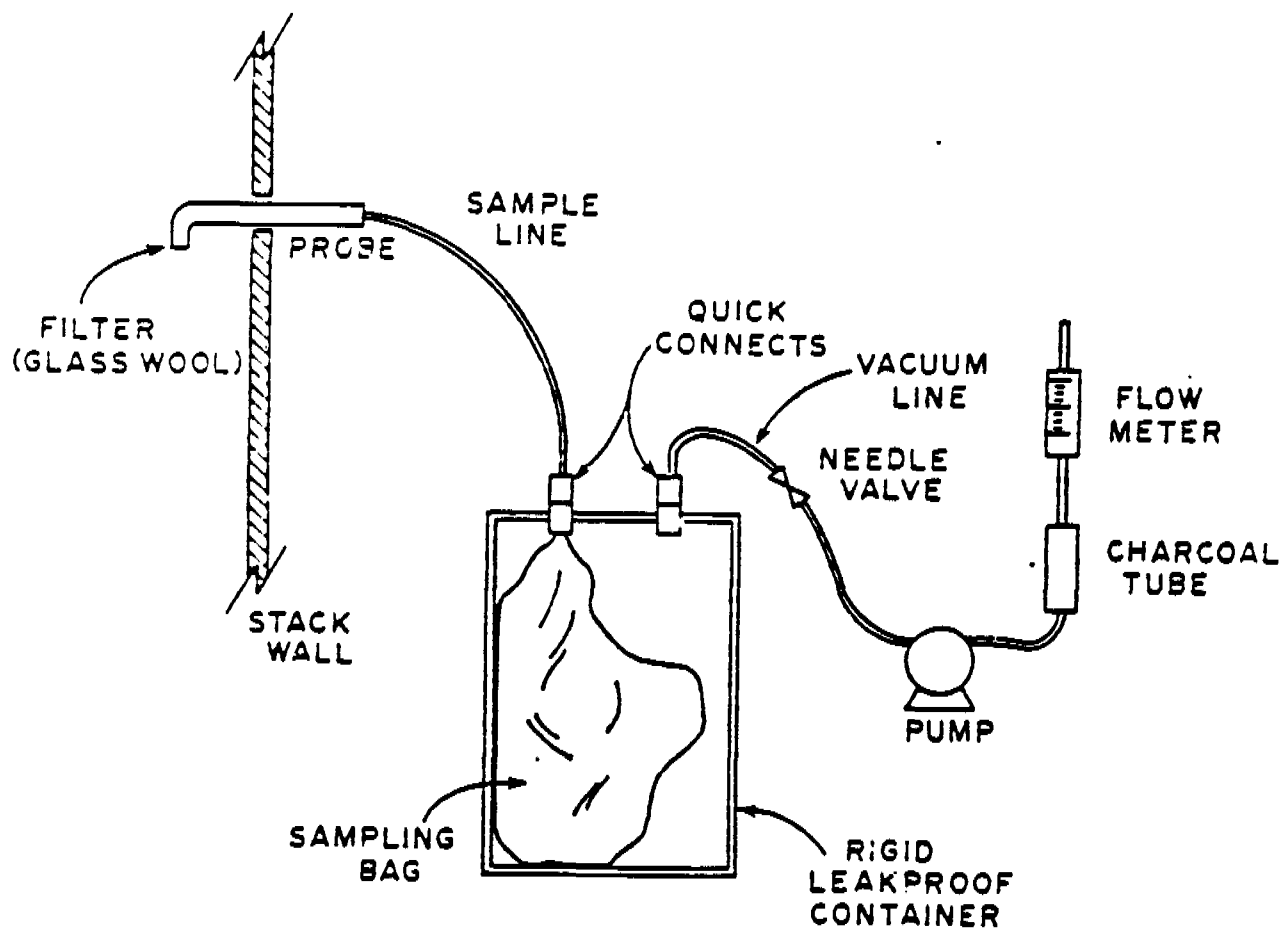


Figure 9. Method 23 sampling train.³⁵

soon as possible after collection, preferably on the same day. The method does not apply when vinylidene chloride is contained in particulate matter.

REFERENCES

1. Hushon, J., and M. Kornreich. Air Pollution Assessment of Vinylidene Chloride. EPA-450/3-78-015. U.S. Environmental Protection Agency, Washington, DC. February 1978. pp. 7-20.
2. Grayson, M., ed. Kirk-Othmer Encyclopedia of Chemical Technology. Third Edition, Volume 23. John Wiley and Sons, New York, NY, 1983. pp. 764-798.
3. Edney, E., S. Mitchell, and J. Bufalini. Atmospheric Chemistry of Several Toxic Chemicals. EPA-600/3-82-092. U.S. Environmental Protection Agency, Research Triangle Park, NC. November 1982. pp. 31-35.
4. Cuppitt, Larry. Fate of Toxic and Hazardous Materials in the Air Environment. EPA-600/3-80-084. U.S. Environmental Protection Agency, Research Triangle Park, NC. August 1980. pp. 3-6.
5. Standifer, R.L., and J.A. Key. Report 4: 1,1,1-Trichloroethane, Perchloroethylene, Trichloroethylene, and Vinylidene Chloride. In: Organic Chemical Manufacturing--Volume 8: Selected Processes. EPA-450/3-80-028c. U.S. Environmental Protection Agency, Research Triangle Park, NC. December 1980. pp. III-1 to III-17.
6. Neufeld, M.L., M. Sittenfield, M.J. Plotkin, K.F. Wolk, and R.E. Boyd. Market Input/Output Studies--Task I: Vinylidene Chloride. EPA-560/6-77-033. U.S. Environmental Protection Agency, Washington, DC. October 1977. pp. 67-70, 156-163.
7. Hawley, Cessner G. The Condensed Chemical Dictionary. Tenth Edition. Van Nostrand Reinhold Co., New York, NY. 1981. pg. 232.
8. Modern Plastics Encyclopedia. Modern Plastics. 59(10A):113-114. October 1982.
9. Reference 6. pg. 156.
10. Reference 5. pp. II-1 to II-6.
11. Reference 5. pp. III-15 to III-17.
12. Reference 6. pp. 67-70.
13. Reference 5. pp. IV-15, IV-18, and IV-19.
14. Reference 5. pp. V-5 to V-7.

15. Mascone, D., U.S. Environmental Protection Agency. Memo and Addendum to J.R. Farmer, EPA, entitled "Thermal Incinerator Performance for NSPS", June 11, 1980.
16. Eisen, P., M. Sanders, and M. Samuels. Human Exposure to Atmospheric Concentrations of Vinylidene Chloride. Prepared by Wapora, Inc. (Project 507-13) for the U.S. Environmental Protection Agency, Research Triangle Park, NC. February 4, 1982. pp. 2-1 and D-1 to D-3.
17. Reference 6. pp. 84-86.
18. Letter from Alice R. Myer, Chemical Manufacturers' Association, to Thomas F. Lahre, U.S. Environmental Protection Agency. March 19, 1985.
19. Letter from Thomas E. Lingafelter, Dow Chemical, to Thomas F. Lahre, U.S. Environmental Protection Agency. February 13, 1985.
20. 1983 Directory of Chemical Producers, United States of America. SRI International. Menlo Park, CA. 1983.
21. Reference 5. pp. III-8 to III-14.
22. Reference 5. pp. IV-11 to IV-18.
23. Reference 5. pp. III-4 to III-8.
24. Reference 5. pp. IV-6 to IV-10.
25. Vinylidene Chloride Monomer Emissions from the Monomer, Polymer, and Polymer Processing Industries. Prepared by Arthur D. Little, Inc. (ADL Reference 76086-31) for the U.S. Environmental Protection Agency, Research Triangle Park, NC. April 1976. pp. 16-42.
26. Reference 6. pp. 9-20.
27. Wilkins, Glynda E. Industrial Process Profiles for Environmental Use: Chapter 10. Plastics and Resins Industry. EPA-600/2-77-023j. U.S. Environmental Protection Agency, Research Triangle Park, NC. February 1977. pp. 55-58.
28. Synthetic Fiber Production Facilities--Background Information for Proposed Standards. EPA-450/3-82-011a. U.S. Environmental Protection Agency, Research Triangle Park, NC. October 1982. pp. 3-1 to 3-77.
29. Control of Volatile Organic Compound Leaks from Synthetic Organic Chemical and Polymer Manufacturing Equipment. EPA 450/3-83-006. U.S. Environmental Protection Agency, Research Triangle Park, NC. March 1984. pg. 4-3.

30. Vinyl Chloride - A Review of National Emission Standards. EPA-450/3-82-003, U.S. Environmental Protection Agency, Research Triangle Park, NC. February 1982. pg. 4-2.
31. Reference 16. pp. 1-3 to 1-4.
32. Reference 25. pp. 43-61.
33. Evaluation and Selection of Models for Estimating Air Emissions from Hazardous Waste Treatment, Storage and Disposal Facilities. EPA-450/3-84-020. Prepared for the U.S. Environmental Protection Agency by GCA, Corp., Bedford, MA. Dec. 1984.
34. Petrasek, A.C., Jr., Barry M. Austern, and Timothy W. Neiheisel. Removal and Partitioning of Volatile Organic Priority Pollutants in Wastewater Treatment. Paper presented at the Ninth U.S.-Japan Conference on Sewage Treatment Technology, Tokyo, Japan, September 13-29, 1983. 20 pp.
35. Method 23. Determination of Halogenated Organics from Stationary Sources. Federal Register. 45(114):39776-39784. June 11, 1980.
36. Forest, Denis. A Sampling and Analytical Method for Vinylidene Chloride in Air. American Industrial Hygiene Association Journal. October 1979. pp. 888-893.
37. Severs, L.W. and L.K. Skory. Monitoring Personnel Exposure to Vinyl Chloride, Vinylidene Chloride and Methyl Chloride in an Industrial Work Environment. American Industrial Hygiene Association Journal. September 1975. pp. 669-676.
38. Telecon. Joseph Knoll, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, with William Battye, GCA/Technology Division. EPA Reference Method 23. January 26, 1984.
39. Memorandum from R. Rosensteel, U.S. Environmental Protection Agency to T. Lahre, U.S. Environmental Protection Agency, entitled "Review of Draft Reports on Emission Factors for Potentially Toxic Substances." November 10, 1984.

APPENDIX A

PROCESS FUGITIVE EMISSION CALCULATIONS FOR VINYLIDENE CHLORIDE PRODUCTION FROM 1,1,2-TRICHLOROETHANE

Fugitive emissions of vinylidene/chloride (VDC) and other volatile organics result from leaks in process valves, pump seals, compressors, sample connections, open-ended lines and pressure relief valves. Fugitive VDC emission rates from these sources were based on a process flow diagram (Figure 2), process operation data, a fugitive source inventory for a hypothetical plant,¹ and EPA emission factors for process fugitive sources.²

The first step in estimating fugitive emissions of VDC was to list the process streams in the hypothetical plant. Their phases (i.e., gaseous or liquid) were then identified from the process flow diagram and their compositions estimated. For the reactor product stream, the composition was estimated based on reaction completion data. For a stream from a distillation column or other separator, the composition was estimated 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 were estimated by dividing the total number of valves at the plant equally among the process streams. Similarly, pumps were apportioned equally among liquid process streams, and relief valves were apportioned equally among all reactors, columns, and other separators. The locations of any compressors were determined from the process flow diagram. Although the above sources probably are not apportioned equally among the process lines at an actual plant, the equal apportionment algorithm provides the best estimate of the number of sources per line given the available data.

Emissions were then calculated for pumps, compressors, valves in liquid and gas line service, and relief valves. Emissions from flanges

and drains are minor in comparison with these sources and were therefore neglected. Fugitive emissions from a particular component were assumed to have the same composition as the process fluid flowing through each component. For valves in liquid service, for instance, VDC emissions were determined by taking the product of: (1) the total number of liquid valves in VDC service; (2) the average VDC content of the streams passing through these valves; and (3) the average fugitive emission rate per valve per unit time as measured by EPA. Emissions from valves in gas service, pumps and compressors were calculated in the same manner. For relief valves, fugitive emissions were assumed to have the composition of the overhead stream from the reactor or column served by the relief valve. Emissions from the various fugitive source types were summed to obtain total process fugitive emissions of VDC.

Because emissions from process fugitive sources do not depend on their size, but only on their number, total process fugitive emissions are not dependent on plant capacity. Thus, the overall emissions are expressed in terms of kilograms per hour of operation.

HYPOTHETICAL PLANT FUGITIVE SOURCE INVENTORY

- 725 process valves
- 15 pumps (not including spares)
- 2 compressors
- 25 safety relief valves

PROCESS LINE COMPOSITION AND FUGITIVE SOURCE INVENTORY

Of the approximately 16 major process lines in the production process, 9 contain at least some fraction of volatile organics compounds (VOC) and 6 contain vinylidene chloride (VDC). Compositions of the major process streams (identified in Figure 2 in the section on VINYLIDENE CHLORIDE PRODUCTION) are estimated in Table A-1.

A fugitive emission equipment count was not available for a VDC production plant. However, studies of other synthetic organic chemical manufacturing plants indicate that a typical fugitive equipment count is as follows:¹

TABLE A-1. ESTIMATED PROCESS LINE COMPOSITION IN VDC PRODUCTION¹

Stream number ^a	Phase	----Stream composition (weight fraction)----					Other
		Water	NaOH	NaCl	Cl ₂ HC-CH ₂ Cl	VDC	
1	Liquid	0	1.000	0	0	0	0
2	Liquid	1.00	0	0	0	0	0
3	Liquid	0	0	0	1.000	0	0
4	Liquid	0.75	0.061	0	0.191	0	0
5	Liquid	0	0	0	0	0	1.00
6	Liquid	0.77	0.011	0.073	0.024	0.121	0
7	Liquid	0.90	0.012	0.086	0	0	0
8	Liquid	0	0	0	0.164	0.836	0
9	Liquid	0.90	0.012	0.086	0	0	0
10	Liquid	0.90	0.012	0.086	0	0	0
11	Liquid	0	0	0	0.164	0.836	0
12	Liquid	0	0	0	0.164	0.836	0
13	Liquid	0.90	0.012	0.086	0	0	0
14	Vapor	0	0	0	0.164	0.836	0
15	Liquid	0	0	0	1.000	0	0
16	Liquid	0	0	0	0	1.000	0

^aStream numbers correspond to those shown in Figure 2.

- 15 process valves per major process line,
- 1 pump (not including spares) per major liquid process line,
- 1 compressor for each gas line requiring pressurization, and
- 2 relief valves per pressure vessel or column.

EMISSION CALCULATIONS

VDC emissions from valves in liquid and gas service, and for pumps were calculated as follows:

$$\begin{aligned}
 (\text{Total VDC emission rate for stream type}) = & \\
 & (\# \text{ of streams}) \times \\
 & (\text{Average VDC content for stream type}) \times \\
 & (\# \text{ of pumps or valves per stream}) \times \\
 & (\text{Emission rate for individual rate for individual pumps or} \\
 & \text{valves})
 \end{aligned}$$

These calculations are summarized in Table A-2. Similarly, emissions from relief valves were calculated for each vessel or column processing VDC:

$$\begin{aligned}
 (\text{VDC emissions rate}) = & \\
 & (2 \text{ relief valves per vessel}) \times \\
 & (\text{VDC fraction in vessel overheads}) \times \\
 & (0.104 \text{ kg emissions/hr/relief valve})
 \end{aligned}$$

These calculations are summarized in Table A-3. No compressors are expected to be in VDC service in the VDC-from-1,1,2-trichloroethane process.

Total uncontrolled process fugitive emission rates for VDC production are given in Table A-4, along with controlled emission rates for various combinations of emission reduction techniques. The emission reduction techniques studied were quarterly and monthly inspection of valves and pumps, the use of double mechanical sealed pumps, and the use of rupture disk in tandem with or in place of relief valves.

TABLE A-2. ESTIMATED VDC EMISSIONS FROM VALVES AND PUMPS

Source type	Number of streams	Average VDC weight fraction ^a	Number of sources	Source VOC emission rate ² (kg/hr-source)	Emissions (kg/hr)
Valves					
vapor	2	0.84	30	0.0036	0.140
liquid	3	0.60	45	0.0071	0.191
Pumps	3	0.60	3	0.0494	0.089
TOTAL					0.42

^aFraction of VOC stream in each source type comprised of VDC.

TABLE A-3. ESTIMATED VDC EMISSIONS FROM RELIEF VALVES

Vessel	Number of relief valves	VDC weight fraction in overheads	Emissions ^a (kg/hr)
Reactor	2	0.56	0.12
Phase separator	2	0.56	0.12
Drying column	2	0.50	0.10
Finishing column	2	0.50	0.10
Stripping column	2	0.50	0.10
TOTAL			0.54

^aRelief valve emission rate of 0.104 kg/hr-valve was used to calculate emissions.²

TABLE A-4. FUGITIVE EMISSION CONTROLS AND ESTIMATED CONTROLLED EMISSION RATES

Source class	Uncontrolled VDC emission rate (kg/hr)	Controlled emission rates					
		Quarterly I/M ^a		Monthly I/M		Monthly I/M double seals; rupture disks	
		Percent control	Emissions (kg/hr)	Percent control	Emissions (kg/hr)	Percent control	Emissions (kg/hr)
Vapor valves	0.140	64.0	0.051	73.0	0.038	73.0	0.038
Liquid valves	0.191	44.0	0.107	59.0	0.078	59.0	0.078
Pumps	0.089	32.5	0.060	60.8	0.035	100.0	0
Relief valves	0.545	0	0.545	0	0.545	100.0	0
OVERALL	0.965	21.0	0.762	29.0	0.696	88.0	0.116

^aI/M refers to inspection and maintenance of valves and pumps. Control percentages are from Reference 2.

REFERENCES FOR APPENDIX

1. Standifer, R.L., and J.A. Key. Report 4: 1,1,1-Trichloroethane, Perchloroethylene, Trichloroethylene, and Vinylidene Chloride. In: Organic Chemical Manufacturing--Volume 8: Selected Processes. EPA-450/3-80-028c, U.S. Environmental Protection Agency, Research Triangle Park, NC. December 1980. pp. IV-1 to IV-22.
2. Fugitive Emission Sources of Organic Compounds--Additional Information on Emissions, Emission Reductions, and Costs. EPA-450/3-82-010, U.S. Environmental Protection Agency, Research Triangle Park, NC. April 1982.

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