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Air Pollution Emissions and Control Technology: Vinyl Chloride Industry



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AIR POLLUTION EMISSIONS AND CONTROL TECHNOLOGY: VINYL CHLORIDE INDUSTRY

by

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ABSTRACT

Canadian industrial operations that are potential sources of vinyl chloride emissions to the atmosphere are reviewed. Abatement technology available to reduce the level of vinyl chloride emissions from these sources is highlighted.

For the year 1973, the total atmospheric emission of vinyl chloride from Canadian industrial operations was estimated at 5000 short tons. The polyvinyl chloride manufacturing industry was responsible for an estimated 89% of the emission and vinyl chloride manufacturing operations accounted for 10%. The plastics fabrication industry, which processes polyvinyl chloride into end-use plastic products, was responsible for the remainder, about 1%. Effective control measures, using available technology, can achieve an estimated 95% reduction in these emissions.

RÉSUMÉ

Au Canada, les sources industrielles potentielles de dégagement de chlorure de vinyle sont examinées, et les techniques antipollution disponibles pour réduire leurs dégagements sont indiquées.

En 1973, les dégagements de chlorure de vinyle par l'ensemble de l'industrie canadienne ont été estimés à 5000 tonnes courtes. De ce total, 89% étaient attribuables à la fabrication du chlorure de polyvinyle et 10%, à celle du chlorure de vinyle. Le reste, environ 1% provenait de la fabrication de matières plastiques à base de chlorure de polyvinyle. On estime que des mesures antipollution efficaces utilisant les techniques disponsibles peuvent réduire de 95% ces dégagements.

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1 INTRODUCTION

1.1 Background

In January 1974, it was reported (1) that several workers who had been exposed to an in-plant atmosphere containing measureable concentrations of vinyl chloride had died of angiosarcoma, a rare liver cancer. Following this disclosure, much has been done by concerned industry, government and independent research groups to generate and assess medical and scientific data pertaining to this problem.

The effect of vinyl chloride on humans has been studied by medical researchers on a limited scale since the early 1940's. Initially this compound was believed to be virtually harmless to humans and several experiments were carried out to assess its anaesthetic properties (2). However, during the 1950's, medical reports suggested a possible link between vinyl chloride and such diseases and disorders as skin lesions, circulatory impairment and gastritis (3). By the mid 1960's, researchers reported several cases of acroosteolysis, a degenerative disease of the finger bones, among workers involved in the manual cleaning of vinyl chloride polymerization reactors (4). The results of animal experiments, released in the early 1970's, revealed a notable incidence of carcinogenic tumors of the skin and lungs of rats exposed to a controlled atmosphere of vinyl chloride (5). A continuation of these animal studies along with epidemiological studies of the mortality of workers exposed to vinyl chloride revealed that it is a casual agent in the formation of angiosarcoma (1, 6).

Vinyl chloride monomer (VCM) is a chlorinated hydrocarbon having the chemical formula CH_2CHCI . The compound is a colourless, flammable gas with an etherial odour. Under atmospheric conditions it boils at -14°C (7). Vinyl chloride released to the atmosphere will decompose in the presence of sunlight to carbon oxides, hydrogen chloride and water. It does not persist indefinitely in the atmosphere (8). The estimated half life of this compound, depending on light intensity, nitrogen oxide concentrations, etc., is about 2 days (9).

In September 1974, the U.S. Environmental Protection Agency announced plans to establish a national emission standard for vinyl chloride. This standard has been developed under Section 112 of the U.S. Clean Air Act, which deals with hazardous air pollutants, and was promulgated in the October 21, 1976, issue of the U.S. Federal Register.

To date, no safe exposure level has been established for vinyl chloride. In recognizing the potential seriousness of the problem, however, Health and Welfare Canada has recommended that vinyl chloride emissions from stationary sources in Canada be controlled and maintained at the lowest possible level, as a public health protection measure. Consequently, Environment Canada intends to prescribe national emission standards regulations for vinyl chloride under Section 7 of the Clean Air Act. These regulations must establish the maximum quantities of vinyl chloride that may be emitted into the ambient air from stationary sources.

1.2 Purpose

The primary purpose of this report is to provide the technical information required for the development of national emission standards regulations for vinyl chloride.

1.3 Scope

This report presents technical and statistical information pertaining to the principal stationary sources of vinyl chloride emissions in Canada. The stationary sources investigated in this report encompass manufacturing facilities operated to produce vinyl chloride and polyvinyl chloride. These operations constitute the principal stationary sources of vinyl chloride emissions to the environment.

The manufacturing processes currently being operated in Canada are discussed. The report also depicts the known vinyl chloride emission sources within these plants and presents a review of the emission control techniques that can be used to abate these emissions.

The plant emission figures presented reflect the Canadian industrial situation as it was in 1973. Plants which were operated to produce vinyl chloride or polyvinyl chloride at that time are considered to be typical of 'uncontrolled' operations. The effectiveness of the control measures discussed in this report is appraised in terms of the percentage reduction in vinyl chloride emissions from a specific source, relative to the situation in 1973. Therefore, 1973 is considered to be the 'base year' of operation for those plants referred to in this report.

In addition to the detailed information presented for the vinyl chloride and polyvinyl chloride processes, the report briefly reviews two other operations that are potential sources of vinyl chloride emissions, the ethylene dichloride process and the 1,1,1 trichloroethane process. Whether or not vinyl chloride emissions emanate from these operations depends on the process technology used to manufacture the respective products.

Another stationary source of vinyl chloride emissions to the environment is polyvinyl chloride fabrication plants. These plants transform polyvinyl chloride resin into plastic products. More than 150 such plants were operating in Canada in 1973 (10).

Collectively, polyvinyl chloride fabrication plants account for an estimated 1% of the total vinyl chloride lost to the environment from all stationary sources in Canada (the estimate includes product transfer and weathering losses). Because this contribution is derived from many plants, particulars regarding these fabrication processes have been excluded from this report.

Many reference sources were used to compile the information presented in this report. Because the Canadian manufacturing operations under review use essentially the same process technology that is used to manufacture similar products in the U.S.A., emission data compiled by the Environmental Protection Agency are used extensively throughout this report (11). Additional information was received from the Canadian industry in response to the EPS (Environmental Protection Service) Petrochemical/Synthetic Resin Industries Atmospheric Emissions and State-of-the-Art Questionnaire in 1974. Supplemental information was obtained from individual companies during plant visits and from the literature.

2 INDUSTRY DESCRIPTION

During the 'base year' 1973, two companies operated plants in Canada to produce an estimated 245 million lb of vinyl chloride - Dow Chemical Canada Ltd., at Sarnia, Ontario, and Gulf Oil Canada Ltd., at Varennes, Quebec. Production capacity figures for each of these operations are given in Table 1.

TABLE 1VINYL CHLORIDE PLANT OPERATORS - 1973 (12, 13)

Operator	Production Capacity 10 ⁶ lb/yr		
Dow Chemical Canada Ltd. Sarnia, Ontario	200		
Gulf Oil Canada Ltd.* Varennes, Quebec	120		

* Gulf Oil terminated operations at this plant in 1975.

Both Dow Chemical Canada Ltd. and Gulf Oil Canada Ltd. cracked ethylene dichloride (EDC) to produce vinyl chloride. More than 90% of vinyl chloride produced in Canada in 1973 was used to produce polyvinyl chloride resins. The remainder was used in the production of 1,1,1 trichloroethane.

In 1973, four plants were operated in Canada to produce an estimated 228 million lb of polyvinyl chloride resin (12, 13). At that time, these plants were operated at approximately 90% of their combined annual rated capacity of 252 million lb (12, 13). The location and rated capacity of the plants are shown in Table 2.

Plastic fabricators consumed an estimated 257 million lb of resin (excluding additives) during 1973 (13). Incremental quantities of resin over that purchased from Canadian suppliers were imported, principally from the United States. Table 3 summarizes the principal uses of polyvinyl chloride resins in Canada.

Operator	Rated Plant Capacity 10 ⁶ lb/yr
Esso Chemical Canada Sarnia, Ontario	90
B.F. Goodrich Canada Ltd. Niagara Falls, Ontarìo	72
B.F. Goodrich Canada Ltd. Shawinigan, Quebec	50
Monsanto Chemical Co.* LaSálle, Quebec	40
, TOTAL	252

TABLE 2POLYVINYL CHLORIDE PLANT OPERATORS - 1973 (12, 13)

* Monsanto terminated operations at this plant in 1975.

3 PROCESS DESCRIPTION

The processes described in the following subsections are considered to be the principal industrial sources of vinyl chloride emissions to the environment.

3.1 Vinyl Chloride Manufacturing Processes

In North America, vinyl chloride is produced commercially, as a liquid, using one of two common manufacturing processes:

- (1) pyrolysis of ethylene dichloride C2H4 Cl2
- (2) vapour phase reaction of acetylene and hydrogen chloride

The pyrolysis of ethylene dichloride is the only process used in Canada to produce vinyl chloride. In the United States, this process accounts for about 92% of current vinyl chloride production capacity (11). Recognizing the present Canadian situation and considering that it is unlikely any new plants brought on stream in Canada will use the outdated acetylene-hydrogen chloride technology, the pyrolysis of ethylene dichloride is the only process described in this report. Because vinyl chloride

End Use	% of Total Industry Consumption		
Film and Sheet	15.8		
Wire and Cable Insulation	14.2		
Pipe and Conduit	13.6		
Other Extrusion and Molded Products	10.7		
Flooring	13.6		
Phonograph Records	3.3		
Other Plastisols	20.3		
Blowmolded Products	2.6		
Other Applications	5.9		

TABLE 3 USES OF POLYVINYL CHLORIDE RESIN (14)

production sites generally include facilities to manufacture ethylene dichloride, as an integral part of the operation, the principal processes used to manufacture ethylene dichloride are also described.

(A) Processes Used to Manufacture Ethylene Dichloride

Two of the most widely used commercial processes to produce ethylene dichloride are the direct chlorination of ethylene process and the oxychlorination process. Figures 1 and 2 are simplified flow diagrams depicting typical processing schemes to manufacture ethylene dichloride.

Direct chlorination of ethylene to produce ethylene dichloride involves the reaction of

= C 14

ethylene and chlorine in the presence of a catalyst according to the following chemical equation: H $C_2H_4 + Cl_2 \longrightarrow CICH_2CH_2CI \qquad H - C = C - 14$ H

Reaction conditions of temperature and pressure range from about 40°-130°C and 5-10 atm respectively depending on the process technology used (15). Excessive reaction temperatures promote the formation of over-chlorinated ethane products such as 1,1,2 trichloroethane. The yield of ethylene dichloride is typically about 90% (16). Fractionation is used to recover the principal reaction products.

The oxychlorination process involves the reaction of ethylene, hydrogen chloride and oxygen in a catalytic process according to the following chemical equation:



LEGEND: EDC-ETHYLENE DICHLORIDE

.



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 $\frac{\partial R}{\partial t} = \frac{\partial R}{\partial t}$ C=C(H

 $2C_2H_4 + 4HCI + O_2 \rightarrow 2CICH_2CH_2CI + 2H_2O$

Reactor operating conditions of about 200°C and 15 atm are typical (15). Overall yields of ethylene dichloride are about 95% (15). The reaction products are usually caustic washed before final separation and recovery.

(B) Pyrolysis of Ethylene Dichloride

1- C- C- H

The pyrolysis of ethylene dichloride involves the dehydrochlorination of ethylene dichloride to produce vinyl chloride and hydrogen chloride according to the reaction: $\frac{\mathcal{O}}{L}$

CICH₂CH₂CI
$$\longrightarrow$$
 CH₂CHCI + HCI $\frac{1}{1} - \frac{1}{1} = C - H$

Figure 3 is a simplified flow diagram of the ethylene dichloride process for the production of vinyl chloride. This flow diagram includes the facilities used to produce ethylene dichloride via either the direct chlorination of ethylene process or the oxychlorination process. Those vinyl chloride operations in which the hydrogen chloride produced during the dehydrochlorination step is recycled to an oxychlorination reactor are referred to as balanced processes.

The dehydrochlorination reaction takes place in a cracking furnace at temperatures between 350°C and 550°C and pressures of 10 to 30 atm, depending on the process technology employed (15). The typical yield of vinyl chloride is about 95% (15, 17).

The hot effluent gases formed during the pyrolysis reaction are quenched and condensed upon discharge from the cracking furnace. The effluent stream, comprised of vinyl chloride, hydrogen chloride, unreacted ethylene dichloride and light and heavy ends (the products of side reactions), is then processed in the separation/purification section of the plant.

The principal compounds in the cracking furnace discharge stream are recovered by fractional distillation. The number of individual products recovered determines the complexity of this recovery section (i.e. the number of fractionation towers used). In general, the first step involves the separation of the hydrogen chloride and light hydrocarbons from the vinyl chloride, chlorinated hydrocarbons and heavy ends. A subsequent tower is used to recover the vinyl chloride and another may be used to separate the other chlorinated hydrocarbons from the heavy ends. Unreacted ethylene dichloride is usually recycled for reprocessing.

3.2 Processes Using Vinyl Chloride as a Principal Feed

More than 90% of the vinyl chloride consumed by Canadian manufacturers, is used in the production of polyvinyl chloride. The remainder is used in the production of 1,1,1, trichloroethane. The following sections describe each of these manufacturing operations.

3.2.1 Polyvinyl Chloride Processes. Polyvinyl chloride (PVC) resin is produced as a white granular solid formed by a free radical polymerization reaction of vinyl chloride molecules. Polyvinyl chloride is described by the generalized chemical formula $(CH_2CHCI)_n$ where 'n' denotes the number of CH₂CHCI units linked together to yield the desired molecular weight for a particular grade of this

$$\begin{array}{c} H \\ C = C \\ H \end{array}$$



LEGEND: EDC-ETHYLENE DICHLORIDE VCM-VINYL CHLORIDE MONOMER compound. Commercial grades of polyvinyl chloride exhibit average molecular weights ranging from about 40,000 to 480,000 (18).

More than 400 different grades of polyvinyl chloride resin have been offered on the world market during the past years (17). The different grades of resin are characterized by properties such as molecular weight, particle size, porosity, tensile strength and bulk density. The variety of grades are produced to meet the requirements of well-established product fabrication techniques (e.g. extrusion, calendering and moulding) and to satisfy varied consumer requirements.

Polyvinyl chloride may be manufactured commercially by four general methods of polymerization:

- suspension polymerization
- mass or bulk polymerization
- emulsion or dispersion polymerization
- solution polymerization

Each method involves the batch polymerization of vinyl chloride monomer in a vessel under relatively moderate operating conditions of temperature and pressure.

The suspension polymerization of vinyl chloride is by far the most important commercial process used to manufacture polyvinyl chloride. Approximately 95% of the polyvinyl chloride resin manufactured in Canada is produced by the suspension process (12). The remainder is manufactured by the emulsion or dispersion process. The suspension polymerization process is the only one of the four commercial manufacturing methods described in detail in this report.

In suspension polymerization, vigorous agitation is used to disperse the vinyl chloride monomer in water as fine droplets. Dispersing agents are used to prevent agglomeration of the droplets. Some resins produced by the suspension process exhibit a high degree of porosity which is required for the addition of plasticizers and/or other additives.

In mass or bulk polymerization processes only the monomer and small amounts of additives are charged to the reactor (diluents are not used). The reaction mass is very viscous and heat transfer is poor. This technique is often used to produce resins exhibiting special physical properties which may not be attainable by other methods. For example, some very high molecular weight grades of polyvinyl chloride can only be produced by bulk polymerization.

Emulsion polymerization is similar to suspension polymerization except that the particle size of the resin is small and the system is stabilized by emulsifiers and additives to yield non-settling emulsions. This method is generally used when the polymer is required in a latex state.

Solution polymerization of vinyl chloride monomer is carried out in a solution of organic solvent. Solution polymerization will generally yield lower molecular weight grades of resin than those obtained from using other polymerization techniques.

3.2.2 Polyvinyl Chloride Manufacture - **The Suspension Process.** Figure 4 is a simplified process flow diagram of the suspension process. During the polymerization reaction, vinyl chloride molecules are linked to form a chain-like compound of high molecular weight. Different grades of polyvinyl chloride resin can be produced by varying the recipe formulation and/or the reaction conditions. Temperature is probably the most important control variable in the reaction mechanism because the molecular weight of the resin is mainly a function of the polymerization temperature (17).

The suspension polymerization reaction is carried out in an aqueous medium in a glass-lined or stainless steel vessel (Figure 5). This reaction is highly exothermic and the temperature of the reaction mass must be maintained at a predetermined level at all points within the vessel to ensure product uniformity.

A suitable organic peroxide such as lauryl peroxide is used to initiate the reaction. A typical recipe of ingredients (17) charged to a reactor is:

INGREDIENT	PARTS BY WEIGHT
Water	100
Protective colloid	0.1–0.5
Buffer salt	0-0.1
Initiator	0.05-0.3
Antifoam agent	0-0.002
Vinyl chloride monomer	50-70

Polymerization conditions between 45° -70°C and pressures of about 8 atm are typical (15). The reaction is normally terminated when 85%-90% of the monomer has been converted to the polymer. When the conversion exceeds 90%, the rate of polymerization decreases and degradation of the product begins (18).

A complete cycle for a batch run involves several time-consuming steps. The time required for each step will vary with the procedures used by a particular manufacturer and the type of initiator used. Batch cycle times vary from 10-20 h (18).

The suspension polymerization plant usually consists of a battery of reactors which are tied into a common vessel known as a stripper (Figure 6). At the completion of a cycle, the polymerization reactor contents are dumped into the stripper where unreacted monomer is removed from the wet polymer and recovered for reprocessing. The stripped material is then transferred to a blend tank as a slurry where it is combined with material from other batches. Water is subsequently removed from the slurry mix by centrifuging and drying. After drying, the resin is screened and then pneumatically conveyed to central storage silos for bagging or bulk transport loading.

3.2.3 1,1,1 Trichloroethane Manufacture. Vinyl chloride can be chlorinated to 1,1,1 trichloroethane which is used primarily as an industrial degreasing solvent. Only one Canadian manufacturer currently produces this product and process information is limited. Figure 7 is a simplified



LEGEND: VCM-VINYL CHLORIDE MONOMER PVC-POLYVINYL CHLORIDE

FIGURE 4 SUSPENSION POLYVINYL CHLORIDE PROCESS



SV-SAFETY VALVE

FIGURE 5 POLYVINYL CHLORIDE REACTOR VESSEL



LEGEND:

PVC-POLYVINYL CHLORIDE VCM-VINYL CHLORIDE MONOMER

FIGURE 6 STRIPPER SYSTEM

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flow diagram of the process which involves chlorinating vinyl chloride over a suitable catalyst according to the following chemical reactions:



4 EMISSION RATES

For the purpose of this report vinyl chloride emissions are classified into two general categories - captive and fugitive. Captive emissions include those from sources which can be readily identified, monitored and measured. Emissions from sources which cannot be specifically identified and quantified are referred to as fugitive.

For 1973, the estimated total atmospheric emissions of vinyl chloride from all stationary sources in Canada is 5000 short tons. Of this amount, polyvinyl chloride manufacturing operations contributed approximately 89%, vinyl chloride and associated manufacturing operations accounted for about 10% and polyvinyl chloride fabrication processes accounted for about 1%.

4.1 Polyvinyl Chloride Manufacture

In response to the EPS Petrochemical/Synthetic Resin Industries Atmospheric Emissions and State-of-the-Art Questionnaire in 1974, three out of four Canadian polyvinyl chloride producers reported estimates of their vinyl chloride emissions for 1973. The weighted average rate of captive emissions resulting from these operations was computed to be 2.15 lb/100 lb of polyvinyl chloride produced. Emergency venting resulting from plant malfunctions accounted for an additional 0.19 lb/100 lb of polyvinyl chloride produced. Very little information pertaining to fugitive emissions was given. Table 4 presents a summary of available data plus comparable figures for American plants as reported by EPA.

An assumption of a 1.53 lb/100 lb fugitive emission factor for vinyl chloride losses from Canadian plants results in an overall emission factor of 3.9 lb/100 lb for the total level of vinyl chloride losses from polyvinyl chloride manufacturing operations. The aggregate vinyl chloride emissions from these plants was estimated at 4450 short tons for 1973 based on a nationwide polyvinyl chloride production figure of 228 million lb.

4.2 Vinyl Chloride Manufacture

The EPA developed a vinyl chloride emission factor of 0.4 lb/100 lb of monomer based on data received from 15 monomer-producing plants (19). Other reference sources suggest emission factors of 0.1 - 0.5 lb/100 lb of monomer as being representative of vinyl chloride losses from this type of process (12, 20). A representative emission factor could not be determined from available Canadian plant

	Captive Sources	Emergency Venting	Fugitive Sources	Total
EPS Survey				
Results	2.15	O . 19	No Data	-
EPA Survey				
Results	2.19	0.20	1.53	3.92

data because only two plants were operated in Canada in 1973 and operational data were submitted for only one of these in response to the EPS survey.

For 1973, total vinyl chloride emissions from the monomer-producing plants in Canada are estimated at 490 short tons. This estimate is based on a nationwide vinyl chloride production figure of 245 million lb and a plant emission factor of 0.4 lb/100 lb of vinyl chloride produced (this emission factor includes the contribution from the associated ethylene dichloride production facilities).

4.3 1,1,1 Trichloroethane Manufacture

For 1973, total emissions of vinyl chloride from the 1,1,1 trichloroethane process are estimated at less than 5 short tons. This estimate is based on an emission factor of 0.05 lb of vinyl chloride/100 lb of vinyl chloride consumed (21). Because the emissions from this source are considered insignificant, the 1,1,1 trichloroethane process will not be discussed in detail. It should be noted, however, that this process is continuous and the emission sources associated with it are similar to those characterizing the vinyl chloride/ethylene dichloride processes (i.e., process vent streams, storage vessel vents and fugitive sources). In general, the abatement techniques which are effective in reducing the level of emissions from the vinyl chloride manufacturing operation may also be applied to the 1,1,1 trichloroethane process.

4.4 Manufacture of Plastic Products

Total vinyl chloride emissions resulting from plastic fabrication operations were about 60 short tons in 1973. This estimate is based on the assumption that the polyvinyl chloride resin produced in Canada in 1973 (257 million lb) contained an average of 500 ppm (11) residual vinyl chloride and that virtually all of this residual monomer was released to the atmosphere during the fabrication process.

(A small fraction of this residual vinyl chloride was lost to atmosphere during transport operations and during storage.)

5

EMISSION SOURCES AND CONTROL TECHNOLOGY

The following sections deal with the principal sources of vinyl chloride emissions associated with the vinyl chloride industry.

5.1 Fugitive Emissions

Fugitive emission sources account for a significant portion of the total vinyl chloride emissions from industrial operations. Of the 490 short tons of vinyl chloride lost to the atmosphere from vinyl chloride manufacturing plants in operation in 1973, an estimated 27% (11) of these losses were from fugitive sources. Similarly, fugitive sources accounted for an estimated 38% (11) of the 4450 short tons of vinyl chloride emissions from polyvinyl chloride manufacturing operations.

There are hundreds of points within the VCM/PVC plant from which vinyl chloride leakage to the atmosphere can occur. The principal fugitive sources include:

- pump, compressor and agitator seals
- pipe flanges and manhole seals
- valve stems
- leaking pressure relief valves
- process quality control sampling sites
- vinyl chloride loading and unloading sites
- equipment purging operations (prior to inspection and maintenance).

The quantity of vinyl chloride lost to the atmosphere via the sources noted varies markedly from plant to plant. Fugitive losses within a plant are affected by the type of equipment used, the operating procedures and the leak detection and maintenance procedures that are instituted. Thus it is impractical to assign an emission factor to each fugitive source. For these reasons, fugitive emission sources have been grouped together and treated as a single entity in the following section dealing with control technology.

5.1.1 Control Technology - **Fugitive Emissions**. Four basic techniques can be used to reduce vinyl chloride emissions from fugitive sources:

(1) Establish improved in-plant maintenance and operating procedures. The improved procedures should be directed towards achieving a reduction in the number of equipment leakages resulting from inadequate work practices and/or check procedures. (2) Install 'leak proof' equipment to reduce the quantity of vinyl chloride lost to the atmosphere via rotating equipment seals, gate valve bonnets, leaking safety valves and the like. Equipment such as double mechanical seals and 'canned' pumps (11, 19) can be used to virtually eliminate vinyl chloride losses from rotating equipment seals. Ball valves can replace gate valves and rupture discs can be installed upstream of safety valves to reduce emissions from this source.

(3) Establish an early warning leak detection program with an effective and complementary maintenance program so that equipment repairs can be made as quickly as possible. Many plants have installed fixed multipoint detectors which are used to monitor the air in specific areas of the plant periodically. Portable detection equipment can be used to locate the exact source of the emission within any problem area. Portable detectors can also be used to monitor other points of potential vinyl chloride leakage on a routine basis.

(4) Install a blow-down facility as a 'catch-all' device for miscellaneous streams containing vinyl chloride. All purging operations which at present result in the release of vinyl chloride laden streams to the atmosphere can be tied into this blow-down facility (e.g. purging process lines, loading/unloading lines, sample lines as well as vessels and rotating equipment in vinyl chloride service). The vinyl chloride which is handled in this system may be recovered subsequently for reprocessing or incineration. Vinyl chloride vapours which are displaced during product transfer operations can also be tied into this blow-down system.

Assuming that best control technology is applied to all known fugitive sources, it has been estimated that the base year (1973) level of vinyl chloride emissions from these sources can be reduced by about 90% (10). This estimate applies to the level of improvement which can be achieved within both vinyl chloride and polyvinyl chloride manufacturing operations.

5.2 Captive Emissions

5.2.1 Vinyl Chloride Manufacture. Emissions of vinyl chloride from the pyrolysis of ethylene dichloride process will vary with the specific processing scheme used and the operating/maintenance procedures that are established by the processor. Probably no two processors using the pyrolysis of ethylene dichloride to produce vinyl chloride will use identical processing sequences. Available data indicate that the processing scheme used has a bearing on the location of the principal sources of vinyl chloride emissions.

The principal sources of vinyl chloride emissions from the ethylene dichloride/vinyl chloride balanced process are summarized in Table 5. These captive sources are vent streams which contain varying quantities of vinyl chloride. The relative importance of each source associated with this processing scheme is depicted in Table 5. The schematic location of these sources is shown in Figure 8.





FIGURE 8 VINYL CHLORIDE MANUFACTURE-BALANCED PROCESS EMISSION SOURCES

Percentage values in parentheses are estimated contributions to total plant Vinyl Chloride emissions

-20~

Losses of vinyl chloride to process water streams are less than 0.2% of total plant losses (11).

The Oxychlorination Reactor System Vent

As noted earlier, the oxychlorination process involves reacting ethylene, hydrogen chloride and air (oxygen) in the presence of a catalyst to produce ethylene dichloride. In some operations all or part of the hydrogen chloride required for the reaction is derived from the vinyl chloride plant.

The by-product hydrogen chloride which is recycled from the vinyl chloride plant will contain some unreacted vinyl chloride. Additional quantities of vinyl chloride may also be produced as a side reaction (22). Much of this vinyl chloride is continuously released from the system via the reactor vent along with varying quantities of other light compounds generated during the reaction. For those plants using the balanced process, the oxychlorination reactor vent may account for upwards of 8% of total vinyl chloride emissions from the vinyl chloride manufacturing complex.

The Ethylene Dichloride Finishing Section Vent

The location of this vent is depicted in Figure 8. The finishing section is operated to produce specification-grade ethylene dichloride which is fed to a cracking furnace where it is converted to vinyl chloride.

The principal source of feed to the finishing section is crude ethylene dichloride from the chlorination or the oxychlorination reactor. Some operators also process an ethylene dichloride rejects stream through this section of the plant. The rejects stream, from the vinyl chloride product recovery section of the plant, is comprised of unreacted ethylene dichloride, miscellaneous hydrocarbons and some unrecovered vinyl chloride.

Any vinyl chloride present in the crude ethylene dichloride will be removed from this stream along with other light hydrocarbons by fractional distillation. Under the processing arrangement being described, the ethylene dichloride finishing section may account for about 11% of the vinyl chloride emissions from the complex.

The Vinyl Chloride Recovery Section Vent(s)

This section of the vinyl chloride manufacturing process includes all facilities located downstream of the cracking furnace. The facilities shown in Figure 8 include the quench tower, the hydrogen chloride recovery system and the vinyl chloride purification system. The principal sources of emissions associated with this section of the process are the light ends column vent and the hydrogen chloride purification system vent. Unreacted vinyl chloride present in streams which are recycled to the ethylene dichloride manufacturing facilities constitutes a potential source of vinyl chloride emissions from these facilities.

The location and need for vent streams seem to vary from plant to plant depending on the specific processing sequence used. It may be concluded, however, that all streams in this section of the

TABLE 5	POTENTIAL VINYL CHLORIDE	EMISSION SOURCES (11):
	BALANCED ETHYLENE DICHLO	DRIDE PROCESS TO PRODUCE
	VINYL CHLORIDE	
		% of Total Plant
Source		Vinyl Chloride Losses
Captive		
Reactor	Vent	8
Ethylene	Dichloride	
Finishing	Section Vent	1 1
Vinyl Ch	loride Recovery	
Section	Vent(s)	54
Fugitive		27
TOTAL		100

vinyl chloride manufacturing process which must be continuously or periodically vented will in fact contain some vinyl chloride.

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The recovery section accounts for an estimated 54% of the total vinyl chloride losses.

5.2.2 Control Technology - **Vinyl Chloride Manufacture.** Captive emission streams which characterize the ethylene dichloride/vinyl chloride manufacturing operation are similar in that they are low volume - low temperature, continuous flow vent streams. Based on the information available, add-on control technology may be the only effective means of abating vinyl chloride emissions from these sources. Abatement systems using adsorption, absorption, hydrogenation or incineration techniques can be used to abate the quantity of vinyl chloride released to the atmosphere via these vent streams. Properly designed add-on control schemes will effectively reduce the vinyl chloride content of these vent streams to a concentration less than 10 ppm (11). These control measures are capable of effecting a 99 + % reduction of the base year level of vinyl chloride emissions from captive sources (11) associated with the ethylene dichloride/vinyl chloride manufacturing complex.

5.2.3 Polyvinyl Chloride Manufacture - **The Suspension Process.** The principal sources of vinyl chloride emissions from this process are summarized in Table 6. The schematic location of these sources is shown in Figure 9.



LEGEND: VCM- VINYL CHLORIDE MONOMER PVC- POLYVINYL CHLORIDE

FIGURE 9 POLYVINYL CHLORIDE PLANT EMISSION SOURCES

Percentage values in parentheses are estimated contributions to total plant Vinyl Chloride emissions

POLYVINYL CHLORIDE MANUFACTU	RE - THE SUSPENSION PROCESS
Source	% of Total Plant Vinyl Chloride Losses
Captive	
Monomer Recovery System Vent	12
Exhaust System Vents	12
Slurry Blend Tank Vent	11
Centrifuge Vent	3
Dryer Vent	16
Storage Silo Vent	2
Fugitive	38
Emergency Upsets	5
Process Water	1
TOTAL	100

5.2.3.1 Monomer Recovery System Emissions and Control Technology. The recovery system noncondensable vent is part of the vinyl chloride monomer recovery/recycle section. The location of this vent is depicted in a simplified flow diagram of this section of the plant (Figure 10). The purpose of this vent and its associated pressure control valve is to release inerts (mostly air) from the system periodically to prevent a pressure buildup within the equipment. During these periodic purging operations, some vinyl chloride is also released to the atmosphere.

The polymerization reaction is normally terminated when about 85% to 90% of the monomer has been converted to polyvinyl chloride (18). Approximately 10% of the unreacted monomer is trapped within the polyvinyl chloride particles, the remainder being present as a dispersed phase in the water or in the vapour phase above the slurry. Most of the unreacted monomer present in the system at this stage of the processing sequence is separated and transferred to the recovery facilities for reprocessing. Unreacted monomer which is not recovered is eventually released to the environment.

The unreacted monomer trapped within the polymer after the reaction mass is dumped from the reactor vessel, is commonly removed from the polymer by vacuum stripping with steam. Vacuum systems are used to remove the unreacted monomer, water vapour and air from the vapour space within

TABLE 6POTENTIAL VINYL CHLORIDE EMISSION SOURCES (11):



FIGURE 10 MONOMER RECOVERY SYSTEM

the reactor and stripper vessels. These streams are tied into the monomer recovery system. During these operations, inerts are admitted to the monomer recovery system and, along with some vinyl chloride, must be periodically released from the system via the monomer recovery system vent.

At conventional recovery system operating conditions of about 10°C and 3 atm vented gas from this system will contain about 50% by volume vinyl chloride (23), accounting for an estimated 12% of total plant vinyl chloride emissions.

Control Technology. - Monomer Recovery System Vent

The following techniques may be used to reduce the level of atmospheric emissions from the monomer recovery system vent:

- add-on control technology using carbon adsorption, solvent absorption or incineration
- lowering condenser operating temperature and/or increasing recovery system operating pressure
- reducing the quantity of inerts which enter the recovery system.

In Table 7, estimates of the effect each of the principal control techniques would have on the level of vinyl chloride emissions from the monomer recovery system vent are given.

5.2.3.2 Exhaust System Emissions and Control Technology. Vinyl chloride monomer may be emitted directly to the atmosphere as a result of several procedures used in the reactor/stripper unit operating sequence. Emissions resulting from these procedures account for about 12% of the total vinyl chloride emissions from the suspension polymerization process.

After a polymerization or stripping operation is completed and the batch is dumped, an atmosphere of vinyl chloride remains in the vessel cavity. Many operators apply a vacuum to remove as much of this residual vinyl chloride as possible for subsequent recovery and reuse. The monomer recovery system vacuum pump is normally used to remove this residual.

When maximum vacuum conditions are attained, air is usually admitted into the vessel to break the vacuum. The ensuing vessel atmosphere consists of air mixed with a relatively small volume of vinyl chloride. It is impractical to use the monomer recovery system to recover this residual of vinyl chloride. Since at a particular set of condenser conditions the ratio of vinyl chloride to air is constant, the quantity of vinyl chloride released from this system is dependent on the amount of air present. Therefore, steam ejectors are commonly used to exhaust the air and the residual vinyl chloride from these vessels. This air/vinyl chloride stream is usually exhausted directly to atmosphere.

The procedure of pulling and breaking a vacuum may have to be repeated several times in preparing the vessel for a subsequent charge or in preparation for vessel entry prior to manual cleaning. The operating procedures which result in these periodic emissions to atmosphere are referred to as vessel exhaust procedures.

TABLE 7 MONOMER RECOVERY SYSTEM VENT: ESTIMATED EFFECT OF CONTROL TECHNIQUES (19)

(Relative to uncontrolled plant emissions)

Aba	tement Technology	% Reduction in VCM Emissions From this Source	Resultant Stack Gas VCM Conc
1.	Add-on control facilities		
	- Carbon adsorption	99+	10 ppm by Vol.
	- Solvent absorption	99 +	10 ppm by Vol.
	 Thermal oxidation 	99 +	10 ppm by Vol.
2.	Refrigeration (Remove the water vapour & . lower condenser temp . from 45°F to 15°F)	90	10 Vol. %
3.	Reduce the quantity of inerts present in the system	80*	50 Vol. %

*Estimate based on the operation of closed reactor and stripper facilities for at least four batch cycles versus opening these vessels after each cycle.

Control Technology - Exhaust Vents

As noted above, atmospheric emissions of vinyl chloride occurring as a result of vessel exhaust procedures, represent a substantial portion of total plant emissions of this compound. The following techniques may be used to achieve an estimated 95% reduction in the quantity of vinyl chloride emissions from these vessel exhaust procedures:

(1) Increase the number of batch runs between the occasions when vessel exhaust procedures are initiated. This can be achieved by:

- instituting closed reactor high pressure water cleaning techniques
- instituting closed reactor charging techniques
- periodically coating the vessel walls to minimize adherence of the polymer.

(2) Use steam purging procedures to remove the residual vinyl chloride from the vessel vapour space. The vinyl chloride removed by this purge medium can be condensed in the monomer recovery facilities (along with the steam) and effectively separated from the condensate.

(3) Install a 'gasholder' or other suitable device to contain the vessel exhaust streams. This device can be used to store other miscellaneous plant streams which also contain vinyl chloride. In general the 'gasholder' serves as surge or hold-up capacity for many vinyl chloride-laden gas streams which can subsequently be processed through the monomer recovery facilities on a controlled and uniform basis.

(4) Remove the residual vinyl chloride from the vessel vapour space by displacing it with water to a 'gasholder' or other suitable containment device.

5.2.3.3 Emissions Downstream of the Stripper and Associated Control Technology. Sources of captive emissions of vinyl chloride located downstream of the stripper (see Figure 11) account for an estimated 32% of total plant emissions of this compound (11). The principal atmospheric emission sources in this section of the plant include:

- the slurry blend tank vents
- the centrifuge vent
- the polymer drying and storage silo vents.

The Slurry Blend Tank Vents

Following the stripping operation, the polymer slurry is transferred to one of a number of slurry blend tanks. The slurry blend tanks are usually designed to hold more than one reactor charge. These tanks provide the surge capacity required for uniform operation of the subsequent water removal facilities. They also facilitate scheduling of the different grades of product through the back end of the plant.

It is common practice to purge the slurry blend tanks continuously with air or nitrogen to maintain a vapour space atmosphere below the flammability range for mixtures of vinyl chloride and air (4%-22% vinyl chloride in air) (16, 24). The purge stream, containing some vinyl chloride is normally released directly to atmosphere via the tank vent stack. This source of vinyl chloride emissions represents about 11% of total plant emissions.

The Centrifuge Vent

The slurry from the blend tank is transferred to a centrifuge for separation into a water solution and a wet polyvinyl chloride cake containing 20%-25% water (15). In some operations, vinyl chloride may leak around the centrifuge casing. This source accounts for an estimated 3% of total plant



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VCM-VINYL CHLORIDE MONOMER

emissions. The magnitude of the release is, however, directly proportional to the level of efficiency achieved in the upstream stripper.

Some vinyl chloride dissolves in the waste water removed during centrifuging (probably less than 1% of total plant emissions). Most of the vinyl chloride present in the waste water is eventually released to the atmosphere via the sewer disengaging facilities and/or the water treatment facilities.

Polymer Drying and Storage

The 20%-25% moisture which remains in the polyvinyl chloride resin particles, after centrifuging, is reduced to about 0.25% in a subsequent drying step (15). Several techniques may be used to dry the resin. Rotary systems and flash systems are the most widely used.

Most of the residual vinyl chloride in the wet resin is removed during the drying phase of the operation. The principal drying methods involve contacting the cake with a large volume of hot air which, in addition to being the drying medium, also serves as a vinyl chloride stripping medium. In most plants, the moisture-laden air containing vinyl chloride is released to the atmosphere via particulate removal facilities. This source of vinyl chloride release represents about 16% of total plant emissions.

After the resin has been dried, it is transferred to storage silos via pneumatic conveying systems. A fraction of the residual vinyl chloride tied up in the finished resin (typically about 50-1000 ppm, depending on the stripper efficiency and the type of resin being produced) is removed with this air conveying stream. The quantity of vinyl chloride removed by this stream represents about 2% of total plant emissions.

Control Technology - Captive Sources Downstream of the Stripper

Stripping efficiency is the most important manufacturing procedure in the control of vinyl chloride emissions from point sources downstream of the stripper. All of the residual vinyl chloride left in the resin slurry after the stripping operation, less that which remains in the finished product, is released to the environment via these sources. The captive sources located in this section of the plant account for about 32% of the total plant vinyl chloride losses.

There are two basic approaches used to reduce the level of vinyl chloride emissions which occur downstream of the stripper:

- improve stripping efficiency
- add-on control technology.

Improved Stripping

The amount of vinyl chloride left in the resin after the stripping operation is a function of the stripping temperature, the degree of vacuum applied, the stripping time and the resin properties.

Most stripping operations are carried out on a batch basis for a fixed time under specific conditions of temperature and pressure. The stripping may be done in the polymerization reactor. Generally, however, this unit operation is carried out in a separate vessel as depicted in Figure 6.

Prior to 1974, typical concentration levels of vinyl chloride in the stripped slurry were between 5000 and 10,000 ppm. These levels were established by the manufacturer, based on economic considerations. Since 1974, however, research studies and plant trials have resulted in many improvements in the efficiency of the stripper. Indications are that batch strippers can be operated to reduce the vinyl chloride cncentrations in the slurry (for the various grades of suspension type resins) to 400 ppm or less (11, 19, 23). Comparing these residual levels to those which were typical prior to 1974, indicates that the batch stripping technology which currently exists can be used to effectively reduce vinyl chloride emissions from all sources downstream of the stripper by 90% – 95%.

In addition to the improvements made in the operating efficiency of batch stripping systems, a new continuous stripping technique is being operated. This technique involves contacting the slurry with steam using a multistage counter current contacting device. The developers of this new technology claim that vinyl chloride concentrations in the slurry can be reduced to levels well below 100 ppm (11). These claims suggest that vinyl chloride losses from sources downstream of the stripper can be reduced by about 99%.

Add-On Control Technology

As an alternative to improved stripping, add-on control devices may be used to reduce vinyl chloride emissions from the above mentioned captive sources. Carbon adsorption, solvent absorption or incineration type control systems can be used to reduce these vinyl chloride emissions.

Theoretically, it is feasible to use add-on control systems to reduce vinyl chloride emissions from the principal captive sources located downstream of the stripper. However, when factors such as feed utilization, the creation of secondary pollution problems (e.g. hydrogen chloride formed during incineration of vinyl chloride) and capital/operating costs are considered, improved stripping would appear to be the most effective means of controlling these emissions. Moreover, improved stripping lowers the residual vinyl chloride content of the finished resin. Thus, improved stripping reduces the risk to the fabrication plant workers exposed to the residual vinyl chloride released during the heating processes used in their operations.

Of the captive sources located downstream of the stripper, the slurry blend tank vents and the centrifuge vent would appear to be the most readily adaptable to add-on control techniques. All three control techniques, i.e. carbon adsorption, solvent absorption and incineration, can be used to control vinyl chloride emissions from these vents. For example, because some slurry blend tank vent streams are low volume (in the order of 70 ft³/min) and contain relatively high concentrations of vinyl chloride (100,000-300,000 ppm), it is feasible, in some instances, to control emissions from this source by using add-on type control technology. Application of any one of the above-mentioned add-on control techniques can effectively reduce vinyl chloride emissions from this source and from the centrifuge vent by more than 99% (11).

Vinyl chloride emissions released via the dryer vents and storage silo vents are much more difficult to control with add-on technology. Typically these sources are high-volume (in excess of 50,000 ft³/min), low-concentration (about 350 ppm vinyl chloride) streams, and prove to be both technically

difficult and very costly to control using add-on techniques. They can be more effectively controlled by using other abatement methods such as improved stripping.

5.2.3.4 *Miscellaneous Emission Sources and Their Control: Emergency Venting.* Pressure vessels used in manufacturing operations must be equipped with protective devices to prevent rupture of that vessel during conditions resulting from operational 'upset' or fire. Either safety valves or rupture discs can be used to afford this protection and both types of device are used in the polyvinyl chloride manufacturing industry.

The polymerization reaction is a highly exothermic addition reaction. Thus, as noted in Section 3.2.2, the temperature of the reaction mass within the vessel must be properly controlled at all times to prevent a 'runaway' temperature from developing. Runaway temperatures arise when the heat of the polymerization reaction cannot be removed from the reaction mass at the rate at which it is generated. Therefore, during a runaway condition, there is an extremely rapid and uncontrolled increase in temperature within the reactor which can cause overpressure and possible rupture of the vessel.

The quantity of vinyl chloride released during an emergency situation varies with the size of the reactor vessel, the time during the reaction sequence at which the incident occurs, and the effectiveness of emergency procedures. In many instances, upon observing the onset of a runaway temperature condition, the plant operator manually vents part of the reacting mass to the atmosphere in an effort to bring the system under control. During this procedure, the safety device is by-passed with the intent of avoiding reactor pressure conditions which will cause this device to activate. For the purpose of this report, releases of vinyl chloride via the safety device and the by-pass vent are referred to as emergency venting.

The number of emergency incidents per year varies from plant to plant, depending on the number of reactor vessels, the operating procedures, and the type of instrumentation used. The quantity of vinyl chloride released during an incident cannot be accurately determined, but available data suggest that discharges of 5000 lb over a period of 5-10 minutes may occur under some emergency venting conditions (11). However, while this source of emission can result in release rates which far exceed any other plant source, major venting incidents are relatively few (1-20/yr) and of short duration. Annual losses of vinyl chloride as a result of emergency venting incidents are estimated at less than 5% of total plant vinyl chloride emissions (11).

Control Technology - Emergency Venting

The principal causes of a runaway reactor temperature condition and, in turn, emergency venting of vinyl chloride are:

- Control instrument malfunction
- interruption of cooling water supply (e.g. pump failure)
- interruption of electrical power supply
- operator error or negligence.

Depending on the stage of the reaction cycle at which the upset is triggered, the operator has about 10-15 minutes to take corrective action before conditions within the reactor are out of control

and safety devices are actuated. During this period, several things can be done to virtually eliminate the release of vinyl chloride to the atmosphere through emergency venting.

In the case of a single reactor upset, all or part of the reactor contents may be vented to a 'gasholder' or an equivalent containment device. Since the gasholder may be used to temporarily contain vinyl chloride laden gas streams from other plant sources, this vessel should be sized to hold more than the equivalent of one reactor charge. Under this control scheme, vinyl chloride contained in the vessel may be recovered for reuse or destroyed by incineration. However, if several or all of the reactors are simultaneously affected by a single emergency (such as an area wide power failure) the only course of action to avoid emergency venting to atmosphere would be to stop the reaction by injecting a chemical inhibitor into each reactor (11, 23).

Other measures used to reduce the vinyl chloride released to the atmosphere through emergency venting include:

- installation of a twin power line from the main electrical supply grid
- an emergency power generator
- computerized control of the reaction process to achieve a greater degree of surveillance and control of operating conditions.

Slurry Screening

In addition to the fugitive sources highlighted in Section 5.1, a slurry screening operation, which is peculiar to the polyvinyl chloride manufacturing operation, is a potential fugitive source of vinyl chloride emissions.

Some polyvinyl chloride manufacturers screen the slurry in an open box as it is dumped from the reactor to remove any lumps that may be present. The quantity of vinyl chloride released to atmosphere at this point is directly proportional to the level of unreacted vinyl chloride present in the slurry as it leaves the reactor.

Control Technology - Slurry Screening

Effective control measures include:

- the installation of an inline ''delumper'' which continuously breaks up lumps with a propeller device and does not require frequent maintenance (19)
- the relocation of the screening operation to a point in the process downstream of the stripper
- enclosing the screening operation and purging the vinyl chloride vapours to a blow-down system.

Process Water

Vinyl chloride is slightly soluble in water (1.33 lb/1000 lb of water at 38°C and 1 atm). The total process water effluent flow rate from a polyvinyl chloride plant is about 1.5 IG/lb of product (19, 25). Studies indicate that this effluent contains an average of 0.016 lb of vinyl chloride per 1000

Ib of water. Assuming that all of the vinyl chloride present in the process water is eventually released to the atmosphere, an estimated 0.025 lb would be released from this source per 100 lb of polyvinyl chloride produced (19). This assumption is based on the fact that plants generally aerate the process water in a central treatment facility before final discharge, and that the vinyl chloride which is contained in the process water is released to atmosphere during this aeration process.

Control Technology - Process Water Emissions

Vinyl chloride present in process water effluent streams can be effectively removed by stripping with either air or steam in a stripping column. Under this arrangement, contaminated effleunt streams can be collected and then processed through a stripping column prior to discharge to central water treatment facilities. It has been estimated that stripping can result in a 99 + % reduction in the vinyl chloride content of the process waste water effluent (19). The vinyl chloride that is removed from the process water can be recovered for reuse or destroyed by incineration.

Building Ventilation Exhaust

As mentioned earlier, most polyvinyl chloride manufacturing operations are carried out within an enclosed area (e.g. a building). Since 1973, plant operators have installed elaborate building ventilation exhaust systems as part of a work area clean-up program designed to meet recently established occupational exposure limits for vinyl chloride. These systems are designed to replace the air within the enclosed manufacturing and resin storage areas of a building, several times per hour. Ventilation hoods and air hoses are commonly used to sweep the vinyl chloride gases away from the worker in areas where significant exposure is likely to occur.

The building ventilation exhaust system has been estimated to contribute 0.5% - 1% of total plant vinyl chloride emissions (23). Operational sources contributing to the ventilation system vinyl chloride losses are many and can be classified as fugitive sources. The quantity of vinyl chloride emitted to the atmosphere via this route has been included in the overall estimate of fugitive losses emanating from the plant (Section 5.1).

Control Technology - Building Ventilation Exhaust

Building ventilation exhausts are typically high flow rate streams (in excess of 50,000 ft³/min) containing low concentrations of vinyl chloride (10 ppm). It is, therefore, difficult to contain vinyl chloride emissions from this source using available add-on control technology. However, many of the control measures which can be used to effectively abate captive and fugitive emissions from specific plant sources will in turn reduce the level of emissions released to atmosphere via the ventilation exhaust system.

5.3 Attainable Levels of Emission Control

As noted in Section 4, the estimated total emissions of vinyl chloride from stationary sources in Canada during 1973 is estimated at 5000 short tons. Of these emissions, approximately 4940 short tons were emitted from polyvinyl chloride and vinyl chloride manufacturing operations. Technology to effect an estimated 95% reduction in vinyl chloride emissions from these two principal manufacturing operations exists. Emissions from captive sources associated with these operations can be reduced by approximately 98% while improved operating practices and control strategies can be used to reduce emissions from fugitive sources by an estimated 90% (11).

Attainable captive source emission limits, using what is considered to be best available control technology, are shown in Table 8 (available control schemes are reviewed in Section 5.2).

TABLE 8ATTAINABLE LEVELS OF EMISSION CONTROL - CAPTIVE SOURCES (26):VINYL CHLORIDE MANUFACTURE; POLYVINYL CHLORIDE MANUFACTURE

	Vinyl Chloride Emissions	
Source	Ib/100 Ib Product	Concentration ppm by volume
Vinyl Chloride Manufacture:		
All process vent streams emitting more than 4.5 Ib/day vinyl chloride	-	10
Polyvinyl Chloride Manufacture:		
Monomer recovery system vent	_	10
Reactor/stripper exhaust system vents	-	10
Reactor opening losses	0.002	<u> </u>
Total from all sources downstream of the stripper operated in the production of each of the following types of resin;		
	0.00	
Suspension resin	0.02	-
Bulk resin	0.04	_
Copolymer resin	0.20	-

5.4 Cost of Pollution Control

Pollution control costs to attain the emission limits depicted in Table 8 will vary from plant to plant throughout the vinyl chloride industry. Factors such as the age of the plant, its location and its layout will influence these costs. For these reasons, amongst others, only order of magnitude estimates of expected total industry expenditures will be mentioned here.

For the purpose of this report, the Canadian vinyl chloride industry is comprised of one remaining vinyl chloride plant and three polyvinyl chloride plants. The total cost of additional controls (relative to 1973) to minimize emissions from the captive sources associated with these four plants would be in the order of \$6 million-\$9 million, depending on the control options selected at the various plant sites. Control schemes to abate emission from fugitive sources will likely cost an additional \$1 million-\$2 million. These estimates are based on 1st quarter 1975 U.S. dollars and are based on the results of a control cost study of the U.S. vinyl chloride industry by EPA (11).

REFERENCES

- 1. C. + E. News, p. 6, (January 28, 1974).
- Mastromatteo, E., A.M. Fisher, H. Christie and H. Danziger, "Acute Inhalation Toxicity of Vinyl Chloride to Laboratory Animals", *J. Amer. Indust. Hyg. Assoc. 21*, pp. 394-397, (1960).
- Weaver, P.H., 'On the Horns of the Vinyl Chloride Dilemma', Fortune, pp. 150-153, 202-204, (October 1974).
- Dinman, B.D., W.A. Cook, W.M. Whitehouse, H.J. Magnuson and Th. Ditcheck, 'Occupational Acroosteolysis I. An Epidemiological Study', Arch. Env. Health 2,, p. 61, (1971).
- Viola, P.L., A. Bigotti and A. Caputo, 'Oncogenic Response of Rat Skin, Lungs and Bones to Vinyl Chloride', *Cancer Res. 31*, pp. 516-522, (1971).
- Tabershaw, I.R. and W.R. Graffey, "Mortality Study of Workers in the Manufacture of Vinyl Chloride and its Polymers", *J. Occ. Med.* 16, pp. 509-516, (August 1974).
- 7. National Inventory of Sources and Emissions of Vinyl Chloride (1973) Internal Report APCD 75-1, (February 1975).
- 8. McConnell, G., Degradation of Vinyl Chloride in the Atmosphere: Research Study Findings (May 1975).
- 9. Status Report On Vinyl Chloride, Dow Chemical of Canada Ltd., (December 19, 1974).
- 10. IT&C, Plastics Processing Industry Survey (1975).
- 11. Standard Support and Environmental Impact Statement: Emission Standard for Vinyl Chloride, EPA-450/2-75-009, (October 1975).
- 12. EPS, Petrochemical/Synthetic Resin Industries Atmospheric Emissions and State-of-the-Art Questionnaire Replies.
- 13. "Product Profile: Vinyl Chloride", Can. Chem. Proc., (January 1974).
- 14. Plastic Industry Council Data File Series, Volume I; Canadian Plastic Resin Consumption 1973, (May 1974).
- Albright, L.F., Processes for Major Addition Type Plastics and Their Monomers, McGraw-Hill, New York, N.Y. (1974).
- Faith, W.I., D.B. Keyes and R.I. Clark, *Industrial Chemicals* 3rd ed., John Wiley and Sons Inc., New York, N.Y. (1965).

- 17. Matthews, G., *Vinyl and Allied Polymers Volume II*, Butterworth and Co. Ltd., London, England (1972).
- 18. Smith, M.W., Manufacture of Plastics Volume I, Reinhold, New York, N.Y. (1964).
- 19. Standard Support Environmental Impact Document: Emission Sources and A-atement Technology Volume II, (March 1975).
- 20. Hedley, W.H., et al, Potential Pollutants from Petrochemical Final Report by the Monsanto Research Corporation, Dayton, Ohio, (December 1973).
- 21. Dow Chemical Canada Ltd., Personal Communication to EPS by Mr. D. Evans, (March 18, 1976).
- 22. Vinyl Chloride An Assessment of Emission Control Techniques and Costs, EPA-650/2-74-097, (September 1974).
- 23. Esso Chemical Canada, Plant data submitted EPS, (October 21, 1975).
- 24. Scientific and Technical Assessment Report on Vinyl Chloride and Polyvinyl Chloride, EPA-600/6-75-004, (June 1975).
- 25. MOE, Environmental Engineering Survey of B.F. Goodrich Canada Ltd., Thorold, Ontario (July 25, 1974).
- 26. Canadian Government/Vinyl Chloride Industry Task Force Meetings (Unpublished Proceedings Oct. 20, 1976).

BIBLIOGRAPHY

"Activated Carbon Effective for Removing VCM", *Env. Sci.* + *Tech., 8:* 10, p. 872, (October 1974).

Air Products and Chemicals Inc., Stripping of Vinyl Chloride Monomer from Resins in Aqueous Slurries and from Dry Resin Powders.

"Battle Lines Drawn on Vinyl Chloride Issue", C. + E. News, p. 16, (February 25, 1974).

Bell, Z.G., J.C. Lafleur, R.P. Lynch and G.S. Work, PPG Industries Inc., "Control Methods for Vinyl Chloride", *Chem. Eng. Prog.* 71: 9, pp. 45-48, (September 1975).

"Withholding of Vinyl Chloride Data Hinted", C. + E. News, p. 16, (May 20, 1974).

Cook, W.A., et al, "Occupational Acroosteolysis", Arch. Env. Health, 2, (January 1971).

"Curtail Vinyl Chloride Exposure", Hydrocarb. Proc., (February 1976).

"Diamond Shamrock's Gamble in Alberta", Can. Chem. Proc. pp. 25-28, (July 1976).

Harper, C.A., Handbook of Plastics and Elastomers, McGraw-Hill, New York, N.Y. (1975).

Kent, J.A., *Handbook of Industrial Chemistry*, 7th ed., Van Nostrand Reinhold, New York, N.Y. (1974).

Monsanto Research Corporation, *Potential Pollutants from Petrochemical Processes*, MRC-DA-406 (December 1973).

Mutchler, J.E. and T.A. Loch, "Potential Air Pollution Problems from Vinyl Chloride and Polyvinyl Chloride', *Vinyl Chloride Seminar Presentations*, G.D. Clayton and Associates, Southfield, Michigan.

Ontario Ministry of the Environment, Vinyl Chloride as an Airborne Hazardous Contaminant I, (October 1974).

Ontario Ministry of the Environment, *Vinyl Chloride as an Airborne Hazardous Contaminant I, Progress Report No. 1*, Report Number ARB-TDA-02-75 (March 1975).

Preliminary Assessment of Environmental Problems Associated with Vinyl Chloride and Polyvinyl Chloride: Report on Activities and Findings of the EPS Vinyl Chloride Task Force, September 1974.

Schweitzer, G.E., *'Environmental Concerns Beyond the Work-Place''*. Presentation to the Working Group on Toxicity of Vinyl Chloride and Polyvinyl Chloride, New York Academy of Sciences, May 11, 1974.

Selikoff I.J., Statement at *Hearings on Standard for Control of Vinyl Chloride Hazards*, June 25, 1974.

Shreve, R.N., Chemical Process Industries, McGraw-Hill, New York, N.Y. (1957).

Society of the Plastics Industry, Inc., Comments on Environmental Protection Agency's Proposed Standard for Vinyl Chloride, (March 1975).

Torkelson, T.R., F. Oyen and V.K. Rowe, "The Toxicity of Vinyl Chloride as Determined by Repeated Exposure of Laboratory Animals", *J. Amer. Indust. Hyg. Assoc. 2,:* 5, (October 1969).

U.S. Federal Register, 39: 92, p. 16896, (May 10, 1974).

U.S. Federal Register, 40: 248, p. 59531, (December 24, 1975).

Vinyl Chloride Task Force, Preliminary Assessment of Environmental Problems Associated with Vinyl Chloride and Polyvinyl Chloride - Report on the Activities and Findings of the Vinyl Chloride Task Force for the United States Environmental Protection Agency (September 1974).