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Vinyl Chloride - A Review Of National Emission Standards

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ABSTRACT

This VC NESHAP Review Study assesses the current VC regulation through an investigation of emission control techniques and technological developments in the industry. The study encompasses evaluations of existing and new control technologies, sources not regulated by the standard, and enforcement and compliance experience since promulgation of the standard. Information and data evaluated during this study were obtained through literature searches, plant visits, and interviews with industrial representatives and EPA Regional Office personnel. The results of this review study will form the basis for possible revison of the existing standard.

ACKNOWLEDGEMENTS

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Several regional EPA personnel also contributed extensive information and provided data necessary to evaluate the current status of emission control in the industry.

ABBREVIATIONS AND ACRONYMS USED IN THIS REPORT

AAQS	Ambient Air Quality Standard
APRS	Automatic Pressure Reduction System
BACT	Best Available Control Technology
BAT	Best Available Technology
BID	Background Information Document
CAA	Clean Air Act
CARB	California Air Resources Board
CFR	Code of Federal Regulations
CMA	Chemical Manufacturers Association
CTA	Chain Transfer Agent
CTG	Control Techniques Guidelines
DOT	Department of Transportation
DSSE	Division of Stationary Source Enforcement
EDC	Ethylene Dichloride
EPA	Environmental Protection Agency
FDA	Food and Drug Administration
FID	Flame ionization detector
FR	Federal Register
HC	Hydrocarbon
KO	Knock-out (vessel)
LEL	Lower explosive limit
NAAQS	National Ambient Air Quality Standards
NESHAP	National Emission Standard for Hazardous Air Pollutants
NIOSH	National Institute for Occupational Safety and Health

NPDES	National Pollution Discharge Elimination System
NSPS	New Source Performance Standards
OAQPS	Office of Air Quality Planning and Standards
OSHA	Occupational Safety and Health Administration
OVA	Organic vapor analyzer
PMN	Premanufacturing Notice
ppm	Parts per million
PSD	Prevention of significant deterioration
PVC	Polyvinyl chloride
RACT	Reasonably Available Control Technology
RCRA	Resource Conservation and Recovery Act
ROL	Reactor opening loss
RVC	Residual vinyl chloride
RVD	Relief valve discharge
SCAQMD	South Coast Air Quality Monitoring District
SIP	State Implementation Plans
SOCMI	Synthetic Organic Chemical Manufacturing Industry
SPI	Society for the Plastics Industry
SSEIS	Standard Support and Environmental Impact Statement
TSCA	Toxic Substances Control Act
VC	Vinyl chloride
VOC	Volatile organic compounds

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1.0 EXECUTIVE SUMMARY

1.1 INTRODUCTION

This Phase I review study assesses the current National Emission Standard for vinyl chloride (VC) by investigating emission control techniques. This review evaluates technological developments in the industry and provides a preliminary basis for possible standard revision. Recommendations to revise the standard would be supported by a more detailed Phase II study that would develop a Background Information Document (BID). This review study was conducted under a contract awarded to TRW's Environmental Engineering Division by the U.S. Environmental Protection Agency (EPA).

The review study focused on four areas which are summarized below:

- Technologies currently used for compliance.
- Existing sources identified during the original support study but not subject to the current regulation.
- Emission sources not identified during the original support study.
- Enforcement and compliance experience.

Additional details can be found in corresponding sections of the text (indicated in parentheses). A description of the processes involved in VC production and polymerization is presented in Chapter 3.

1.2 PROCESS DEVELOPMENTS

The sources subject to the VC regulation are ethylene dichloride (EDC) produced by oxychlorination, VC, and polyvinyl chloride (PVC) facilities. Recent modifications of processes in these facilities include:

- EDC/VC - The "balanced process" utilizing direct chlorination and oxychlorination is the most common process used for production of EDC and VC. Many newer plants and some existing plants have incorporated oxygen oxychlorination plants as part of the EDC process. The change from air to pure oxygen as a feedstock can make combustion more feasible and therefore could result in reduced emissions from the oxychlorination vent.

  (Section 3.2.1 and 3.2.2)

- PVC - Newer plants are incorporating larger reactor systems resulting in increased capacity, fewer reactor openings and reduced emissions. These large reactor systems have also accounted for a decrease in the production of specialty PVC resins.

  (Section 4.2.3.1)

1.3 CONTROL TECHNOLOGY SUMMARY

Most of the discussion regarding VC control technology is focused on PVC plants because these facilities contribute proportionately more emissions. For this reason, most of the requirements in the VC regulations pertain to PVC plants. The characteristics inherent in the batch processes of these plants account for the relative difficulty in emission control implementation.

1.4 PRIMARY CONTROLS

Control devices, applied to reduce VC emissions when exhaust gases are discharged to the atmosphere, include:

- Incineration - This method represents the most prevalent means of primary control and is the only one used by both EDC/VC and PVC plants. (Solvent absorption and carbon adsorption are also used as primary controls in PVC plants, but in EDC/VC plants they are used on a smaller scale as part of the process or as a means to reduce fugitive emissions.)

  Although thermal incineration is most commonly used, two plants are using catalytic oxidation systems. In most cases,

thermal incineration is reducing emissions below the required 10 ppm. Most units have scrubbers to prevent HCl emissions.

(Section 4.1.2)

- Solvent Absorption - This method is effective in reducing emissions below 10 ppm. It is used as primary control only in PVC plants. VC is recovered by this method rather than destroyed (as with incineration).

  (Section 4.1.6)

- Carbon Adsorption - As a primary control, this method is not as effective (in most cases) as incineration or solvent absorption in achieving the 10 ppm level. Usually, carbon adsorbers must be supplemented by other primary controls (e.g., incineration). Some plants that initially selected carbon adsorption as a primary control for exhaust gases have replaced the carbon beds totally with another control device. Carbon adsorption is effective on a smaller scale for reducing fugitive emissions or for recovering VC from some exhaust gases.

  (Section 4.1.5)

- Other Controls - These include steam boilers, flares, refrigeration systems and containment devices. Boilers are not usually used for primary control due to corrosion problems. Efficiency of VC reduction in flares has not been determined. Secondary pollutants (e.g., noise, smoke) have also been noted as a disadvantage of flares. Refrigeration systems are generally used as part of recovery systems or as back-up control in case of primary control breakdown. Containment devices are used to reduce emissions to the atomosphere and include gasholders and pressurized holding vessels. These devices collect vapors from various equipment vents and feed the VC recovery system and/or primary control device. They are also used in some cases to collect and hold emissions when the primary control is down for maintenance.

  (Sections 4.1.3, 4.1.4, 4.1.7, 4.1.8, and 4.2.3.3.1)

1.5 RELIEF VALVE DISCHARGES

Relief valve discharges cause short term excursions of VC emissions and, according to EPA regional enforcement personnel, represent the single most difficult enforcement problem.

- Contention is caused by the wording in the regulation that allows only "emergency" relief valve discharges.

  (Sections 4.2.1 and 5.7)

- Regional personnel indicate relief valve discharges continue to occur, but the frequency and magnitude vary throughout the industry. PVC reactors are responsible for the greatest frequency and largest quantities of emissions, but nonreactor-related discharges contribute approximately 34 percent of the relief valve events and 20 percent of the total quantity discharged.

  (Section 4.2.2)

- Reactor releases are affected by the type of polymerization process and whether the newer reactors are employed. The newer reactors are larger and incorporate more instrumentation. They appear to provide better control over upset conditions that could result in a relief valve discharge.

  (Section 4.2.3)

- Procedures for prevention of relief valve discharges vary from plant to plant. Many of these procedures have reduced the frequency of discharges.

1.6 RESIN STRIPPING

Because stripping techniques are different for each type and grade of resin, a wide range of residual VC (RVC) content in the stripped resin has been noted.

- Suspension Resins - These resins represent the highest percentage of total PVC production. The most widely used stripping method is continuous steam stripping. Many processors are attaining levels much lower than the required 400 ppm RVC - some less than 20 ppm.

  (Section 4.3.2)

- Dispersion Resins - Dispersion or emulsion resins are usually vacuum stripped batchwise in the reactor or in separate batch stripping vessels. Continuous stripping technologies for dispersion resins are not as advanced as for suspension resins. Required emission levels for dispersion resins (2,000 ppm) are being met and, in some cases, processors are regularly achieving levels below 1,000 ppm. Latex resins, produced by the dispersion process and usually sold undried, are required to meet a 400 ppm level. These resins are sensitive to heat and shear stress, creating difficulties in stripping efficiently.

  (Section 4.3.2)

- Bulk Resins - The characteristics of these resins (e.g., uniform porosity and size) enhance stripping efficiency. Steam stripping (under vacuum) in the reactor is used for these resins.

  (Section 4.3.4)

- Solution Resins - Only one plant produces solution resins. This process is unique among stripping procedures because no particulate resin form exists. Stripping is a distillation process with a high efficiency averaging levels of 10 ppm RVC.

  (Section 4.3.5)

1.7 FUGITIVE EMISSIONS

Fugitive emissions represent one of the larger contributions to VC emissions at EDC/VC and PVC plants.

- PVC plants appear to contribute more fugitives because of the batch process characteristics and the prevalence of plants with many old small reactors. One study done by a PVC processor indicated that, after installation of required equipment to control fugitives and implementation of leak detection and elimination programs, a large reduction was achieved in fugitive emissions. Emissions from their old small reactor system are now 75 percent lower than the industry average fugitive emissions as estimated in the original standard support study. Those

from their newer large reactor systems are now 95 percent lower.

(Section 4.4.1)

- EPA Regional personnel indicate that almost all plants have installed the required equipment specified in the current regulation and are following the required operational procedures. Some plants have received approval for equivalent equipment.

(Sections 4.4.2 and 4.4.3)

- The leak detection and elimination programs represent the greatest variability among plants surveyed. Leak detection programs and routine surveys with portable monitors vary widely among the plants. In most cases, other requirements have been addressed adequately (e.g., area monitoring and plans to eliminate leaks) and fugitives have been lowered.

(Section 4.4.4)

1.8 REACTOR OPENING LOSS (ROL)

Control of this emission source is achieved through various technologies and process modifications. Several methods have been developed that are effective in reducing ROL emissions to levels below those required by the regulation. "Clean reactor" technology has also contributed to a reduction in emissions from this source. Selection of the type of control (reactor purging) is based primarily on operating preferences and economics.

There is a problem in emission level determination for those processors whose resins are stripped in the reactor. Because actual measurements cannot be made to ascertain RVC levels, determination is based on calculations. These may not always be indicative of actual emissions.

(Section 4.5)

1.9 ENFORCEMENT AND COMPLIANCE EXPERIENCE

Industrial representatives and regional EPA personnel cited several areas of concern regarding enforcement and compliance experiences under the existing VC NESHAP. While many of these points were specific to either industry or the EPA, several areas reflected viewpoints common to

both. Chapter 5 lists and discusses these concerns. Enforcement of relief valve discharges is the most common concern.

(Chapter 5)

1.10 UNREGULATED SOURCES

Many of the sources not currently regulated under the VC standard were identified during the original study. These include PVC compounders and fabricators as well as processors using VC as a chemical intermediate or producing it as a byproduct. The implementation of the OSHA workplace standard for VC has resulted in fabricators' receiving resins with RVC levels of 10 ppm or lower. This has greatly reduced emission levels from fabricating facilities. Facilities manufacturing certain pesticides and trichloroethanes use VC as an intermediate, and emission information on these processes was not obtained during this study phase.

Unregulated sources producing VC as a byproduct were contacted and they reported that the small amount of VC involved was either incinerated or recycled through recovery systems for use in polymerization processes in another facility.

Other sources include mobile sources, nonplant transfer facilities, solid waste drying facilities and disposal sites (landfills). Each of these represents a potential VC emission source and each has been identified as an area of concern by regional EPA personnel.

(Chapter 6)

1.11 IMPACT OF OTHER REGULATIONS

There has been substantial regulatory activity since promulgation of the current VC NESHAP. The new regulations that will have an effect in reducing VC emissions to the atmosphere are Prevention of Significant Deterioration (PSD) of Air Quality, plans for nonattainment review, and delegation of NESHAP authority, all under the Clean Air Act. These regulations call for the reduction of VC emissions below those previously required by the VC NESHAP. Other new regulations that will also have an effect on levels of VC emissions include the Resource Conservation and Recovery Act (RCRA) for the control of hazardous wastes, the Toxic Substances Control Act (TSCA) which regulates any new chemicals involved in polymer development, and the Clean Water Act requiring the development of effluent guidelines for VC as well as a possible VC drinking water standard.

(Chapter 7)

2.0 INTRODUCTION

2.1 BACKGROUND INFORMATION

The vinyl chloride (VC) standard was promulgated in 1976 under Section 112 of the Clean Air Act (CAA), National Emission Standards for Hazardous Air Pollutants (NESHAP), and is applicable to new and existing sources of VC – those plants producing VC and/or polymerizing VC into polyvinyl chloride (PVC). The proposed NESHAP "Policy and Procedures for Identifying, Assessing, and Regulating Airborne Substances Posing a Risk of Cancer" would require that emission standards promulgated under Section 112 be reviewed at intervals of no more than 5 years. These reviews would be used to determine the need for revision of the emission standard.

VC was first implicated as a highly specific cause of angiosarcoma, a rare cancer of the liver, by evidence from occupational exposures. Following intensive study, the Occupational Safety and Health Administration (OSHA) promulgated a standard in 1975 to reduce occupational exposure to VC, and the EPA promulgated a standard in 1976 to reduce atmospheric VC emissions. Waivers of compliance were granted, in some cases for up to 2 years, allowing industry to incorporate necessary controls.

The existing VC NESHAP (henceforth referred to as the regulation) is one of the most complex air emissions standards promulgated by the EPA. The regulation is applicable to three different types of facilities – plants producing ethylene dichloride (EDC) by the reaction of oxygen and hydrogen chloride with ethylene, plants producing VC by any process, and plants producing one or more polymers containing any fraction of VC. Research and development facilities containing a polymerization reactor capacity greater than 0.2 cubic meters (50 gallons) but no more than 4 cubic meters (1100 gallons) are exempt from all parts of the regulation

except the 10 ppm emission limit. Reactors less than 0.2 cubic meters (50 gallons) are not regulated. Those reactors greater than 4 cubic meters (1100 gallons) are subject to all requirements of the regulation.

Each of these facilities are subject to different standards at numerous points in the manufacturing process - numerical emission limits, equipment specifications, and work practice requirements (i.e., working procedures that must be followed by plant personnel). Table 2-1 lists each section of the regulation requiring a specific standard and the type of plant subject to that standard. The current regulation is reproduced in Appendix A.

Compliance with the current regulation is determined through testing and monitoring results and extensive reporting and recordkeeping requirements (all of which are conducted by the plant). The plants are required to report to the responsible Regional EPA office and EPA enforcement personnel conduct standard compliance tests and review plant procedures and records periodically. Requirements for reporting and recordkeeping are summarized in Table 2-2.

2.2 SCOPE OF THE REVIEW STUDY

Periodic review of regulations is an important part of the standards development program. The purpose of these reviews is to investigate the control techniques applied to industrial processes for reducing VC air emissions.

2.2.1 Areas of Concern

The review study conducted to assess the current VC regulation concentrated on four areas of concern:

- Technologies being used for compliance,
- Existing sources identified during the original support study but not subject to the current regulation,
- New emission sources not identified during the original support study, and
- Enforcement and compliance experience.

Each of these areas served as focal points for research and appropriate study methodology. The original study supporting the current regulation (EPA, 1975) was thoroughly reviewed including all the information submitted

Table 2-1. EMISSION STANDARDS IN THE VC NESHAP

Section	Applicability	Standard	Plants Involved
61.62(a)	Exhaust gases discharged to the atmosphere from any equipment used in EDC purification.	≤ 10 ppm	EDC
61.62(b)	Emissions of VC to the atmosphere from oxychlorination reactors.	0.2 g/kg 100% EDC product	EDC
61.63(a)	Discharge of exhaust gases to the atmosphere from any equipment used in VC formation and/or purification.	≤ 10 ppm	VC
61.64(a)(1)	PVC reactor exhaust gases discharged to the atmosphere.	≤ 10 ppm	PVC
61.64(a)(2)	Allowable reactor opening losses of vinyl chloride based on the amount of product produced between openings.	0.02 g VC/kg PVC	PVC
61.64(a)(3)	Discharge to the atmosphere from any manual vent valve on a PVC reactor.	none (except for an emergency)	PVC
61.64(b)	Exhaust gases discharged to the atmosphere from a stripper.	≤ 10 ppm	PVC
61.64(c)	Exhaust gases discharged to the atmosphere from mixing, weighing, and holding containers which precede reactors.	≤ 10 ppm	PVC
61.64(d)	Exhaust gases discharged to the atmosphere from monomer-recovery systems.	≤ 10 ppm	PVC
61.64(e)(1)	Emissions of vinyl chloride to the atmosphere from the combination of all sources following the stripper. Pertains to the requirements of residual VC (RVC) levels attained with the stripping process.	2000 ppm - dispersion resins (excluding latex) 400 ppm - all other resins (including latex)	PVC

(continued)

Table 2-1. Continued

Section	Applicability	Standard	Plants Involved
61.64(e)(2)	Emissions of vinyl chloride to the atmosphere from the combination of all sources following the reactor if the plant has no stripper; or from sources following the stripper if the plant uses technology in addition to stripping.	2 g/kg product from the stripper (or reactor) for dispersion PVC resins (excluding latex) 0.4 g/kg product from the stripper (or reactor) for all other PVC resins (including latex)	PVC
61.65(a)	Discharge to the atmosphere from any relief valve on any equipment in VC service (equipment contains or contacts either a liquid at least 10% by weight VC or gas 10% by volume VC).	none (except for an emergency)	EDC, VC and PVC
61.65(b)(1)	Fugitive emissions to the atmosphere from loading and unloading lines in VC service (i) opening of the lines (ii) VC removed from these lines to meet (i) and ducted to a control system	 (i) 0.0038 m^3 VC @ STP (ii) $\leq$ 10 ppm	EDC, VC, PVC
61.65(b)(2)	Fugitive emissions to the atmosphere from slip gauges (in VC service) used during loading and unloading operations.	$\leq$ 10 ppm	EDC, VC, PVC
61.65(b)(3)	Fugitive emissions to the atmosphere from pump, compressor, and agitator seal leakage.	$\leq$ 10 ppm	EDC, VC, PVC
61.65(b)(4)	Fugitive emissions to the atmosphere from leakage of relief valves on equipment in VC service.	minimized by installation of a rupture disk or by connection of discharge to a process line or recovery system	EDC, VC, PVC

(continued)

Table 2-1. Concluded

Section	Applicability	Standard	Plants Involved
61.65(b)(5)	Fugitive emissions to the atmosphere from manual venting of gases.	≤ 10 ppm	EDC, VC, PVC
61.65(b)(6)	Fugitive emissions to the atmosphere from opening of equipment.		EDC, VC, PVC
	(i) before opening	(i) total amount discharged per opening must be 2% by volume VC or 0.95 m^3 (whichever is larger)	
	(ii) VC removed from equipment to meet (i) and ducted to a control system	(ii) ≤ 10 ppm	
61.65(b)(7)	Fugitive emissions to the atmosphere from sampling.		EDC, VC, PVC
	• unused sample portions containing ≥ 10% by weight VC	return to process	
	• sample containers in VC service	purge into closed process system	
61.65(b)(8)	VC emissions due to leaks from equipment in VC service.	minimize via formal leak detection and elimination (LD & E) program, designed by operator and approved by the Administrator.	EDC, VC, PVC

Table 2-2. SUMMARY OF REPORTING AND RECORDKEEPING REQUIREMENTS IN VC NESHAP

Section	Applicability	Requirements	Category
61.69(a)	Owner or operator of any source to which this subpart applies	Initial Report: Notification that equipment and procedural specifications required in Section 61.65 (fugitive emission control) have been implemented.	Initial Reporting
61.69(b)(1)	Existing source or new source having start-up date preceding effective date of regulation.	Submittal of above notification within 90 days of effective date of regulation (unless waiver granted).	
(2)	New source having start-up date after effective date.	Submittal of above notification within 90 days of initial start-up date.	
61.69(c)	Owners or operators of above sources	Notification inclusions: • List of equipment installed for compliance • Description of physical and functional characteristics of equipment • Description of methods used for measuring or calculating emissions • Statement verifying that equipment is installed and procedures are being used	
61.70(a)	Owner or operator of any source to which this subpart applies	Semi-annual reporting to Administrator (September 15 and March 15 of each year) containing the information described in subsequent sections.	Semi-Annual Reporting
61.70(b)(1)	Existing source or new source having start-up date preceding effective date.	Submittal of notification within 180 days of the effective date (unless waiver granted).	
(2)	New source having start-up date after effective date.	Submittal of notification within 180 days of initial start-up date.	

(continued)

Table 2-2. Continued

Section	Applicability	Requirements	Category
61.70(c)	Owner or operator of above sources	Use specified test methods (from Appendix B) unless equivalency or alternative method approved.	Semi-Annual Reporting
(1)	Same	Reporting of any emissions averaged over one hour which are in excess of limits prescribed for emissions from: • EDC purification equipment • Oxychlorination reactors • Equipment used for VC formation/purification • PVC reactor exhaust gases • Control systems for reactor emissions for ROL • Fugitives from loading/unloading lines • Fugitives from slip gauges • Fugitives from manual venting of gauges • Fugitives from equipment opening emissions ducted through a control system • Fugitives from inprocess wastewater emissions ducted through a control system	
(2)	Owner or operator of PVC plants in which stripping operations are used	Reporting of a record of the VC content in the PVC resin using method 107 as follows: • If batch stripped, sample each batch of each grade of resin immediately after stripping • If continuously stripped, sample each grade of resin or at 8 hour intervals (whichever is more frequent) • Determine the quantity of materials processed by the stripper on a dry solids basis • Report VC content found in each sample, averaged separately for each type of resin, over each calendar day and weighted according to the quantity of each grade of resin produced that day • Retain records for at least two years	
(3)	Same	Report record of Reactor Opening Loss (ROL) emissions	

(continued)

Table 2-2. Concluded

Section	Applicability	Requirements	Category
61.71(a)	Owner or operator of any source to which this subpart applies	Retention of the following information (for minimum of two years):	Recordkeeping
(1)	Same	• Record of leaks detected by the VC monitoring system	
(2)	Same	• Record of leaks detected during routine monitoring with the portable hydrocarbon detector and action taken to repair the leaks	
(3)	Same	• Record of emissions measured by the continuous VC monitoring of sources listed in 61.70(c)(1)	
(4)	Same	• Daily operating record for each PVC reactor including pressures and temperatures	
61.64(a)(3)	PVC plants only	Manual vent valve discharge. Operator of source must notify Administrator within 10 days of occurrence and submit a report containing the following: • Source of relief valve discharge • Nature and cause of discharge • Date and time of discharge • Approximate quantity of VC lost during discharge • Method used for determining VC loss • Action taken to stop discharge • Action to be taken to prevent future discharges	Exception Reporting
61.65(a)	EDC, VC and PVC plants	Relief valve discharge. Operator of source must notify Administrator within 10 days of occurrence and submit a report containing the following: (Same as requirements for "Manual vent valve discharge" above).	

to EPA under authority of Section 114 of the Clean Air Act (CAA). Section 114 authority was also used to review Regional source files, but no Section 114 information requests were sent to any subject sources. All responses were given voluntarily and cleared of any confidential material prior to inclusion in this report. The results presented here will form the basis for preliminary recommendations for revision of the current regulation and will identify additional research that is needed to support these revisions.

2.2.2 Review Study Methods

The following methods were used to conduct the review study.

- A literature review was conducted using published and unpublished information found in trade journals, EPA studies, EPA contractor-conducted studies, other governmental agency studies, and other pertinent references.
- EPA Regional personnel involved in enforcement and surveillance of the VC emitting industries from Regions I, II, III, IV, V, VI, and IX were consulted. Discussions were conducted during regional office visits, by telephone, and by mail.
- Representative plants in each region were visited (three EDC/VC plants and eight PVC plants). An effort was made to include old and new plants of each type as well as plants using the various process types.
- Meetings were held with industrial representatives to discuss control technologies currently used by their plants. Discussions were also held with representatives of two of the industry's trade organizations – the Society for the Plastics Industry (SPI) and the Chemical Manufacturers Association (CMA).
- The EPA OAQPS and the Division of Stationary Source Enforcement (DSSE) were also consulted.

Appendix B lists the locations, dates, and purposes of the meetings held with industry and EPA personnel.

2.3 THE VC EMITTING INDUSTRY

2.3.1 Current Number And Geographical Distribution

There are 39 operating PVC plants and 18 operating EDC/VC plants (1 producing EDC only) in 18 states and 7 EPA regions. Table 2-3 shows the

Table 2-3. GEOGRAPHIC DISTRIBUTION OF OPERATING VINYL CHLORIDE-EMITTING PLANTS

Region	State	No. of PVC plants	No. of EDC/VC plants
I	Massachusetts	3	0
II	New Jersey	6	0
	New York	1	0
III	Delaware	2	0
	Maryland	1	0
	Pennsylvania	1	0
	West Virginia	1	0
IV	Florida	1	0
	Georgia	1	0
	Kentucky	2	1
	Mississippi	1	0
V	Illinois	2	0
	Michigan	1	0
	Ohio	2	0
VI	Louisiana	5	11
	Oklahoma	2	0
	Texas	4	5
IX	California	3	1
	TOTAL PLANTS	39	18

distribution of these plants throughout the United States. (See Appendix C for identification of these plants). The number of EDC/VC plants has increased from 15 prior to promulgation of the regulation to 17 plants currently in operation. Two of the original plants discontinued operation and four new plants began operation. These new plants are identified in Appendix C. During this period the approximate VC nameplate production capacity increased from 3.1 teragrams (6820 million pounds) per year in 1974 to 3.7 teragrams (8200 million pounds) per year in 1980 (EPA, 1975; Chemical Week, 1980a).

The number of operating PVC plants has remained consistent since promulgation of the regulation. Of the 41 original PVC plants, 4 plants have discontinued operation and 3 new plants have begun operation. These newer larger plants, along with extensive expansions at several other existing plants, have resulted in an approximate increase in PVC nameplate production capacity from 2.6 teragrams (5739 million pounds) per year in 1975 to 3.4 teragrams (7600 million pounds) per year in 1980 (EPA, 1975; Chemical Week, 1980b).

2.3.2 Influence of the Standard on Industry

Promulgation of the regulation was followed by significant changes in the VC industry. These changes included plant and equipment modernization, process modifications, and redirection of some research and development resources from the product itself to the areas of environmental control. Economically, these changes were felt most acutely by the older PVC plants that had to retrofit their processes with new controls. Several EDC/VC and PVC plants were still in the design phase during development of the regulation and the engineering was altered to accommodate the new requirements.

The cost (of compliance) to the VC industry for a 10-year period (1977-1986) is estimated to be $765.7 million (1977 dollars). This includes investments, capital, operating and maintenance costs for new and existing plants (EPA, 1979).

A survey of 14 PVC producers indicated a 10-to-12 percent average loss in production capacity as a result of compliance requirements (Chemical Week, 1979). The reasons for lost capacity were due mainly to the time needed to clean reactors and purge the different systems in an

effort to reduce VC emissions prior to opening to the atmosphere. The PVC process may also need to be operated at a slower rate to strip residual VC (RVC) from PVC resins in order to reduce emissions. The production loss varies with the type of resin produced and stripping technology used.

EDC/VC plants have expended capital to comply with the regulations, mainly for add-on control equipment and modifications to processes. Furthermore, state agencies regulating hydrocarbon emissions are stimulating new technology for emission reduction. The main emphasis has been in changing from air processes to oxygen processes in the EDC process. This results in a lower volume emission to be combusted.

At the time of this review study, most of the EDC/VC and PVC plants have completed many of the modifications discussed above and are channeling their research and development resources back to product development. Relatively few plants have ceased production during the last 4 years. No EDC/VC plants have shut down; seven PVC plants have closed (four on a temporary basis). Construction of new or modified sources is currently underway in many regions.

2.3.3 Industrial Trends

From the standpoint of process and control, there is a significant trend in the industry towards automation and computerization. Among plants surveyed during the review study, processors utilizing these types of advanced systems have attained a high level of compliance.

There is a definite trend toward the use of larger reactors in the PVC industry. Economic and emission control advantages of these larger systems are discussed in Section 4.0.

The tendency to minimize the number of PVC resin grades has also been noted. The "grocery store" processor, with many small reactors producing multiple grades of resin, is leaning towards the processing of fewer grades. One reason for this change is the difficulty and amount of time required for stripping RVC from certain specialty resins (as mentioned above).

Reduction of energy consumption at EDC/VC plants is also being achieved through various process modifications. Steam consumption has been greatly reduced by Stauffer Chemical who uses the EDC reactor heat

in their purification reboilers and B.F. Goodrich who uses the heat of reaction for purification (McPherson, 1979). Many companies are also devoting more effort to make the "cracking" of EDC to form VC more efficient and eliminate unwanted byproducts originating from side reactions during the cracking. These trends will be discussed in more detail in later sections.

The VC industry is currently experiencing a sales decline due to the recession that occurred in early 1980. This decline is due mainly to the depressed construction industry, a major consumer of PVC pipe. (Forty percent of the PVC used in the United States goes into the manufacture of pipe.) Because 96 percent of the VC produced by EDC/VC plants is used in the PVC industry, a domino effect occurs. Currently, EDC/VC producers are running their plants at an average 86 percent of the first-quarter 1980 nameplate capacity while PVC producers are running their plants at an average 65 percent of the first-quarter 1980 nameplate capacity (Chemical and Engineering News, 1980a; 1980b).

2.5 REFERENCES FOR CHAPTER 2

Chemical and Engineering News. 1980a. "Vinyl Chloride." July 7, 1980, p. 9.

Chemical and Engineering News. 1980b. "Polyvinyl Chloride." October 6, 1980, p. 13.

Chemical Week. 1979. "At PVC Plants, Compliance Curbs Capacity." March 28, 1979, p. 36.

Chemical Week. 1980a. "PVC Growth Plans Lead to Big VCM Expansions." February 13, 1980, p. 26.

Chemical Week. 1980b. "PVC: Big Plans Match Growth Forecasts." January 16, 1980, p. 33.

Environmental Protection Agency. 1975. Standard Support and Environmental Impact Statement: Emission Standard for Vinyl Chloride, EPA-450/2-75-009. October 1975.

Environmental Protection Agency. 1979. Report to Congress. Document #96-38. "Cost of Clean Air and Clean Water," Vinyl Chloride Air Pollution Control Costs. December 1979, p. 56.

McPherson, R. W.; Starks, C. M.; and Fryar, G. I. 1979. "Vinyl Chloride Monomer . . . What You Should Know," Hydrocarbon Processing. March 1979, p. 36.

3.0 PROCESS DESCRIPTION

3.1 INTRODUCTION

This chapter describes processes used to produce vinyl chloride (VC) and to polymerize VC into polyvinyl chloride (PVC) resins. The most common method used for production of VC is dehydrochlorination (cracking) of ethylene dichloride (EDC). Currently, there are four polymerization processes being used to produce polyvinyl chloride resins from VC.

Approximately 87 percent of the EDC, or 1,2 dichloroethane, produced in the United States is used to produce VC. Current commercial processes that manufacture EDC for production of VC use a combination of ethylene, chlorine, and oxygen (usually in the form of air) for feedstocks. Hydrogen chloride (HCl) recycled from the cracking of EDC is also used as feedstock. In general, the production of EDC is an intermediate step in a combination of processes known as the "balanced process" for the production of VC. Figure 3-1 shows a simplified process flow diagram of an EDC/VC plant using the "balanced process." Table 3-1 summarizes the potential emission points and regulation requirements for control of each point in each process step shown in Figure 3-1. The requirements of the regulation will be discussed in more detail as the different process steps are described.

Polyvinyl chloride is one of the most versatile thermoplastics manufactured in the United States today. PVC resins are noted for their excellent chemical and physical properties. They are easy to process, cost relatively little to make, are self-extinguishing (when ignition source is removed) and can be compounded with other resins (Shreve, 1977, p. 589). Products fabricated from PVC resins can be either flexible or rigid.

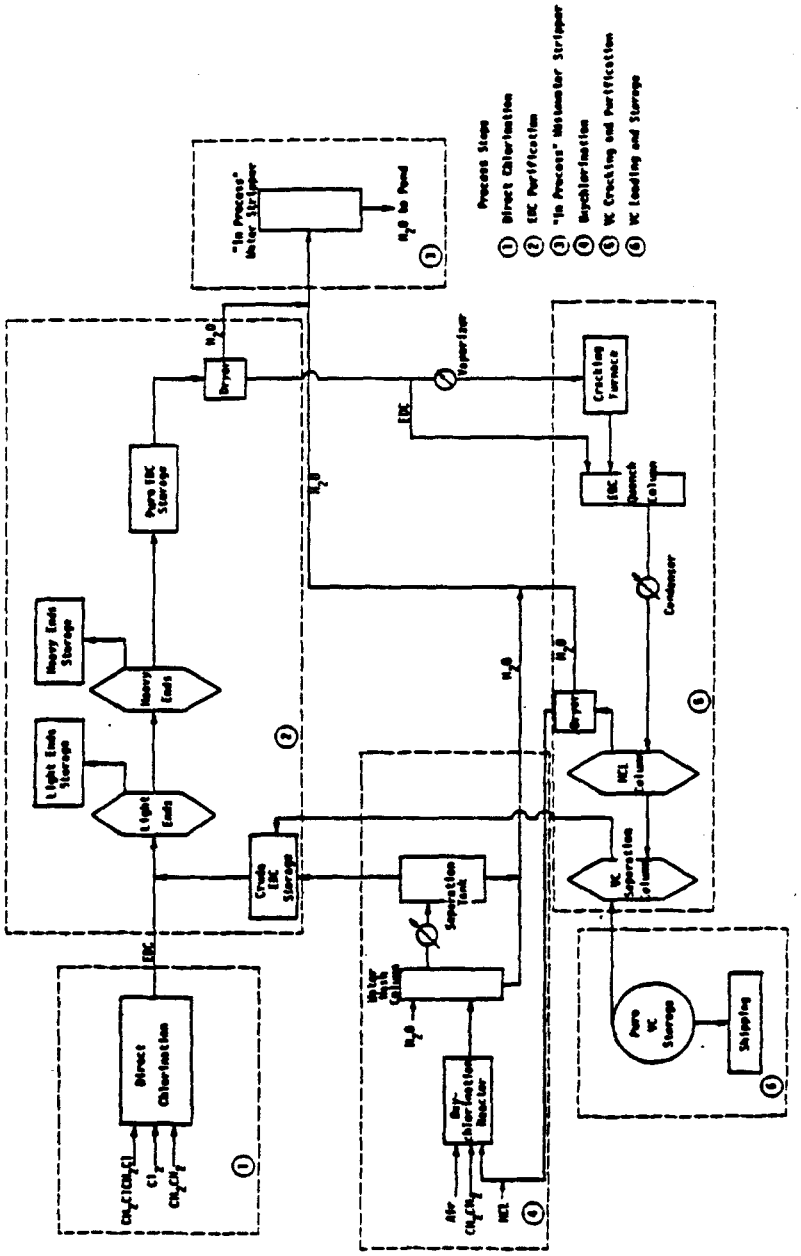


Figure 3-1. EDC/VC "Balanced Process" flow diagram.

Table 3-1. POINT SOURCE EMISSIONS
"BALANCED PROCESS" EDC/VC PLANTS

	Process step	Potential emission points	Regulation requirements
1	Direct chlorination	Product condenser	Not regulated
2	EDC purification	EDC crude storage, light ends column condenser, light ends storage tank, heavy ends column condenser, heavy ends storage tank	All emission points are required to be controlled to $\leq$ 10 ppm
3	"Inprocess" wastewater stripper	Wastewater storage tank Wastewater stripper column	VC removed from inprocess water is to be ducted to a control system from which concentration of VC in exhaust gas does not exceed 10 ppm
4	Oxychlorination	Water wash column Oxychlorination process vent Separator tank	Emissions from reactor are not to exceed 0.2 g VC/kg of the 100 percent EDC product
5	VC cracking and purification	EDC quench column HCl column vent VC column condensor	Concentration in all exhaust gases must not exceed 10 ppm
6	VC loading and storage	Loading lines VC storage tanks	Emissions from loading lines must be reduced so that upon opening of line to the atmosphere emissions do not exceed 0.0038m^3 of VC at STP. VC removed from lines to meet this criteria must be controlled to $\leq$ 10 ppm upon exhaust to the atmosphere. Concentration of VC in exhaust gases discharged to the atmosphere from storage tanks must not exceed 10 ppm.

Consumption of PVC resins totalled 2.6 teragrams (5.6×10^9 pounds) in the United States in 1978, and consumption of PVC thermoplastics was second only to consumption of low density polyethylene (Hatch, 1979, p. 176).

3.2 PRODUCTION OF ETHYLENE DICHLORIDE (EDC)

In the "balanced process" (see Figure 3-1), ethylene dichloride is produced by two different methods 1) direct chlorination, and 2) oxychlorination. EDC is first produced by direct chlorination of ethylene (CH_2CH_2) with chlorine (Cl_2). Direct chlorination may be simply expressed as

$$CH_2CH_2 + Cl_2 \xrightarrow{\text{catalyst}} CH_2ClCH_2Cl.$$

This process varies with the technology employed but usually yields a high conversion rate; approximately 95 percent to 98 percent of the ethylene reacts and 99 percent of the chlorine reacts (Nass, 1977, p. 20). Byproducts and unreacted chlorine and ethylene are removed during purification by scrubbing and distillation. The purified and dried EDC is then "cracked" (dehydrochlorination by pyrolysis) to produce VC. Approximately one mole of hydrogen chloride (HCl) is produced for every mole of VC formed during the cracking process.

The HCl byproduct from cracking is recycled as a feedstock to form EDC by a second process, oxychlorination. The reaction that occurs in the oxychlorination reactor may be simply expressed as

$$CH_2CH_2 + 2HCl + \tfrac{1}{2}O_2 \xrightarrow{\text{catalyst}} CH_2ClCH_2Cl + H_2O.$$

An oxychlorination reactor uses the available HCl formed from the EDC cracking process in the "balanced process." EDC produced in the oxychlorination reactor is usually routed through the same purification system used for the direct chlorination reactor.

There are currently a number of licensed process variations for EDC/VC production. The most common licensors in the United States are B. F. Goodrich, Stauffer Chemical, Pittsburgh Plate Glass, Dow Chemical, and Ethyl. In some instances, combinations of these process variations are used.

Section 61.60(a)(1) of the regulation states that EDC production by reaction of O_2 and HCl with CH_2CH_2 (oxychlorination) is subject to

requirements in the regulation of EDC production (see Table 2-1). The direct chlorination step used to produce EDC is not required to meet stipulations of the regulation. Regulation of the oxychlorination step is needed because HCl generated in the cracking furnace, which is recycled for oxychlorination feedstock, contains VC, which is also formed as a byproduct in the oxychlorination reactor. Therefore, VC may be released from the oxychlorination vent and may contaminate the EDC product stream.

3.2.1 Direct Chlorination of Ethylene

Typically, direct chlorination of ethylene is carried out in a liquid-phase reactor. Although vapor-phase reactors are available, better temperature control is realized with the liquid EDC medium, and dilution gas for safety reasons is not necessary. In the liquid-phase reactor, the reactants (ethylene and chlorine) are bubbled up through liquid EDC. Mechanical agitation may also be used to promote solubility (Nass, 1977). Operating temperatures normally range from 50°C (120°F) to 70°C (160°F) and pressures range from 400 kilopascals to 500 kilopascals (4 atmospheres to 5 atmospheres) (Nass, 1977, p. 20). Metallic chlorides may be used as catalysts for this free radical process. Iron chlorides seem to be most prevalant in commercial processes, although aluminum, copper, and antimony chlorides are also used (Milby, 1978, p. 16).

The EDC product from direct chlorination may be contaminated with 1,1,2 trichlorethane and the metal chloride catalyst, both of which must be removed before the EDC can be cracked to VC. Although direct chlorination has not been cited as being a source of VC emissions and is not subject to the regulation, the operations could possibly become contaminated by VC. If ethylene separated from vent or product gases in the oxychlorination reactor is recycled to the direct chlorination process (McPherson, 1979, p. 78), the ethylene could be contaminated by VC formed as a byproduct in the oxychlorination reactor.

3.2.2 Oxychlorination of Ethylene

An important development in the "balanced process" was the start-up of the first large scale oxychlorination unit in 1958. The oxychlorination process (see Figure 3-1) allows the production of VC from two

chemical feedstocks, chlorine and ethylene, without coproduct formation (McPherson, 1979). The process can take place in two types of reactors, a fixed-bed reactor or fluidized-bed reactor. Fluidized-bed reactors are capable of better temperature control because of the excellent intermixing of reactants and catalyst.

In the fixed-bed reactor, the catalyst is packed in tubes; however, hot spots can form in the reactor tubes if the catalyst migrates (usually in the direction of process flow). Heavy concentrations of catalyst in one or more areas accelerates the reaction rate and the subsequent heating may cause an increase in byproduct formation.

Temperature control in the oxychlorination reactor is important whether fixed-bed or fluidized-bed configurations are used. If temperatures exceed 325°C (600°F), an increase in byproducts such as VC is noted along with the burning of ethylene to form carbon monoxide (CO) and carbon dioxide (CO_2). An increased deactivation of the catalyst may also occur at the higher temperatures (McPherson, 1979, p. 78).

All oxychlorination reactors use copper chloride for the reaction catalyst (Albright, 1967, p. 219). Sodium or potassium chloride can be mixed with the copper chloride to lower the melting temperature of the salt mixture and to reduce the vapor pressure of the copper chloride, hence increasing catalyst life. Catalyst for both types of reactors is supported on a solid porous material such as alumina or silica.

A new oxychlorination process has been developed by the M. W. Kellogg Company. In this process an aqueous solution of copper chlorides is used as catalyst and reactants are bubbled up through the catalyst. Some of the advantages of this process are high product yield, excellent temperature control, the use of aqueous solutions of HCl as feedstock, and simultaneous chlorination as well as oxychlorination (Nass, 1977, p. 23). There are no known commercial producers currently using the M. W. Kellogg process of oxychlorination.

Oxychlorination reactors incorporate large rupture discs as a safety measure. The rupture disc would allow pressure to escape to the atmosphere in the event of an explosion. Over-pressure due to an accelerated reaction is not an item of concern (DiBernardi, 1980). Thus, there are no specific requirements in the regulation for rupture discs on oxychlorination reactors.

The oxychlorination process vent is subject to the current regulation. Emissions from oxychlorination reactors must not exceed 0.2 grams of VC per kilogram of the 100 percent EDC product. This emission limit can be met by an add-on control device such as an incinerator or by process modifications.

The use of oxygen instead of air in the formation of EDC by this process greatly affects the quantity of inerts (e.g., nitrogen) that are vented from the oxychlorination process. When air is used as a feedstock material, emissions from the oxychlorination vent are large in volume and low in hydrocarbon content. Large amounts of inerts increase the work that must be done to condense the product stream in order to separate EDC and unreacted ethylene.

Byproducts found in the oxychlorination product stream can include VC, vinylidene chloride, ethyl chloride, 1,1-dichloroethane, 1,2-dichloroethylene, trichloroethylene, chloroform, carbon tetrachloride, methyl chloride, methylene chloride, chloral, and high boiling compounds (McPherson, 1979, p. 78). These byproducts must be removed prior to cracking the EDC to produce VC.

Acetylene in the HCl feedstock recycled from the cracking furnace is used to form 1,1,2 trichloroethylene. This byproduct is not easily removed in the EDC purification step and reduces product yield in the cracking furnace. One method of eliminating 1,1,2 trichloroethylene formation is hydrogenation of the HCl feedstock. Hydrogenation is a catalytic reaction that eliminates the acetylene by converting it to ethylene.

3.2.3 Purification of Ethylene Dichloride

In order to prevent fouling of the dehydrochlorination reactor (cracking furnace), the EDC cracked to form VC must be highly pure, at least 99.5 percent. Also, any moisture in the stream must be removed to prevent corrosion in equipment from the HCl generated during the cracking process. Typically, process vent streams purified are those from direct chlorination of ethylene, oxychlorination of ethylene, and EDC recovered from the dehydrochlorination process (see Figure 3-1). Because the purification process is used to purify EDC recycled from the oxychlorination

unit and the cracking furnace, VC contamination is possible. For this reason Section 61.62 requires that all exhaust gases discharged to the atmosphere from the purification process not exceed 10 ppm VC unless the equipment is out of service or opened. Prior to opening any equipment, Section 61.65(b)(6) of the regulation requires that the quantity of VC in the purification equipment be reduced to 2.0 percent by volume or 0.0950 cubic meters (25 gallons), whichever is larger, at standard temperature and pressure (STP).

The first step of EDC purification is usually a water quench followed by caustic scrubbing. This step removes catalyst and unreacted chlorine from the direct chlorination process stream.

Water that comes in contact with VC is termed "inprocess wastewater." This water is returned to the process or must meet "inprocess wastewater" requirements of the regulation before being discharged to other wastewater treatment facilities. The current regulation prohibits the discharge of "inprocess wastewater" containing more than 10 ppm VC.

Water and low-boiling impurities such as VC, ethyl chloride, vinylidene chloride, chloroform, and methyl chloride, generated in the oxychlorination reactor, are removed by a light ends distillation column. Pure, dry EDC is taken overhead from a second distillation column which removes compounds of a higher boiling temperature. Gases taken overhead from the light ends distillation column are stored in a recovery tank and may subsequently be sold. Tars from the heavy ends distillation column can be fractionated to recover soluble components and the remains incinerated to recover chlorine as HCl (McPherson, 1979, p. 80). All vent gases from processes and storage vessels in VC service (defined in the regulation as containing 10 percent by volume or more VC) are required to be controlled to 10 ppm or less VC.

Ethylene dichloride condensed from the dehydrochlorination process stream requires purification to remove byproducts formed during cracking. Special treatment is needed to remove chloroprene which can polymerize inside the light ends distillation column and trichloroethylene which forms an azeotrope (mixture with constant boiling point and distilling off in a fixed ratio) with EDC. Trichloroethylene may inhibit dehydrochlorination if allowed to accumulate in the EDC. These two byproducts

are usually removed by chlorination prior to distillation (McPherson, 1979, p. 79).

A method for formation of HCl from the light and heavy ends distillation column byproducts has been developed. The method employs catalytic oxidation of the byproducts separated by the purification columns with air and other added reactants. The HCl formed by this method is used as feedstock for the oxychlorination unit.

3.3 PRODUCTION OF VINYL CHLORIDE

All VC is currently produced in the United States jointly with EDC using the "balanced process" method; however, VC manufactured by any process is covered by the current regulation (see Table 2-1). VC concentrations in all exhaust gases from the formation (cracking) and purification of VC cannot exceed 10 ppm.

3.3.1 Formation of Vinyl Chloride by Dehydrochlorination of EDC

Thermal dehydrochlorination, commonly known as cracking, is the separation of hydrogen and chlorine from 1,2-dichloroethane (EDC) yielding vinyl chloride (CH_2=CHCl) and hydrogen chloride (HCl) at about a one to one molar ratio. The cracking of EDC may be simply expressed as

$$CH_2ClCH_2Cl \longrightarrow CH_2CHCl + HCl.$$

The non-catalytic method seems to be preferred over the catalytic method (Nass, 1977). The typical cracking furnace operates at pressures between 2 megapascals to 3 megapascals (20.0 atmospheres to 30.0 atmospheres) and at temperatures between 450°C to 650°C (840°F to 1,200°F) (Albright, 1967, p. 223). Operating the furnace at high pressures results in an increased yield, fewer byproducts, and allows easier separation of the VC product from unreacted EDC and byproducts. Conversion rates are normally kept between 50 percent and 60 percent in order to minimize byproduct formation. Research is continuing in the development of cracking promoters and inhibitors of side reactions in pyrolysis chemistry. Considerable energy and cost savings could be achieved through increased conversion levels without concurrent losses of EDC to undesirable side reactions (McPherson, 1979, p. 87).

The process stream from the cracking furnace is condensed to separate the VC product and unreacted EDC which is recycled back to the process

(see Figure 3-1). Some systems quench the process stream with crude EDC to reduce formation of byproducts and to partially condense EDC from the product. Byproducts formed in the furnace reactor tubes in addition to HCl are tars, carbon, chloroprene, butadiene, and trichloroethane. Carbon and tars tend to foul reactor tubes in the furnace so the tubes need to be opened and cleaned periodically.

3.3.2 Purification of Vinyl Chloride

The VC in the product stream from the cracking furnace must be separated from byproducts formed during cracking and unreacted EDC (see Figure 3-1). The first step in purification of the product stream as mentioned above is normally a quench of the hot effluent with liquid EDC or the condensation product from the cracking furnace. The product stream exits the quench column and is condensed and fed to a distillation column. In this column, HCl is separated from the product stream. Acetylene and some ethylene byproducts will also come off with the HCl, and HCl treatment by hydrogenation may be necessary if the HCl is to be used as a feedstock for the oxychlorination step. The EDC, VC, and remaining byproducts are then fed to a second distillation column where VC is distilled.

Methyl chloride and butadiene will come off with VC, depending on the efficiency of the fractional distillation system. Methyl chloride formation in the cracking furnace can be reduced by addition of chlorine or anhydrous HCl, or by selective hydrogenation (Nass, 1977). The remaining crude EDC is returned to the EDC purification step of the process. The VC taken overhead from the second column is stored in pressurized vessels for eventual shipment to PVC plants or other facilities using VC. In instances where the PVC plant is very close to the VC producer, VC can be delivered by pipeline.

3.3.3 Emissions for Typical EDC/VC Plants

Prior to promulgation, EPA estimated VC emissions from the 17 existing EDC/VC plants to be approximately 11 gigagrams (24.2 million pounds) or approximately 15 percent of the nationwide VC emissions (EPA, 1975). The original study done in support of the existing regulation identified uncontrolled VC emissions from four areas within an EDC/VC

plant producing 316 gigagrams per year (700 million pounds per year). These four areas were the EDC purification light ends vents, the VC finishing column, the oxychlorination vent and fugitive emissions sources (see Figure 3-1). Total emissions from this plant were calculated to be approximately 1.4 gigagrams (3.1 million pounds) of VC per year.

3.4 PRODUCTION OF POLYVINYL CHLORIDE

Four polymerization processes are being used currently to manufacture PVC resins:

- suspension,
- dispersion (emulsion),
- bulk (mass), and
- solution.

Figure 3-2 shows a generic flow diagram for PVC production by the suspension and dispersion processes. The potential emission points for each of the process steps shown in Figure 3-2 are listed in Table 3-2 along with a summary of regulation requirements for control of emissions.

Many companies have licensed some phase of their particular process such as stripping technology or clean reactor technology which will be discussed in subsequent sections. The licensing of these process phases has evolved from the intensive research work done to reduce residual VC (RVC) levels in finished resins, limit worker exposure, and reduce emissions to the atmosphere.

After polymerization, VC may be present in any of three forms in the polymerization reactor depending on the particular process. VC will always be present separately as a gas or liquid in the reactor and will also be trapped within the newly formed polymer resin. In the suspension, dispersion, and solution processes, VC will also be trapped in the process water.

The resins produced by a process are categorized as to the "type" of resin. Those processes responsible for more than one variation of their type of resin are further subdivided into "grades." The resin grade is developed to allow compounding and fabrication to yield the desired product. Figure 3-3 shows the resin types, the compounds, and the various fabrication processes. PVC fabrication will be discussed in more detail in Section 6.1.1.

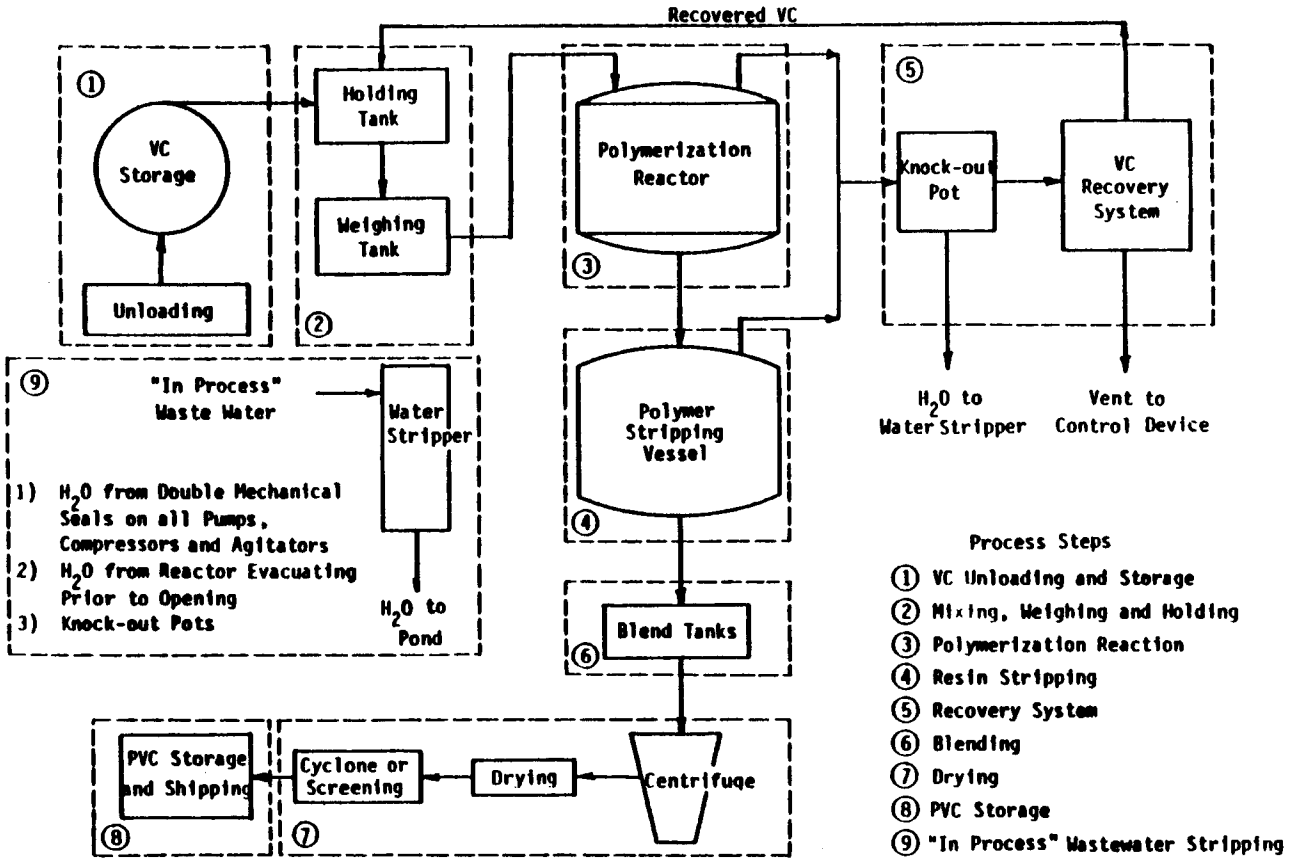


Figure 3-2. Suspension and dispersion processes flow diagram.

Table 3-2. POINT SOURCE EMISSIONS TYPICAL OF SUSPENSION AND DISPERSION PVC PLANTS

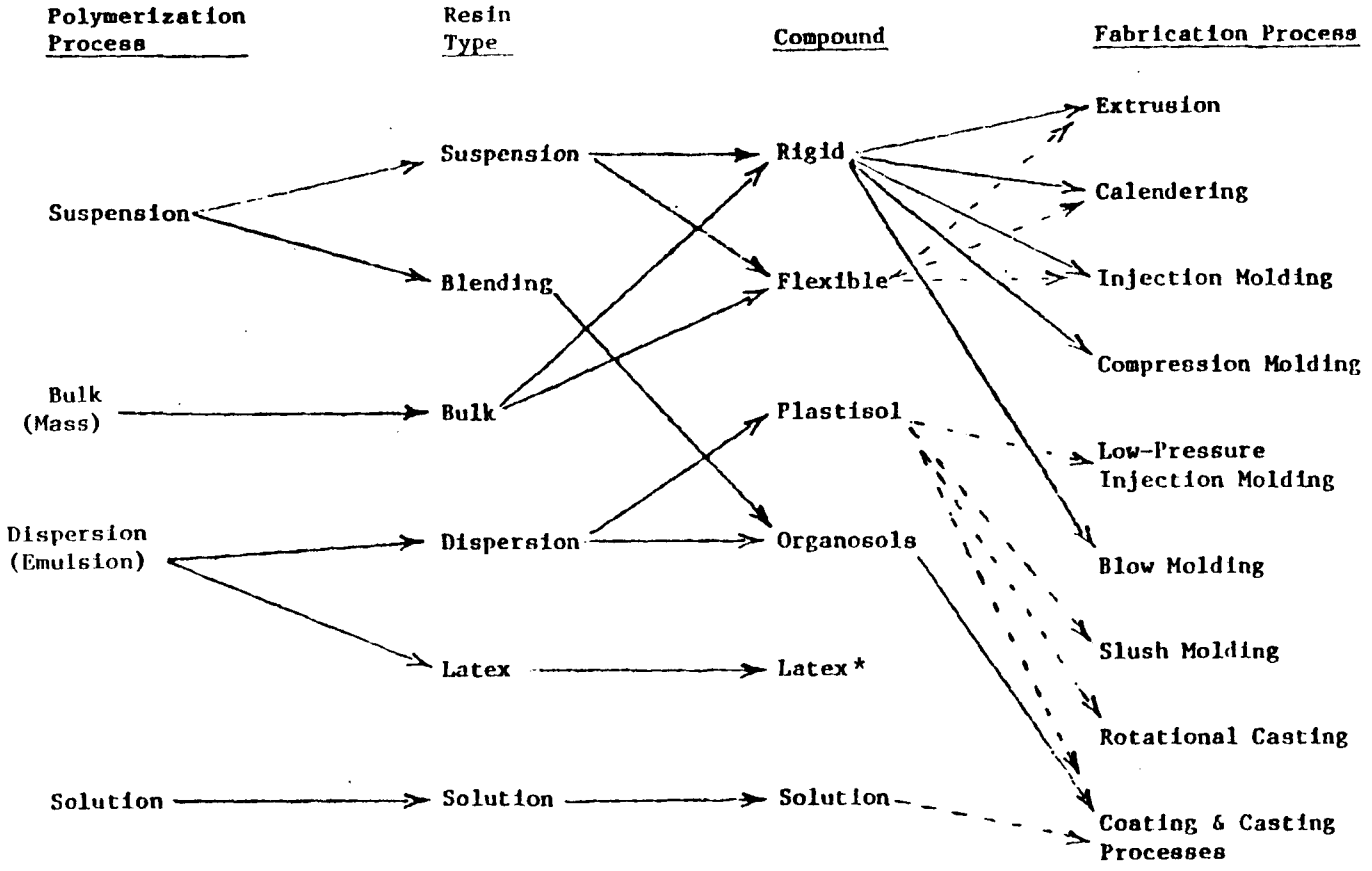
	Process step	Potential emission points	Regulation requirements
1	VC unloading and storage	Loading lines, VC storage tank	Emissions from loading lines must be reduced so that upon opening of line to the atmosphere emissions do not exceed 0.0038m^3 of VC at STP. VC removed from lines to meet this criteria must be controlled to $\leq$ 10 ppm upon exhaust to the atmosphere. Concentration of exhaust gases discharged to the atmosphere from storage tanks must not exceed 10 ppm.
2	Mixing, weighing and holding tanks before stripping operation	Mixing, weighing and holding tank vents	Concentration of VC exhaust gases discharged to the atmosphere must not exceed 10 ppm.
3	Polymerization	Polymerization reactor opening loss (ROL)	ROL from each reactor is not to exceed 0.02 g VC/kg PVC products.
		Polymerization reactor relief valve discharges	No discharge to the atmosphere except for an emergency relief discharge
		Polymerization reactor rupture disc discharges	Concentration of VC exhaust gases discharged to the atmosphere must not exceed 10 ppm. Not required to be reported.
4	Stripping	Stripping vessel vent	Concentration of VC exhaust gases discharged to the atmosphere must not exceed 10 ppm.

(continued)

Table 3-2. Concluded

	Process step	Potential emission points	Regulation requirements
5	Monomer recovery system	Recovery system exhaust vent knock-out pot	Concentration of VC exhaust gases discharged to the atmosphere must not exceed 10 ppm.
6	Blending (mixing, weighing and holding tanks after stripping operation)	Slurry blend tanks and holding tank vents	Not regulated.*
7	Drying, sizing, screening of dewatered resin	Centrifuge vents, dryer vent stacks, storage silos, baghouse vents, screening operation vents	Not regulated.*
8	PVC loading and storage	Storage silos	Not regulated.*
9	"In Process" wastewater stripper	Waste-water storage tank waste-water stripper column	VC removed from in process water is to be ducted to a control system from which concentration of VC in exhaust gas does not exceed 10 ppm.

*If a PVC plant is using stripping to control VC emissions, emission sources beyond the stripper are not regulated.



*Latices are usually sold directly to the consumer rather than being used in later fabrication processes.

Figure 3-3. Polyvinyl chloride resins, PVC compounds and PVC fabrication processes.

A plant manufacturing polymers containing any amount of polymerized VC is subject to the current regulation. The requirements of the regulation listed in Table 3-2 will be discussed in more detail below.

3.4.1 Free Radical Polymerization

Polymerization is the chemistry of combining simple molecules (monomers) into long chains of repeating molecular units (polymers). There are two types of polymerization - addition and condensation. PVC resins are commerically produced by addition polymerization and, in general, polymerization is induced by the use of free radical initiators (Nass, 1977, p. 34). Thermal decomposition of the initiator, which is combined with the VC and other constituents in the polymerization reactor, yields free radical molecules having one unshared electron. This free radical reacts with additional VC molecules by removing an electron from the VC double covalent bond and sharing an electron with the free radical. The remaining unshared electron moves along the chain becoming the new radical bond site. Another VC molecule may then become a part of the polymer chain by reacting with the polymer radical,

Radical + VC molecule ⟶ Polymer radical

Radicals are transferred from the polymer by a reaction with a VC monomer to yield a polymer and free radical. The transfer reaction increases with increasing temperatures. This characteristic of the reaction kinetics allows a desired molecular weight to be obtained by controlling reaction temperature (Cameron, 1979, p. 39). Radicals are also transferred by reacting with hydrogen atoms obtained from VC or solvent in the reactor. Another way of transferring radical sites from the growing polymer chain is by using chain transfer agents (CTA). These CTA's are used to regulate the molecular weight of the polymer to a desired level. In all transfer reactions, the radical is released and able to initiate another polymerization reaction. The reaction is terminated when two polymers with radical sites are combined. Polymerization rate is controlled by choice of the appropriate initiator.

The polymerization reaction is exothermic and the reaction rate must not be allowed to accelerate to the extent that the heat of reaction cannot be removed by reactor cooling devices. Reaction rates tend to increase as the temperature increases. If the heat of reaction is not removed, a runaway reaction can develop and the rapid increase in temperature will increase the pressure inside the reactor vessel beyond safe limits.

The monomer structure of VC is capable of several variations in chain structure, but free radical polymerizations generally produce atactic structures (random orientation of monomer unit in chain structure) (Nass, 1977, p. 46). Tendency towards syndiotactic structure (regular alternating orientation of the monomer unit in the chain structure) and crystallinity are both increased by reduced polymerization temperatures.

3.4.2 Unloading of VC at PVC Plant Sites

Under the current regulation VC emissions from loading and unloading lines, which are opened to the atmosphere, must be reduced in the opened lines to 0.0038 cubic meters (0.13 cubic feet) or less at standard temperature and pressure. Also, the VC removed from loading and unloading lines in order to meet this requirement of the regulation must be vented to a control system from which the concentration of VC in the exhaust gas does not exceed 10 ppm (see Table 3-2). When PVC plants are not located close enough to receive VC by pipeline, it is shipped by railcar, tank car, barge or marine vessels.

The VC is normally unloaded at PVC plants by displacement. This is accomplished by pumping vapor from storage tanks into the transfer vessel which displaces the liquid VC from the transport vessel through the unloading line. When the liquid VC is displaced, the compressor line is reversed and used as suction to evacuate remaining liquid as vapor. The remaining liquid VC is allowed to boil during tank car evacuation for its removal as a gas. This vaporization of the VC usually takes 20 to 30 minutes (Mukerji, 1977, p. 155). Lines between tank car compressor and storage tank can be switched without disconnection by incorporating a 4-way valve in the pumping lines. Instrumentation of

the system usually incorporates a turbine meter, a flow totalizer to measure the VC flowrate and quantities unloaded, and storage tank level indicators.

Unloading and transfer lines may be purged with nitrogen to reduce VC to the required level before disconnection of the unloading lines. In some cases, the portion of the unloading line which is opened to the atmosphere has been reduced to diminish the amount of VC that will escape to levels below those required by the regulation.

3.4.3 Mixing, Weighing and Holding Vessels

Storage spheres, storage tanks, weigh tanks, gasholders, wastewater storage tanks, knockout pots, and surge tanks are representative of vessels covered under Section 61.64(c) of the regulation for mixing, weighing, and holding vessel (see Table 2-1). These vessels are used to hold liquid or gaseous VC and PVC slurry during various stages of the PVC process. Some of these vessels were open to the atmosphere prior to promulgation of the VC regulations, but have since been enclosed and are usually ducted to the recovery system and/or the primary control device. The number and types of vessels will vary from plant to plant depending on the size and type of process used to produce the PVC resin.

Section 61.64(c) of the regulation requires the concentration of VC in all exhaust gases discharged to the atmosphere from mixing, weighing, and holding containers "in-VC-service" not to exceed 10 ppm (see Table 3-2). Any piece of equipment that contains or contacts a fluid that is 10 percent by weight, VC, or gas that is at least 10 percent by volume, is considered "in-VC-service." There are no requirements in the regulation for mixing, weighing or holding containers used in the process after the stripping of the PVC resin provided resin stripping is used.

3.4.4 Suspension Polymerization

The suspension process for producing PVC resins (see Figure 3-3) is characterized by the formation of polymers in droplets of the liquid VC (or other co-monomers) suspended in water. These droplets are formed by agitation and the use of protective colloids or suspending agents. Protective colloids commonly used are water-soluble polymers such as modified cellulose or partially hydrolyzed polyvinyl acetate. The

process is started by evacuating the polymerization reactor to remove oxygen and other contaminants that may inhibit the reaction initiator (see Section 3.3.1). Water and VC may be simultaneously added to the reactor with the protective colloids, or they may be added separately (water and colloids first, followed by the liquid monomer). The water used is deionized and deaerated in order not to inhibit free radical initiator formation. Water and other ingredients charged to the reactor must be carefully measured prior to charging because a level indicator for reactors has not been commercially developed. In some cases the reactor is on a scale and the amount of material charged is weighed in the reactor. More often, a separate weigh tank is used to measure materials charged to the reactor. A flow meter can be used to record the amount of water added. Reactor operators manually charge additives that are used in small proportions. The initiator is usually the last ingredient charged to the reactor. Initiators commonly used in the suspension process are peresters, peroxycarbonates, peroxides, or azo compounds. The initiators are soluble in VC and allow formation of PVC in the monomer droplets.

After all materials are in the reactor, the batch is brought up to the reaction temperature by passing steam through the reactor jackets which allows free radical initiators to be formed. Reaction temperatures are varied in order to produce a resin grade of a particular molecular weight. Once polymerization is initiated, the reaction becomes exothermic and cooling water must be circulated through the reactor jacket to remove heat of reaction. In some instances reflux condensers have also been used to control reaction temperature and remove excess heat.

After approximately 6 hours in the reactor, the batch temperature and pressure drop. This signifies that nearly all the VC has reacted (75 percent to 90 percent of the VC usually reacts) and the remaining or residual VC (RVC), which is in a liquid or gaseous state or trapped in the resin particles, must be stripped. This RVC is usually stripped with steam under vacuum. The suspension process yields a particle size distribution of a much wider range than the other polymerization processes. Particle size may range from 90 micrometers to 130 micrometers (0.0035 inches to 0.0050 inches) with low to medium molecular weights.

The regulation requires that RVC levels for suspension resins not exceed 400 ppm of the PVC product. PVC resin, unreacted VC (in the water, in the headspace, and trapped in the resin) and water are the constituents remaining in the reactor after polymerization. This polymer slurry may be steam-stripped of RVC batchwise in the reactor or in a separate vessel. B. F. Goodrich has developed a continuous stripping operation which strips the resin with steam running countercurrent to the PVC slurry. Most plants strip batchwise with steam in separate vessels or in the continuous stripping column. In all cases, water accompanying the PVC product is stripped with the slurry and then removed by centrifugation.

Batch stripping procedures use temperatures up to 87°C (190°F) and a vacuum of 91 kilopascals (27 inches of mercury) or more (Nass, 1977, p. 83). Heat is applied by steam injected directly into the batch or by steam passed through the reactor wall jackets. If stripping is used to meet RVC levels, any downstream processes or equipment (e.g., water treatment, vents from mixing tanks, centrifuges, dryers, etc.) are not required to meet any other requirements of the regulation.

After stripping, the batch is transferred to blend tanks which mix the batch with other batches to ensure product uniformity. The mixed batches are then fed to a continuous centrifuging operation that separates the polymer from the water in the slurry. Both mixing tanks and centrifuges are vented to the atmosphere if stripping is utilized. The water from centrifuging is not required to be stripped of VC because most of the VC is removed during resin stripping. Therefore, the centrifuge water is recycled back to the process or discharged to the plant's wastewater treatment system.

The wet cake from centrifuging is conveyed to a rotary dryer for further removal of the remaining (usually 25 percent) moisture (Nass, 1977, p. 83). Most of the RVC not removed during stripping will be released during the drying operation. Counter-current air temperatures in the dryer range from 65°C to 100°C (150°F to 210°F). Drying time is generally short, but large volumes of air containing RVC are released. After drying, the resin may be screened to remove agglomerates. The resin is then bagged or stored in silos for bulk shipment by trucks or rail car.

Uniformity of suspension resin batches is dependent on control of variables such as:

- impurities (noncondensable gases present in the reactor prior to polymerization or impurities in raw materials charged to the reactor),
- rate of temperature increase to reaction temperature,
- agitation speed and schedule (speed varies as the slurry becomes more dense),
- charging rate of raw materials, and
- temperatures of raw materials charged.

In some of the newer PVC facilities these variables are closely monitored by levels of computer control. In the older plants many variables such as cooling water flow rates, pump operation, agitator motors, temperature, and pressure are monitored and controlled manually from the control room panel or at the reactor. More versatility is possible with computer assistance. A reactor linked to computerized control elements can produce different grades of resin by using programs designed to yield specific reactor conditions (e.g., agitation, temperature, amount, and type of materials charged) that will produce the desired resin product. Computers can also monitor operating conditions and respond to emergencies (such as high pressure in the reactor). They can be programmed to take necessary action to bring an upset condition under control, e.g., choosing the best compensatory action.

The use of large reactor systems has increased quality control and allowed incorporation of equipment and procedures that reduce VC emissions. Large reactors, approximately 8,000 gallons (30 cubic meters) and up, offer lower plant cost, improved product uniformity, and increased productivity. A more detailed discussion of reactors is included in Section 3.4.8.

3.4.5 Dispersion Polymerization

Although dispersion (emulsion) resins are formed in reactors similar to those used for suspension type resins, reaction kinetics of polymer formation vary greatly. In general, dispersion resins are of a high density with small particle size. The process is initiated by charging the necessary ingredients (water, liquid, VC, emulsifiers, and a free

radical initiator) to an evacuated reactor. Proportions of these ingredients and other minor additives will vary depending on the type of resin and the resin grade. Emulsifiers (soaps and surfactants) are used to disperse VC in the water phase. Soap micelles (i.e., colloidal aggregates that are formed above a critical emulsifier concentration) also contain small amounts of VC and are the site of polymer formation. Initiators used are water soluble (versus VC soluble initiators used in suspension polymerization) and penetrate soap micelles to begin polymerization. Commonly used initiators are hydrogen peroxide, organic peroxides, and peroxydisulfates.

Two general types of resin are produced by the dispersion process - latex and dispersion. If the latex type resin is to be produced, only a small amount of VC and initiator are normally charged. The reactor is heated by injecting steam into the reactor jackets to initiate formation of free radicals. Agitation is used to disperse the monomer and other ingredients in the water medium. Once polymerization begins, the heat of reaction is removed by circulation of cooling water through the reactor jackets. Small amounts of initiator and monomer are then continuously added during polymerization until the correct particle size is attained. Conversion of VC to latex polymer is almost complete. Latex resin particle sizes range from 0.05 micrometers to 2 micrometers.

The residual VC is removed from latex resins by completely reacting the free VC with additional catalyst (post-catalysis). This is done in the reactor or in a separate vessel. The regulation requires that latex resins be stripped to 400 ppm RVC. Latex resins are usually sold in solution, and drying or separation of resin from the polymer slurry is not necessary.

The process for formation of dispersion type resins follows that described for latex resins except that more monomer is added to allow particles to grow to a larger size. In some cases the process may call for "seed" latex. The "seed" latex is formed by starting a batch in a separate reactor. Before this batch reaches 60 percent conversion it is transferred to other reactors with more VC and emulsifiers. This allows formation of larger emulsion particles which are used in plastisol and stir-in resins. These dispersion type resins range from 0.2 micrometers

to 5 micrometers in particle size and are more sensitive to heat and mechanical agitation than suspension resins. Because the dispersion resins are more sensitive, stripping the resin may take longer because lower stripping temperatures are used. The regulation requires that dispersion type resins be stripped to 2,000 ppm RVC.

After polymerization is complete, the dispersion resins are usually spray dried. Spray-dried resins contain emulsifiers that inhibit the absorption of plasticizers. In many applications where heat is applied during fabrication, this property is acceptable because the heat melts the resins which allows plasticizer absorption. In some fabrication processes (such as calendering), plasticizers must be absorbed prior to fabrication because temperatures used are not high enough to melt the resin. If removal of the soaps from the dispersion resin is desired, coagulation of emulsifiers with salts is usually performed. The salts (calcium or magnesium) are added to the polymer slurry and the emulsifiers precipitate and are rinsed out with water. The resin and water are then separated and the resin is dried in a rotary or pan dryer (Erdman, 1980).

3.4.6 Bulk Polymerization

Bulk (mass) polymer resins are produced by a two-stage polymerization process. A simple diagram of the bulk process is shown in Figure 3-4 and requirements of the regulation for bulk plants are summarized in Table 3-3. The first stage is the formation of a "seed" resin in a vertical pre-polymerization (Pre-Po) reactor. The "seed" resin is transferred to a horizontal post-polymerization (Po-Po) reactor in the second stage of the process. More VC is added to the Po-Po which allows the "seed" resin to grow in size to the finished resin product. The bulk process differs from the dispersion process in that no water is used in the reaction - the process is anhydrous. The bulk process used in this country is licensed by Rhone-Poulenc of France. A new version of the Rhone-Poulenc process utilizing a vertical Po-Po reactor is now available, but is not currently being used in the United States.

The Pre-Po reactor is charged with liquid VC and enough initiator to carry the reaction to approximately seven to twelve percent conversion. Initiators used are those commonly used in the suspension process - an

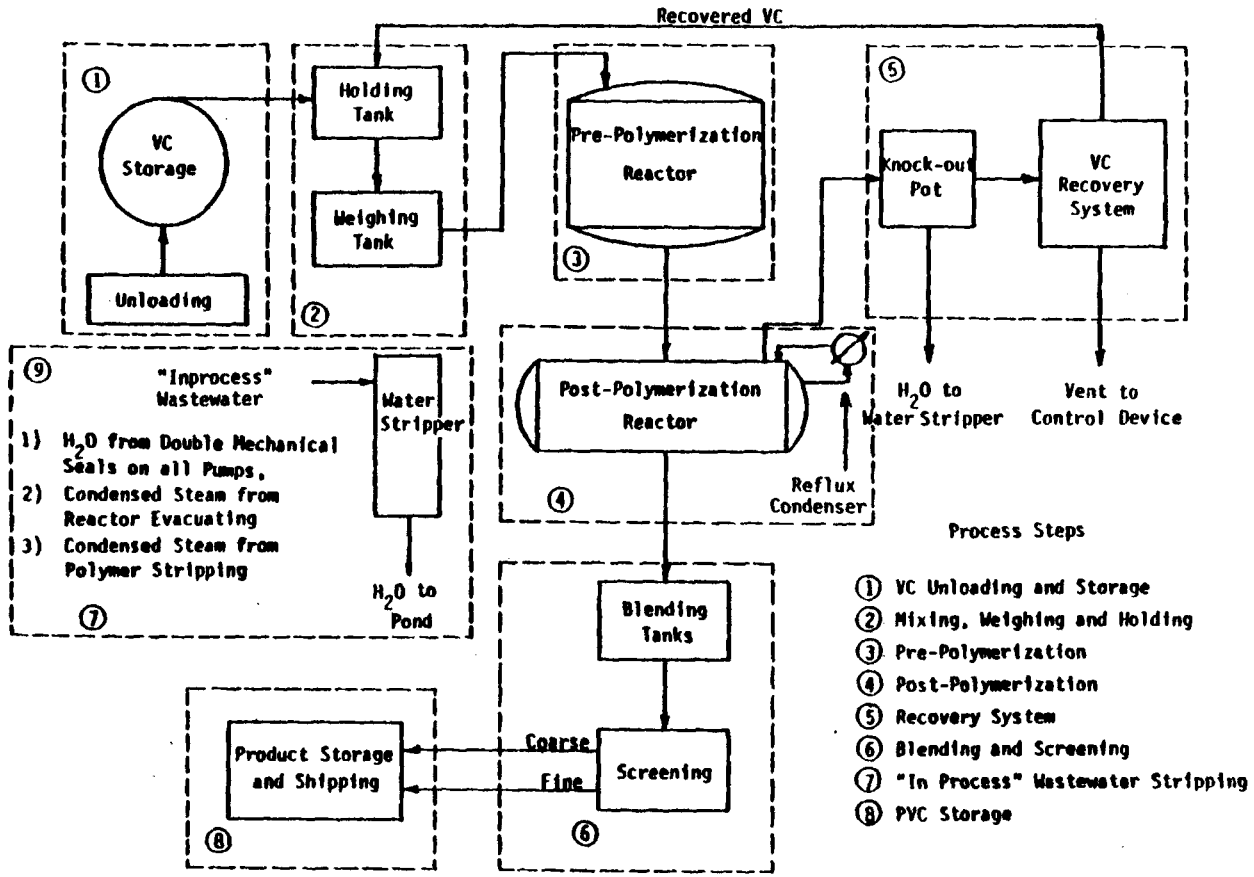


Figure 3-4. Bulk process flow diagram.

Table 3-3. POINT SOURCE EMISSIONS TYPICAL OF BULK PVC PLANTS

	Process step	Potential emission points	Regulation requirements
1	VC unloading and storage	Loading lines, VC storage tank	Emissions from loading lines must be reduced so that upon opening of line to the atmosphere emissions do not exceed 0.0038m^3 of VC at STP. VC removed from lines to meet this criteria must be controlled to $\leq$ 10 ppm upon exhaust to the atmosphere. Concentration of exhaust gases discharged to the atmosphere from storage tanks must not exceed 10 ppm.
2	Mixing, weighing and holding tanks before stripping operation	Mixing, weighing and holding tank vents	Concentration of VC exhaust gases discharged to the atmosphere must not exceed 10 ppm.
3	Pre-polymerization	Polymerization reactor opening loss (ROL)	ROL from each reactor is not to exceed 0.02 g VC/kg PVC products.
		Polymerization reactor relief valve discharges	No discharge to the atmosphere except for an emergency relief discharge.
		Polymerization reactor rupture disc discharges	Concentration of VC exhaust gases discharged to the atmosphere must not exceed 10 ppm. Not required to be reported.
4	Post-polymerization (stripping in reactor)	Polymerization reactor opening loss (ROL)	ROL from each reactor is not to exceed 0.02 g VC/kg PVC products.

(continued)

Table 3-3. Concluded

	Process step	Potential emission points	Regulation requirements
		Polymerization reactor relief valve discharges	No discharge to the atmosphere except for an emergency relief discharge
		Polymerization reactor rupture disc discharges	Concentration of VC exhaust gases discharged to the atmosphere must not exceed 10 ppm. Not required to be reported.
5	Monomer recovery system	Recovery system exhaust vent knock-out pot	Concentration of VC exhaust gases discharged to the atmosphere must not exceed 10 ppm.
6	Blending (mixing, weighing and holding tanks after stripping operation)	Dry resin blend tanks and screening operation baghouse vents	Not regulated.*
7	"Inprocess" wastewater stripper	Wastewater storage tank Wastewater stripper column	VC removed from in process water is to be ducted to a control system from which concentration of VC in exhaust gas does not exceed 10 ppm.
8	PVC loading and storage	Storage silos	Not regulated.*

*If a PVC plant is using stripping technology to control VC emissions, emission sources beyond the stripper are not regulated.

oil soluble, free radical catalyst (Nass, 1977). The Pre-Po reactor is brought to an operating temperature of 40°C to 70°C (130°F to 184°F) by injecting steam into the reactor jackets. Strong agitation is used to form small particles of approximately 1 micrometer (Nass, 1977, p. 75). These small particles provide the "seed" that grows in size to form resin beads in the Po-Po reactor. The remaining liquid VC and seed resin are pumped to the Po-Po reactor at approximately 7 to 12 percent conversion.

Total cycle time for the Pre-Po is 2 hours (Dubec, 1980) which is normally one-fifth the duration of the Po-Po cycle. Thus, one Pre-Po reactor can be used to feed as many as six Po-Po reactors.

After the "seed" polymer and remaining liquid VC is pumped from the Pre-Po to the Po-Po, more VC and initiator are added to the Po-Po for completion of the reaction. Small amounts of additional additives may be charged to the reactor for heat stability and particle size control (Dubec, 1980). The number of PVC particles in the Po-Po is determined by the amount of seed resin charged from the Pre-Po. The "seed" resin absorbs the VC and at about 20 percent conversion the batch becomes solid and powdery, thus the agitator in the Po-Po must be of rugged construction. When the conversion to PVC has reached 70 percent to 90 percent, steam is injected and a vacuum is pulled on the reactor to remove RVC from the resin particles. This represents the bulk stripping procedure that takes place in the Po-Po reactor. Exhaust gases from this stripping procedure are vented to recovery and the primary control so that VC emissions do not exceed 10 ppm. VC recovered from the reactors is sent back to the charge tank for reuse. The regulation requires bulk resins to be stripped to 400 ppm RVC as determined on a dry solids basis.

In producing PVC resins by the bulk process, temperature is the major control variable for determining the molecular weight of the polymer. One disadvantage of the bulk process is that there is not a good medium for heat transfer from the polymer reaction to the reactor wall. Reflux condensers are used to help control the reactor vessel temperature. The condensers remove gas from the reactor headspace, condense the gas, and then return the liquid VC to the reactor. Heat from the gas is removed by cooling water in the reflux condensers.

The Po-Po is opened after every batch for cleaning. VC concentrations that are emitted when the Po-Po reactor is opened may be determined by actual measurement or by calculation as approved by the Administrator. Polymer removed from the Po-Po reactor (already dry) is pneumatically conveyed to screens that remove oversize particles. Batches may be blended to improve product uniformity.

Bulk resins range in size from 0.1 to 1.0 micrometers and exhibit excellent qualities for dry-blending compounds. The beads are of uniform size and porosity which allows uniform absorption of plasticizer. Also, because suspending agents and surfactants are not used, the finished resin has a higher purity and therefore better heat stability than suspension or dispersion resins (Nass, 1977, p. 75).

3.4.7 Solution Polymerization

PVC produced by the solution process typically consists of copolymers of VC and polyvinyl acetate. Only one company is producing resins by this process in the United States. A simple diagram of the solution process is shown in Figure 3-5 and requirements of the regulation are summarized in Table 3-4.

The solution process is continuous and liquid VC, vinyl acetate, solvent, and initiator in solution are fed to a polymerization reactor which operates at low temperatures. Conversion to copolymer is approximately 60 percent to 70 percent. The copolymer resin solution is removed continuously and fed to a stripping operation that removes the solvent.

VC and vinyl acetate are soluble in the solvent. The monomers and solvents are mixed and charged to the reactor separately from the initiator solution. The copolymer formed is soluble in the solvent and forms a homogeneous solution. Typical solvents listed in the literature for this type of process are N-butane; aliphatic alcohols, ketones, esters, and hydrocarbons; aromatic hydrocarbons; and chlorinated hydrocarbons.

No resin particles are formed by the solution process and RVC is stripped by distillation. Distillation takes place in a conventional trayed column. Acetone vapors are used to strip VC from the copolymer resin solution. The acetone vapors taken overhead from the distillation column are sent to a VC recovery system and then recycled back to the process.

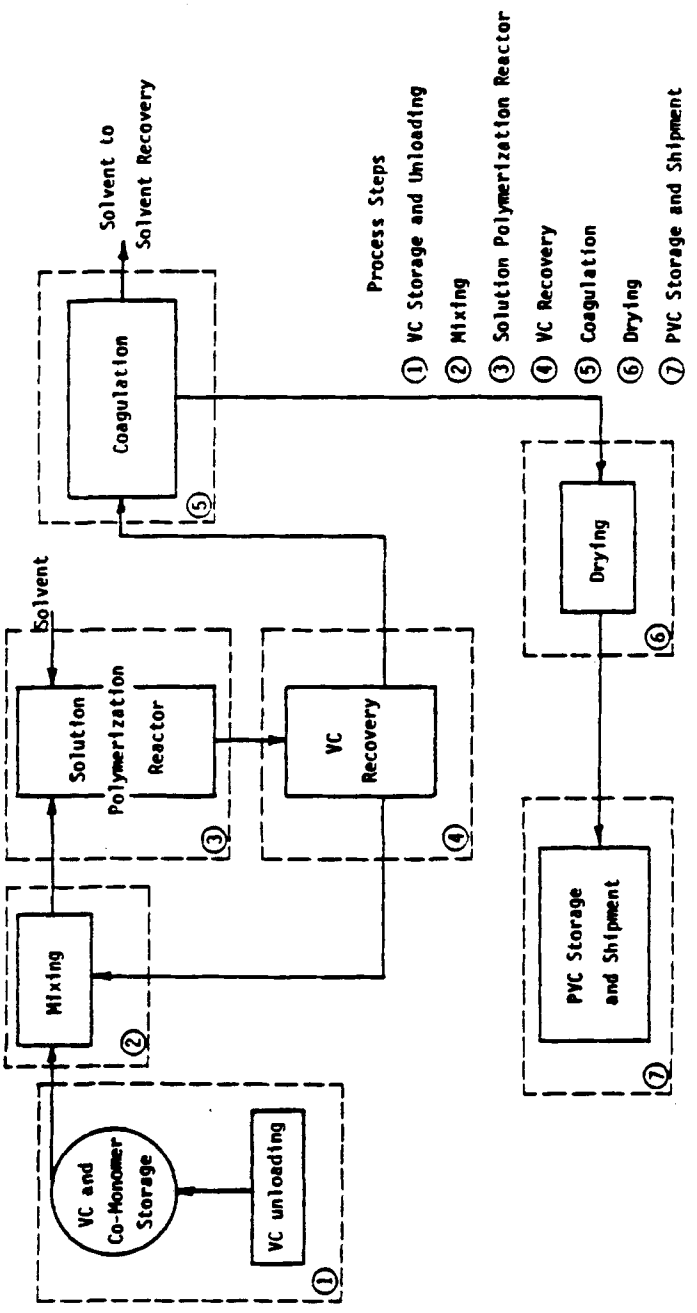


Figure 3-5. Solution process flow diagram.

Table 3-4. POINT SOURCE EMISSIONS TYPICAL OF SOLUTION PROCESS PVC PLANTS

	Process step	Potential emission points	Regulation requirements
1	VC unloading and storage	Loading lines, VC storage tanks	Emissions from loading lines must be reduced so that upon opening of line to the atmosphere emissions do not exceed 0.0038m^3 of VC at STP. VC removed from lines to meet this criteria must be controlled to < 10 ppm upon exhaust to the atmosphere. Concentration of exhaust gases discharged to the atmosphere from storage tanks must not exceed 10 ppm.
2	Mixing, weighing and holding tanks before stripping operation	Mixing, weighing and holding tank vents	Concentration of VC exhaust gases discharged to the atmosphere must not exceed 10 ppm.
3	Solution Polymerization Reactor	Polymerization reactor opening loss (ROL)	ROL from each reactor is not to exceed 0.02 g VC/kg PVC products.
		Polymerization reactor relief valve discharges	No discharge to the atmosphere except for an emergency relief discharge.
		Polymerization reactor rupture disc discharges	Concentration of VC exhaust gases discharged to the atmosphere must not exceed 10 ppm. Not required to be reported.
4	VC recovery (stripping)	Recovery condenser vent	Concentration of VC exhaust gases discharged to the atmosphere must not exceed 10 ppm.

(continued)

Table 3-4. Concluded

	Process step	Potential emission points	Regulation requirements
5	Coagulation	Resin solution storage tank condenser vent, resin precipitation vent	Not regulated.
6	Resin drying	Dryer vent	Not regulated.
7	PVC storage and loading	Silo vents	Not regulated.

After stripping, the resin in solution is recovered by precipitation. A constituent is added to the solution reducing the solution solubility of the copolymer resin and allowing the copolymer to precipitate. Copolymer resins are then separated by centrifugation. The resins are rinsed with water to prevent the particles from sticking together. The rinsed resins are flash dried and then are penumatically conveyed to storage silos or packaged for shipment. Solution resins are used by casting and coating fabricators to provide thin coatings for food and beverage containers. Solution resins are highly pure because emulsifiers or suspending agents are not used in the process.

3.4.8 Polymerization Reactors

The design of the reactors used in the various polymerization processes is important for controlling resin quality. Polymerization conditions (e.g., temperature, pressure, and agitation) within the reactor are primary control variables in the production of PVC resins. These operating conditions along with reactive constituents charged to the reactor produce the various resin grades.

Reactor emissions are subject to several sections of the current regulation (see Table 2-1). Requirements of Section 61.64 of the regulation specify the following emissions limits:

- Concentration of VC in all exhaust gases discharged to the atmosphere must not exceed 10 ppm except for emergency relief valve discharges.
- Reactor opening loss (ROL) emissions are not to exceed 0.02 grams VC per kilogram of PVC product.

Leakage from reactor agitator seals and relief valves are covered under subsections 61.65(b)(3v) and 61.65(b)(4), respectively, which require installation of double-mechanical seals on agitator shafts and installation of rupture discs upstream of relief valves; connecting relief valves to process lines or recovery system or equivalent as approved by the Administrator. Equivalency clauses for these equipment requirements are included under Sections 61.65(b)(3v) and 61.65(b)(4).

Both suspension and dispersion (emulsion) type resins are produced in a similar reactor under similar conditions and thus will be discussed together. Bulk (mass) type resins are produced in a two-reactor system. Solution type resins are the only PVC resins commercially produced by a

continuous process in a reactor similar to a distillation column. A discussion of various reactors follows.

Reactors for Suspension and Dispersion (Emulsion) Type Resins

The following reactor parameters are common to suspension and dispersion processes:

- Reactor Size and Number - each plant may have from 4 to more than 50 reactors. Reactors currently being used in the United States range in size from 11.3 cubic meters to 169.5 cubic meters (3,000 gallons to 45,000 gallons) (Khan, 1978, p. 17). The larger reactors with a 23 cubic meter (6,000 gallon) capacity and larger are relatively new (early 1970's) and are being used to reduce variability in product quality and increase production capacity. With larger and fewer reactors, incorporation of sophisticated controls is less expensive on a cost-per-pound basis.
- Reactor Construction - reactors are of stainless steel, glass-lined carbon steel, glass-lined stainless steel or stainless steel-lined carbon steel construction. Choice of material is dependent on corrosion resistance required and desired lifetime of reactors (Khan, 1978, p. 17). In larger reactors where wall thickness approaches 0.025 meters (1 inch), a stainless steel-lined carbon steel reactor offers an advantage for thermal conductivity (Cameron, 1979, p. 45). This is necessary in order to dissipate heat of reaction from the larger amounts of polymer slurry. In small reactors, where heat conduction is not as critical, glass-lined reactors are used. The glass lining on the smaller reactors helps to prevent polymer build-up on the reactor wall which will normally be hotter than the reactor wall on a large reactor.
- Operating Temperature and Pressure - for suspension resins, temperature of the reactor is usually about 55°C (Khan, 1979, p. 75) and is maintained as a function of the resin properties desired. This normally produces reactor pressures of 515 kilopascals to 810 kilopascals (5.1 to 8.0 atmospheres). Dispersion resins are more sensitive to heat and are processed at lower temperatures (Lamorte, 1978, p. 23).

- Agitation - mixing blades are usually of either retreat curve or turbine-type and provide the agitation speed that directly affects product quality (Cameron, 1979, p. 45). In suspension polymerization, agitation is often operated at lower speeds than in dispersion polymerization because intense agitation of dispersion resins results in poor control of particle size (Nass, 1977, p. 94). Agitation speed is variable and is determined by the type of resin particle desired. The use of baffles in the reactor is also important to produce a better size distribution of particles. The tubular-finger baffle and single-blade baffle are used and in some instances their positioning can be set from outside the reactor. Power requirements of the agitator drive motor are usually monitored by an amperage meter. This monitoring instrument is important because loss of agitation reduces heat transfer to reactor walls and a runaway reaction could occur.
- Cleaning - in order to produce high quality resins, the internal surface of the reactor must be kept clean. After several batches, polymer build-up occurs where liquid polymer slurry contacts the reactor walls. Polymer build-up is also formed on areas of the reactor that are not in contact with the slurry. This formation on surfaces other than the walls is due mostly to a reaction of VC in the gas phase with oxygen, a common contaminant in the reactor. Regardless of cause, if polymer build-up is not removed, small flakes of the polymer will contaminate the next batch. These flakes do not absorb compounding ingredients (e.g., plasticizers, stabilizers) and produce areas known as "fish eyes" in the finished resin product.

  The most common cleaning practice involves opening the reactor manways to allow plant personnel access to clean the reactor interior. This may be done manually by scraping the walls or by fitting a high pressure water cleaning system into the reactor manway. Prior to opening, the ROL requirement must be attained. In order to meet this requirement some

method of reactor evacuation is required. The evacuation method used to attain the ROL is usually a time-consuming procedure and results in reduced production capacity. These procedures will be discussed in detail in Section 4.5. To reduce these reactor openings for cleaning purposes, high pressure water jets have been installed within some of the newer reactor vessels. Also, solvent cleaning systems have been used by several companies – a solvent solution is passed through the reactor several times to remove polymer build-up. Some have found this technique successful while others have abandoned the approach because of high cost and potential toxicity of the solvent. The use of a chemical treatment of the the reactor walls after cleaning has also been successful in preventing polymer build-up. This chemical, which is usually proprietary, is applied to the reactor walls prior to polymerization.

- Relief Valves and Rupture Disks - relief valves and rupture discs are safety devices on the polymerization reactor vessel. These devices open directly to the atmosphere under abnormal high-pressure conditions. If the pressure in the reactor vessel increases beyond a safe limit, the relief valve or rupture disc relieves the pressure in the vessel. Without this safety feature a vessel could rupture. Causes of increased pressure conditions will be discussed in Section 4.2. Relief valves used for reactor safety are set at approximately 50 to 100 pounds over normal operating pressure. Conventional relief valves allow a reactor to depressurize and, if operating properly, the relief valve will close or reseat again after pressure is reduced.

Reactors for Bulk Resins

A description of bulk reactors follows:

- Reactor Size and Number - the bulk process uses two types of reactors for polymerization of VC - the pre-polymerization (Pre-Po) reactor where the reaction is initiated and the

post-polymerization (Po-Po) reactor where the reaction is completed. The Pre-Po reactor usually has a 2,200 gallon capacity (Dubec. 1980) and cycle time is short (about 2 hours) in order to supply seed resins to other Po-Po reactor. The Po-Po capacity is normally 4,400 gallons (Holbrook, 1980).

- Reactor Construction - both Pre-Po and Po-Po reactors are of stainless steel construction with water jackets for cooling. The Pre-Po reactor vessel stands upright with the agitator shaft entering at the top. The Po-Po reactor vessel is horizontal with the agitator shaft entering at one end.
- Operating Temperature and Pressure - polymerization temperature in the reactors is normally between 40°C to 70°C (120°F to 158°F) producing VC vapor pressures in the reactor of between 500 kilopascals to 1,200 kilopascals (5 atmospheres to 12 atmospheres). Temperature control is much more critical in the bulk process because there is no water to transfer heat to reactor walls. In addition to reactor jacket cooling water, reflux condensers are used to remove heat by condensing gaseous VC from the reactor and returning it as liquid VC.
- Agitation - agitation in the Pre-Po is by a flat bladed, turbine-type agitator and is much stronger than the agitation used in the Po-Po. This stronger agitation is necessary to produce small seed particles of the required size distribution (Goiran, 1980). Baffles are used to prevent formation of a vortex (whirlpool). Agitation in the Po-Po is by a ribbon blender which results in less extensive and slower agitation (Schoultz, 1977, p. 654). The particle size produced is dependent on the agitation history in the Pre-Po reactor.
- Cleaning - polymer build-up in the Pre-Po is slow because polymerization only reacts to 7 to 12 percent conversion. Cleaning may only be necessary every 5 to 50 batches depending on the resin product (Dubec, 1980). The Po-Po is opened for cleaning after every batch for manual cleaning because the dry, powdery resin adheres to the reactor walls and agitator blades (Dubec, 1980).

- Rupture Disc and Relief Valves - the same as those used on suspension/dispersion reactors.

Reactors for Solution Resins

Polymerization reactors in the solution process operate on a continuous cycle as opposed to the batch cycle of reactors used in suspension, dispersion, and bulk processes. Heating to initiate the solution process is supplied by hot water that is passed through coils inside the reactor. The solution process is run at lower temperatures than the other processes and over-pressure problems are rare (Erdmann, 1980). Heat of reaction is removed by reflux condensers. Agitation is provided by an external pump cycle that circulates the reactants through the reactor.

Relief valves and rupture discs are used on the solution reactor for safety purposes. Rupture discs are set at pressures higher than the relief valve. Reactor relief valve discharges from an accelerated reaction are uncommon in the solution process. Most relief valve releases that occur are due to premature rupture disc failure.

Polymer build-up is not a problem in the solution reactors. When cleaning is necessary, pure solvent is circulated through the reactors for cleaning. Reactors are only opened for maintenance and inspection procedures.

3.4.9 Emissions for a Typical PVC Plant

The study done in support of the current regulation identified 41 existing PVC plants. The VC emissions from these 41 PVC plants totaled 85 gigagrams (187 million pounds) per year in 1974, which represented approximately 85 percent of the total nationwide emissions of VC. Emissions data submitted by PVC producers were used to calculate emissions estimates for seven areas within a typical PVC plant producing 68 gigagrams (150 million pounds) of PVC resin per year. These four areas of potential emissions from the typical plant were as follows:

- Reactor and Stripper Losses - this area includes safety relief valve and reactor opening losses.
- Monomer Recovery System - after recovery of VC from the process, the unrecoverable VC was discharged to the atmosphere (these emissions are now controlled with the primary control device).

- Slurry Blend Tank, Centrifuges, Dryers and Storage Silos - these four areas are combined into sources after resin stripping.
- Fugitive Emissions Sources.

The total emissions from the typical PVC plant were approximately 2.7 gigagrams (6.0 million pounds) of VC per year.

Emission data were also compiled for VC losses during equipment purges. These purges represent VC lost when equipment is taken out of service for maintenance or inspection. This equipment purging contributed an additional 833 kilograms (1834 pounds) per year.

3.5 REFERENCES FOR CHAPTER 3

Albright, Lyle F. 1967a. Manufacture of Vinyl Chloride. Chemical Engineering (a).

Albright, Lyle F. 1967b. Vinyl Chloride Polymerization by Suspension Process Yields Polyvinyl Chloride Resins. Chemical Engineering (b).

Cameron, J. B. Lundeen, A. J. McCulley, J. H., Jr. 1979. Trends in Suspension PVC Manufacture. Hydrocarbon Processing.

Chemical Week. 1976. PVC Rolls Out of Jeopardy into Jubilation.

DeBernardi, James, Plant Manager, Lake Charles, La. Conoco Plant. Telecon with Matthew Boss, TRW, November 26, 1980.

Dubec, Harold. 1980. Manager of Environmental Compliance. Trip report - visit to Hooker Chemical Company, Ruco Division. Burlington, N. J. September 15, 1980.

Erdman, J. F., Environmental Protection Coordinator, Union Carbide Corporation, Texas City, Texas. Telecon with Matthew Boss, TRW Environmental Engineering Division. December 14, 1980.

Goiran, L. Polyvinyl Chloride (PVC) Manufacturing Equipment: Permit Application for Approval of Modification. Letter to David C. Hawkins, May 4, 1980.

Hatch, Lewis F., and Matar, Sami. 1979. From Hydrocarbons to Petrochemicals. Hydrocarbon Processing.

Holbrook, W. C., Director of Toxicology and Environmental Affairs. Trip report - visit to B. F. Goodrich Chemical Company, Pedricktown Plant. Pedricktown, N. J. September 17, 1980.

Khan, Z. S., and Hughes, T. W. 1978. Source Assessment: Polyvinyl Chloride. Industrial Pollution Control Division, Industrial Environmental Research Laboratory. Cincinnati, Ohio.

Lamorte, Michael F. 1978. National Emission Standards for Hazardous Air Pollutants Inspection Manual for Vinyl Chloride. Research Triangle Institute.

Little, Arthur D., Inc. Vinyl Chloride Monomer Emissions From the PVC Processing Industries. Contract No. 68-02-1332, Task No. 10. August 1975.

McCulley, J., Process Engineer, Conoco. Telecon with Matthew Boss, TRW. November 24, 1980. Use of Relief Valves and Rupture Discs at PVC Facilities.

McPherson, R. W.; Starks, C. M.; Fryar, G. J. 1979. Vinyl Chloride Monomer . . . What You Should Know. Hydrocarbon Processing.

Milby, Thomas H. 1978. Vinyl Chloride an Information Resource. Stanford Research Institute. Menlo Park, California.

Mukerji, Asu. 1977. Unloading and Storage Technique for Vinyl Chloride Monomer. Chemical Engineering.

Nass, Leonard I. 1977. Encyclopedia of PVC. Society of Plastic Engineers, Inc., Vol. 3. New York. Marcel Dekker, Inc.

Schoultz, Kenneth S.; Bochinski, Julius H.; Goeon, James A. 1977. Engineering Control Assessment of the Plastics and Resins Industry . . . Case Study: Manufacture of PVC by Bulk Polymerization. American Industrial Hygiene Association Journal.

Shreve, R. N.; Brink, Joseph A., Jr. Chemical Process Industries. McGraw-Hill Book Company. New York, N. Y. 1977.

Sorenson, Wayne R. 1977. A Close Look at PVC Today. Plastics Engineering.

U.S. Environmental Protection Agency. 1975. Standard Support and Environmental Impact Statement: Emission Standard for Vinyl Chloride. Emission Standards and Engineering Division. Research Triangle Park, North Carolina.

4.0 CONTROL TECHNIQUES USED TO COMPLY WITH THE EXISTING EMISSION STANDARD

Tables 4-1 and 4-2 identify control technologies that can be applied to potential emission points from EDC/VC and PVC plants. Tables 4-3 and 4-4 show the estimated emissions reductions that result when the typical EDC/VC and PVC plants, developed during the original standard support study (EPA, 1975), comply with the applicable current standard. Actual emissions are lower because the majority of plants surveyed have lower levels than required by the current standard with the possible exception of relief valve discharges. Primary control devices are reducing emissions, in most cases, well below the 10 ppm level for exhaust gases. EDC/VC plants using a pure oxygen (or combination oxygen and air) feedstock for the oxychlorination reactor and/or incinerating the oxy vent have reduced emissions below the standard. Fugitive emissions from new large reactor plants are 95 percent lower than those emissions from typical plants in 1975 (Holbrook, 1980a). Most PVC plants are stripping resins to lower levels than required and new purging methods have been developed to reduce reactor opening losses.

The following sections discuss the control technologies that industry is currently using to accomplish the various requirements of the regulation and to achieve actual emissions reductions. Improvements and new developments in control technology since promulgation of the regulations are also discussed.

4.1 DISCHARGE OF EXHAUST GASES TO THE ATMOSPHERE

4.1.1 Introduction

The current regulations require that the discharge of exhaust gases to the atmosphere be controlled to meet a set standard. The sources of these exhaust gases, the applicable standards, and control technologies

Table 4-1. POINT SOURCE EMISSIONS AND TECHNOLOGIES FOR CONTROL IN TYPICAL SUSPENSION, DISPERSION AND BULK PVC PLANT

	Process step	Potential emission points	Regulation requirements	Control technology
1	VC unloading and storage	Loading lines, VC storage tank	Emissions from loading lines must be reduced so that upon opening of line to the atmosphere emissions do not exceed 0.003m^3 of VC at STP.	Purged to monomer recovery system
			VC removed from lines to meet this criteria must be controlled to $\leq$ 10 ppm upon exhaust to the atmosphere. Concentration of exhaust gases discharged to the atmosphere from storage tanks must not exceed 10 ppm.	Incineration, solvent absorption or carbon adsorption
2	Mixing, weighing and holding tanks before stripping operation	Mixing, weighing and holding tank vents	Concentration of VC exhaust gases discharged to the atmosphere must not exceed 10 ppm.	Vented to monomer recovery system followed by incineration, solvent absorption, carbon adsorption, or combinations of these
3	Polymerization	Polymerization reactor opening loss (ROL)	ROL from each reactor is not to exceed 0.02 g VC/kg PVC products.	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	No discharge to the atmosphere except for an emergency relief discharge.	Shortstop, containment, instrumentation, improved operator training, etc.
4	Stripping	Stripping vessel vent	Concentration of VC exhaust gases discharged to the atmosphere must not exceed 10 ppm.	Vented to monomer recovery system followed by incineration, solvent absorption or carbon adsorption
5	Monomer recovery system	Recovery system exhaust vents and knock-out pot	Concentration of VC exhaust gases discharged to the atmosphere must not exceed 10 ppm.	Gasholders used in some instances to collect all recovery vents and/or refrigeration to condense VC followed by incineration, solvent absorption or carbon adsorption
6	(Blending, mixing, weighing and holding after stripping operation)	Slurry blend tanks and holding tank vents	Controlled by stripping standards	Stripping technology

(continued)

Table 4-1. Concluded.

	Process step	Potential emission points	Regulation requirements	Control technology
7	Drying, sizing, screening of dewatered resin	Centrifuge vents, dryer vent stacks, storage silos, bag-house vents, screening operation vents	Controlled by stripping standards.	Stripping technology
8	PVC loading and storage	Storage silos	Controlled by stripping standards.	Stripping technology
9	"Inprocess" wastewater stripper	Wastewater storage tank Wastewater stripper column	VC removed from in process water is to be ducted to a control system from which concentration of VC in exhaust gas does not exceed 10 ppm.	VC removed from wastewater by steam stripping in column or batch vessel, vented to monomer recovery system followed by incineration, solvent absorption or carbon adsorption
10	All of the above process steps	Fugitive emissions sources	Equipment specifications, operational procedures and leak detection and elimination programs.	Double mechanical seals, double outboard seals, rupture discs or equivalent equipment; closed systems and equipment purging to monomer recovery system; area monitors, portable monitors, routine leak surveys and maintenance programs
			VC collected from equipment seals and operational procedures are to be controlled to $\leq$ 10 ppm upon exhaust to atmosphere.	Vented to monomer recovery system followed by incineration, solvent absorption or carbon adsorption

Table 4-2. PO T SOURCE EMISSIONS AND TECHNOLOGIES FOR CONTROL IN "BALANCED PROCESS" EDC/VC PLANTS

	Process step		ential emission points	Regulation requirements	Contr	echnology
1	Direct chlorination	Produc	ndenser	Not regulated.	Not regulated	
2	EDC purification	EDC cr column storag column storag	storage, light ends denser, light ends nk, heavy ends denser, heavy ends nk	All emission points are required to be controlled to ≤ 10 ppm.	Incineration	
3	"Inprocess" wastewater stripper	Wastew Wastew	storage tank stripper column	VC removed from inprocess water is to be ducted to a control system from which concentration of VC in exhaust gas does not exceed 10 ppm.	Wastewater steam batch vessel, VC refrigeration an incinerated	ipped in column or be recovered by haust gases
4	Oxychlorination	Water Oxychl Separa	column ation process vent tank	Emissions from reactor are not to exceed 0.2 g VC/kg of the 100 percent EDC product.	Process modifica pure oxygen feed	s; incineration; incineration
5	VC cracking and purification	EDC qu HCl co VCM co	column vent condenser	Concentration in all exhaust gases must not exceed 10 ppm.	Incineration	
6	VC loading and storage	Loadin VC sto	nes tanks	Emissions from loading lines (and any other equipment in VC service) must be reduced so that upon opening of line to the atmosphere emissions do not exceed 0.003m^3 of VC at STP.	Closed systems, purge to monomer	bon adsorption and covery system
				VC removed from lines to meet this criteria must be controlled to ≤ 10 ppm upon exhaust to the atmosphere. Concentration of exhaust gases discharged to the atmosphere from storage tanks must not exceed 10 ppm.	Incineration	
7	All of the above process steps	Fugiti	missions	Equipment specifications, operational procedures and leak detection and elimination programs.	Double mechanica seals, rupture d to monomer recov monitors, portab leak surveys and	als, double outboard or equivalent; purge system; and area monitors, routine intenance programs
				VC collected from equipment seals and operational procedures controlled to ≤ 10 ppm upon exhaust to the atmosphere.	Incineration	

Table 4-3. EMISSION REDUCTION FOR 316 Gg/yr EDC/VC FACILITY IN COMPLIANCE WITH CURRENT REGULATION

Emission source	Current standard	Uncontrolled[a] emissions (kg/yr)	Regulated[b] emissions (kg/yr)	Estimated actual emissions (kg/yr)
Relief valve discharges	Non-preventable discharges only	Unknown	Non-preventable discharge	1,950[c]
Primary control	10 ppm	916,400	3,160	3,160[d]
Oxychlorination vent	0.02 kg/100 kg EDC product	113,760	50,150[e]	25,000[f]
Fugitive emissions	Work practice and equipment standard	379,200	37,920[g]	10,000[h]
Total emissions		1,409,360	91,230 + non-preventable discharges	40,110

[a] Based on EPA emissions estimates developed from emissions data submitted by industrial sources.

[b] Represents emissions from EDC/VC meeting current standard; actual emissions are lower.

[c] Based on relief valve discharge data from Table 4-7 and EDC/VC production data for 1977-1980 (Chemical and Engineering News, 1980a). Production for the 9 EDC/VC plants was estimated to be 6,325 million kg for the 4-year period. An emission factor of 6.2 kg VC per million kg produced was used.

[d] Due to the relatively small amount of emissions involved, a new estimate of emissions was not made in this study. Data on hand indicate that emissions may be lower than those shown.

[e] Assumes balanced process and 100 percent conversion during EDC cracking.

[f] Estimate represents an average of emission levels ranging from plants using only air and not incinerating the oxy vent (and still meeting the standard) to those using oxygen and incinerating. This estimate is based on very limited data (DeBernardi, 1981).

[g] Assumes 90 percent reduction following installation of required equipment and implementation of leak detection and elimination programs.

[h] Based on results of a fugitive emission study done in an EDC/VC plant (Blacksmith, et al., 1980).

Table 4-4. EMISSIONS REDUCTION FOR 68 Gg/yr PVC FACILITY IN COMPLIANCE WITH CURRENT REGULATION

Emission source	Current standard	Uncontrolled[a] emissions (kg/yr)	Regulated[b] emissions (kg/yr)	Estimated actual emissions (kg/yr)
Primary control	10 ppm	326,400	680	680[c]
Relief valve discharges	Non-preventable discharges only	136,000	Non-preventable discharges	4,780[d]
Combined sources after resin stripping	400 ppm - suspension, latex, and bulk [2000 ppm - dispersion]	850,000	27,200 [136,000]	13,600[e] [74,800]
Fugitive emissions	Work practice and equipment standard	1,040,400	108,800	25,500[f]
Reactor opening loss	0.002 kg/100 kg PVC product	312,800	1,360	1,360[g]
Total emissions		2,665,600	138,040 [246,840] + non-preventable discharges	45,920 [107,120]

[a] Based on EPA emissions estimates developed from emissions data submitted by industrial sources.

[b] Represents emissions from PVC plant meeting current standard; actual emissions are lower except for relief valve discharges.

[c] Because of the relatively small amount of emissions involved, a new estimate of emissions was not made in this study. Emissions may be lower than those shown here because plants are presently controlled lower than 10 ppm.

[d] Based on relief valve discharge data from Table 4-6 and total PVC production for 1977-1980 (Chemical and Engineering News, 1978; ibid. 1980b). Emission value includes 580 kg/yr for nonreactor relief valve discharges and 4,200 kg/yr for reactor relief valve discharges. Production for the 23 PVC plants was estimated to be 5800 million kg for the 4-year period. An emission factor of 70.2 kg VC per million kg PVC product was used.

[e] Based on an average of stripping levels reported by industrial sources.

[f] Estimation quoted from SPI, based on B.F. Goodrich fugitive emission study (delaCruz, 1981).

[g] Because of the relatively small amount of emissions involved, a new estimate of emissions was not made. Emissions may be lower than those shown.

are presented in Tables 4-1 and 4-2. (See Figure 3-1 and 3-2 in Section 3.0 (Process Description) for locations of process steps). A complete copy of the regulation can be found in Appendix A.

The most common primary control technologies currently used for exhaust gases from EDC/VC plants and PVC plants are incineration, solvent absorption, and carbon adsorption.

Because only emission levels greater than 10 ppm are currently reported, there is no way to know how effectively exhaust gas controls are working. In fact, levels may be much less than 10 ppm most of the time. Results of the initial compliance tests required for primary control devices following the 2 year waiver period give an indication of the effectiveness of these devices. However, only one initial source test was required and, in most cases, the control device was operating at peak performance. The effectiveness of the control devices over long periods of time and under variable plant conditions is not known.

The current standard allows no excess emissions during periods of control equipment shutdown and for this reason most plants maintain back-up control equipment to provide emission control when primary exhaust gas control equipment is not operating. Some of these secondary devices are duplicates of the primary systems (e.g., parallel incinerators) that are capable of handling 100 percent of plant exhaust gas discharge emissions, enabling the plant to maintain full production status. Other back-up systems are potential primary control devices (e.g., incinerator back-up for a solvent absorption system). Some plants use temporary measures for back-up control such as short term storage vessels while others merely maintain an inventory of spare parts for the single primary control device. There are several plants that do not have any back-up control systems.

In the original standard support document, several technologies were identified for possible control of VC emissions in exhaust vents. These control technologies are being used by the industry and are discussed in the following sections.

4.1.2 Incineration

In the plants surveyed during this review study, incineration represented the most prevalent method of exhaust gas emission control.

In those plants not using incineration as primary control, it is usually used as a back-up for the primary control system. Many of the plants maintain two incinerators so that control is provided if one is out of service.

Waste streams containing chlorinated hydrocarbons such as VC are more difficult to combust and higher temperatures of combustion are usually required in comparison with non-chlorinated hydrocarbon waste streams. Combustion temperatures of 980° to 1,100°C (1,800° to 3,000°F) have been recommended for efficient destruction of halogen-containing hydrocarbons by thermal oxidation. However, many of the VC sources surveyed that use thermal oxidation are operating their incinerators at much lower combustion temperatures.

A disadvantage to incineration is that it is a destructive control method. No VC is recovered and in those cases when waste heat has been recovered, no return has been shown.

The methods of incineration used in the VC industry are thermal and catalytic. The incineration method used most often is thermal oxidation. Incineration temperatures for VC emission control range from 760°C to 1,290°C (1,400°F to 2,350°F) with residence times of 0.5 seconds to 2.0 seconds. One company has recently tested a back-up incinerator at a combustion temperature of 540°C (1,000°F). Results showed average VC concentrations of 0.26 ppm. The following data show the results of their tests with a range of incineration temperatures. These tests were performed to determine compliance and were observed by a Region IV representative as well as members of the Kentucky Division of Air Pollution Control. At the time of the tests, the plant (an EDC/VC facility) was operating under conditions stipulated by EPA compliance test parameters, i.e., at least 90 percent capacity (Holbrook, 1980b).

Combustion temperature	Average VC concentration
540°C (1,000°F)	0.26 ppm
650°C (1,200°F)	None detected
870°C (1,600°F)	None detected
980°C (1,800°F)	0.18 ppm

One of the major VC and PVC producers has extensively studied incineration technology and they report that the large size and high temperatures (used in conventional thermal incineration) are not always necessary for efficient combustion of VC. This manufacturer uses a smaller (Brulé) incinerator as a back-up control in its PVC plants. The incinerator and stack are lined with a ceramic material that allows the unit to reach optimum temperature within a few hours. A large surge tank contains the exhaust gases until the incinerator comes up to temperature and regulates the flow to the unit. The incinerator is heated to 704° to 760°C (1,300° to 1,400°F) using supplemental fuel. At this point the vinyl chloride waste stream is fed to the incinerator which raises the energy content of the stream, thus causing a reduction of the supplemental fuel feed. A temperature of 870° to 980°C (1,600° to 1,800°F) is maintained which burns the exhaust gases to less than 10 ppm VC (Varner, 1980).

Auxiliary fuel usage in thermal oxidation systems varies according to processes. One EDC/VC plant adds methane during direct chlorination. This both enhances the combustion of vinyl chloride as well as provides a "fuel-rich" mixture in the reactor to avoid explosion. Some EDC/VC plants use pure oxygen instead of air as feedstock for the oxychlorination reactor. As mentioned in Section 3.1.2, this minimizes the venting of inerts, provides more efficient incineration, and greatly reduces auxiliary fuel usage. These plants view the reduced energy consumption as an economic advantage. The use of pure oxygen would seem to be a measure to attain compliance with other hydrocarbon standards (such as volatile organic compounds (VOC)) (Brittain, 1980a).

There are several approaches to the control of the EDC oxychlorination reactor vent (oxy vent). Some EDC/VC plants do not incinerate the oxychlorination vent gas but, instead, meet the standard by process modifications (e.g., incorporation of vapor phase catalytic reaction) (DeBernardi, 1980). There may be high concentrations of VC emissions during start-up, shutdown and unstable operating conditions. Some plants incinerate the oxy vent during these periods (Brittain, 1980b). Oxy vent emissions are potential candidates for regulation (for VOC) by State Implementation Plans (SIP) and New Source Performance Standards (NSPS) programs.

Incinerators are equipped with flame arresters or flash-back preventative devices necessitated by the hydrocarbon-oxygen content of the waste streams. Because combustion of halogen-containing hydrocarbons results in the formation of HCl, quench systems for cooling and caustic scrubbers for HCl removal are incorporated when required by state regulations.

Continuous monitoring of incineration stacks and compliance tests have shown VC levels ranging from "non-detectable at 0.1 ppm" to "less than 10 ppm" according to regional enforcement personnel.

The following problems have been identified with thermal incineration systems.

- Incinerator overloading. When VC levels are too high the rich mixture of combustibles leads to elevated temperatures and results in maintenance problems. Some plants have solved this problem by using a surge vessel (such as a gasholder) to provide a constant feed to the incinerator.
- The thermal incineration process can be a source of secondary air and water pollution (e.g., HCl and Cl_2 generation from combustion and high total dissolved solids (TDS) levels from scrubbing).
- Supplemental fuel and high maintenance requirements represent additional expenses. One of the major maintenance items - "downcomers" (connections between furnace and quench system) - has been estimated to cost $6,000 to replace when corroded, and replacement may be necessary as often as once each month. Overall annual maintenance costs for incineration have been reported around $100,000 (for PVC plant incinerators designed to handle over 45 kilograms per hour VC). A PVC plant (with a production rate of 68 gigagrams of PVC resins per year) uses 26.5 cubic meters (7,000 gallons) of No. 2 fuel oil per month to keep their dual incincerators hot (Dubec, 1980).
- Monitoring is difficult due to temperature fluctuations and moisture condensation. Some plants have solved this problem

by using a system that removes moisture prior to analysis (Laundrie, 1980).

- Location of the incinerator requires "safe radius" considerations.

Catalytic incineration systems are currently used by at least one plant for primary control, and at least one other plant is experimenting with them. Energy requirements for catalytic oxidation are approximately one-third of that used for thermal oxidation without heat recovery. The plant using catalytic incineration passes the exhaust gas vapors through a wash oil scrubbing system. This hydrocarbon oil contacts the stream in the vent condenser line countercurrently, recovers vinyl chloride, and provides a stable load to the incinerator. This is an experimental procedure serving more of a VC recovery function than an emission control purpose.

Problems with catalytic incineration include:

- Surge capacity. Assuring even flow into the incinerator has presented a problem for some plants.
- Catalyst pollution. Organic halides pollute and degrade the catalyst which is expensive to replace.
- Conversion to other chlorinated hydrocarbons.
- Efficiency. These units reportedly remove less than 60 percent of the VC in the oxychlorination process.

Waste heat boilers can be used in conjunction with incinerators; they are used for steam generation for heat recovery.

4.1.3 Steam Boilers

None of the plants surveyed use steam boilers as primary control. When used, they are maintained for back-up control. The long term reliability of these units is limited by the corrosivity of the vinyl chloride stream. One plant is considering the use of "expendable" boilers as a back-up for this reason.

4.1.4 Flares

The use of flares is generally restricted to back-up control. Generally speaking, a flare would be installed to accommodate streams from a large chemical complex in order to reduce hydrocarbon emissions. One plant uses a flare as an equivalency to the use of a rupture disc

upstream from the safety valve. (This represented an approval on the basis of an equipment standard as opposed to an emission standard.) In this case the relief valve would discharge directly to the flare. Parameters for usage were specified (Brittain, 1980a). Regional EPA personnel discourage the use of flares because they cannot be tested or monitored reliably. There are other objections to the use of flares.

- A destruction efficiency of 90 percent can be calculated and therefore it is Agency policy to allow their use only on exhaust gas streams containing 100 ppm VC or less (Ullrich, 1981).
- There is a need for a large capacity, low pressure vapor/liquid separator.
- The safe radius restriction can be prohibitive for flare location. For example, this radius would be 170 meters (560 feet) for a 17,000 kilojoule per square meter (1,500 Btu per square foot) per hour radiation density at ground level (Finch, 1980).
- Secondary pollutants (e.g., noise, hydrogen chloride, smoke) are produced by the flaring process, thus elevation or isolation of the flare is required.
- Capital costs. Installed capital costs for elevated flares range between $40,000 and $700,000; ground flares cost between $30,000 and $900,000.
- Energy use consideration. For general consideration, the quantity of steam required can be assumed to be 0.4 kilogram steam per kilogram of hydrocarbon (0.4 pounds of steam per pound of hydrocarbon) (Neveril, 1978, p. 5-76). Also, the dilute gas streams present in both EDC/VC and PVC plants cannot burn without the addition of natural gas or other fuel. All the heat produced is wasted.

One company has two flares – one servicing the large chemical complex and the other installed specifically for PVC process emissions. The latter was originally designed for emergency releases. The stack is 99 meters (325 feet) tall, thus overcoming the "safe radiation distance"

problem. Two vessels (one dry knock-out (KO) drum and one water-sealed drum) provide enough knock-out volume capacity to keep the liquid from the top of the stack. The flare has never been used for that "worst-case" condition but it does handle periodic small relief valve discharges (non-routine emergencies). Ninety-eight percent of the rupture disc/relief valve combinations are tied into the flare at that facility. One disadvantage of the use of a flare for VC emissions is the smoke inherent in burning the emissions. Even with a discharge of 15 to 20 seconds duration, the smoke emanating from the flare lasts for 1 to 2 hours, creating problems with state opacity regulation (Kachtick, 1980).

4.1.5 Carbon Adsorption

This method is used as primary control in only a few of the plants surveyed. More often it is used in conjunction with other control devices (usually incineration). Most of the regional EPA personnel and industrial representatives felt that carbon adsorption alone is not effective in reducing discharge emissions to below 10 ppm.

PVC plants are successfully using carbon adsorption systems as primary control. (It is possible that the competition from hydrocarbons, other than VC, found in exhaust streams at EDC/VC plants prevent the use of carbon adsorption systems.) The most practical application of carbon adsorption control technology would be in PVC plant monomer recovery systems, closed slurry blend tanks, and storage areas because of the high VC concentration and low volume streams found in these areas. One EDC/VC plant uses a very small carbon adsorption system – two 0.4 cubic meter (110 gallon) carbon-filled vessels run in series – at their marine loading dock. This is a portable system which is regenerated by passing hot nitrogen through the carbon beds and into the incinerator (DeBernardi, 1980).

Two PVC plants using carbon adsorption as primary control for exhaust gases use a double bed system. When a probe at the outlet of the bed indicates an approaching 5 ppm level (as an indicator of break-through), the waste stream is diverted to the other bed while the first bed is being regenerated. Continuous monitors on these units show the systems to be effective in reducing VC emission levels to below 10 ppm

(Battye, 1978). Back-up control for one plant is a boiler. With the VC levels from carbon adsorption below 10 ppm, the boiler can also accommodate effluent from the adsorber without HCl corrosion problems.

The following disadvantages have been cited for carbon adsorption systems.

- Regeneration of the beds requires high energy usage.
- Treatment of regenerating gas streams requires another control device (e.g., incineration).
- Polymerization of VC on the carbon beds is a potential problem.
- With new regulations on hazardous waste treatment and disposal (RCRA), eventual disposition of the contaminated carbon could be a problem.
- Carbon adsorption represents higher capital costs than solvent absorption and incineration.

4.1.6 Solvent Absorption

Four of the plants surveyed use solvent absorption as primary control for exhaust gases. (All of these are PVC plants although the principles of solvent absorption can apply to exhaust gas control in EDC/VC plants.)

The vent gas absorber system used by the major producers incorporates the same figure-eight solvent absorption technology described in the original standard support document, with proprietary modifications to improve efficiency. The function of the vent gas absorber is to strip and recover residual VC. The recovered VC is then reused in polymerization.

The vent gas absorber system consists of two packed columns. In the first column the VC gas is absorbed by the lean solvent which enters at the top. The non-absorbables and a small quantity of solvent are then vented to the atmosphere from the top of the column.

The VC-rich solvent is passed through a heat exchanger on its way to the stripping column. In the stripping column the solvent is heated to remove the VC that comes off at the top and is returned to the process. The lean solvent comes off at the bottom of the column. The warm, lean solvent passes back through the heat exchanger and another cooler before returning to the stripping column for another cycle. The vent gas

absorber system described above was developed by B. F. Goodrich who plans to license the technology; it is commercially available. The only other solvent absorption system used by the plants surveyed in this study is a proprietary system designed by the company using it.

The efficiency claimed by the plants using the vent gas absorber system is 99.99 percent. Capital investment is slightly more than for incineration but less than for carbon adsorption. Utility costs for the solvent absorption system are greater than for incineration but less than those for carbon adsorption; however, VC recovery, achieved in the vent gas absorber system, results in a substantial credit to the system.

B. F. Goodrich regards the safety advantages of their vent gas absorber system as significant. The VC from the feed stream is absorbed in cold solvent and the non-absorbables (containing oxygen) and a small quantity of solvent are vented to the atmosphere at the top of the absorbing column. In this operation the cold solvent acts as a built-in heat sink. As the VC is absorbed by the solvent, it is removed from the absorber and further contact with any oxygen in the feed stream. Even though a small volume of gas passes through the explosive range, the cold solvent heat sink makes the operation safe.

Because there is no flame associated with the operation of a vent gas absorber (as with incineration) it can be located close to other parts of the PVC process. In addition, B. F. Goodrich claims that the unit has a low environmental pollution potential even though some small amount of solvent is released to the atmosphere. The solvent is proprietary, commercially available, inexpensive, and reputed to be low in toxicity.

4.1.7 Refrigeration

This method of controlling exhaust gases is used only in conjunction with other control devices to reduce the load on these downstream systems. Condensation of VC and water reduces the volume of gases to be handled by primary control systems. Use of refrigeration is usually limited to monomer-recovery systems and in some cases, installation of refrigeration units was in response to hydrocarbon control for SIP compliance.

A typical application of this control technology in a recovery system can be illustrated as follows: Vents from compressor relief valves, pumps, transfer lines, weigh scales, condensers and knockout pots, and slurry and wastewater strippers would go to a common holding vessel. VC from this vessel would be recovered through compressing and condensing the monomer in a refrigeration unit. The noncondensable stream from the recovery system would be vented to a surge tank or gasholder which would vent to the incinerator (Laundrie, 1980).

The above description represents a monomer-recovery system for a plant utilizing 18 reactors with an average capacity of 19 cubic meters (5,000 gallons). Equipment includes seven 0.2 cubic meters per second (400 cfm) vacuum pumps, two compressors (one 0.2 cubic meters per second (400 cfm) and one 0.1 cubic meters per second (200 cfm)) and two 0.01 cubic meters per second (30 cfm) vent compressors.

4.1.8 Other Controls

One EDC/VC plant in Region VI uses a separate fixed-bed oxychlorination reactor to receive only the oxy vent exhaust stream. The reactor converts VC to heavier chlorinated hydrocarbons which are used in other processes (Brittain, 1980a).

In the past several years a number of procedures have been proposed for the removal of vinyl chloride from gas streams. Some of these systems that have been developed, but are not in current use by the plants surveyed in this study, follow (Sittig, 1977).

Reaction with ozone. The disadvantage of this method is that it is slow and requires long residence times to reduce the VC content of the gas stream to 1 ppm or less. In addition, it is difficult to meter ozone into the gas streams in amounts that will destroy substantially all of the VC without leaving an appreciable amount of ozone in the effluent gas. There are also environmental problems arising from the presence in the effluent gas of ozonides formed by the reaction of vinyl chloride with ozone.

Reaction with ozone in the presence of activated carbon. This process (patent assigned to Tenneco Chemicals, Inc.) is one in which VC is removed from gas streams that contain from 10 ppm to 1,000 ppm of VC by contacting the gas stream with ozone in the presence of activated

carbon. The gas streams treated in this way contain less than approximately 1 ppm of vinyl chloride and no detectable amount of ozone or ozonides. Another process (patent assigned to Stauffer Chemical Company) is also one in which the stream contacts ozone but without activated carbon. The process can be used to treat gas streams that arise in the ethylene oxychlorination processes, ethylene dichloride cracking operations, VC polymerization processes in which VC is a monomer or comonomer, ventilation streams from areas in which VC is or may be present, processes for preparing vinylidene chloride, and polymerization processes in which vinylidene chloride is utilized as a monomer or comonomer.

After reaction with ozone, the gas stream contains hydrogen chloride, oxygenated compounds such as carbon dioxide and water, and can contain phosgene and partially oxygenated hydrocarbons such as methanol.

Contacting the treated gas stream with an aqueous medium is advantageous because products of the reaction are removed from the gas stream and partially oxidized hydrocarbons can further react with any unreacted ozone present in the gas stream. The aqueous medium also aids in hydrolysis of reaction products of ozone and the chlorinated hydrocarbons present.

4.2 RELIEF VALVE DISCHARGES

4.2.1 Introduction

Pressure vessels, transfer lines, and other equipment in EDC/VC and PVC plants are equipped with safety relief valves, rupture discs or a combination rupture disc/relief valve assembly to prevent overpressurization which might cause a rupture to occur. The size of polymerization reactors, which can range from several thousand liters for the older reactors to the new reactors of up to approximately 190,000 liters (50,000 gallons) used by Hüls of Germany (the largest reactors currently being used in the United States range from 35,000 to 40,000 gallons) plus the close proximity of the reactors to each other, represents the greatest potential for an explosion hazard. It is for this reason that existing safety regulations and insurance companies require and strictly enforce the use of safety relief devices on pressurized equipment.

Relief valve discharges, which cause short-term peak emissions, represented approximately 4 percent of total emissions from a typical PVC plant prior to promulgation of the regulation (EPA, 1975, p. 5-6). Relief valve discharge emissions were not quantified for a typical EDC/VC plant. The major concern during the original standard support study was for relief valves located on PVC reactors because these relief valves represented a large source of emissions. PVC plants prevented reactor relief valve discharges by equipping reactors with instruments to warn personnel of an emergency condition. Preventive measures could then be taken such as injecting a short-stop agent to kill the reaction or manually relieving pressure to the recovery system. One plant used a gasholder to prevent relief valve discharges and EPA indicated that a gasholder could be sized to hold all the VC present in an entire reactor batch (EPA, 1975, p. 4-30).

Based on this information, relief valve emissions were addressed in Section 61.65(a) which states,

> Except for an emergency relief valve discharge, there is to be no discharge to the atmosphere from any relief valve on any equipment in vinyl chloride service. An emergency relief discharge means a discharge [that] could not have been avoided by taking measures to prevent the discharge.

When a relief valve discharge occurs, the plant is required to notify EPA and submit such data as the source (specific piece of equipment), cause, quantity, and measures that would be taken to prevent future discharges.

4.2.2 Emissions from Safety Relief Valves

The intention of Section 61.65(a) was to reduce relief valve discharges through the proper combination of control equipment and operating procedures. If a release then occurred, it would be considered either an emergency condition or one in which a plant had not implemented the proper combination of control techniques.

EPA Regional enforcement personnel indicate that releases are continuing to occur. As mentioned, the concern during the original standard support study was for relief valve discharges from PVC reactors

that have the potential to discharge the entire reactor contents. Prior to the regulation, relief valve discharges were not accurately measured but typically 2,200 kg (5,000 lb) of VC was released in a 5 to 10 minute period (EPA 1975, p. 4-30). With the change to larger reactor systems, the potential quantity of emissions from the relief valve is increased.

Relief valve discharge data from EPA Regional Offices substantiate the fact that releases are continuing to occur and reactors account for the largest quantities per release. Table 4-5 shows a compilation of reactor and non-reactor relief valve discharge data for 32 regulated sources (55 percent of all sources) for the period 1977 to 1980 (Brittain, 1980; Diem, 1980; Aronson, 1980; West, 1981). These 32 plants were responsible for 533 relief valve discharge events totalling approximately 450,000 kilograms (1 million pounds) of VC emissions over the 4 year period.

PVC plants experience both reactor and non-reactor relief valve discharges. Table 4-6 shows that portion of the relief valve discharge data in Table 4-5 contributed from PVC plants, which is approximately 82 percent of the total events and 91 percent of the quantity of VC emitted. Based on these data, an average reactor relief valve discharge accounted for approximately 1,025 kilograms (2,275 pounds) of VC being released to the atmosphere. The time period for a reactor relief valve discharge event ranged from less than 1 minute to 115 minutes, with typical events less than 10 minutes in duration. The average PVC non-reactor relief valve discharge was approximately 540 kilograms (1,200 pounds) of VC emissions over a period of 10 minutes or less.

EDC/VC plants experience non-reactor related relief valve discharges. Table 4-7 shows that a portion of the relief valve discharge data in Table 4-5 was contributed from EDC/VC plants. Based on these data, the average non-reactor relief valve discharge from EDC/VC plants was approximately 430 kilograms (950 pounds) of VC emissions. The duration of the EDC/VC non-reactor relief valve discharges was not determined. Together, the EDC/VC and PVC non-reactor relief valve discharges represented 34 percent of the total events and 20 percent of the total quantity of VC emitted by relief valve discharge.

Table 4-5. TOTAL NUMBER OF RELIEF VALVE DISCHARGES AND QUANTITY OF VC EMITTED FROM 32 REGULATED SOURCES[a] FOR THE PERIOD 1977 to 1980

	Reactor and non-reactor relief valve discharges		
	Events	kg VC	(lb VC)
1977[b]	149	90,804	(201,787)
1978[b]	130	126,835	(281,856)
1979	156	153,212	(340,472)
1980[c]	97	75,718	(168,260)
TOTALS	533	446,569	(992,375)

[a]The 32 regulated sources are 9 EDC/VC plants and 23 PVC plants.

[b]Relief valve discharge data for 1977 does not reflect data from 1 EDC/VC plant and 5 PVC plants; these same plants reported data for only 3 months of 1978.

[c]Relief valve discharge data for 1980 ranges from 8 to 12 months.

Table 4-6. RELIEF VALVE DISCHARGES FROM PVC PLANTS FOR THE PERIOD 1977 to 1980

	PVC plants[a]	Non-reactor relief valve discharges			Reactor relief valve discharges		
		Events	kg VC	(lb VC)	Events	kg VC	(lb VC)
1977	18	9	17,550	(38,999)	118	65,028	(144,507)
1978[b]	23	6	1,742	(3,869)	102	111,375	(247,500)
1979	23	50	11,912	(26,471)	77	129,689	(288,199)
1980[c]	23	26	17,998	(39,996)	53	52,174	(115,941)
	TOTALS	91	49,202	(109,335)	350	358,266	(796,147)

[a]The 23 PVC plants represent 58 percent of the total number of PVC plants in the U.S.; 2 of these PVC plants reported no relief valve discharges for the 4 year period.

[b]Relief valve discharge data from 5 plants is for 3 months of 1978.

[c]Relief valve discharge data for 1980 ranges from 8 to 12 months.

Table 4-7. RELIEF VALVE DISCHARGES FROM EDC/VC PLANTS FOR THE PERIOD 1977 to 1980

	EDC/VC plants[a]	Non-reactor relief valve discharges		
		Events	kg VC	(lb VC)
1977	8	22	8,226	(18,281)
1978[b]	9	22	13,719	(30,487)
1979	9	29	11,611	(25,802)
1980[c]	9	18	5,545	(12,323)
	TOTALS	91	39,101	(86,893)

[a]The 9 EDC/VC plants represent 50 percent of the total number of EDC/VC plants in the U.S.

[b]Relief valve discharge data from 1 plant is for 3 months of 1978.

[c]Relief valve discharge data for 1980 ranges from 8 to 10 months.

Based on the relief valve discharge reports submitted to Regional offices, the rate of reactor and non-reactor discharges are not consistent throughout the industry. Many sources have reported few, if any, releases during the past several years, while other sources continue to have releases on a regular basis. The decline (or absence) of any relief valve discharges may also be due to the wording of the regulation that states only "relief valve" discharges are required to be reported. Plants using other safety relief devices (e.g., rupture discs only) are not required to report discharges through these devices. The reported releases that continue to occur are more prevalent among the older sources using small reactor technology; however, some of these older sources have reduced releases through application of available control technology.

4.2.3 Relief Valve Discharges from Reactors

Relief valve discharges are classified as either reactor releases or non-reactor releases - PVC plants experience both types while EDC/VC plants only experience non-reactor releases. The causes of reactor releases and measures that can be taken to prevent them are discussed in the following sections.

4.2.3.1 Process Variations. The frequency of, and ability to control, relief valve discharges from reactors vary among the different polymerization processes. In addition, the frequency of discharges is dependent on the age of the plant. Newer (and larger) reactor systems are replacing the older systems which usually consisted of many small reactors. These newer reactor systems provide better process control, fewer upset conditions, and fewer emissions to the atmosphere.

Suspension/dispersion.

The newer and larger reactors are most often applied to the suspension and dispersion processes. As mentioned above, these newer systems provide better process control and reduce emissions. Newer reactors have fewer piping connections, valves, and mechanical operations per kilogram of monomer transformed to resin. The fewer number of batches and reactors that need to be monitored when larger reactors are utilized results in a lessened probability of relief valve discharges. Also, relief valve discharge control equipment and procedures can be more economically applied to new plants with large reactors.

Older smaller reactors are usually operated closer to the rated pressure and when an upset condition develops it becomes more difficult to short-stop the reaction before the relief valve set pressure is attained. Construction materials in the newer reactor systems (e.g., stainless steel, carbon steel) contribute to better heat transfer and control of the reaction. The older smaller reactors are usually glass-lined which has an insulating effect on the reactor and results in poorer heat transfer and less control over the reaction.

Bulk polymerization.

The bulk (or mass) polymerization process has some advantages over polymerization conducted in the aqueous medium used in the suspension and dispersion processes. Because the bulk process is anhydrous and no water or suspending agents are used, the process generates no foam and energy consumption is low. Exothermic heat is removed by water-cooled reflux condensers. The bulk process currently used in the United States utilizes a vertical pre-polymerization (Pre-Po) reactor and a horizontal post-polymerization (Po-Po) reactor. A new bulk process has been developed that utilizes a vertical Po-Po reactor, but it is not currently in use in the United States. These bulk processes have several unique aspects that affect relief valve discharges.

Relief valve discharges from the Pre-Po reactor are unlikely because the reaction only goes to 8 to 12 percent conversion. If a high temperature or pressure is detected in the Pre-Po, the slurry can be dropped to an empty Po-Po reactor where the larger volume allows the low level of initiator charged to the Pre-Po to be used up and complete the reaction. However, reaction control is more difficult in the Po-Po reactor because the bulk reaction is anhydrous and this results in less efficient heat transfer to the walls of the reactor. Almost all of the liquid VC charged to the Po-Po is used during the early stages of the reaction and it is during this early stage that auto-acceleration of the reaction and a rapid increase in temperature can occur. Therefore, process control is more critical during this initial reaction stage.

If an upset situation is detected in the Po-Po reactor, the conventional short-stopping techniques, effectively used in the suspension and dispersion processes, can not be used to terminate the bulk

reaction because the contents of the Po-Po reactor are not fluid and mixing is not turbulent. As a result, the short-stop agent is not distributed rapidly or completely enough throughout the slurry. Rhône-Poulenc has developed a short-stopping procedure, but it is only applicable to their newer process technology utilizing vertical Po-Po reactors (Dubec, 1980). B. F. Goodrich operates two bulk plants in the United States and has developed a more effective gaseous short-stop system that may be available for licensing in the future (Dubec, 1980).

Solution process.

Union Carbide operates the only facility in the United States using the solution polymerization process. The solution process is a continuous, homogeneous process - it is not a batch flow system like the other processes. The solvent, which is always present, provides a heat sink capable of preventing an accelerated reaction. In over 30 years of operating the solution process, Union Carbide has not experienced a reactor relief valve discharge to the atmosphere caused by an accelerated reaction. Reactor relief valve discharges that have occurred were due to a premature failure of the rupture disc under the relief valve (Erdman, 1980).

4.2.3.2 Causes of Reactor Discharges. There can be many causes of reactor relief valve discharges ranging from total power failure caused by a natural disaster to mechanical failure of process equipment to operator errors. Two of the more frequent causes of relief valve discharges common to suspension and dispersion processes follow.

- The hydraulically full (hydroful) condition resulting from too much liquid or the presence of noncondensable gases in the reactor. This condition can be caused by instrumentation errors or an overcharging of the reactor and usually results in a small release to the atmosphere.
- High temperature in the reactor from an accelerated reaction. This condition is caused by inadequate cooling and can result in a discharge of the entire reactor contents.

Both of these conditions can result in high pressure in the reactor and a substantial, multiphase discharge through the relief valve to the atmosphere.

Hydroful condition.

The VC liquid charge expands up to 13 percent when heated to reaction temperature. Therefore, an overcharging of the reactor may not be detected when raw materials are initially charged and the resulting increase in pressure above the normal operating pressure will open the relief valve when the slurry reaches the top of the reactor. Overcharging of the reactor can result from charge meter or weigh tank errors, leaking reactor valves, and wash-water or solvent cleaning solution incompletely drained from the reactor.

The presence of noncondensable gases in the reactor will also cause high pressure to develop resulting in a hydroful condition. The operating procedure for a typical suspension or dispersion process is to charge a reactor with water, initiator, and other constituents (depending on the process and resin qualities desired) to about 50 percent of reactor volume. Pressure is then reduced to about 5 kPa (0.05 atmospheres). Vaporization of the water will sweep some noncondensable gases from the reactor if present. Liquid VC is added under vacuum to raise the slurry level to about 80 percent reactor volume. Liquid expansion from the reaction temperature then raises the slurry level to about 90 percent reactor volume. The concentration of any noncondensable gases present at 50 percent reactor volume can be increased by up to five times. Because the combined VC and water vapor pressure at normal operating temperatures can reach about 1,000 kPa (150 psia) and relief valve systems are usually set at 1,300 kPa (195 psia), the presence of only 5 percent noncondensable gases in the vapor space prior to VC liquid charging could trigger a release. The sources of noncondensable gases in the reactor include:

- gases not removed by initial evacuation during preparation for a new batch,
- gases dissolved or entrained in the VC liquid charge, and
- leakage from reactor valves into the reactor after vacuum treatment and before heating to reaction temperature.

In the case of a hydroful condition caused by overcharging or the presence of noncondensable gases, the increased pressure causing the relief valve to open is quickly relieved by liquid and vapor flows

through the valve. The relief valve will reseat itself under most circumstances after pressure is released. However, if the relief valve does not reseat properly or pieces of a blown rupture disc become lodged in the valve preventing complete closure, a larger volume of reactor contents will continue to be discharged until temperature and pressure are brought under control.

Accelerated reaction.

The polymerization reaction is exothermic and the reaction heat produced is controlled by circulating cooling water through the reactor jacket. The reaction normally takes place at a temperature and pressure of approximately 55°C (130°F) and 1,000 kPa (150 psia). As the reaction proceeds, the polymer tends to coat the inner walls of the reactor reducing heat transfer effectiveness and, because reactors are no longer opened as often, more consecutive batches are run and polymer continues to coat the inner reactor walls. However, new clean reactor technology has reduced this polymer build-up even though reactors are not opened as often. In some of the newer systems, water jets clean the inner walls after each batch to prevent polymer build-up and loss of heat transfer effectiveness. The use of clean reactor technology or other proprietary methods for reduction of polymer build-up allows the most efficient heat transfer through reactor walls and thus reduces the danger of auto-acceleration due to high reaction temperatures.

For suspension and dispersion processes, an auto-acceleration of the reaction occurs with increased heat evolution at some point around the 50 percent conversion level. Heat transfer effectiveness and control of the reaction during this period depend on vigorous agitation of the slurry and an adequate supply of cooling water applied to the reactor jacket. A malfunction of these systems will result in rapid heating and an increase in pressure that could cause the relief valve to open.

The loss of agitation is the greatest concern because heat transfer is significantly reduced. Inadequate heat removal during the auto-acceleration period will usually result in a major discharge (possibly the entire contents of the reactor) because of the rapid rise in temperature. An increase from the normal reaction temperature of 55°C (130°F) to 72°C (162°F) or a total increase of 17C° (32F°) can result in

the sum of the VC and water vapor pressures reaching the relief valve discharge pressure setting.

However, if the reaction is in its later stages (greater than 80 percent conversion), most of the VC will have been used up. This decreases the potential quantity of emissions through the relief valve. In the earlier stages of the reaction all of the VC would be vaporized, unless a shortstop agent were added to the reactor to kill the reaction. Addition of a shortstop agent usually requires that agitation still be available for distribution throughout the slurry. Conoco has developed a shortstop agent that is effective without agitation. This new development will be discussed in a subsequent section.

4.2.3.3 Prevention of Reactor Discharges. Proper instrumentation to detect upset conditions, gasholder equipment, and an automatic inhibitor solution (shortstop agent) addition systems can be used to eliminate many of these relief valve discharges (EPA, 1975). However, there are many other variables that must be considered for the above three controls to be successful. The following sections discuss other generic control measures, in addition to the EPA-recommended methods, used in the VC industry to prevent relief valve discharges.

4.2.3.3.1 Current generic preventive methods. Methods currently used by PVC plants to prevent emergency relief valve discharges follow.

Shortstop systems.

A shortstop or kill agent system can be used to stop the polymerization reaction when upset conditions develop. A shortstop system injects a chemical agent into the reactor which terminates the reaction by inhibiting the action of the initiator. The system is either manual, automated, or a combination of the two. The manual system generally uses high pressure water injection with the same equipment used to charge the reactor with initiator (Ledvina, 1980). Depending on the kill agent system used, success of the manual system is usually dependent on having agitation for complete dispersion of the shortstop throughout the slurry, the charge manifold being clear (this is a manifold used to charge ingredients to the reactor) and the availability of necessary personnel.

Several variations of the automated shortstop system exist. The newer computer-controlled plants have built-in programs that recognize the upset condition by monitoring operating parameters and automatically injecting the shortstop agent. For example, one plant has installed motion sensors on the reactor agitator that sense when power has been lost and a pressure build-up is beginning. A shortstop agent is then automatically injected into the reactor (Ethyl, 1980). Under this particular condition, an alternative source of pressure would be needed to open the valve and inject the shortstop agent if power loss were the cause of agitator failure. Any shortstop system employed would have to be connected to other vessels that might receive the slurry under upset conditions because active initiator may still be present in the slurry even if it is dumped to a blowdown or holding tank.

Instrumentation.

The degree of instrumentation is important in preventing relief valve discharges and varies greatly among plants. Those plants most successful in preventing discharges have several levels of back-up instrumentation. The instrumentation monitors reactor operating parameters (e.g., pressure, temperature) and either warns operators of an emergency condition or takes action automatically. Instruments monitoring the reaction can be tied into a computer system receiving data from instruments on and in the reactor or they can be locally mounted units on each reactor. Selection of operating parameters to be monitored is critical. For example, a temperature sensor mounted on a baffle can become fouled by polymer build-up. The temperature reported by the sensor can lag behind the actual temperature of reaction. Therefore, pressure sensors may be a better indicator of the actual temperature. In most cases a combination of the two is more reliable.

Other instruments, in addition to those monitoring actual reaction conditions, will contribute to the prevention of an upset condition. For example, overcharging a reactor is a common cause of relief valve discharges. A metering system for charging exact amounts of liquid VC and other ingredients in combination with accurate weigh tanks can prevent overcharging and the subsequent hydroful condition. Dual metering in series for both VC and water can help prevent overcharging.

Upstream filters can help maintain meter accuracy (Ullrich, 1981). A level control on the reactor that is attached to an alarm system would indicate overcharging. One company indicated success in using a radioactive source detected by ion chamber sensing to determine the level in the reactor prior to beginning the reaction. Reactors mounted on scales help to prevent overcharging. Agitator seal-water leaking back into reactors could also cause an overcharging condition. This leakage can be prevented with an electrically operated shut-off valve for the seal-water system. Other examples of instrumentation to prevent relief valve discharges will be discussed in more detail in the next section describing some of the preventive systems currently used by the VC industry.

Auxiliary power supply.

The effectiveness of the above examples of instrumentation systems as well as other preventive systems is dependent on the availability of power to run these systems. Auxiliary sources of power are necessary to maintain agitation, cooling, and instrumentation in the event of losing the main power source to a plant. No auxiliary power systems currently found in PVC plants are designed to operate the entire plant -- enough power is usually only available to safely shut down the plant by allowing those polymerization reactions in progress to be terminated or finished. Most plants have dual power lines into the plant to provide primary power. The dual lines keep power constant and prevent sudden surges and dips in power or a complete loss of power. Emergency back-up power is usually supplied by diesel-driven generators.

Back-up power may also be supplied in the form of an auxiliary source of instrument "air" that would be necessary to open valves to recovery or for the injection of shortstop agents. One plant uses high pressure, precharged nitrogen to provide pressure. All other valves needed for operation during an upset condition for an orderly shut-down are also nitrogen operated (Ledvina, 1980).

Auxiliary venting system.

An auxiliary venting system could be used to prevent the minor releases usually caused by the hydroful condition. The venting system

would be connected to existing recovery systems or control devices. Variations of this type of system are currently used by some PVC plants.

The auxiliary venting system is designed for two-phase relief and blowdown flows and can be used for minor events in which removal of a small quantity of material from the reactor will prevent over-pressuring and a more serious condition from developing. This auxiliary venting system could be used for the following conditions:

- overcharge of the reactor,
- presence of noncondensable gases,
- moderate reaction rate increase, and
- heat transfer reduction.

The vent line would be set at a pressure above normal operation pressure, but below the safety relief valve pressure. The vent line would then automatically open at this pressure or it could be activated from the control panel.

A computer program developed for two-phase flow through a relief valve is used in conjunction with the specific process design to select the relief valve opening pressure and size the necessary equipment. The program simulates the rate of pressure rise in the reactor and rate of venting from the reactor. Using this program, the relief valve and header system are sized and the pressure profile in the relief header is determined for the required relief flow rate so that all back pressure limitations at various points along the system are met. The program also determines maximum possible blowdown flow rate for given inlet and outlet pressures and for a given pipe header configuration (Richter, 1978, pp. 145-152).

A typical auxiliary relief valve system would consist of the following:

- polymerization reactor,
- relief valve (not open to atmosphere),
- knock-out drum for liquid/vapor separation,
- header system connecting relief valve and knock-out drum,
- blowdown tank, and
- blowdown header system.

The auxiliary vent line would be connected into a knock-out tank to prevent a carryover of liquid or solid. Vapor from the knock-out drum

can be vented to the existing recovery system, a gasholder, or control device; slurry is pumped from the blowdown tank. It is assumed that pressure in the system is atmospheric and back-pressure from the vent to recovery or control is negligible (which may not always be the case (Richter, 1978)). Sizing of all equipment is based on the computer program results that also give a history of conditions in the reactor and determine when the relief valve will close. The estimated the cost of an auxiliary venting system for a 38,000 liter (10,000 gallon) reactor system, assuming availability of a blowdown tank, using December, 1979, dollars. These costs are shown in Table 4-8.

Table 4-8
ESTIMATED COSTS FOR AN AUXILIARY VENTING SYSTEM

Auxiliary venting system	Eight 38,000 liter (10,000 gallon) reactor*
Knockout tank	419,300
Pump and motor	15,800
Piping	224,500
Instruments, control valves and safety devices	65,200
Building and site development	95,700
Total Physical Cost	$820,500

*The venting system proposed would accommodate an eight reactor line.

Chilled Water System

Many plants maintain a separate supply of chilled water other than normal jacket cooling water for upset conditions resulting from reduced heat transfer. The water is usually brine-cooled and temperatures range from 4°C (40°F) to 10°C (50°F). In the event of an increase in temperature, the chilled water can be pumped into the reactor jacket to slow the reaction. This replacement can be done in approximately 5 minutes. The chilled water can also be injected directly into the batch or into a blowdown tank where the batch might be dumped.

Operator Training Programs

A staff of qualified operators able to recognize a potential emergency situation and take appropriate measures to prevent the situation will

help to minimze relief valve discharges. The different levels of computer control help to eliminate common operator errors and aid the operator in detecting potential problems, but the computer does not provide the decision-making capabilities that are only found in experienced operations personnel. The right combination of operator experience and computer control can help to eliminate relief valve discharges.

Operator training programs vary from company to company. Training programs range from several weeks to over a month with year-to-year retraining and refresher programs also offered. Polymer operators are trained to deal with run-away reactions - how to recognize them and what steps are necessary to bring them under control. At least one company has instituted a disciplinary system for those operators responsible for a run-away reaction and the relief valve discharge if it occurs (Laundrie, 1980).

Flares.

A flare can also be used to help control a relief valve discharge. As mentioned in Section 4.1.4, one company uses a flare as an equivalency to a rupture disc in order to prevent fugitive emissions through the relief valve - the relief valve is connected directly to the flare. The flare is designed for relief valve discharges originating from upset process conditions and will accommodate two reactors simultaneously. A knock-out drum is installed between the relief valve and flare to prevent liquid entrainment. The flare has only handled minor discharges but could receive the entire reactor contents (i.e., worst-case condition). This method does not eliminate relief valve discharges, but only helps to minimize the emissions from this source. Safety and cost considerations (e.g., supplemental fuel needs) must be evaluated before applying this control method to relief valve discharges.

Gasholders and other containment methods.

A gasholder is a cylindrical, variable-volume vessel. The most common type of gasholder is a vessel with a floating roof with either a water seal or a double inner synthetic seal that expands to accommodate the influx of gas. The water-sealed gasholder has a longer life because there is no seal failure, but the water seal is a constant source of VC fugitive emissions and freezing must be prevented in colder climates.

The operating principle of a gasholder is based on piston displacement. A frictionless movable piston floats on the confined gas - rising and falling with changes in the volume of stored gas. As gas enters and builds up to the designed operating pressure, the piston rises and floats on the gas.

Gasholders are currently being used as part of the recovery system to contain and store VC gas collected from various emission sources in the plant. The gases stored can be fed to the recovery system or the gasholder can serve as a surge vessel feeding the primary control device (incinerators must receive a near constant flow and concentration of combustibles for proper operation).

Gasholders can be used to help prevent relief valve discharges without actually receiving or containing the entire reactor charge. Currently there is no plant that has connected a relief valve directly to a gasholder or uses a gasholder only for relief valve discharges. One plant manually relieves pressure to the monomer recovery system gasholder when a batch is out of control (Brumbaugh, 1980). The plant identified several problems that can occur if the gasholder is used for this purpose. As discussed previously, a multi-phased discharge can occur and slurry can carryover to the gasholder. The plant installed a knock-out tank to prevent this carryover, but it does not always handle the relief valve flow. Also, this plant's gasholder is part of the recovery system and capacity is not always available to handle the entire VC charge to a reactor.

The auxiliary vent system previously described for minor relief valve discharges would not be as effective in preventing a discharge caused by an accelerated reaction that could result in a major release or release of the entire reactor batch. Prevention of the major relief valve discharge would require two different types of control technology - the auxiliary vent system and a containment system such as a gasholder.

A gasholder for the purpose of containing a major relief valve discharge would have to be designed to accommodate a worst-case condition for one reactor (the entire reactor charge), and would have to be dedicated to that service only. Simultaneous discharges from many reactors would require many gasholders. The same knock-out tank described for the

auxiliary venting system would be a part of the gasholder containment system. There would be a separate line from the knock-out tank that would go directly to the existing recovery system or control device for the purpose of controlling minor releases. However, the knock-out tank would have a back pressure valve set to open to the gasholder in the event of a major release.

This review study, Conoco Research Division (Ledvina, 1980) and the B.F. Goodrich Chemical Group (Holbrook, 1980b) have evaluated the gasholder potential for containing relief valve discharges only and the following discussion is based on this research.

Typical specifications for a gasholder to contain a relief valve discharge from a 38,000 liter (10,000 gallon) reactor (assuming 1.4:1.0 water to VC charge ratio) is shown in Table 4-9.

Table 4-9
TYPICAL GASHOLDER SPECIFICATIONS
FOR 38,000 LITER (10,000 GALLON) REACTOR

Dimension	Specification
Volume	5,700 m^3 (200,000 ft^3)
Diameter	24 m (75 ft)
Height	15 m (48 ft)
Seal	water

The estimated capital costs for installation of the above gasholder for a 38,000 liter (10,000 gallon) reactor, assuming the use of an existing recovery system for the vapors in the gasholder, based on December, 1979, dollars is indicated in Table 4-10. The estimated total cost does not include the cost of the auxiliary vent system with knockout tank in Table 4-8 which increases the total system cost by approximately $821,000 to $4,802,100. Accuracy of these costs are ± 30 percent. Insurance, taxes, recovery credits and other miscellaneous charges are not included.

B.F. Goodrich estimated the cost of a similar gasholder system with 14,000 m^3 (500,000 ft^3) capacity to be approximately $3,000,000

Table 4-10. ESTIMATED COST FOR INSTALLATION OF A GASHOLDER

Equipment	Cost for 38,000 liter (10,000 gallon) reactor
Gasholder	$ 883,400
Piping	382,200
Safety	70,400
Site development	232,900
Header extension from KO tank	600,000
Engineering and construction	1,070,000
Contingency	648,000
Operation and maintenance	94,200
Total System Cost	$3,981,100

(Holbrook, 1979). Their cost was based on earlier dollar values and did not include operation and maintenance costs. Conoco estimated a gasholder system alone without the auxiliary venting system (i.e., knock-out tank and blowdown tank) to be between $2,000,000 and $4,000,000 for fabrication and installation of a gasholder with synthetic rubber seal and 14,000 m^3 (500,000 ft^3) to 42,000 m^3 (1,500,000 ft^3) capacity. The life of the synthetic rubber seal is estimated at about 2 years and the replacement cost is 5 to 10 percent of the original gasholder cost. Replacement time is 4 to 6 weeks and seal delivery takes 20 to 22 weeks. Thus, a second gasholder would be required to prevent potential emissions from relief valves during downtime for seal replacement.

Therefore, the estimated capital cost for installation of a gasholder system for containment of a relief valve discharge will approach $5,000,000 (and several gasholders may be required). This system would be for containment of one 38,000 liter (10,000 gallon) reactor and does not take into consideration the possibility of multiple reactor relief valve discharges.

Experience with gasholders indicates that the following conditions and considerations must be evaluated to ensure trouble-free operation:

- The gas from the reactor must be clean and free of suspended solids and liquids. Polymer carryover could cause line plugging which can result in backpressure to the reactor.
- The gas or mixture must be unreactive, non-corrosive, and non-explosive.
- There must be no condensation in the gasholder system or transfer lines could freeze.
- Water seals probably represent the best type of seal for trouble-free operation.
- Based on a computer simulation assuming adiabatic cooling conditions for the reactor, transfer of reactor contents at a limited rate that would allow only vapor to be vented would result in a gain of 0.1 to 1.5 minutes until the safety device to the atmosphere would open. Transfer is limited to this rate to avoid slurry (and foam) carryover.
- The maximum fill rate of a conventional gasholder, which is limited by expansion of the inner seal, will also limit the

venting rate. The maximum piston velocity for a rubber-sealed gasholder is approximately 4.6 m (15 ft) per minute and would require about 6 to 8 minutes to fill - this seal expansion rate thus may limit the venting rate of the reactor contents. A venting system to the atmosphere must be present on the gasholder should the gasholder not be able to accommodate the discharge.

- For a gasholder with a capacity of 14,000 m^3 (500,000 ft^3) to 42,000 m^3 (1,500,000 ft^3) a horizontal knock out vessel with a capacity of 8,000 m^3 (300,000 ft^3) to 14,000 m^3 (500,000 ft^3) would be required. The length of the vessel would be 46 m (150 ft) to 54 m (175 ft). The pressure drop in the line from the gasholder to the knock out drum can not be controlled, therefore the KO drum pressure must be atmospheric.
- The potential for back-pressure on the reactor relief valve must be evaluated. Conventional relief valves can take up to 10 percent of the set pressure before it reseats. A balanced-bellows relief valve can take 40 to 50 percent of the set pressure. A pitot-operated relief valve can be opened on a differential pressure basis, but because of the small pitot tube diameter, this type is only intended for clean service.
- Relief valves to the atmosphere are designed to discharge directly to the atmosphere such that the explosion risk caused by VC flammability levels of 3 to 30 percent and worker exposure are minimized. Failure of the gasholder during an upset condition could result in a vapor cloud at low level because of the high concentration of VC at low pressure in the gasholder and low velocity of the vapor.

The above gasholder containment system could be designed into a PVC plant. Techniques such as elaborate monitoring and alarm systems, freeze protection, inert gas purging systems, strict personnel training programs, and inspection routines would be necessary to minimize some of the safety hazards. There are other systems that minimize relief valve discharges, including the use of a gasholder to help prevent these discharges. However, no matter what system or combination of systems is

utilized, a safety relief device directly to the atmosphere will always be required.

Another containment device that can be used to help prevent relief valve discharges is a blowdown or spare slurry-holding vessel. These vessels are usually used for stripping the batch of residual VC or for blending with other batches. A blowdown or holding tank is a constant volume, nonpressurized vessel (some may be pressurized) that would allow an influx of gas until the pressure of the tank and the source of pressure are equalized. The tank can also take the slurry directly and have chilled water and short-stop agent waiting for control of a run-away reaction. Discharge of the slurry to this tank can be manual or auto-activated. The timing of gas venting, slurry dump, or both, is critical in order to prevent the relief valve on this holding vessel from opening. These holding vessels can be used in combination with a gasholder or the recovery system to successfully control an upset condition--the reactor vapors are vented to the gasholder or recovery while the polymer slurry is dumped to the blowdown tank, or the entire reactor contents are dumped to the blowdown tank and pressure relieved from this tank to the gasholder or recovery system.

Pressurized containment can also be used to help prevent a relief valve discharge. B.F. Goodrich replaced their gasholders with this type of pressurized containment which they refer to as a "burp" tank. The purpose of the burp tank is to prevent emissions to the atmosphere as part of the VC recovery system, but the tank can also be used to assist in preventing relief valve discharges (Holbrook, 1980a). This automatic pressure reduction system usually will open at a pressure between operating pressure and the pressure relief valve setting. The vapors from this system go to recovery or the primary control device.

Other methods for preventing relief valve discharges.

Periodic pressure tests run on the reactor will decrease the likelihood of premature failure of rupture discs. Other preventive maintenance areas pertaining to rupture discs include (Ullrich, 1981):

- Premature disc failure can be caused by defective metal. This can be minimized by paying the disc supplier to pre-test a fraction of the lots before shipment.

- Premature disc failure is likely if the maximum operating pressure is exceeded. This pressure ranges from 70 to 90 percent of the burst pressure, depending on the type of disc. Once the maximum operating pressure is exceeded, the disc is deformed and must be replaced to ensure that it does not fail below the burst pressure. It is believed that in a computer-controlled plant, the chance of exceeding the maximum operating pressure, and thus the frequency of premature disc failure, is reduced.
- Rupture discs in vinyl chloride service, particularly on PVC ractors, are subject to pressure cycling, and therefore must possess the best fatigue resistance. The discs should also be replaced at a frequency determined by operating experience.

One plant also monitors all plant devices (e.g., valves, pumps, flowmeters, instruments, controllers) before charging the reactor to verify their successful operation and ensure safe operation during the polymerization reaction (Holbrook, 1980).

Another newer preventive method is a multiple initiator system. This system maintains a high initiator rate early in the reaction cycle and a slower initiator rate during that part of the cycle when auto-acceleration is expected to occur. The system thus maintains a near constant temperature and pressure during the reaction.

4.2.3.3.2 Preventive systems currently in use. Several systems for prevention of relief valve discharges have been installed by PVC plants. These plants all use a combination of equipment and work practice procedures to prevent or minimize relief valve discharges to the atmosphere. Several of these systems are discussed in the following subsections.

B. F. Goodrich Company. B. F. Goodrich produces PVC resins by the suspension, dispersion, and bulk polymerization processes. The new, larger reactors as well as the older, smaller reactors are utilized in their processes. B. F. Goodrich used gasholders extensively as part of their recovery system, but have since replaced the gasholders with pressurized burp tanks (that provide direct recovery) with high volume liquid ring compressors. Following is a discussion of their relief valve discharge prevention systems (Holbrook, 1980c).

B. F. Goodrich has reduced releases from reactor safety relief valves in their large reactor suspension PVC systems. This was accomplished through process control with emphasis on early detection and analysis of abnormal conditions. A totally computer-controlled system was installed to detect these abnormal conditions and take the appropriate action with a minimum of operator involvement. A thermal model was developed to simulate the typical controlled polymerization reaction and a kinetic model was developed to compare the typical reaction with an actual reaction. When the computer recognizes a potential upset condition, preventive control methods can be implemented and the upset conditions are then brought under control.

B. F. Goodrich identified three conditions that can result in a relief valve discharge from the large reactors – equipment failure, hydroful conditions, and an accelerated polymerization reaction. Some equipment can be kept in service with an emergency generator and back-up instrumentation. Equipment failure can be minimized by preventive maintenance following a regular schedule. The other conditions are minimized by computer control, but in the event of a high pressure situation in the reactor preventive steps are taken immediately. The large suspension reactor system is followed by a larger blowdown or flash tank which is generally 1.5 times as large as the reactor. Normally, the purpose of the blowdown tank is to receive the polymer slurry before the process is complete so the reactor can be prepared for the next charge. The blowdown tank has both an agitation and a shortstop system and thus can also receive the slurry under upset conditions so that an accelerated reaction can be brought under control. A recovery separator tank, preceding the recovery system, knocks out entrained liquid that would be vented during an abnormal condition. To relieve reactor pressure, if a hydroful condition exists, the computer immediately stops the addition of reaction ingredients. If the pressure is not due to a hydroful condition, but is due to a runaway reaction, the following control functions are triggered:

- Full cooling to the reactor and blowdown tank.
- Addition of reaction shortstop.

- Recovery of VC from the reactor.
- Opening of exhaust vents to a recovery separator to relieve pressure.
- Pump-out of reactor into a blowdown tank.

In addition to the above process controls, all plant devices (e.g., valves, pumps, flowmeters, instruments, and controllers) are monitored before the reactor is charged to verify their successful operation and ensure safe operation during the polymerization reaction.

The computer control system information display has been centralized and the following back-up systems have been installed:

- Dual power lines into the plant.
- Emergency power generation to maintain cooling and agitation should a primary power failure occur.
- Emergency power supply for computer and instruments.
- Manual control of instruments should a power failure occur.
- Instrumentation backup for computer.
- Installation of redundant equipment (pumps, compressors, and flowmeters).

The above combination of control technologies for relief valve discharge prevention has resulted in no reactor relief valve releases for 31,000 charges at their large reactor facilities.

B. F. Goodrich has also developed an effective relief valve discharge prevention program for their smaller reactors using many of the preventive measures described earlier. Similar to the large reactor systems, there are three conditions that B. F. Goodrich feels can result in releases from the small reactor suspension and dispersion processes - equipment failure, hydroful conditions and accelerated polymerization. Equipment failure is prevented by an emergency generator, backup instrumentation, and preventive maintenance that follows a regular schedule.

A hydroful condition is controlled in a manner similar to the large reactor system described above. When the computer detects excessive pressure in the reactor caused by a hydroful condition, all valves are closed to the reactor except cooling water, charging is stopped, the

slurry is sent to a blowdown tank, and vents are opened to a separator recovery tank (knockout tank) to relieve reactor pressure. The accelerated polymerization reaction (high reactor pressure and temperature) prevention follows the same initial preventive steps for the hydroful condition. In addition, water is injected directly into the reactor to cool the contents. The reactor is then vented to the prevent or burp tank (pressurized containment vessel) to relieve pressure, and a shortstop agent is injected to kill the reaction.

Conoco Chemical Division. Conoco has done research at their pilot facility to develop a prevention for relief valve discharges. An elaborate kill system is the primary method for preventing a discharge to the atmosphere. Tests were conducted in Conoco's large reactor pilot plant to determine the effectiveness of their kill system in stopping the polymerization reaction and the resulting pressure rise in a PVC reactor (McCulley, 1980). The tests were planned to simulate the concurrent loss of reactor agitation and cooling that would occur during a power failure or a worst-case situation. In each of the test runs, the simulated power failure was started 3 hours into the polymerization reaction to ensure that the reaction rate was near its maximum. Also, the reactor pressure was allowed to increase from its normal pressure of 118 to 119 psig up to 140 psig before injecting the killing agent. The 7 to 11 minutes required for this pressure increase provided sufficient time for the swirling inside the reactor to stop; this minimized mixing of the kill agent with the reaction mass.

The kill agent was pressured through a nozzle (no spray nozzle or other distribution device was used) into the vapor space of the reactor. The investigators suspected that the kill agent simply ran down the sides of the reactor into the slurry and did not benefit from injection-caused mixing. The liquid kill agent used is soluble in the liquid VC. Results showed that after injection of the killing agent at 140 psig, reactor pressure continued to increase to a maximum of 150 psig over approximately 8 minutes (about 20 minutes into test). The reactor pressure then slowly decreased to 146.5 psig 70 minutes into the test run – the gradual pressure drop probably was due to heat losses from the reactor to the atmosphere.

These tests confirmed that, if sufficient killing agent is injected, the polymerization reaction can be stopped and the rising reactor pressure can be controlled during a major power failure or other condition that results in total loss of cooling and/or agitation.

Early detection of an upset condition and control equipment redundancy are the most important requisites to preventing an emergency situation from reaching the kill system stage of control.

Conoco feels there are four major causes of a relief valve discharge:

- operator error,
- general equipment malfunction,
- events external to the system, and
- specific failure of the kill system.

In order for any of the first three events to result in a release, the fourth event, failure of the kill system, must occur. Specific examples of operator error and equipment malfunction (overcharging reactor, cooling system failure, etc.) have already been discussed. Examples of external events are power failures, fires, or some natural disaster.

The early detection program includes the following:

- Two sets of reactor temperature and pressure indicators on the control panel (from separate transmitters) are supplemented by pressure gauges on each reactor. (Use of temperature indicators represents a level of redundancy because an increase in VC vapor pressure will be accompanied by a rise in temperature.)
- Operators are always in 2-way radio contact with control panel personnel.
- High pressure and high temperature alarms sound in the control room and, if acknowledged, turn off. If the pressure continues to rise, a second alarm, set at a higher pressure, sounds and cannot be shut off until the reactor pressure drops below its set point. This alarm also sets off a siren which can be heard throughout the plant.
- A temperature control instrument on the control panel regulates the water flow to a reactor. If this flow is improperly regulated,

a panel switch can be used to override the controller, sending maximum cooling water flow to the reactor.

- The panel has reactor amperage indicators with alarms. A low amperage reading is used to confirm that the reactor has emptied after stripping to avoid overfilling the reactor on the next charge. Low amperage can result from a failure in the agitation system.
- There is a back-up power system for the control panel.
- Cooling water for reactors. Provisions are made to supply water to the reactor from cross-ties with city water or from the fire-water pumps (diesel-driven). Each of these capabilities is checked once each week. Also, instrumentation prevents this backup cooling water flow from going to users other than the reactors.
- A severe-weather radio provides current weather conditions that may affect the plant (e.g., storm conditions that could cause a total power failure to the plant).
- A reactor can be vented to an empty vessel or the recovery system to reduce pressure.

If the above early-detection prevention methods and redundant equipment are not adequate to bring the reaction under control, then the kill system is implemented. Two kill systems are maintained. The first kill system uses high pressure water injection. It is a completely manual system and is used to control reactor pressure increases during normal plant operation. It cannot be used in the event of a power failure.

If agitation is lost due to equipment failure or loss of power, the second kill system can be used. This second system uses high pressure nitrogen injection (precharged), and is a remotely operated system backed up by a manual injection line. In this situation, valves are also nitrogen operated. This kill agent is effective without mixing. The system has been tested in Conoco's pilot plant and has proven to be effective under worst-case conditions including loss of reactor cooling or agitation.

The kill systems for each reactor can be activated from the control board or locally at the reactor. The system from one reactor can be used on a different reactor, and each system contains enough shortstop

agent for two complete kills in one reactor. Two racks of back-up nitrogen bottles are available for instrumentation use.

To contain a plant fire, which could result in an an emergency discharge, a fixed-spray fire fighting system was installed throughout the VC areas of the plant. Hydrocarbon (HC) sensors detect explosive concentrations with an alarm set at 20 percent of the lower explosive limit (LEL) and watering systems are triggered at 40 percent of the LEL. These HC detectors are independent of the fugitive emission detection system required by the current regulation. Fire sensors throughout the areas where VC is handled monitor on a rate-of-temperature-rise basis.

Back-up cooling is used instead of a back-up power system. The rationale is that if the emergency situation is due to a broken agitator shaft, motor, pump, etc., back-up power will not alleviate the situation. The second kill system described above always accommodates these types of situations.

Both of Conoco's plants use an extensive interlock system to prevent mistakes that could release VCM to the atmosphere, damage equipment, or otherwise seriously effect the plant operation. For example, there is an interlock which prevents the reactor dump valve from opening if the reactor is under pressure, thereby avoiding the accidental dumping of a reactor containing a large amount of VCM. The Aberdeen plant uses programmable logic controllers for its interlock control system. The Oklahoma City plant uses a hard-wired relay logic system.

Hooker Chemical Company. As discussed previously, the bulk polymerization process presents some disadvantages for prevention of a relief valve discharge. The process is anhydrous resulting in poor heat transfer and agitation is slow which makes shortstop agents difficult to disperse throughout the dry slurry. Pre-Po reactor control is easier because the reaction only goes to 8 to 12 percent conversion and if a high pressure condition develops, the slurry is dropped to an empty, larger Po-Po reactor where the initiator is used up and the reaction brought under control. Also, the liquid VC charged to a Pre-Po provides some heat transfer and better temperature monitoring. Therefore, Po-Po reactor control is more important in the bulk process.

Hooker Chemical Company prevents relief valve discharges through a combination of equipment installations and work practice procedures (Dubec, 1980). Pre-Po and Po-Po reactors are mounted on scales that provide back up control for overcharging of reactors. In order to better monitor temperature in the Po-Po, reflux condensers were retrofitted to the reactor so exothermic heat of reaction can be removed by the circulation of water through the condensers.

If upset conditions develop in the Po-Po reactor, the following manual procedure is followed:

- The Po-Po reactors are equipped with pressure alarms that activate when the reaction pressure increases above normal operating pressure, thus alerting operators of the upset condition.
- The reflux condensers are flooded with water to control the temperature.
- The Po-Po reactor undergoes degassing.
- Valves are opened back to the recovery system which is a brine-cooled system.
- Cooling water at 10°C (50°F) from chilled tanks (also a brine-cooled system) is pumped into the reactor jacket to slow the reaction.
- At this point if the above steps have not brought the reaction under control and time is still available, pressure will be manually released to keep the rupture disc from blowing.

When the above steps are not effective, then the rupture disc will eventually rupture and the reactor will discharge to the atmosphere. As mentioned previously, the critical time for the bulk process is the first half of the reaction. Beyond this midway point, the unreacted VC has been substantially reduced and the reaction is more easily controlled. This particular plant does not use a shortstop agent in the procedure, but such an agent may be available in the future.

Also, two power lines have been run into the plant to prevent a total loss of power. In the event that total power is lost to the plant, two emergency generators provide the power necessary to control the reactions in progress and safely bring the plant down in about 12 hours without any relief valve discharges.

General Tire Chemical Division. General Tire has older, small reactor technology for the suspension process and uses a gasholder with a capacity of 1,400 m^3 (50,000 ft^3) to help prevent relief valve discharges from the suspension reactors (Laundrie, 1980). The main purpose of the gasholder is for venting compressor relief valves, pumps, transfer lines, weigh scales, condensers and knock-out tanks. Emissions from reactor opening and the slurry and wastewater strippers are also vented to the gasholder. VC collected in the gasholder is recovered and returned to the process.

When an upset situation is detected in a reactor, the following procedure is followed:

- Each reactor is equipped with a high pressure alarm which signals a potential upset situation.
- If possible, the reaction is vented to the gasholder to relieve pressure. A KO tank prevents entrained slurry from reaching the gasholder, but this is not always possible.
- A chemical shortstop agent is manually added to the reactor.
- The batch is dropped into a stripper vessel or pressure is equalized to an empty reactor.
- Cooling water pumps are on separate electrical circuits to prevent a loss of cooling water during power supply outages. A back-up water supply is available if primary cooling water is lost.
- Electrical power is supplied to the plant by two separate feeders. The system automatically switches to the other feeder if power fails on one feeder.

If the above procedure is not successful, then the reactor is manually vented to the atmosphere. Because this is an older plant with less sophisticated instrumentation, more responsibility for prevention of relief valve discharges falls upon the operators. Polymer operators have been trained to deal with runaway reactions - how to recognize them and what steps are necessary to bring them under control.

4.2.4 Non-Reactor Relief Valve Discharges.

Safety relief devices are found on all pressurized equipment in EDC/VC plants and PVC plants. These devices may be rupture discs,

single or in series, or combination in-line rupture disc and relief valve. In most cases non-reactor relief valves discharge less than reactor relief valves. During the original standard-support study (EPA, 1975), emphasis for control was placed on reactor safety relief valves. However, Regional offices indicate that the non-reactor releases are equally important. Tables 4-6 and 4-7 shows the frequency and quantity of VC discharged through non-reactor relief valves.

The following section describes some of the typical causes of non-reactor relief valve discharges and some of the actions taken to prevent their occurrence. Some of the discussion pertains to reactor relief valve discharges where common equipment is utilized.

Failure of rupture discs. The premature failure of rupture discs alone, in series or in combination with relief valves is the most common cause of discharges. Section 61.65(b)(4) requires a rupture disc to be installed between equipment and relief valves to prevent fugitive emissions from these relief valves. Rupture discs were installed for this purpose and failure of these discs was responsible for the majority of the non-reactor (as well as reactor) relief valve discharges reported initially after the waiver period. Some of the causes (and corrective measures taken) for rupture disk failure include:

- Overrated pressure capacity. Many rupture disc manufacturers rated their discs at a specific pressure, but failure sometimes occurred at a much lower pressure. This problem was usually solved by a reliable quality-assurance program that guarantees the rated capacities on the discs.
- Compatibility with process design. There are several types of rupture discs commercially available, but not all are compatible with a specific process design. For example, one bulk plant installed rupture discs on all pressure vessels and they continually failed below their rated capacity even though testing showed the disc capable of handling that capacity. After experimentation with several different types, reverse buckling discs were found to be successful, but only after the process piping was replaced. Another plant could not use knife-head discs because, with their process, these discs were

susceptible to cracking at the welds. Finding the compatible rupture disc sometimes requires trial-and-error.

- Corrosion of rupture discs. Failure of many discs is caused by corrosion from process material coming into contact with the disc. Corrosion caused by plant location is also a problem. Plants located near ocean shorelines experience corrosion problems caused by the salt-water mist. Corrosion problems are usually solved by finding the right disc material such as nickel or stainless steel, or by coating the disc with a material such as teflon.
- Disc leakage. Leaks are caused by pin-holes and irregularities already present in the disc, or result from improper handling by plant personnel. The first cause is a function of cost. The more a plant is willing to pay for a disc, the more the manufacturer will test and guarantee their disc. Although even with the most expensive discs, there is always the possibility of a poor quality disc in a batch. Most plants maintain a rigorous inspection program for discs prior to installation. A potential stress problem that results in a leak can also be detected by gauging the space between the rupture disc and relief valve for pressure - many plants currently follow this practice even though it is not required by the regulation. The other cause of failure, poor handling, is minimized by instituting good maintenance and installation procedures.

Failure of rupture discs from most of the above causes can be reduced by following a good quality control program. Many plants have found it necessary to bring in a representative from the rupture disc manufacturer to train plant personnel in proper handling and installation procedures. In most cases this has eliminated failure of rupture discs. An example of Conoco's testing/maintenance program includes the following (Ledvina, 1980):

- The rupture disc is assembled in the shop between two flanges prior to installation below the relief valve on a reactor or other piece of equipment. This allows the disc to be pre-torqued in a safety head device and reduces handling during installation.

- After installation and before the equipment is put in service, discs are hydrostatically tested to insure reliability. The discs are tested up to 90 percent of burst pressure after installation. (Reactors are pressurized above normal operating pressure before charging).
- Upon receipt of a disc shipment a percentage of each lot is randomly selected and pressure checked for quality and actual pressure. The lot is rejected or accepted by this procedure.
- Discs are changed every 6 months and those removed are tested to verify actual rupture pressure.
- Relief valves are replaced every twelve months.
- Emergency procedures involving non-reactor and reactor discharges are updated once every year.
- The rupture disc manufacturer's representative visits the plant each year for retraining purposes.

Failure of level controls. Slip gauges, which have a probe that moves through the gas/liquid interface in storage or transfer vessels indicating the level in the vessel by the physical state of the material discharged, have been replaced with more sophisticated level controllers. The new level controllers are used on charge tanks, storage spheres and tanks, rail cars, tank cars and marine transport vessels, all of which are under pressure and have some type of safety relief valve. However, the new level controllers are not always reliable and inaccurate readings on these controllers can cause an overpressurized condition during the filling operation resulting in a relief valve discharge.

Many times these discharges are significant. One plant released approximately 17,200 kg (38,000 pounds) of liquid VC from a storage sphere during barge unloading (Battye, 1978). This was a combination operator error and level control failure. Most of the discharges are much lower and usually involve operator error caused by inattentiveness during the filling operation.

High pressure in transfer lines and equipment. An overpressurization can develop in the transfer lines during transfer of VC from storage areas to process units. The pressure surge (hydraulic hammer) may be

caused by closing a valve too quickly and can be prevented by manually closing the valve slowly or instrumenting the valve to close slowly.

This condition can also be prevented by installing an emergency high-pressure trip-switch or using a small, in-line surge vessel (Brittain, 1980a). The high-pressure-sensitive switches can be used to prevent relief valve discharges from other equipment such as recovery compressors. The compressor automatically shuts off when overpressured, a condition usually caused by clogging of the compressor lines (Moulthrop, 1980).

Other causes of non-reactor discharges. Cold weather can be a cause for non-reactor discharges. For example, one plant had an automatic valve (to the VC reclaim vent) freeze shut causing the secondary decant tank to overpressurize which caused a rupture disc to burst (Battye, 1978).

4.3 RESIN STRIPPING

4.3.1 Introduction

Because one of the greatest sources of emissions is from those points downstream of the resin stripper, the effectiveness of the polymer stripping process is of prime importance in controlling emissions of RVC lost to the atmosphere. The release of unreacted VC from the polymer resin in the stripper is a function of time, temperature, and pressure of the stripping process, in addition to particle size distribution and porosity of the resin.

Prior to the current VC standard, stripping was done by PVC manufacturers for economic reasons; i.e., recovery of VC for reuse in the process. Reduction of RVC concentration in the resin to meet regulated emission levels now represents a primary reason for stripping to lower levels.

In PVC plants using stripping technology to control vinyl chloride emissions, the daily weighted average of the residual VC (RVC) concentration in the stripped resin must meet the following limits as required by Section 61.64(e)(1):

- 2,000 ppm for dispersion resins (excluding latex).

- 400 ppm for all other resins (including latex) averaged separately for each type of resin. Included in this category are suspension, bulk and solution resins.

The prescribed emission levels are assigned without regard to grades of the resin types although different grades of resin have unique characteristics with respect to stripping efficiencies. Determination of the RVC concentration is to be made by sampling immediately after the stripping process and using a prescribed method (EPA Method 107). The quantity of materials processed by each stripper is determined on a dry solids basis. If batch stripping is used, one representative sample of PVC resin is taken from each batch of each grade resin. If continuous stripping is used, one representative sample of PVC resin is taken for each grade of resin processed or at 8 hour intervals. Results of the RVC analyses are submitted in the semi-annual report required from each processor regulated by the standard.

Variables that affect stripping levels are: batch vs. continuous stripping, homopolymer vs. copolymer resins, and reactor vs. non-reactor stripping. Molecular weight and porosity of the resins influence stripping rates. Stripping VC from PVC resin involves (Ullrich, 1981):

- VC migration to resin particle surface,
- VC dissolution in slurry liquid, and
- VC vaporization and evacuation.

The first step is rate controlling. Suspension resin particles are porous while dispersion and latex resin particles are not. Dispersion particles are smaller than suspension, and latex smaller than dispersion. For suspension resin, particle porosity enhances migration and allows stripping below the 400 parts per million (ppm) residual vinyl chloride (RVC) standard. For latex resin, the short migration distance allows stripping below the 400 ppm RVC standard. For dispersion resin, the longer migration distance and the particle non-porosity, in addition to thermal and mechanical stress sensitivity, make stripping more difficult. Each of these determines resin stripping methodologies.

Lower stripping levels, required by the standard, sometimes result in the resin being excessively exposed to high temperatures that adversely affect the resin's heat history. This heat history is a critical parameter for the fabricator.

Table 4-11 shows comparative stripping levels reported by PVC plants producing various resin types and using different stripping methods.

4.3.2 Suspension Resin Stripping

Of the 40 operating PVC plants in the United States, 32 of these use the suspension polymerization process. (See Section 3.3.4 for a process description.) These resins are homopolymers and copolymers and are stripped batchwise or continuously, in the reactor or in a separate vessel. Suspension resins have many grades with variable heat and shear-stress tolerances.

One continuous stripping system for suspension resins has been developed by B. F. Goodrich and is widely used throughout the industry. In this process a pressurized stripping column feed tank is used to release excess VC. This tank forms a transition from the batch reactor to the continuous, multi-stage stripping column. The hot slurry is pumped continuously from the feed tank to the stripping column through a vapor liquid separator. The liquid slurry enters the top of a counter-current steam stripping column and the vapor streams from the feed tank separator and column are sent to the VC recovery system. The system can be designed to handle porous or non-porous slurry feed with RVC content ranging from 5,000 to 200,000 ppm. This process uses high temperatures 80° - 90°C (180° - 190°F) and a short residence time (Varner, 1980). Levels attained in this process are often less than 10 ppm RVC in the stripped slurry. Disadvantages of continuous column stripping are (Fannin, 1981):

- Decreased scheduling flexibility. Processors requiring frequent changes in batch sizes and/or recipe modifications cannot use column stripping efficiently.
- Difficulty in cleaning column. Due to the column's shape, internal cleaning is not as convenient as in an open vessel.
- Increased potential for burned particles. Crevices within the column, resulting from the contact of trays and relatively greater number of joints, tend to retain resin particles. This results in a long exposure to heat and consequent burned particles.

Table 4-11. PERCENT DISTRIBUTION OF STRIPPING LEVELS BEING ACHIEVED BY INDUSTRY[a]

Suspension				Concentration of residual vinyl chloride in ppm[b]							
		Range of daily average (ppm)									
Plant	Method[c]	High	Low	400	350	300	250	200	150	100	50
1	c	123	0.5	100	100	100	100	100	100	99.3	97.3
2	b	1,629	0.4	98.8	98.8	98.8	98.3	98.3	96.5	95.9	89.0
3	c	388	3	100	99.4	98.9	97.7	96.0	89.3	80.2	42.9
4	c	303	19	100	100	99.4	97.6	93.9	89.0	72.6	27.4
5	b	576	3	96.8	96.8	95.5	94.2	91.6	80.6	54.8	30.3
6	b	634	5	98.3	95.7	89.7	84.5	75.9	61.2	45.7	19.0
7	b	631	8	98.4	95.9	87.7	81.1	68.0	50.8	29.5	11.5
8	c	382	16	100	98.3	94.5	89.5	72.9	47.5	24.9	3.3
9	c	1,214	4	81.8	75.5	67.8	58.7	46.2	40.6	35.0	30.1
10	c	1,385	22	82.5	74.6	65.8	58.8	50.0	35.1	17.5	1.8
11		541	70	92.7	90.2	78.0	63.4	41.5	26.8	14.6	0
12	b	514	51	93.2	85.7	72.9	59.4	37.6	21.8	9.8	0.8
13	b	684	63	95.0	90.8	80.9	63.8	41.1	20.6	6.4	0
14	b	1,099	71	93.8	86.9	81.8	68.7	51.1	15.9	2.8	0
15		1,056	96	75.9	60.3	46.6	37.9	20.7	6.9	0	0
Bulk											
1	b	166	12	100	100	100	100	100	99.4	97.5	78.3
2	b	293	3	100	100	100	99.3	99.3	97.9	95.2	84.9
3	b	672	56	84.3	77.7	58.1	46.4	25.1	8.9	1.1	0
Latex											
1	b	15	0.2	100	100	100	100	100	100	100	100
2	b	310	8	100	100	99.4	99.4	98.8	96.9	74.5	24.2

[a]Based on EPA semi-annual reports for March through September 1980 obtained from Regional EPA offices. Data represents approximately 50% of suspension, 75% of bulk, and 33% of latex plants.

[b]Individual data are percentages of time that concentration falls below specified levels. Values represent daily averages weighted on a production basis.

[c]Method: b = batch; c = continuous

(continued)

Table 4-11 (Concluded)

Dispersion		Range of daily average (ppm)		Concentration of residual vinyl chloride in ppm[b]																		
Plant	Method[c]	High	Low	2000	1900	1800	1700	1600	1500	1400	1300	1200	1100	1000	900	800	700	600	500	400	300	200	100
1	b	1,245	15	100	100	100	100	100	100	100	100	99.4	98.8	98.8	98.8	98.2	97.6	97.6	95.8	89.3	75.0	38.1	9.5
2	c	1,949	132	100	99.3	93.7	90.9	84.6	79.0	71.3	61.5	54.5	42.7	39.9	32.2	20.3	19.5	14.0	9.1	6.3	2.8	1.4	0
3	b	2,364	418	99.4	96.6	92.2	87.2	82.7	70.9	62.0	50.8	43.0	33.5	27.4	21.2	11.2	8.4	3.9	1.7	0	0	0	0
4	b	5,515	49	85.6	83.5	81.4	79.4	76.3	73.7	73.2	68.6	65.0	61.3	55.2	51.5	45.9	36.6	28.4	18.6	9.3	5.1	2.1	0.5
5	b	14,092	297	80.3	78.0	76.4	76.4	74.0	72.4	71.7	68.5	66.1	59.1	51.2	37.8	23.6	15.0	7.9	3.1	1.6	0.8	0	0
6	b	4,129	89	83.8	80.2	78.4	74.3	71.3	67.1	64.1	56.9	52.7	45.5	39.5	31.1	24.0	16.2	10.2	7.8	4.2	2.4	0.6	0
7	c	6,066	644	70.7	62.6	58.5	55.3	45.5	37.4	26.0	22.8	14.6	10.6	8.9	7.3	4.1	0.8	0	0	0	0	0	0

[a]Based on EPA semi-annual reports for March through September 1980 obtained from Regional EPA offices. Data represents approximately 40% of dispersion plants.

[b]Individual data are percentages of time that concentration falls below specified levels. Values represent daily averages weighted on a production basis.

[c]Method: b = batch; c = continuous

- Mechanical stress. Because of the pumping system used in continuous stripping columns, mechanical stress is imposed on the slurry. For resins with a high sensitivity to this stress, the particles can agglomerate resulting in poor uniformity and an increased tendency for those particles to be retained and burned. An extreme of this situation can be equipment fouling (i.e., plugging of filters, screens, and orifices).
- Complex process control. Continuous stripping columns must be fed at a rate controlled to maintain certain target temperatures and pressures. There are more variables to be controlled simultaneously than in an open vessel.

Continuous steam stripping represents the most widely used method for suspension resins. Many of the processors using this technology are achieving less than 400 ppm stripping levels ranging as low as 25 ppm RVC (Pucci, 1980). One plant using a steam stripping method, but stripping batchwise, reports typical daily averages of 200 - 250 ppm RVC (Laundrie, 1980). Reportedly, this plant is unable to use continuous stripping due to the many (17) different grades of resins produced. Generally speaking, those plants attaining the lowest RVC levels have chosen to produce one or two resin grades with heat and shear stresses compatible with their continuous stripping technology. In some cases "specialty" has been sacrificed for increased production capacity.

Firestone Corporation continuously strips suspension resins to levels less than 100 ppm RVC using their own proprietary technology. This system uses less steam than other known counter-current continuous strippers and may be marketed in the future (Schaul, 1980).

4.3.3 Emulsion Resin Stripping

About half (21) of the PVC plants have dispersion polymerization facilities. Of these, 6 are latex resin processes. Dispersion resins are more sensitive to heat and shear stress than are suspension resins. Latexes are susceptible to these stresses and when exposed to shear the emulsion can degrade into an unstable latex with a poor heat transfer property. (See Section 3.3.5.1 for Emulsion Resin Stripping Process description.)

Dispersion resin slurry is usually either vacuum stripped in the reactor or transferred to a separate vessel (blowdown tank) where it is steam sparged. Due to their thermal instability, dispersion resins are most often batch stripped under vacuum. Inert-gas sparging is sometimes used instead of steam when dilution of the emulsion has to be avoided.

At least one manufacturer (B. F. Goodrich) does use a continuous stripping procedure for its dispersion resins. The process was developed by the company specifically for one of its dispersion facilities (Holbrook, 1980c).

Daily averages of stripping levels for dispersion resins have been reported as low as 15 ppm for one plant (Gilmore, 1980). Typical RVC levels for dispersion resins in comparison to other resins are shown in Table 4-11.

4.3.4 Bulk (Mass) Resin Stripping

Four of the forty PVC manufacturing plants produce bulk resins. Characteristics of bulk resins resemble those of suspension resins but the bulk resin beads are more uniform in porosity and size. These characteristics enhance stripping efficiency. Three of the bulk polymerization plants surveyed strip in the reactor using steam stripping technologies. In bulk resin stripping processes, steam must be injected under a vacuum to avoid contaminating the process with water because bulk polymerization is a dry process. One plant reports achieving daily emission levels of less than 150 ppm RVC and another, less than 250 ppm RVC.

Because the bulk polymerization process is anhydrous there are no dryer emissions. However, those emission downstream of the stripping process are still governed by the level of RVC removal during stripping.

4.3.5 Solution (Solvent) Resin Stripping

Only one plant produces PVC by the solution process. This plant operates a process for the copolymerization of vinyl chloride with vinyl acetate and other comonomers. The solvent process is unique, from the standpoint of stripping procedures, in that no particulate resin form exists and thus stripping can be accomplished by distillation. The efficiency of the distillation process results in average levels of 10 ppm RVC or less on a consistent basis.

The stripper still operates on a conventional distillation principle using acetone and acetone vapors. The column is fitted with perforated trays designed to accommodate the viscous resin solution.

This company is seeking approval for a less rigorous (and less costly) sampling/analysis plan to assure compliance (Erdman, 1980).

4.3.6 Other Stripping Technologies

A short-residence-time device, adaptable to continuous processing, is a proprietary thin-film evaporator. This device is reported to exhibit diffusivities of 1,000 to 10,000 times greater than those for simple molecular diffusion. In this system, heat is transferred through a metallic wall to a thin film of liquid. A mechanical agitator distributes the liquid evenly over the heat-transfer surface. Disadvantages of this device are: design criteria limits heat transfer area of each unit, more maintenance is required than for a non-mechanical device, and foaming may occur.

Another device, the Parkson stripper, is a non-mechanical, plate-type, dispersed-flow contactor. The latex is dispersed into a controlled, high velocity stream of steam and the resulting two phase flow passes turbulently through a plate-type stripper. The stripped latex then discharges into a cyclone separator, usually operated under vacuum, where the latex is disengaged from the vapor. Multistage units may be used to achieve desired residual monomer level. This unit is applicable to foamy, heat-sensitive or viscous products. Its advantages are: complete absence of foam, lack of moving parts, low holdup, low residence time, and reduced surface fouling. The main disadvantage is that the plate design permits only a limited capacity range.

One company's latex emulsion PVC facilities do not strip the resin but instead uses a proprietary post-polymerizer. This involves the use of a catalyst to react left-over VC. This process yields RVC levels less than 10 ppm, which is a level mandated by the company's internal standard for their particular product (Smith, 1980).

4.4 FUGITIVE EMISSIONS

4.4.1 Introduction

Fugitive emissions represent one of the most difficult emission sources in EDC/VC and PVC plants to quantify and control. Most of the

original fugitive emissions estimates were calculated by a mass balance. For EDC/VC plants a mass balance calculation is less accurate because several gas streams into and out of the plant are not measured accurately (e.g., gaseous chlorine and ethylene feedstocks). PVC plant liquid and solid streams are somewhat easier to measure and fugitive emission estimates are more accurate. The accuracy of fugitive emissions estimates is also affected by whether the plant is open or enclosed, and new or old. An enclosed plant's fugitive emissions can be determined by using roof monitors and ventilation flow rates through the building. Fugitive emissions from an open plant are more difficult to measure because of the variable wind patterns causing dispersion. The newer sources have larger and fewer reactors and fewer piping connections which reduces fugitive emissions. These variables must be considered when assessing fugitive emissions losses from EDC/VC and PVC plants.

Based on a recent study done by B. F. Goodrich (Holbrook, 1980a), fugitive emissions from their enclosed existing small reactor suspension and dispersion processes were determined (by actual measurement) to be 0.034 kg/100 kg of PVC produced or approximately 20 percent of the EPA estimated controlled 1975 rate (de la Cruz, 1981). New large reactor suspension processes were determined to be 0.0085 kg/100 kg of PVC produced or only 5 percent of the EPA estimated controlled 1975 rate (de la Cruz, 1981). This study was conducted following the implementation of controls required by the current regulation and reflects the effect of the regulation and new process technology on fugitive emissions reduction. Sources of fugitive emissions in EDC/VC and PVC plants include the following common equipment and operations:

- Pump, compressor and agitator seals,
- Loading, unloading and storage operation,
- Inprocess wastewater,
- Sampling and laboratory analysis,
- Equipment opening for cleaning and maintenance,
- Pipe and equipment flanges,
- Process drains and manhole cover seals,
- Process valves and pressure relief valves, and

- Open-ended lines.

In order to reduce the fugitive emissions from the above sources, Section 61.65(b) outlined the following three requirements for EDC/VC and PVC plants:

- Equipment modifications,
- Operational procedures, and
- Leak detection and elimination programs.

These three requirements will be discussed in detail in the subsequent sections.

In addition to the above three requirements for control of equipment leaks, fugitive emissions that could originate from water used in the various processes or water used to meet other requirements of the regulation (e.g., reactor purging at PVC plants) are required to be controlled. Control of these inprocess wastewater fugitive emissions will also be discussed in a subsequent section.

EPA has published an advanced notice of proposed rulemaking for generic standards for airborne carcinogens (44 FR 58662). These generic standards would reduce fugitive emissions of organic chemical carcinogens listed in the future under Section 112 of the CAA. The standards will provide a quick and simplified first step in regulating chemical air carcinogens by leak detection and repair programs.

The generic standards are independent of process or chemical and are based on the similarity of operations and equipment throughout an industry such as the Synthetic Organic Chemical Manufacturing Industry (SOCMI). Depending on the nature of the listed organic chemical and emission sources of this chemical, the generic standards may require "tailoring" in certain cases to reflect unique and unusual situations. Generic standards would be followed in most cases by additional standards that would be developed under the proposed Policy and Procedures for Airborne Carcinogens.

The draft generic standards need not be considered in any revision to the VC NESHAP. The standards focus primarily on reducing fugitive emissions through the use of an effective leak detection and repair program. This type of program is similar to the programs currently being used in the VC industry. In addition, EPA recently proposed

regulations under Section 112 of the CAA that would limit benzene emissions from fugitive sources in new and existing petroleum refineries and organic chemical plants. The proposed regulation is similar in many ways to requirements that the VC NESHAP outlined for prevention of fugitive emissions (e.g., leak detection and repair program and equipment specifications).

The following sections describe requirements of the regulation for control of VC fugitive emissions. These sections also discuss new developments resulting from the above draft generic standards and proposed benzene regulations.

4.4.2 Equipment Specifications

Valves, pumps, flanges and other pieces of equipment are used to move streams of liquid VC, PVC slurry, and VC-contaminated gases to and from various process vessels or control devices. Equipment incorporating sealed interfaces develop leaks after some period of operation, usually because of seal failure. The regulation requires specifications for the following equipment used in VC service:

- loading/unloading lines,
- slip gauges,
- pump seals,
- compressor seals, and
- agitator seals.

Double mechanical seals are required on rotating pumps, rotating compressors, and agitators. Double mechanical seals are preferred over conventional seals to provide the greatest reduction of fugitive emissions because they have less leakage over a long service life. The inner and outer mechanical seals of this system provide double seal protection from leaks, where failure of either seal does not result in emissions to the atmosphere.

Some plants are using tandem mechanical seals instead of double mechanical seals for better product control. Typically, EDC/VC plants are using tandem seals to prevent contamination of the VC product stream by water. The double mechanical seal allows seal fluid to leak into the product line while the tandem seal arrangement allows product to leak

into the seal fluid. When water is used as sealing fluid, the water is required to be collected and stripped to 10 ppm or less VC. Other sealing fluids (e.g., oils) are not required to be collected and stripped of VC contamination.

Regulations proposed for benzene fugitive emissions specify properties of the seal or barrier fluid. The fluid must have a vapor pressure less than 0.4 kPa (0.1 lb/in^2) at 20°C (68°F) or it can be a heavy fluid such as kerosene or diesel oil. No such requirement is specified by the VC regulation.

Other equipment requirements are double outboard seals on reciprocating pumps and compressors, and rupture discs upstream from relief valves. The double outboard seals provide double protection against leakage of emissions to the atmosphere. Relief valves can be a continuous source of fugitive emissions especially those that do not reseat properly after relieving pressure. Rupture discs installed under the relief valve prevent this leakage if properly installed.

Slip gauges are no longer being used to measure the level of VC in storage, holding, and transfer vessels. These gauges have been replaced by more reliable level controllers that are not a source of fugitive emissions. Loading and unloading lines have been modified in most cases to reduce the VC remaining to required levels following purging and prior to opening.

Section 61.65(b)(4) allows an equivalency to the rupture disc and Section 61.66 allows equivalent equipment to be proposed other than that required by the regulation. For example, instead of installing a rupture disc, leakage through the relief valve can be eliminated by connecting the discharge line from the relief valve to process equipment or the recovery system. As mentioned in a previous section (Section 4.1.4), one PVC plant has connected many of their safety relief valves on reactors to a flare as an equivalency for a rupture disc. VC emissions from the polymerization reactor leaking through the relief valve are combusted in the flare. Table 4-12 lists equivalency determinations approved or conditionally approved by the EPA since promulgation of the standard (Brittain, 1980c; Legro, 1977).

Table 4-12. APPROVEI OR CONDITIONALLY APPROVED EQUIPMENT EQUIVALENCY DETERMINATIONS

Equipment Required By Regulation	Equi	ent Equivalency Request	Discussion
Rupture discs under all relief valves (RV) (Section 61.65(b)(4))	1. RV's rinc seal	equipped with "0" seat pressure	1. Approved under following conditions: • Ethylene propylene rubber (EPR) rings must be used unless other material approved. • Only can be used with RV having disc seat such that no leaks occur during simmering. • Must be maintenance program for replacement (per year, each RV event and when leakage occurs). • Maintenance program records (keep 2 years). • Describe affected RV's prior to modification.
Double outboard seals on all reciprocating compressors (Section 61.65(b)(3)(iv))	1. Pres the the pres gas	urized system – ent space between wo seals is urized with inert	1. Volume between the inboard and outboard seals will be pressurized with inert gas that will be continuously purged to recovery and primary control device. Leakage is into the compressor rather than to the atmosphere and less maintenance is required.
	2. Pacl of :	ng rings in place als	2. Conditional approval if packing rings are vented at low pressure to a control device. Venting at pressures below atmosphere could lead to dilution with ambient air. Pressure between seals must be specified and flow rate monitored for leakage.
Double mechanical seals on rotating compressors and vacuum pumps (Section 61.65(b)(3)(i) and (iii))	1. Liq pacl add pla dri	d seals with ng modified by g two "boxes" d over idle and ends of unit	1. Conditional approval provided mechanical seal used on drive shaft. Idle end will not penetrate "box" which has a vapor tight seal. Drive end will have similar "box" containing mechanical seal. Both "boxes" are vented back into process at 1 psig to reduce emissions.
	2. Lab	inth seals	2. Used on centrifugal compressors.

(continued)

Table 4-12. Concluded

Equipment Required By Regulation	Equipment Equivalency Request	Discussion
Double outboard seals on reciprocating pumps (Section 61.65 (b)(3)(ii))	1. Reciprocating Hill-McCanna Type K pump with seals, shaft lubrication, regular leakage inspections and monitoring	1. This pump equipped with four separate layers of packing material combined with a Merco Nardstrom lubricator. A sealed pump must be used to lubricate the stuffing box and lubricant levels checked on regular basis. A VC monitoring point must be close.
	2. Double packing pumps with venting of water lubricant to a control device	2. Water lubricant between the seals would be vented to the wastewater stripper which controls VC emissions to 10 ppm or less.
Double mechanical seals for horizontal agitators (Section 61.65(b)(3)(v))	1. Pressurized grease system	1. Would only be applicable to the bulk PVC process which employs horizontal agitation.

The "O" ring equivalency determination for rupture discs listed in Table 4-12 can represent a reduction in emissions and equipment maintenance. In the normal operation of a relief valve without a rupture disc, the relief valve seat (metal to metal seat) lifts off the nozzle slightly as the operating pressure approaches the set pressure of the relief valve, and the relief valve begins to "simmer." "Simmering" occurs with fluctuations in operating pressures, but many times the "simmering" does not cause the relief valve to fully open. The result can be a misalignment of the relief valve seat and continuous leakage when the operating perssure returns to normal. If properly installed and maintained, the use of an "O" ring between the relief valve metal-to-metal seat prevents the continual leakage from improper reseating. The purpose of the relief valve/rupture disc combination was to eliminate "simmering." If the rupture disc bursts, however, and the relief valve does not reseat properly, then "simmering" will occur until the rupture disc is replaced. The "O" ring does not completely eliminate "simmering" if it is improperly installed or not maintained, but it will eliminate the need to replace the rupture disc every time a relief valve opens.

4.4.3 Operational Procedures

The regulation requires EDC/VC and PVC plants to use the following operational procedures to reduce fugitive emissions:

- Manual (non-emergency) venting of equipment. All gases vented from equipment in VC service are to be ducted through a control device which reduces emissions to 10 ppm or less.
- Opening of equipment (including loading and unloading lines). Before opening equipment in VC service, the quantity of VC in the equipment is to be reduced to no more than 2.0 percent by volume or 0.0950 m^3 (25 gallons) of VC, whichever is larger, at standard temperature and pressure. The quantity of VC removed in order to meet the requirement is then to be ducted to a control device that reduces VC in the exhaust gases to 10 ppm or less.
- Sampling procedures. Unused samples containing at least 10 percent VC by weight are to be returned to the process and sampling techniques should employ closed-loop systems.

Requirements of this section of the regulation have been met through modification of equipment that formerly discharged directly to the atmosphere. In most cases, the vents from equipment subject to these requirements have been enclosed and are ducted to the plant's VC recovery system which is then ducted to the final control device to reduce VC emissions to the atmosphere to 10 ppm or less. All routine manual venting of equipment is to the recovery system. Most plants use a positive-displacement unloading procedure and transfer lines are only open to the atmosphere when maintenance is required. When disconnection for maintenance is required, transfer lines are purged to the recovery system. One plant has modified the unloading lines from railcars so that after purging the lines to recovery, the volume remaining in the lines is less than the allowed volume of 0.0950 m^3 (25 gallons) (Laundrie, 1980). Plants surveyed during this study sample with closed-loop systems and return unused sample to the process.

4.4.4 Leak Detection And Elimination Programs

The third requirement for reducing fugitive emissions from EDC/VC and PVC plants is instituting and implementing a leak detection and elimination program. As mentioned above, the major focus of the draft generic standards is a leak detection and elimination program. The VC sources were given the opportunity to develop their own program and submit it to the responsible Regional office for approval. The regulation listed the following six requirements for an adequate program:

- a reliable and accurate VC area or fixed monitoring system,
- a reliable and accurate portable hydrocarbon (HC) detector to be used to pinpoint leaks indicated by the area monitoring system and to make routine checks of the plant for small leaks,
- an acceptable calibration and maintenance schedule for the area monitoring system and the portable HC detector,
- an acceptable number and location of monitoring points and an acceptable frequency of monitoring,
- an acceptable plan of action to be taken when a leak is detected, and

- a definition of a leak which is acceptable when compared with the background concentration in the plant.

In addition, plants are required to maintain records for at least two years. A record of leaks detected by the area monitors must include VC concentrations measured and recorded, and the location, date, and time of each measurement. A record of the leaks detected during routine monitoring by the portable HC detector must also include action taken to repair the leak in addition to the above same area monitor recordkeeping requirements.

The intention of the fugitive emissions control requirements is to first establish a background level of VC in the plant following installation of required equipment and implementation of operational procedures described above. A leak definition would then be set based on the plant's background level of fugitive emissions. The purpose of the leak detection and elimination program would then be to monitor for leaks based on the definition and eliminate these leaks over time, thus continuously lowering the background levels as well as fugitive emissions. The background levels and leak definition would be reevaluated and redefined as the fugitive emissions level decreased over time.

After any initial waiver period for compliance, a few of the EPA Regions evaluated the adequacy of the leak detection and elimination programs (Battye, 1978; Battye and Hall, 1978). Evaluations were also made during these review study plant visits. These evaluations provide the background for the following discussion of leak detection and elimination program requirements.

Many inconsistencies were found among the plants because each plant designed their own leak detection and elimination programs based on the above six requirements for an adequate program. The site-specific differences among the plants also contributed to inconsistencies. In most cases the requirements were addressed adequately with minimal changes recommended by the EPA Regions (e.g., number and location of area sampling probes). However, other requirements such as leak definitions, background concentrations and routine plant surveys were not adequate in many cases. An example of the variability of the leak detection and elimination programs among five plants is shown in

Table 4-13. Each of the requirements for an adequate program are discussed in more detail in the following subsections.

Leak definition.

A leak is defined on the basis of the plant's background concentration of VC which not only varies among plants but may vary among different areas of a plant. The background level for open plants or outdoor equipment is usually set at zero. The regulation requires that the leak concentration initially defined is to be reduced over time as background concentrations in the plant are reduced. It is for these reasons that leak definitions varied among plants and that one definition cannot be applied to all plants. In most cases the leak definition was regarded by the Regions to be adequate while in other cases the defined value was too high.

A separate leak definition was usually identified for area monitors versus portable monitors. Table 4-14 shows the range of leak definitions for 12 PVC plants. As indicated by these leak definitions, there is a great deal of variability. Many plants had not compiled data from which to determine background levels, others had not defined a distance from the leak for the portable monitoring leak definition and many plants neglected the storage and handling areas completely.

Area monitoring system.

According to EPA Regional personnel an adequate area monitoring system should accomplish four purposes:

- monitor processes for leaks,
- protect employees from occupational exposures (OSHA requirements),
- identify process conditions (e.g., start-up, shut-down, upset conditions) that precipitate VC fugitive emissions, and
- provide background data base for relocation of sampling probes and redefinition of leak.

The draft generic standards considered continuous area-wide monitoring to measure ambient concentrations of hazardous chemicals, but found this type of monitoring not as effective in locating leaks as a seal-by-seal routine inspection. Any added effectiveness from area-wide monitoring is minimal, plus it is a capital intensive technique. In the VC industry

Table 4-13. LEAK DETECTION AND ELIMINATION PROGRAMS

Plant	Type of area monitor/ points	Area monitoring sampling interval	Background concentration level	Action level for area monitor — Response/ party responsible for repair	Calibration and maintenance schedules	Walk-through program	Process equipment check program	Action level for portable H.C.
A	Gas chromatograph		25 ppm	Two consecutive readings greater than 5 ppm Foreman - non-written	Area monitor-span checked daily, GC's calibrated weekly; equipment checked weekly, annual tear-down. Portable-calibrated and checked weekly.	No program-areas checked dictated by area monitoring system. All areas checked occasionally	None.	25 ppm above back-ground level.
B	Mirian II Infrared Analyzers Six twelve-stream units. Total of 66 points.	Each unit samples one stream per minute	Area Averages- I - 5 ppm II - 5 ppm Tank Farm - 5 ppm	Three consecutive readings greater than 25 ppm. Monitor print reading once per week. Foreman - written (OSHA Worklist)	Area monitor-calibrated daily with 10 ppm standard. Portable-100 ppm standard.	No program-weekly area checking as directed by area monitoring system.	No pro-gram, checked about once every two weeks.	N/A
C	Mirian II Infrared Spectrometers One six-stream unit Two twelve-stream units Arcas gas chroma-tograph with FID One six-stream unit Total of 42 points.	Each unit samples one stream per minute Samples one stream per minute	5 ppm	One reading greater than 25 ppm or four consecutive readings of 10 ppm above background level. Area monitor checked every shift by portable HC detection operation. Portable HC detector operator - non-written.	Area monitor-calibrated daily with 15.5 ppm standard. Equipment checked weekly. Portable-calibrated weekly.	No program-areas checked three shifts daily as directed by area monitoring system.	None.	N/A

(continued)

Table 4-13. Concluded

Plant	Type of area monitor/ points	Area monitoring sampling interval	Background concentration level	Action level for area monitor --- Response/ party responsible for repair	Calibration and maintenance schedules	Walk-through program	Process equipment check program	Action level for portable H.C.
D	EOCOM Fourier Multiplex I.R. spectrometer sensitive to less than 1 ppm. Incorporates microcomputer (Indoor area). Two Mirian I.R. spectrometers (Outdoor area). Total of 47 points	EOCOM - non-cyclic, may mix streams to find a group with highest ppm, then breaks down this group. Computes statistical probability of an excursion in a given area. Can analyze a sample in 20 seconds. Mirian - continuous monitor.	1-2 ppm	100 ppm concentration over a 5 minute period. Respond with portable H.C. checking. Foreman	EOCOM - claims no calibration is needed. Checked twice daily with oscilloscope. Portable (Century) calibrated electronically once daily.	Entire plant three times each week.	None.	N/A
E	Three Arcas 505 G.C.'s with FID. Total of 48 points	Each stream every ten minutes. One screen per minute.	Less than 1.2 ppm	Two consecutive readings greater than 25 ppm for area monitor. Portable - 25 ppm reading. Respond with portable H.C. check. Operator - for minor repairs; shift foreman for more extensive problems.	G.C. checked daily and calibrated twice a week with three different standards. Portable - calibrated weekly.	Thorough check of reactors daily; other areas checked thoroughly once per month. Data is recorded.	Reactors are checked daily at manifolds, agitator seals, rupture disks, manways, condensors and piping.	Single 2.5 ppm reading

ıble 4-14. VARIABILITY IN LEAK DEFINITIONS

Plants	Area Monitoring System		Portable Monitoring System				Storage and Handling Facilities (Area Monitor)		
	Leak Definition (ppm)	Consecutive Readings (or Persistent Time Period)	ckground Level (ppm)	Leak Definition (ppm)	Inches From Source (or Persistent Time Period)	Background Level (ppm)	Leak Definition (ppm)	Consecutive Readings (or Persistent Time Period)	Background Level (ppm)
A	3 >100	2 (10 min.) 1	0.50	>100		0.5	2500		0.1
B	3	1	0.82	100	1 in.	0.82	5	1	0
C	>5 >100	2 1		>50	6 in.		>10 >100	2 1	
D	25	60 min.	None etermined	50-300 >300	3 in. (30 min)	None Determined			
E	20-25	1	1	10	3 in.	1	50	1	
F	1	1	0.5	50	12 in.	0.5	5	1	<0.5
G	25	2	1.2	25		1.2	25	2	1.2
H	5	2	(ıfidential	25		Confidential	5	2	Confidential
I	100	5 min.	1 to 2	100		1 to 2			
J	25 >10	1 4	5	*	•	•	25 >10	1 4	5
K	25	3	1-10	•	•	•	25	3	0.5-5
L	>5	3	).5-5	>5		0.5-5	>5	3	0.5-5

• Routine survey conducted only if area mor :or printout indicates leaks.

the leak detection and repair programs are based on area-wide monitoring for ambient VC concentrations. The effectiveness of this monitoring is discussed below.

The most important variable for an adequate area monitoring system is the location of sampling probes. The number and location of sampling probes for the area monitoring system will vary among plants -- this requirement is too site-specific to set exact numbers and locations. Many plants already had area monitors to protect work areas as required by OSHA. As a result, this same system was utilized for EPA requirements and many probes were located in worker breathing zones instead of fugitive emissions sources. OSHA probes were located where workers spend most of their time, thus many areas (which have a potential for fugitive emissions) are not monitored. Some plants completely neglected storage and handling areas which can be a significant source of fugitive emissions. For example, the area monitors are set at different concentration levels which set off an alarm when this level is exceeded. Some alarm levels were set only for personnel safety, which can be higher than the leak definition for a particular plant, and the EPA leak definition level was neglected. In other cases where the alarm is set to detect fugitive emissions, the alarm is set at a level higher than the leak definition.

Many of the plants had insufficient background data to determine if area sampling locations and background levels set were adequate. Some plants determine how often an alarm is sounded for a particular concentration in different areas of the plant over time and relocate sample probes based on these alarm frequencies. In some cases, background levels, as well as leak definitions, may vary in different areas of a plant. Some plants have located area probes close to exhaust fans and equipment near air ventilation intake fans. The probe near an exhaust fan responds to all leaks but there is a dilution effect, while the probe near the intake fan does not respond at all. A compromise between these two locations based on air flow patterns through enclosed buildings results in the proper placement of probes. The sampling location near an exhaust fan has been used in some cases to provide data for reevaluation

of the program because VC concentrations at this point should decrease with time.

Area sampling lines in some cases are manifolded to two or more sampling probes. The result is that a localized leak near one probe will often be diluted by air from other probes and thus, the leak will not be detected until the concentration is higher than the actual leak definition. Also, there is no way to determine if one probe becomes clogged or broken unless sample line integrity is checked on a regular basis. Probes close to reactors can be easily broken by reactor vibrations. Particle filters or metal shields on outdoor probes help to provide protection from probe and sample contamination and breakage.

Continuous air purging of probes and sample lines is recommended to ensure that the concentration recorded is indicative of the current reading. Also, gases used to calibrate the area monitor provide more representative results when injected at the sampling probe. In a recent study (EPA 1980) done in support of the proposed standard for benzene fugitive emissions, these recommendations were followed. Calibration gases were injected directly into the sample probe to evaluate the response of the area-wide monitor. Results of the calibration are indicated in Table 4-15. The concentrations measured by the area-wide monitor were much lower than the actual concentrations of the calibration gases. The gases were adsorbed to the inner walls of the sampling lines because concentrations continued to increase and then slowly decreased as the gases were desorbed from the sampling line inner walls.

Another important aspect of the area monitoring system is the time interval used to cycle all sampling points. Most plants use more than one instrument and usually each instrument has 10 to 16 sampling streams. Analysis of a sample collected by a stream takes about 1 minute (20 to 90 second range), thus each stream is monitored once every 10 to 16 minutes. However, some plants have different systems, whereby cycle time selection is more elaborate. For example, one plant that produces other chemicals in addition to VC, uses a halogen analyzer and gas chromotograph which chose the point to be analyzed based on four classes of information collected - a halogen alarm level sounded, maximum time

Table 4-15. CALIBRATION RESULTS FOR AREA-WIDE MONITOR

Calibration gases	Vendor analysis (ppm)	Laboratory analysis (ppm)		Area-wide monitor reading (ppm)	
		Sample 1	Sample 2	Probe 1	Probe 2
Benzene	5.37	5.00	6.00	0.04	0.00
Toluene	54.30	53.00	52.00	18.16	44.39
(para)xylene	28.10	48.00*	45.00*	21.29*	19.40*
(ortho)xylene	22.00				

*The laboratory analysis and area-wide monitor measured total xylene.

for a cycle, any alarm level sounded, and if no alarm level is sounded (this is the most frequent choice of system and results in a sample once every 40 to 50 minutes). The maximum sampling time between each point is 1.5 to 3.0 hours with all points monitored at least eight times every 24 hours.

Another plant does not cyclically monitor but instead uses a microprocessor that computes statistically the probability of an excursion over the leak definition in each sampling area and selects the area most likely to be near an excursion. This selection is based on historical data and time elapsed since last analysis. This system also mixes streams to save time and if after mixing the VC concentration is high, the instrument immediately analyzes each stream separately. An operator can also select a stream to see if an excursion has been corrected and review an hourly printout showing time weighted concentration averages.

Plants surveyed use one or more of the following area monitoring systems:

- Arcas 505 gas chromatograph with flame ionization detection (FID),
- Bendix 6000 series gas chromatograph with FID,
- EOCOM Fourier multiplex infrared spectrometer (FMS-7200) with minicomputer, and
- Miran II Infrared Analyzers with infrared spectrophotometry.

The gas chromatographs use columns to separate the VC from other compounds. The FMS-7200 uses two wavelength bands and is therefore more specific for VC. Sensitivity of the FMS-7200 is less than 1 ppm. The Miran II is not as specific or accurate for VC and is usually used to monitor outdoor equipment only. There are other Miran instruments that are more appropriate for indoor monitoring.

Routine surveys with portable detector.

As mentioned above, the draft generic standards emphasize routine leak detection surveys with a portable monitor over area-wide monitors, or a combination of the two. The VC industry uses a combination of routine surveys and area-wide monitors. The portable hydrocarbon (HC) detector is used to immediately identify the leaking equipment source

when an area alarm is sounded and to conduct leak surveys throughout the plant on a regular schedule. The following portable HC detectors were used by the plants surveyed:

- Century Systems Organic Vapor Analyzer (OVA) - the instrument measures total HC by flame ionization.
- H Nu Systems Photoionization Detector (Model P1101) - the instrument has three concentration ranges for total HC.

Some plants favor one of these portable meters over the other or use both, one as primary and one as back-up; both are regarded as adequate for leak detection.

The routine surveys that are required to be conducted on a regular basis probably represented the least consistent area in the leak detection and elimination programs reviewed. The schedule for routine portable monitoring, other than following up an area monitor alarm, varied among the plants -- from a once per shift basis to a weekly or monthly basis or no regular schedule at all. In some cases, the routine survey was conducted on a regular basis and in other cases, on an irregular basis depending on area monitoring print-outs for a particular shift or day. For PVC plants, the most thorough routine programs consisted of monitoring the reactor daily and other equipment and areas of the plant on a weekly, monthly, or quarterly basis. Usually the weekly, monthly, or quarterly frequencies in most cases are determined by historical data and type of equipment service.

Routine leak surveys usually follow an equipment checklist so that the same pieces of equipment are consistently monitored. This not only provides consistency, but also identifies those pieces of equipment that chronically leak and may require more frequent monitoring.

Instrument calibration and maintenance.

Most plants surveyed follow the instrument manufacturer's recommended calibration and maintenance procedures. Standard gases were usually used for instrument calibration and the concentration of these gases was in most cases close to the leak definition. Some plants calibrated portable monitors with a Wheatstone bridge which only provides a check on the internal electronics. As mentioned above for the area monitors,

calibration gases injected at the sample-probe location provided the best method for calibration as opposed to injecting the gas directly into the instrument. Also, there can be interference if other chemicals are being produced at a facility. This should be taken into consideration when developing a calibration and maintenance procedure as well as when locating area sampling probes and conducting routine leak surveys.

Plan of action when leak detected.

In most cases, when an alarm is sounded by the area monitoring system, the following actions are usually activated:

- a leak search is initiated with a portable monitor in that area of the plant,
- the leaking piece of equipment is identified, and
- the leak is eliminated.

There is some variation in procedures taken once the leak is identified, but most plants follow similar actions for elimination based on the severity of the leak. Some leaks can be stopped immediately by turning a valve or tightening a flange or the leak may be severe enough to cause immediate equipment decommissioning, which requires that the equipment be immediately put on recovery and shut down at the earliest and safest time. The leak may also be somewhere between these two extremes, in which case the leaking equipment can be enclosed and ducted out of the building until the maintenance personnel can repair the leaking equipment.

In all cases, it is important that an accurate log be kept on the leaking equipment – date, time, location, cause of leak, quantity of emissions (if possible), corrective action taken, and time until repair. Shift supervisors are usually made responsible for seeing that the leak is properly eliminated. The equipment usually is monitored again immediately after repair to verify repair and elimination of the leak. An accurate record of these leak abatement steps is not only required but also identifies those pieces of equipment that chronically leak and may require more frequent monitoring.

Recordkeeping requirements.

As mentioned previously, detailed records are to be maintained at the facility for at least two years. These data are maintained for

review by EPA personnel during inspections - no records on fugitive emissions are required to be submitted to EPA. Only the original proposed program was to be submitted for approval. Some plants maintain records for their own benefit that are not required by the regulation, such as the number of times a specific area alarm is activated or identification of equipment leaking below the leak definition. These extra data, in conjunction with required data, can be used to determine trends - the number of leaks found as a function of time or the background levels as a function of time. This information can then be evaluated periodically to identify problem areas and seek ways to eliminate the problems (e.g., replace chronically leaking equipment with new or different equipment). The information can also be used periodically to improve the program and reevaluate the leak definition.

Adequate leak detection and elimination programs.

EPA Region VI, which is responsible for the majority of subject sources, evaluated the programs submitted and based on these evaluations and follow-up inspections, determined the following minimum requirements for an acceptable program (Ramirez, 1978):

- A sufficient number of sampling points must be utilized to detect a leak no matter which direction the wind is blowing.
- A leak patrol must survey the entire plant at least once a week.
- An accuracy test of the leak detection system should be conducted by introducing a known concentration of VC into a sampling probe. The complete system should be checked once a year and reported in the semi-annual report.
- The VC calibration gas cylinders should be analyzed when they are received by utilizing Method 106.
- There must be an alarm system (visual or audio) to notify the plant personnel of a leak. This alarm must continue until acknowledged.
- There must be an instantaneous printout showing location and concentration of leaks when they occur.

- The evaluation of each company's background level will be made on a case-by-case basis in order to evaluate their definition of a leak.
- The portable hydrocarbon detector must be calibrated at least once a week.

An additional important requirement is the development of a data base for fugitive emissions through accurate recordkeeping. In some instances, this recordkeeping may require additional data collection other than that required by the regulation. The data base developed could then be evaluated on a regular basis to reevaluate a plant's background level and redefine the leak definition.

4.4.5 Inprocess Wastewater

Water used in the EDC/VC and PVC processes can become contaminated with VC and be a source of secondary emissions if not contained and controlled. Even though the above requirements of the regulation discussed for fugitive emission control (equipment specifications, operational procedures and leak detection and elimination programs) are not applicable to inprocess wastewater, it is still categorized as a fugitive emissions source. The regulation requires the concentration of VC in each wastewater stream containing greater than 10 ppm VC measured immediately as it leaves a piece of equipment, and before being mixed with other wastewater, be reduced to 10 ppm VC or less. This concentration in the water must be attained prior to mixing with other inprocess wastewaters containing 10 ppm or less VC, before being discharged to a wastewater treatment process or plant, or before being discharged untreated to a body of water.

There are several sources of inprocess wastewater in EDC/VC and PVC plants. In EDC/VC plants, water from EDC purification and VC cracking and purification (as shown in Figure 3-1) and equipment seals is contaminated with VC at levels greater than 10 ppm. In PVC plants, VC-contaminated inprocess wastewater is generated from the following sources:

- water used to evacuate reactors prior to opening in order to meet reactor opening loss (ROL) requirements,
- water used as sealing fluid for double mechanical seals on pumps, compressors and agitators,

- water removed by knock-out pots used in the monomer recovery system, and
- water used to seal gasholders.

Depending on the methods used to attain the ROL requirement (e.g., water piston which is discussed in Section 4.5), large quantities of inprocess wastewater can be generated.

Inprocess wastewater from ROL methods, seals, and knock-out pots is usually collected in a vessel and then steam stripped of VC. Water used to seal gasholders is in contact with VC-contaminated gases and by definition is an inprocess wastewater. This water is always exposed to the atmosphere without treatment. Actual VC concentrations of this seal water were not available, but for one plant using a water-sealed gasholder, emissions to the atmosphere from the seal were calculated to be approximately 0.79 kilograms (1.75 pounds) per year (Battye, 1978).

Removal of VC dissolved in water is usually accomplished by a distillation column. The water collected by fugitive emissions sources, and usually held in a vessel prior to the column, is close to saturation. Thus, separation in the stripping column is simple because the vapor pressure of VC is much greater than water.

4.5 REACTOR OPENING LOSS

4.5.1 Introduction

The VC emissions resulting from venting a polymerization reactor to the atmosphere (other than an emergency relief discharge as defined in Section 61.65(a)) constitute reactor opening loss (ROL). The ROL standard is only applicable to PVC plants. These emissions are regulated under Section 61.64(a)(2) and are limited to 0.02 grams VC per kilogram PVC produced (on a dry solids basis). This regulation applies to any vessel used as a reactor or as both a reactor and a stripper.

Determination of ROL emission levels is made by actual sampling and analysis of VC levels at the bottom, middle, and top of the reactor (methodology specified in the standard). A calculation option is primarily used by processors stripping in the reactor and is based on number of evacuations, vacuum applied, and volume of gas. The calculation (if approved) represents a waiver from testing, not an equivalent

method of ROL determination. When the reactor serves as the stripping vessel, the resin (after stripping is completed) contributes VC to the headspace concentration and consequently to the ROL measurement. Reporting of ROL emission levels is made in the semi-annual report submitted by regulated facilities to Regional EPA offices. (See Table 4-16 for representative reported ROL levels).

To maintain product quality, reactors are opened for maintenance or inspection and for removal of residual polymer adhering to reactor walls. The frequency of openings is a function of resin types and grades, reactor size and construction, location and method of the stripping process, and effectiveness of reactor cleaning methods.

ROL emissions control can be achieved through various technologies and process modifications. Basically, the objective is to:

- minimize the amount of VC in the gas phase prior to opening, and/or
- maximize the total PVC production per reactor opening.

Reducing the amount of gaseous VC can be accomplished by evacuation to a low absolute pressure, by displacement with water or an inert gas, by steaming, or by a combination of these. Increasing total PVC production may be achieved by reducing reactor opening frequency. (This also has the advantages of reducing turn around time and minimizing employee exposure to VC). Technologies available for controlling ROL emissions have been developed by the various plants to suit their individual processes. The method identified in the original standard support document, water piston, is not applicable to all processes (EPA, 1975). The water piston method as well as other methods are discussed below.

4.5.2 Solvent Cleaning

Solvent cleaning systems reduce the number of times a reactor has to be opened for cleaning. The solvent, circulated through the reactor, dissolves the solid scale present on the reactor walls, eliminating the need for manual scraping. Several solvents, suitable for reactor cleaning, have been tried by PVC processors. These include di-methylformamide (DMF), tetrahydrofuran (THF) and dichloroethane. However, there are serious disadvantages to the use of these solvents for reactor cleaning. These include:

Table 4-16. REACTOR OPENING LOSS REPORTED BY REPRESENTATIVE COMPANIES
(Data from September 1980 Semi-Annual Reports)

Company (code)	Resin type	Number of openings	Number out of compliance	Compliance rate	Concentration calculated or actual	Control technology
A	suspen.	72	2	97.2%		
B	suspen.	47	1	97.9%	actual	
C	suspen.	757	2	99.7%	calculation	Water Piston (Displacement)
D	suspen.	215	0	100%		Steam Sweep Technology
E	disper.	60	2	96.7%	actual	
F	disper.	766	0	100%		
G	disper.		0	100%		Solvent Cleaning/Closed Charge Technology
H	bulk	5668	18	99.7%	actual	Steam Injection
I	bulk	1340	0	100%	calculation	Steam Sweep Technology
J	latex		0	100%		Redox Catalysis

- The expense of the solvents. THF is approximately $2.00 per liter ($7.00 per gallon). One plant experimenting with this chemical for ROL reduction lost 76,000 to 114,000 liters (20,000 to 30,000 gallons) of solvent per month through the process. This represents a loss of up to $210,000 per month.
- The creation of secondary sources of pollution (solvents appropriate for reactor cleaning pose environmental and work-place hazards).
- The requirement for energy-intensive stripping operations to remove PVC from the solvent so that the solvent can be reused.
- The hydrocarbons present due to solvent cleaning may require that ROL be measured by Method 106 to demonstrate compliance, or that many more batches be produced between reactor opening. This is because the hydrocarbon detector (alternative to using Method 106) will measure these hydrocarbons along with VC (Ullrich, 1981).

Nevertheless, a few processors using solvent cleaning are reporting low ROL levels. A solvent cleaning process using DMF has been patented by Air Products and Chemicals Incorporated and is probably available for license. This process involves filling the reactor with solvent under an inert atmosphere. The reactor is heated and stirred while a small continuous flow of solvent overflows the reactor top. After sufficient time elapses, the solvent is transferred to storage and the reactor is rinsed several times with water. The reactor is then ready for another polymerization cycle. Solvent regeneration includes precipitation of solids, centrifuging to remove solids, and distillation to purify the solvent.

4.5.3 Steam Piston

One PVC manufacturer surveyed uses this technology to control ROL emissions for their suspension and dispersion reactors. The process involves draining the reacted slurry from the reactor and placing a puddle of water in the bottom of the reactor. A vacuum is pulled and steam is applied to the vessel jacket. Under vacuum the water boils and evaporates at low temperatures. The steam rises through the vessel in a

"piston like" manner and is exhausted to the VC recovery system. This technique has proven effective in reducing ROL emissions.

4.5.4 Water Piston

An application of this technology was noted in a PVC suspension homopolymer plant and identified in the standard support document. After the slurry is discharged to another vessel for stripping, the reactor is hydraulically filled to the nozzles with water, displacing VC vapors to recovery. Steam is applied to the jacket to heat the water in the reactor and vacuum is pulled from the top of the reactor. The vapors in the head space are exhausted to the recovery system by way of a knock-out pot (Laundrie, 1980).

One problem encountered in this method is the generation of large amounts of water contaminated with VC. Another consideration is the type of polymer involved. Diffusion rates of VC out of the polymer are not only temperature dependent but also depend on the resin characteristics. If the jacket temperature is too high, polymer degradation can proceed to the point where removal of polymer build-up is difficult after the reactor is opened. Jacket temperatures that are not hot enough result in decreased VC diffusion rates, thereby extending the time required for adequate VC removal and increasing emissions when opened.

4.5.5 Reactor Purge Air Blower

This technology is used by a suspension-polymerization plant manufacturing homopolymer and copolymer resins. This facility strips the slurry in the reactor. Prior to reactor opening, a purge air blower sweeps the vapor space above the slurry. The blower discharges directly to the incinerator. ROL compliance is then determined by calculation (Schaul, 1980).

4.5.6 Steam Purge (Sweep)

This represents the most widely used technology for control of ROL emissions. It involves the injection of live steam under vacuum, condensing the waste steam, and subsequent stripping of the water. Less VC contaminated water is generated by this process. Parameters for this process, reported by a suspension and dispersion resin plant, consist of

a 15-minute purge under vacuum. This procedure has consistently resulted in ROL emission levels well below the standard for this plant (Battye, 1978, Vol. II, p. 30). Vacuum pressures and temperatures vary from plant to plant depending on resin characteristics and process variables.

One problem encountered by a plant using this steam sweep technology involves leakage by shut-off valves back into the reactor, resulting in ROL excursions. This has been attributed to scoring of the valves and subsequent failure to reseal properly.

4.5.7 Redox Catalysis

One company, whose latex PVC facilities substitute a post-polymerization process for resin stripping, eliminates ROL emissions entirely. The method involves removing all equipment from VC service prior to opening by using a caustic wash and pickle rinse. These rinses are treated with a catalyst which scavanges unreacted VC and the rinses are monitored for VC until they are shown to be below 10 ppm prior to release to the sewer. The technology is proprietary (Ferrell, 1980).

4.5.8 Water Jet Cleaning

A procedure reported for suspension resin reactor cleaning - Hydraulic Reactor Cleaning (HRC) - used 28,000 to 41,000 kPa (4,000 to 6,000 psi) water in a water jet cleaning system with the water jet collar fitted directly into the reactor manway. This equipment allowed 25 to 30 batches to be run between reactor openings instead of opening between each batch. An identical system for dispersion resin reactors allowed 5 to 15 batches between openings. With some development expense, a spray system of the type could be developed by any PVC producer. The HRC technology described was developed by B. F. Goodrich and is probably available for licensing.

4.5.9 Clean Reactor (Closed Cleaning) Technology

This technology encompasses a wide range of techniques used to keep reactor walls free of deposits. Included are wall coatings, recipe modifications and mechanical cleaning devices. In conjunction with large reactor utilization, which allows more room for internal cleaning devices, clean reactor technology affords abatement of emissions from

other sources in addition to the ROL. High pressure spray systems and nozzle designs (for removal of deposits) and formulations of dispersants, catalysts and additives (for reduction of deposits) are incorporated in this technology. These are patented and some are available for license.

4.5.10 Nitrogen Purge

Nitrogen, used to purge the reactor under a vacuum, is non-condensable and therefore this method is not easily adaptable to monomer recovery without increased expense. Primary applications of this ROL emissions control method are in Pre-Po reactor preparation for opening. The vacuum is broken three or four times with nitrogen - the final break being made with air. The nitrogen gas, which contains recovered monomer, is subsequently incinerated.

4.5.11 Slurry Backfill

One plant is known to use this method to control ROL emissions for reactors used as strippers. The process involves dispersion resins which are stripped in the reactor. Following polymerization, the slurry is stripped under vacuum in the reactor vessel until the required resin RVC level is attained. The reactor is then backfilled with previously stripped slurry forcing headspace vapors out of the reactor to the recovery system, and thus also eliminating the reactor headspace. No further vacuum is applied because liquid slurry would be evacuated at this point. The ROL requirement is met by this method because the headspace vapors have been eliminated (Konter, 1980). A waiver of testing requirements has been obtained from the Region. Resin RVC emissions lost during transfer of the slurry to another vessel cannot contribute to ROL emissions because these emissions would be considered beyond the stripping operation and therefore not regulated (Section 61.64(e)(1)).

The main advantage of the slurry backfill control technique for ROL is the small amount of water used, eliminating the need for a large VC-contaminated wastewater stripper. In addition to the pumps required for backfilling, a level sensor is required to insure that the slurry is not backed into the recovery system. This process would also appear to be adaptable to suspension processes.

4.5.12 Calculated Emissions

In processes where resin stripping takes place in a separate vessel, the reactor is under pressure which allows the slurry to be evacuated without opening the reactor. The methods described above can then be applied prior to opening in order to attain the ROL standard. However, when the reactor also serves as the stripping vessel, the vacuum (pulled when the slurry is being stripped) must be broken prior to slurry discharge and this constitutes a reportable reactor opening. The required testing procedure for ROL can not be applied until the slurry is removed. The slurry may contribute enough RVC so that the ROL standard is unattainable and these measurements cannot be made until the reactor has cooled.

The prescribed method for measuring ROL is impractical and unsafe for those plants stripping in the reactor. If the probe measurement is taken while the reactor is hot immediately after stripping, the high vapor temperatures present a safety problem to the person making the measurements. If the reactor is allowed to cool, this not only affects productivity (because several hours are required for cooling) but also results in measurements that are not representative.

When ROL measurements are made according to the present regulation, the same VC is essentially "counted twice" (i.e., once in the resin and once in the vapor space).

Through waivers of emission testing for reactor opening loss, PVC plants whose stripping operations take place in the reactor, are considered to be in compliance with Section 61.64(a)(2) if the measured reactor opening loss added to the measured resin RVC is less than the sum of allowable ROL and the allowable resin RVC. For plants stripping below the RVC standard, the processor is not penalized for that portion of the RVC (removed by stripping) that contributes to the ROL. The ROL levels are allowed to be higher when the reduced stripping emissions are used as a credit.

The calculation may present a problem even though the results as calculated are correct. The calculation will not include those emissions from leaking valves or broken equipment that may contribute to ROL emissions, but are only found by an actual test.

It is the policy of some Regions, in keeping with the intent of the standard, to grant waivers of testing to those processors in the above category. These waivers are made on a case-by-case basis, and with the provisions that RVC samples must be taken on each batch. A calculation may then be used to establish ROL. Formulas developed for these calculations are generally treated as confidential by the plants using them because the formulas are considered to be potentially marketable and they can reveal some of the nature of the process. The basis for the ROL calculation is Raoult's Law. The general requirements for using calculated ROL's are:

(1) Calculations must be done for each grade of resin,

(2) Parameters such as number of times a vacuum is pulled, must remain constant, and

(3) Tests must be confirmed by standard methods.

4.6 REFERENCES FOR CHAPTER 4

Aronson, Wayne, J. 1980. Enforcement Division, EPA Region IV, Atlanta, Georgia. Freedom of Information Request from J. W. Bodamer, Jr., TRW Environmental Engineering Division. October 1980.

Battye, William. 1978. GCA Corporation, Technology Division. "Technical Assistance to Region III for Enforcement of Vinyl Chloride Regulations," Contract No. 68-01-4143, Task No. 35, Volumes I, II, III, V and VI. December 1978.

Battye, William and Hall, Robert R. 1978. GCA Corporation, Technology Division, "Technical Assistance to Region V for Evaluating Vinyl Chloride Leak Detection and Elimination Programs," Contract No. 68-01-4143, Task No. 16, Volumes I, III, V, VI and VII. July 1978.

Blacksmith, J.R., G.E. Harris, G.L. Langley. 1980. Radian Corporation, "Frequency of Leak Occurrence for Fittings in Synthetic Organic Chemical Plant Process Units," Contract No. 68-02-3171, Task No. 001. September 1980.

Brittain, Martin. 1980(a). NESHAP Coordinator for EPA Region VI. Meeting report - TRW visit to Region VI offices, Dallas. July 23, 1980.

Brittain, Martin. 1980(b). NESHAP Coordinator for EPA Region VI. Telecon with J. W. Bodamer, Jr., TRW Environmental Engineering Division. November 7, 1980.

Brittain, Martin E. 1980(c). Environmental Protection Agency, NESHAP Coordinator, Region VI. Information supplied during meeting between Region VI and TRW. July 1980.

Brumbaugh, Gerry. General Tire and Rubber Company. Telecon with J. W. Bodamer, Jr., TRW Environmental Engineering Division. November 14, 1980.

Chemical and Engineering News, 1978. "Key Polymers." September 4, 1978, p. 13.

Chemical and Engineering News, 1980(a). "Key Chemicals." July 7, 1980, p. 9.

Chemical and Engineering News, 1980(b). "Key Polymers." October 6, 1980, p. 13.

DeBernardi, James. 1980. Plant Manager, Conoco Chemicals, Lake Charles, Louisiana, EDC/VCM plant. Telecon with M. A. Cassidy, TRW Environmental Engineering Division. November 18, 1980.

DeBernardi, James. 1981. Plant Manager, Conoco Chemicals, Lake Charles, Louisiana, EDC/VCM plant. Telecon with M.A. Cassidy, TRW Environmental Engineering Division. March 6, 1981.

de la Cruz, Peter L., 1981. Assistant General Counsel to the Society of Plastics Industry, Inc. Letter with attachments to Don R. Goodwin, EPA. May 18, 1981.

Diem, Conrad. 1980. Special Enforcement Section, EPA Region III. Letter to J. W. Bodamer, Jr., TRW. December 1980.

Dubec, Harold F. 1980. Manager of Environmental Compliance, Hooker Chemical. Trip report - visit to Hooker Chemical Company, Ruco Division, Burlington, New Jersey. September 1980.

Environmental Protection Agency. 1980. "Emission Test Report Benzene, Fugitive Emissions - Petroleum Refineries," EMB Report No. 78-OCM-12B, October 1980.

Environmental Protection Agency. "Proposed National Emission Standards for Identifying, Assessing and Regulating Airborne Substances Posing a Risk of Cancer," Federal Register/Volume 44, No. 197/Wednesday. October 10, 1979.

Environmental Protection Agency. 1975. Standard Support and Environmental Impact Statement: Emission Standard for Vinyl Chloride. EPA-450/2-75-009, October 1975.

Erdmann, John F. 1980. Environmental Protection Coordinator, Union Carbide. Telecon with J. W. Bodamer, Jr., TRW Environmental Engineering Division. November 4, 1980.

Erdmann, John F. 1980. Environmental Protection Coordinator, Union Carbide Corporation, Texas City, Texas. Telecon with M. A. Cassidy, TRW Environmental Engineering Division. December 4, 1980.

Ethyl Corporation. 1980. Telecon with Joy Reed of TRW Environmental Engineering Division. July 1980.

Fannin, James. 1981. B. F. Goodrich Chemical Division. Telecon with M. A. Cassidy, TRW Environmental Engineering Division. February 18, 1981.

Ferrell, John. 1980. Union Carbide Corporation, Tucker, Georgia PVC Plant. Telecon with M. A. Cassidy, TRW Environmental Engineering Division. December 5, 1980.

Finch, Walter. 1980. Senior Process Engineer, Conoco Chemicals. Meeting report - Conoco/EPA/TRW meeting at RTP. October 17, 1980.

Gilmore, J. M. 1980. Plant Manager, Goodyear Tire and Rubber Company, Niagara Falls, New York PVC plant. Semi-Annual Report. September 10, 1980.

Holbrook, W. C. 1979. Director of Toxicology and Environmental Affairs, B. F. Goodrich Chemical Group. Letter with attachments to Donald R. Goodwin, U.S. EPA. November, 19, 1979.

Holbrook, W. C. 1980(a). Director of Toxicology and Environmental Affairs, B. F. Goodrich Chemical Group. Telecon with J. W. Bodamer, Jr., TRW Environmental Engineering Division. October 17, 1980.

Holbrook, W. C. 1980(b). Director of Toxicology and Environmental Affairs, B. F. Goodrich Chemical Division. Letter with attachments to J. W. Bodamer, Jr., TRW Environmental Engineering Division. December 12, 1980.

Holbrook, W. C. 1980(c). Director of Toxicology and Environmental Affairs, B. F. Goodrich Chemical Division. Trip report - visit to the Pedricktown Polyvinyl Chloride Plant. September 17, 1980.

Kachtick, James. 1980. Tenneco Chemicals, Pasadena Texas PVC plant. Telecon with M. A. Cassidy, TRW Environmental Engineering Division. December 2, 1980.

Konter, Ken. 1980. Senior Environmental Engineer, B. F. Goodrich Chemical Division. Telecon with Matthew Boss, TRW Environmental Engineering Division. December 5, 1980.

Laundrie, Robert. 1980. General Tire and Rubber Company, Chemical and Plastics Division. Trip report - visit to General Tire's polyvinyl chloride facility in Ashtabula, Ohio. September 10, 1980.

Ledvina, Joseph C. 1980. Director of Environmental Activities, Conoco, Inc. Meeting report - representatives from Conoco, TRW, and EPA. October 17, 1980.

Legro, Stanley W. 1977. Environmental Protection Agency, Division of Stationary Source Enforcement. Letter to Regional Enforcement Directors containing determinations of equivalent compliance methods for vinyl chloride. May 26, 1977.

McCulley, John H. 1980. Chemicals Division, Conoco Inc. Letter to J. W. Bodamer, Jr., TRW. December 16, 1980.

Moulthrop, Samuel P. 1980. Enforcement Division, EPA Region II. Telecon with J. W. Bodamer, Jr. of TRW Environmental Engineering Division. November 10, 1980.

Neveril, R. B. 1978. Capital and Operating Costs of Selected Air Pollution Control Systems, GARD, Inc., 1978. EPA Contract No. 68-02-2899. December 1978.

Pucci, Michael. 1980. NESHAP Coordinator for EPA Region II. Meeting report - TRW visit to Region II Offices, New York. August 12, 1980.

Richter, S. H. 1975. Arthur G. McKee and Company, Cleveland, Ohio. "Size Relief Systems for Two-Phase Flow," Hydrocarbon Processing. July 1975.

Schaul, Peter. 1980. EPA Region III. Meeting report - TRW visit to Region III Offices, Philadelphia. September 16, 1980.

Sittig, Marshall. 1977. How to Remove Pollutants and Toxic Materials From Air and Water. Noyes Data Corporation. 1977.

Smith, Cornelius. 1980. Chief Environmental Attorney, Union Carbide Corporate Headquarters, New York, New York. Telecon with M. A. Cassidy, TRW Environmental Engineering Division. December 5, 1980.

Ullrich, David A. 1981. Chief, Air Enforcement Branch EPA Region V. Letter to Jack R. Farmer, EPA. April 28, 1981.

Varner, Bruce. 1980. NESHAP Coordinator for EPA Region V. Meeting report - TRW visit to Region V offices, Chicago. August 19, 1980.

West, Michael. 1981. Air Facilities Branch, EPA Region II. Letter to J. W. Bodamer, Jr., TRW Environmental Engineering Division. January 21, 1981.

Wu, James. 1980. NESHAP Coordinator for EPA Region IV. Telecon with J. W. Bodamer, Jr., TRW Environmental Engineering Division. November 7, 1980.

5.0 ENFORCEMENT AND COMPLIANCE EXPERIENCE

5.1 INTRODUCTION

Industry representatives and Regional EPA personnel presented their viewpoints drawn from experience with enforcement and compliance under the existing VC NESHAP. Many of these points were common to industry and EPA regional personnel while others were specific to enforcement problems or compliance experiences. These comments are reviewed below and have been categorized as they pertain to requirements in the regulation. (All of the following are opinions expressed by industry and/or EPA personnel.)

5.2 INTENT OF THE STANDARD

- Health effects: Nearly all of the industrial representatives contacted (and one Regional EPA person) expressed concern over the potential revision of the NESHAP without a health effects basis (Baise, 1980).
- The intent of the standard (with regard to emergency releases) could be achieved by using a "bubble concept" total plant control as an endpoint (Holbrook, 1980). It is not always possible to achieve the 100 percent compliance required by the current regulation. There should be "malfunction language" written into a revision. A source should be allowed to offset emissions in another area of the plant until inoperative control equipment is repaired. For example, if the source's primary stripping unit goes down but stripping can also be done in the reactor, the slowing of production to allow longer residence time in the reactor is a self-imposed economic penalty and would allow the source to continue operating under a "short-term bubble." In California (South Coast Air Quality

Management District) a bubble or group of emissions from a plant is allowed. Their discharge limit (50 grams per hour) is based on a Dames and Moore study (Fannin, 1980). The California Air Resources Board (CARB) set an ambient VC standard of 10 ppb. This ambient level was based on the lowest possible detectable limit for VC at that time. Dames and Moore then calculated that an emission limit of 50 grams per hour would maintain the ambient level of 10 ppb. (See Chapter 7 for further discussion).

- PVC plants that are regulated by more stringent requirements should receive a blanket exemption from NESHAP (Holbrook, 1980). NESHAP regulations are designed to protect the public from hazardous air pollutants. However, in some cases, regulations designed to protect the public from nonhazardous air pollutants are more stringent than a NESHAP. For example, a new PVC plant constructed in a nonattainment area for hydrocarbons (an area of the country that does not meet the required criteria pollutant limits) may be forced to control VC emissions more strictly than the VC NESHAP requires. A PSD permit will not be issued unless the new plant can show that the lower levels can be attained.

5.3 STANDARDS FOR EDC AND VC PLANTS

- Industry feels that there should be separate sections in the regulation specifically for EDC, VC, and PVC plants (Oubre, 1980). The regulation should identify more specifically those requirements applicable to each plant.
- Regional EPA personnel and industry note that the classification of "in VC service" is a point of contention.

5.4 EXHAUST GASES TO THE ATMOSPHERE

- Industry feels that an allowance should be made for a reasonable amount of down time for control equipment. Emissions from shutdown may actually be greater than emissions that would occur if the plant were to continue operating (Ledvina, 1980;

Holbrook, 1980). The shutdown, as well as start-up, of an EDC/VC plant can create more emissions than are discharged by a plant that is allowed to run for a certain period of time without control devices.

5.5 INPROCESS WASTEWATER

- Under the current regulation, industry is required to measure VC concentration in wastewater following stripping only at the time of start-up of the stripper. Unless monitoring is required on a regular basis, the effectiveness of the wastewater stripper cannot be determined.
- One region felt that daily sampling of inprocess wastewater (following stripping) should be required to ensure proper stripper operation and maintenance. (One plant in that region, Borden Chemical, routinely tests wastewater stripper VC concentrations.) Compliance with the regulations has drastically increased the quantity of inprocess wastewater discharged from many plants (Varner, 1980).
- The wording of the current inprocess wastewater definition includes that water used to seal gasholders. This seal water should be made exempt from the inprocess wastewater definition (Wyatt, 1980).

5.6 REACTOR OPENING LOSS (ROL)

- Industry and regional EPA personnel see a need for a separate standard for processors stripping in the reactor. The current regulation assumed the stripping operation was separate from the polymerization reactor (i.e., took place in a different vessel), which is not always the case. The resulting problem is that the test method developed for measuring the ROL is not applicable to plants stripping in the reactor. It is possible to use the headspace volume of gas above the resin slurry, but the slurry and reactor are too hot to measure immediately, and after the resin is stripped to the required limit, it continues to emit VC into the headspace (Wyatt, 1980). The proposed revision of the standard would be based on a combination of

ROL requirements and resin stripping levels (Ledvina, 1980; Brittain, 1980; Varner, 1980; Holbrook, 1980). Currently, processors stripping in the reactor show compliance by stripping to the required levels and calculating the ROL emissions. The only problem with this method is that the calculation does not show valves that may be leaking back into the reactor, causing emissions to be higher than calculated.

- Industry would like to see a provision for monthly or semi-annual averaging of the ROL (Holbrook, 1980). This would apply mainly to bulk processors and other plants stripping in the reactor.
- Concern was expressed about the prevalence of "ritualistic sampling," in which the reactor is opened before analytical results of the resin samples are available and/or slurry transferred to another vessel. The current regulation requires that the resin must sampled to determine compliance with stripping levels; but before the analysis can be completed, the slurry has already been transferred to the next vessel (Pucci 1980).
- Regional EPA personnel see a need for a prescribed method of testing for opening of the Pre-polymerizer (Pre-Po) in the bulk process. Because the Pre-Po is involved in only 10 percent of the polymerization reaction and is currently defined as a "reactor" under the standard, there are problems associated with determining compliance for these vessels; i.e., should equipment opening loss or reactor opening loss standards be applied. Post-polymerization (Po-Po) reactors are opened after every batch, whereas Pre-Po reactors are not opened as frequently (Brittain, 1980). The intention of the regulation was that the Pre-Po and Po-Po combined meet the ROL standard. Industry currently applies the ROL to each reactor.

5.7 RELIEF VALVE DISCHARGES

- The primary concern about relief valve discharges, shared by industry and regional EPA personnel, is how to determine what

is "preventable." This point was raised more frequently than any other by EPA regions and industries.

- All of the industrial representatives stated that the zero concept for relief valve discharges was unrealistic. Many felt that frequency of discharge and the quantity of VC discharged should be the basis for determining the level of compliance (Holbrook, 1980; Laundrie, 1980).
- Industry pointed out that controls for dispersion, suspension, bulk, and solution processes differ. They suggest that the prevalence of reactor discharges by resin types should be studied (Holbrook, 1980).
- Industrial personnel have cautioned against recommending gasholders as containment for relief valve discharges. They regard this as a safety and economic issue (Holbrook, 1980; Laundrie, 1980; Ledvina, 1980).
- An opinion expressed by industry is that 100 percent compliance 100 percent of the time should not be required and cannot be attained. They suggest that a malfunction clause be incorporated (Holbrook, 1980; Ledvina, 1980).
- Industry suggested that the VC standard could be made more consistent with other standards (e.g., proposed benzene) standards with regard to control of equipment breakdown that results in emergency discharges of a certain level.
- Two regions pointed out that due to substitutions of other devices in place of relief valves (e.g., double rupture discs) the standard should be reworded to change "relief valve (discharge)" to "relief device, including but not limited to . . ." (Brittain, 1980).

5.8 RESIN STRIPPING

- Industry feels that the language used to describe resin "grade" is ambiguous and this affects the resin stripping regulations.
- Industry and Regional EPA personnel state because each resin grade has unique characteristics that require different stripping techniques, allowance should be made in the standard for

stripping levels reflecting pertinent resin requirements (Holbrook, 1980; Laundrie, 1980; Shaul, 1980).

- Industry would like relief from the daily calibration and monitoring requirements of the current regulation (Wyatt, 1980). For example, the suggestion was made by industry that longer averaging periods should be permitted for determining stripping level compliance (Laundrie, 1980; Mercier, 1980). Daily compliance with resin stripping levels could be shown by reporting certain process parameters (e.g., vacuum pulled, temperature, time in stripper) that industry has proven achieve the required levels. Sampling could then be required on a less frequent basis to support the process parameters. (Note: The preamble to the regulation, published in the Federal Register, does make provisions for using process parameters to demonstrate compliance. The preamble states that, "For both reactor opening and improved stripping, it is possible that the relationship between the emissions measured and the corresponding operating procedures used to attain the emissions measured can be established." (40 FR 59543.)
- One region suggested the possibility of applying a standard for new sources (under NESHAP) for stripping with retrofitting requirements for existing sources. This would encourage the industry to pursue the technology available for reducing emission levels below current requirements. Several plants are stripping suspension resins to less than 400 ppm by continuous stripping (Brittain, 1980).
- Sampling and analytical requirements for resin stripping in the solution polymerization process need to be reviewed (Brittain, 1980). The stripping requirements (in the current regulation) were developed for the removal of unreacted VC from solid particles of PVC. However, there is no particulate resin form for solution resins. Solution resin stripping involves a distillation mechanism rather than a diffusion mechanism as in solid particles. Accordingly, solution resins can be stripped to an average level of 10 ppm or less. Therefore, the sampling

and analytical procedures to ensure that the 400 ppm level is met for solution resins are relatively extensive.

5.9 SOURCES AFTER THE STRIPPER

- Regional EPA personnel suggest that dryer emissions be reevaluated. Based on a Prevention of Significant Deterioration (PSD) application, an average suspension plant producing 90 gigagrams (100,000 tons) of PVC resin per year will emit 36 megagrams (40 tons) of VC per year out of the dryer stack. Indirect drying (which would reduce drying air and make add-on control more economical) followed by a control or product recovery device, may be a better way to reduce these emissions (e.g., one PVC plant uses steam coils that indirectly heat the resin in a rotary dryer) (Pucci, 1980).
- Blend tanks and centrifuges, the next steps following the stripping operation, have been suggested as potentially significant emission sources (Pucci, 1980).
- One region's PSD Best Available Control Technology (BACT) analysis shows that 20 to 40 times as much VC is allowed to escape from process units following the stripper as is allowed from ROL and the 10 ppm exhaust emissions (Varner, 1980).

5.10 FUGITIVE EMISSIONS

- One region proposed that plants submit representative data on ambient (background) levels in annual report form, similar to the draft generic standards. This would provide a means to determine the plant's progress in lowering background levels and to establish criteria for evaluating fugitive control. A certain percent deviation would be permitted and if the plant achieved an average of a prescribed level, it would be in compliance (Brittain, 1980b).
- The submission of an annual report as mentioned above would also allow the responsible EPA Region to reevaluate the Leak Detection and Elimination Programs and, thus, reject a previously approved program (Flynn, 1980).
- An industrial source maintains that the levels for fugitives predicted in the Standard Support and Environmental Impact

Statement document for the original standard were considerably higher than actual levels. This company has determined the relationship of fugitive emissions to production rate and has measured suspension and dispersion process fugitives to be 25 percent of the predicted levels for their older small reactor suspension and dispersion plants (Holbrook, 1980).

5.11 LEAK DETECTION AND ELIMINATION PROGRAMS

- Many industrial sources, as well as regional EPA personnel, regard the definition of a leak in the standard as unclear. "Small" and "major" leaks need to be defined. The setting of a de minimus level was suggested (Yonge, 1980; Oubre, 1980; McNair, 1980; Pucci, 1980; Wu, 1980; Flynn, 1980).
- As previously mentioned, regional personnel have no way of determining the success of the programs in lowering fugitive emissions background levels in the plants (Brittain, 1980).
- One region commented that the location of monitors, while serving OSHA purposes, may not be optimal for fugitive detection (e.g., many sources do not monitor storage areas) (Pucci, 1980).
- Several industrial representatives said that their Leak Detection Programs, submitted to Regional EPA offices, are rarely acknowledged (Yonge, 1980; Oubre, 1980; DeBernardi, 1980).

5.12 EMISSIONS TESTING AND ANALYSIS

- Region II commented that the units for allowable emissions from equipment opening are inconsistent. For larger pieces of equipment, such as a surge tank serving an incinerator, the allowable emissions should be similar to the ROL standard. Only the smaller pieces of equipment (e.g., loading/unloading lines) should have the 2 percent by volume or 25 gallon cutoff (Pucci, 1980).
- The continuous emission monitoring standard for the primary control device does not specify whether a "minute to minute" monitor (as for a NSPS) or a sequential leak detection monitor is required (Pucci, 1980). No performance specification

exists for these continuous emission monitors in the current regulation; this requirement of the regulation should be made consistent with the NSPS requirements so that continuous monitoring results can be used for determining violations of emission standards (Varner, 1980; Pucci, 1980).

- Sampling regulations for RVC are currently under the section (61.70(c)(2)(ii) for semi-annual reporting in the standard. It would be more appropriate to locate this regulation under testing (Section 61.67) and monitoring (Section 61.68) (Brittain, 1980).
- Sampling bag sizes, specified in methods 106 and 107, are too large for the sample (Ledvina, 1980).
- Methods 106 and 107 call for "zero-grade" gas for analysis. This method is very expensive to use on a day-to-day basis. Stack sampling should utilize zero-grade gas, but it is not necessary for daily analyses (Holbrook, 1980).
- Industry feels that instrumental calibration on a daily basis is not necessary. Drift history, etc., should be allowed to establish the reliability of the instruments (Holbrook, 1980; Oubre, 1980; DeBernardi, 1980).
- One region said that a source reported calibration requirements for a daily span check actually caused an increase in emissions (Pucci, 1980).
- Industry would like to establish its own program for calibration procedures with periodic checking of internal standard operating procedures by regional EPA personnel (DeBernardi, 1980).
- Some industrial representatives feel that the standard should not restrict analysis to specific instruments. There are questions as to reliability and availability of parts for some of the required instruments (Ledvina, 1980).
- Method 106 for ROL measurements is not considered to be reliable. Corrections for condensing water vapor in the sample cannot be made reliably (Ledvina, 1980).
- Region VI suggested the need for a monitoring performance standard for backup as well as primary control devices. When

VC emissions are bypassed to the atmosphere (e.g., in the case of a malfunction or shutdown of a primary control device), a backup incinerator, or a flare, the downstream monitor does not measure any VC. Region VI feels that monitors for VC should be located so that actual emissions of VC to the atmosphere are always measured during all process operating conditions (Harrison, 1979).

5.13 REPORTING

- Industry made several comments regarding the lack of uniformity in reporting requirements among the regions. Frequency of reports and level of detail required were given as examples of differences (Holbrook, 1980; Laundrie, 1980).
- Industry suggests that the possibility of consolidation of permits be considered (Holbrook, 1980).
- Many comments were made by Regional EPA personnel regarding semi-annual report requirements. The regions do not consider the semi-annual reports effective for enforcement purposes. They feel that excursions should be reported on a 10-day basis or immediately, with a minimum frequency of four times a year (Thompson, 1980; Aronson, 1980; Varner, 1980).
- Industry feels that semi-annual reporting should be replaced with exception reporting (Holbrook, 1980).

5.14 RECORDKEEPING

- Industry feels recordkeeping should be reduced to include only exception or noncompliance data for the pertinent time frame (Holbrook, 1980). This would reduce the amount of records required to be maintained onsite.
- One region pointed out that the standard does not specify a time limit for retention of ROL records (Varner, 1980).

5.15 NESHAP APPLICABILITY DETERMINATIONS

Since promulgation of the VC NESHAP, several inquiries have been made regarding the applicability of VC-use situations to the standard. The following are examples of the type of inquiries directed to the Division of Stationary Source Enforcement (DSSE) (Reich, 1980; King, 1980).

Question	Determination	Discussion
Are duplicate continuous monitoring systems needed for vinyl chloride plants?	No	Although backup monitoring equipment is not required, it is the responsibility of the source to ensure that the monitoring equipment operates continuously.
Is EPA concerned with short-term monitoring malfunctions?	Yes	The vinyl chloride standard does not provide for monitoring malfunctions of any duration - EPA is concerned about any malfunction.
Are relief valve discharges which are due to operator error considered violations of section 61.65(a)?	Conditional	Relief valve discharges resulting from operator error are considered violations if the errors are preventable. The following are examples of preventable operator errors: 1. Errors due to lack of training 2. Negligence
Can a demonstration of noncompliance of the reactor opening loss standard, using an unapproved test method, support an enforcement action?	No	If a source is using a test method which has not been approved by EPA as an equivalent or alternate test method, information pertinent to the method should be submitted to EPA for evaluation.
When is a relief valve discharge a violation of section 61.65(a)?		A relief valve discharge is a violation if it could have been anticipated and preventative measures could have been taken or prevented by proper operating, maintaining and inspecting equipment.
What measures can be taken to prevent relief valve discharges?		Examples of measures that can be taken to prevent relief valve discharges include:

Question	Determination	Discussion
		1. Properly instrumenting the reactor to detect upset conditions. 2. Injecting chemicals to stop polymerization reaction during upset conditions. 3. Venting reactor contents to a gasholder and ultimately to a recovery system. 4. Maintaining a backup source of power. 5. Proper training of employees.
Are vinyl chloride tank cars that are transported by rail to a vinyl chloride plant, "equipment in vinyl chloride service"?	No	Tank cars are not subject to the vinyl chloride regulations, except to the extent that the requirements for purging of loading and unloading apply.
Is a PVC sludge-drying facility, designed to accommodate sludge with some low residual VC content, subject to the VC NESHAP regulations?	No	The regulation applies to plants which produce EDC, VC, or PVC. The standard specifically places requirements on the reactor, stripper, containers (mixing, weighing, and holding), monomer recovery system, and sources following the stripper. If all discharged material meets the requirements of this subpart prior to its exposure to the atmosphere, this subpart does not apply to the PVC sludge drying facility because the process is not considered part of the production processes of EDC, VC, or PVC plants.

These are representative questions directed to many of the EPA Regions and are indicative of the need to clarify some points in the regulation.

5.16 REFERENCES FOR CHAPTER 5

Aronson, Wayne, EPA Region IV, Air Enforcement Branch. Meeting report - TRW visit to Region IV offices. September 3, 1980.

Baise, Gary, Attorney, Beveridge, Fairbanks and Diamond. Meeting report - TRW/EPA/SPI meeting at Durham, N. C. July 31, 1980.

Brittain, Martin, NESHAP Coordinator, EPA Region VI. Meeting report - TRW visit to Region VI offices. October 27, 1980.

DeBernardi, James, Plant Manager, Lake Charles, La. Conoco Plant. Meeting report - TRW visit to Conoco Plant. August 7, 1980.

Fannin, James, B. F. Goodrich Chemical Division. Meeting report - TRW visit to B. F. Goodrich Cleveland office. October 30, 1980.

Environmental Protection Agency. 1975. "NESHAP Proposed Standard for Vinyl Chloride," Federal Register, Vol. 40, No. 248. December 24, 1975.

Flynn, Peter M. Environmental Engineer, Air Facilities Branch, EPA Region II. Letter to J. W. Bodamer, Jr., December 2, 1980.

Fradkoff, Steve, Region I EPA. Meeting report - TRW visit to Region I offices. August 13, 1980.

Harrison, Arlene, Regional Administrator, EPA Region VI. Letter to Don Goodwin. January 29, 1979.

Holbrook, W. C., Director of Toxicology and Environmental Affairs, B. F. Goodrich Chemical Division. Trip report - visit to the Pedricktown Polyvinyl Chloride Plant. September 17, 1980.

King, J. A., DSSE, USEPA. Letter to Regina E. Thompson, EPA Region III, 1980.

Laundrie, Robert W., General Tire and Rubber Co. Trip report - TRW visit to the Ashtabula, Ohio PVC plant. September 10, 1980.

Ledvina, Joseph C., Director of Environmental Activities, Conoco, Inc. Meeting report - representatives from Conoco, TRW and EPA. October 17, 1980.

McNair, Cathy, NESHAP Coordinator, EPA Region I. Meeting report - TRW visit to Region I offices. August 13, 1980.

Oubre, Robert, Technical Manager, Dow Chemical Corp., Oyster Creek Division. Trip report - TRW visit to Oyster Creek plant. August 5, 1980.

Pucci, Michael, NESHAP Coordinator for EPA Region II. Meeting report - TRW visit to Region II offices, New York. August 12, 1980.

Reich, Edward, DSSE, USEPA. Letter to EPA Regional Directors regarding Summary of NESHAP Determinations, 1980.

Schaul, Peter, EPA Region III. Meeting report - TRW visit to Region III offices, Philadelphia. September 16, 1980.

Thompson, Jean, NESHAP Coordinator, EPA Region III. Meeting report - TRW visit to Region III offices. September 16, 1980.

Varner, Bruce, NESHAP Coordinator for EPA Region V. Meeting report - TRW visit to Region V offices, Chicago. August 19, 1980.

Wu, James, NESHAP Coordinator for Region IV. Meeting report - TRW visit to Region IV offices. September 3, 1980.

Wyatt, Susan R. 1980. Office of Air Quality Planning and Standards. U.S. EPA Meeting report – TRW visit to OAQPS. June 16, 1980.

Yonge, John, Environmental Control Supervisor, Shintech, Inc. Trip report - TRW visit to Shintech Plant, Freeport, Texas. August 5, 1980.

6.0 UNREGULATED SOURCES OF VINYL CHLORIDE

6.1 INTRODUCTION

The current regulation is applicable to the following types of facilities:

(1) plants producing EDC by the reaction of oxygen and hydrogen chloride with ethylene,

(2) plants producing VC by any process, and

(3) plants producing one or more polymers containing any fraction of VC.

There are, however, several categories of VC-emitting facilities that are not regulated under the current VC NESHAP. Many of these sources were identified during the original study. These include PVC compounders and fabricators, and processors who use VC as a chemical intermediate or produce it as a byproduct.

New sources of unregulated VC emissions have been identified during this review study. They include mobile-mounted sources, nonplant transfer facilities, solid waste drying facilities, and disposal sites.

Many of the sources not regulated by the VC NESHAP are subject to state hydrocarbon-emission control standards, specifically those plants located in nonattainment areas.

6.2 SOURCES IDENTIFIED DURING THE ORIGINAL STUDY

6.2.1 Fabricating Operations

Following polymerization of VC, two major processes are involved in the conversion of VC to a finished PVC product – compounding and fabricating. Compounding involves the mixing of PVC resins with additives such as plasticizers, stabilizers, pigments, blowing agents and anti-oxidants. These additives impart certain properties that are required for handling the polymer during fabrication as well as in the final product. Compounding

may be done by the fabricator, the resin producer, or by independent compounders.

Fabrication of the polymer consists of melting and shaping the compound by various processes. Some of the major processes are:

- Extrusion - This process consists of mixing and melting a continuous stream of plastic and generating sufficient pressure to force the compound through a die.
- Calendering - The compound is fed through sets of rollers to form continuous sheets of plastic.
- Molding - Several types of molding are used; injection, compression, vacuforming, and embossing constitute the more common processes.
- Bonding - The joining of two or more pieces of PVC can be accomplished using heat (or heat and pressure), adhesives, or hot gas welding.

Most of the residual VC (RVC) in the resin is lost at the PVC plant. Following stripping operations (which remove RVC to levels at or below those required by the regulation) further losses of RVC occur in drying, bagging, and storage operations. More RVC can be lost while the resin is in transit. Thus, operations following the stripper (and prior to compounding operations) account for the reduction in RVC levels entering compounding and fabricating facilities as compared with those found in the stripped resin. The application of heat and pressure during fabrication can cause some of the remaining RVC to diffuse from the resin particles.

A.D. Little (1975) prepared a report on VC emissions from PVC processing industries for the EPA in August 1975. This report quantified the VC emissions from compounders and fabricators of PVC resins. The conclusions drawn from the study were:

- There are more than 8000 PVC fabricating facilities in the United States,
- Emissions from compounding and subsequent fabrication processes together accounted for less than one-half of one percent of the total United States emissions, and

- The most promising control technique to limit VC emissions to the atmosphere from compounding and fabricating facilities appeared to be further reduction of RVC levels in incoming resins. At the time of the 1975 study, average VC content of raw resin was reported to be 300 ppm (in 1974), with PVC production rates of 2.0 teragrams (4.4×10^9 pounds). Total VC release from compounding and fabricating facilities during 1974 was 600 megagrams (1.3×10^6 pounds).

Since promulgation of the OSHA VC workplace standard (permissible occupational exposure level), PVC manufacturers have reduced the RVC content in the resins supplied to compounders and fabricators. To control VC exposure in fabrication facilities, the PVC industry has established a 10 ppm VC concentration limit in dried PVC resins. Surveillance and enforcement of this requirement has been delegated to the Plastic Pipe Institute (Cameron et al., 1980, p. 43).

In addition to the influence of the OSHA standard, requirements by the Food and Drug Administration (FDA) have contributed to the reduction of RVC levels in resins supplied to fabricators. PVC products that will come into contact with humans are required to have very low levels of RVC. Therefore, resins to be used for blood bags, food wrap, drug and beverage bottles, etc., enter the fabricating facilities with RVC levels well below 1 ppm. Bottle resin, for example, is currently provided at levels less than 0.05 ppm (Ter Haar, 1980.)

Of the PVC plants surveyed, all report that average PVC levels in resin leaving the plant range from <0.002 ppm to 10 ppm. Many plants report levels of <0.5 ppm to 1 ppm. Typical reductions in resin RVC since promulgation of the VC NESHAP are shown by the following data from a PVC resin manufacturer (Ter Haar, 1980):

Resin type	RVC Levels (ppm) Prior to 1974	Current
Emulsion Resins	3.0	0.5
Bottle Resins	–	<0.05
Other Suspension Resins	935	2.6

In 1979, PVC production rates were reported to be 2.8 teragrams (6.1 x 10^9 pounds) (Chemical and Engineering News, 1980, p. 13). Assuming that the average RVC content of the resins supplied to compounders and fabricators is 10 ppm and that all of the VC is lost to the atmosphere during fabrication (worst case assumption), total emissions from these sources for 1979 would have been 28 megagrams (6.1 x 10^4 pounds) VC.

The emission levels from these sources would actually be much lower than those cited above since average RVC content of incoming resin is probably less than 10 ppm. In addition, VC migration studies indicate that a very low percentage of monomer is released during fabrication. During extrusion, for example, 10 percent of the monomer is typically released (Ter Haar, 1980).

EPA conducted ambient air studies in which five PVC fabrication plants were monitored. There were no measured concentrations of VC emitted from three of these plants. The highest measured concentration was 0.006 ppm, 24-hour average (Padgett, 1980).

6.2.2 Miscellaneous Sources

In a study done by Arthur D. Little, Inc. for the EPA (Lyman, 1976), miscellaneous sources of VC emissions were categorized as follows:

- Industrial processes in which VC is used as a chemical intermediate for the production of other chemicals,
- Industrial processes in which VC is used as a minor constituent (<50 percent by weight) for the production of resins, and
- Industrial processes in which VC is produced as a byproduct of the chemical reaction involved.

The second category, use of VC as a minor constituent in resin production, no longer represents an unregulated source, as these processes are now subject to the current VC NESHAP regulations (i.e., any amount of VC used for polymerization constitutes a regulated process).

Within the first category (use of VC as a chemical intermediate), two main sources were identified by the Arthur D. Little study: (1) production of 1,1,1-Trichloroethane (1,1,1-TCE) and 1,1,2-Trichloroethane (1,1,2-TCE); and (2) production of other special chemicals such as certain pesticides.

A more recent survey conducted by Conoco (McPherson, 1979, p. 75) attributes three to four percent VC usage to the manufacture of 1,1,1-TCE. Information pertaining to the current status of VC emissions from the manufacture of 1,1,1-TCE and 1,1,2-TCE was not obtained during the review study.

VC emissions from pesticide manufacturing facilities were identified in the Arthur D. Little report. Total VC consumption was estimated to be only two percent of the amount estimated for TCE production. One of the two plants cited in the study, an insecticide manufacturing facility, was contacted during the current VC NESHAP review study. It appears that VC consumption, control technology, and emissions are essentially the same as they were when the Arthur D. Little study was done (Vines, 1981). At that time, VC emissions to the atmosphere were estimated to be about 0.14 kilograms (0.3 pounds) per day.

The third category (VC as a byproduct) encompassed the following processes existing in the United States:

(1) the manufacture of EDC via oxychlorination, and

(2) the manufacture of ethylene amines and ethylene imines from EDC.

The first process is now regulated under the existing VC NESHAP. Current information on VC emissions from ethylene amine production confirms that VC, as a byproduct in these processes, represents a very minor source of emissions (actual amounts not known). A representative of a plant manufacturing ethylene amines stated that the small amount of VC involved is directly vented to the incinerator in one plant. In another plant, VC is sent to the VC recovery column at their PVC facility. In either case, storage and handling of VC is not a factor. VC fugitive emission surveillance in these plants has shown no detectable VC levels (Wise, 1981).

6.3 NEW SOURCES IDENTIFIED DURING THE REVIEW STUDY

6.3.1 Mobile-mounted Sources of Emissions

Three areas of mobile-mounted emission sources have been noted by some regional EPA personnel. These are rail cars, tank cars, and marine unloading facilities. Department of Transportation (DOT) and Coast

Guard regulations are primarily concerned with flammability and water pollution parameters. No designation of responsibility for VC emissions into the air has been assigned for rail car leaks (Aronson, 1980). Several companies have reported relief valve discharges associated with the unloading of VC from ships at marine unloading facilities (Brittain, 1980).

Facilities used for cleaning rail and tank cars transporting liquid VC are often remote from regulated sources. There is a question as to whether these facilities or the VC supplier should assume responsibility for resultant VC emissions.

6.3.2 Nonplant Transfer Facilities

Terminals for transfer and short term storage of VC from marine vessels are under the jurisdiction of the Coast Guard and are not regulated by the VC NESHAP. The significance of emissions from these intermediate facilities is a concern of Regions I and VI (Pucci, 1980; Brittain, 1980). Because 16 of the 18 operating EDC/VC plants are located in Region VI and most of these plants are proximate to marine waters, this potential source of VC emissions is of major concern to Region VI as well as the plants who normally take responsibility for the emissions. In addition, many sources are clustered in the northeastern United States and VC can be transferred by marine vessels to transfer facilities near the sources. One of these transfer facilities was identified in Region II, but has temporarily been shut down.

The unregulated source of emissions is usually from a safety relief valve on the marine vessel (barge or ship) that discharges when overpressurization occurs during loading and unloading. One plant in Region VI reported a total of 871 kilograms (1936 pounds) of VC emitted from marine vessel relief valves over a 3.5 year period since 1977. This is comparable to 58 percent of the total quantity of relief valve discharges reported during this same time period. However, in most cases, the discharges from marine vessels are not reported because this source of emissions is not regulated (Brittain, 1980).

Tank farms, used for temporary VC storage and potentially for emergency stockpiling (due to rail strikes, etc.), are not currently regulated under the standard (Schaul, 1980; Varner, 1980).

6.3.3 Solid Waste Drying Facilities

One facility is currently installing a PVC sludge drying operation, designed to accommodate sludge with some low residual VC content. Such facilities are considered to be potential VC emission sources (Schaul, 1980). However, the sludges to be dried at these facilities contain PVC resins that have already met requirements for resin stripping levels.

6.3.4 Disposal Facilities (Landfill)

VC emissions were recently detected in vents from a landfill in Region II. These vents were installed mainly for the release of methane from the landfill. It is thought that PVC wastes, generated prior to the VC NESHAP's stripping requirements (and therefore unregulated), were disposed of in the landfill (Pucci, 1980). Measurements made at the landfill vents showed levels as high as 90.2 ppm. A review of the design proposed for the new venting system for the landfill included an evaluation of the number and spacing of the vents as well as an acceptable means for dealing with the VC emissions. The recommendation report stated that a manifold burner system would substantially reduce VC concentration, although the report did not state the level of reduction. The burner systems suggested included a Hirt Ground Flare and other waste gas burners. Interim control devices are being evaluated, and these include activated charcoal cannisters and activated charcoal tubes. VC has been measured in another landfill nearby, and Region II suspects that many more exist (Spatola, 1981).

Disposal of off-specification batches of PVC resin has been identified as a potential VC emission problem. These batches cannot always be stripped by conventional methods and thus may contain high levels of RVC. Some off-specification batches can be sold, but many are discarded. The State of California requires that all of these batches be stripped to levels appropriate to that resin type, but industry states that this is not always possible (Fannin, 1980). Ultimate disposition of the off-specification batches has not been determined.

6.4 REFERENCES FOR CHAPTER 6

Aronson, Wayne. 1980. EPA Region IV, Air Enforcement Branch. Meeting report - TRW visit to Region IV offices. September 3, 1980.

Brittain, Martin. 1980. NESHAP Coordinator, EPA Region VI. Meeting report - TRW visit to Region VI offices. October 27, 1980.

Cameron, J. B., A. J. Lundeen, and J. H. McCully, Jr. 1980. "Trends in Suspension PVC Manufacture." Hydrocarbon Processing. March 1980.

Chemical and Engineering News. 1980. "Key Polymers." October 6, 1980.

Fannin, James. 1980. B. F. Goodrich. Meeting with TRW in Cleveland, Ohio. October 30, 1980.

Little, Arthur D., Inc. 1975. Vinyl Chloride Monomer Emissions From the PVC Processing Industries. Contract No. 68-02-1332, Task No. 10. August 1975.

Lyman, Warren J., Arthur D. Little, Inc. 1976. Miscellaneous Industrial Sources of Vinyl Chloride Emissions in the U.S.. Contract No. 68-02-1332, Task No. 13 (Part 1-A, B, C). March 1976.

McPherson, R. W., C. M. Starks, G. F. Fryer. 1979. "Vinyl Chloride Monomer . . . What You Should Know." Hydrocarbon Processing. March 1979.

Padgett, Joseph. 1980. Director SASD, EPA. Letter with enclosures to Al Montague, SAD, EPA. September 23, 1980.

Pucci, Michael. 1980. NESHAP Coordinator for EPA Region II. Meeting report - TRW visit to Region II offices, New York. August 12, 1980.

Schaul, Peter. 1980. EPA Region III. Meeting report - TRW visit to Region III offices, Philadelphia. September 16, 1980.

Spatola, Joseph. 1980. EPA Region II, Air and Hazardous Materials. Telecon with M. A. Cassidy, TRW. January 13, 1981.

Ter Haar, Gary L. 1980. Director of Toxicology and Industrial Hygiene, Ethyl Corporation. Letter with attachments to Docket Officer, DOL - OSHA. May 7, 1980.

Varner, Bruce. 1980. NESHAP Coordinator for EPA Region V. Meeting report - TRW visit to Region V offices, Chicago. August 19, 1980.

Vines, J. H. 1981. Manager Insecticide Production, Chemagro Division of Mobay Chemical Co., Kansas City, Mo. Telecon to M. A. Cassidy, TRW. January 6, 1981.

Wise, R. C. 1981. Union Carbide Corp. Telecon to M. A. Cassidy, TRW. January 7, 1981.

7.0 IMPACT OF OTHER REGULATIONS

7.1 INTRODUCTION

The original study, which was done to support the current regulation, found that existing regulations as well as proposed regulations had little effect, if any, on the reduction of atmospheric VC emissions from EDC/VC and PVC plants. The Occupational Safety and Health Administration's (OSHA) regulations required a combination of ventilation techniques, engineering and work practice controls, and respirators to reduce worker exposure. Many of the engineering controls reduced atmospheric emissions, for example, portable and fixed point monitoring, improved sealing techniques, transfer line purges, reactor cleaning methods, and improved stripping, which not only reduced emissions from PVC plants but satisfied the demands of the fabricators (EPA 1975, p. 9-5). However, it was felt that compliance with the standard would not be uniform throughout the industry or significantly reduce VC emissions to the atmosphere.

Some state regulations existed for hydrocarbons and new construction and they indirectly reduced VC emissions at some plants. Texas regulations required two EDC/VC plants to reduce hydrocarbon emissions from the oxychlorination reactor, thus indirectly reducing VC emissions. Louisiana had similar regulations. New Jersey and Texas both required what was specified by each state as best control technology for any pollutant, including VC, when a source was newly constructed or modified (EPA 1975, p. 9-10). Other regulations concerning water pollution, transport of VC, aerosol products, and food packaging had no effect on reducing VC emissions.

However, since promulgation of the standard in October 1976, other regulations have evolved that can have a potentially greater effect on VC emitted to the total environment. The following is a list of the new

regulations, policies and requirements that have been established or proposed.

- Policy and Procedures for Identifying, Assessing and Regulating Airborne Substances Posing a Risk of Cancer (Proposed Carcinogen Rule)
- Prevention of Significant Deterioration (PSD)
- Resolution of the South Coast Air Quality Management District Board (SCAQMD) adopting Rule 1005.1 - Control of Vinyl Chloride Emissions
- Resource Conservation and Recovery Act (RCRA)
- Toxic Substances Control Act (TSCA)
- Toxic Pollutant Effluent Standards as required by the Clean Water Act of 1977
- Proposed Primary Drinking Water Regulations
- Potential Revision to the OSHA Workplace Standard for VC
- Transport of Hazardous Wastes and Hazardous Substances
- Food and Drug Administration (FDA) regulations
- Other state and local air pollution regulations

These new regulations have made the acquisition of permits necessary for construction and operation increasingly complex. The effect of the new regulatory requirements of the VC NESHAP will be discussed below with the federal and state laws responsible for implementation.

7.2 CLEAN AIR ACT

The Clean Air Act (CAA) Amendments of 1977 provided a mechanism for instituting a program for Prevention of Significant Deterioration (PSD) of Air Quality and plans for nonattainment areas. These regulations provide for continued protection of the existing ambient air quality and, in some cases, have had an effect on reducing VC emissions from new and modified sources. The CAA recently proposed a rule for regulating airborne carcinogens. The proposed Carcinogen Rule directly affects any recommended revisions to the current standard that may result from this review study. In addition, the state of California has established the first ambient air quality standard for VC and the regulations necessary for its enforcement.

7.2.1 Carcinogen Rule

The Carcinogen Rule, proposed on October 10, 1979, considered policies and procedures to:

- determine the carcinogenicity and risks for a specific pollutant,
- establish priorities for regulatory action,
- specify degree of control, and
- provide public input to the decisionmaking process. The proposed rule's requirement for periodic review of NESHAP regulations triggered this review of the current VC regulation. At least every 5 years, regulations would be reviewed for possible modification incorporating technological developments and health effects information. These reviews provide the opportunity to consider revising the standard (EPA, 1979a).

7.2.2 Prevention of Significant Deterioration

The original, and more recently revised, PSD and related nonattainment regulations have been responsible for reducing VC emissions from EDC/VC and PVC plants, in certain respects, beyond the reductions required by the current VC NESHAP. The goal of PSD is to ensure that air quality in clean areas does not significantly deteriorate and yet maintains a margin for future industrial growth. Clean areas, or those areas meeting the National Ambient Air Quality Standards (NAAQS) for criteria pollutants, are classified as attainment areas. New construction or a modification to an existing applicable source may be subject to PSD review and specific required analyses.

New construction or a modification to an existing source in a nonattainment area (an area not achieving the NAAQS) must be reviewed in accordance with the nonattainment provisions of the applicable State Implementation Plan (SIP). SIP's represent the plan of action that a state follows to restore non-attainment areas to attainment areas. EPA is continuing to publish control techniques guidelines (CTG) for those industries that emit significant quantities of air pollutants in areas of the country where NAAQS are not being achieved. CTG's provide information to state and local agencies that can be used in maintaining air quality (i.e., for developing an SIP). The CTG identifies reasonably available control technology (RACT) that can be applied to the industries

to reduce emissions, taking into account technological and economic feasibility. No CTG currently exists that would directly affect a regulated VC source. CTG's are in the developmental stages for air oxidation processes, polymers and resins, which could affect VC sources in the future.

PSD review is required for sources locating in PSD areas, in areas designated attainment, or in areas that are unclassifiable for any criteria pollutant. PSD areas, however, can also be designated non-attainment for one or more pollutants. In such areas, significant increases in pollutants for which the area is designated nonattainment under Section 107 of the CAA are exempt from PSD review. If this is the case, the facility will still be subject to review according to that state's applicable SIP. Therefore, a newly constructed EDC/VC and/or PVC plant (or modification to an existing plant) may be subject to PSD or non-attainment review or both.

PSD applicability is first determined for the new source or for the modification to an existing source. A new source is subject to PSD review if it is: (1) one of the 28 listed sources with the "potential" to emit 100 tons per year or more of a regulated pollutant, or (2) any unlisted source with the "potential" to emit 250 tons per year of a regulated pollutant. Regulated pollutants are the five criteria pollutants and nine non-criteria pollutants (of which VC is one). "Potential" emissions incorporate controls, any federal or state permit requirements and fugitive emissions. A modification to a major source is subject to PSD review if the physical change or change in operation results in a significant net emissions increase. The significance level above which PSD review is required is 1 ton per year for VC and 40 tons per year for volatile organic compounds.

Once it is determined that the source is subject to PSD review, the following three analyses are required:

- Best Available Control Technology (BACT) analysis,
- air quality analysis, and
- additional impact analyses.

The BACT analysis is the most important requirement and it provides the data for the other two requirements. Because NESHAP regulations do

not necessarily require BACT, PSD regulations can override NESHAP provisions and the resulting requirements for BACT may represent a more stringent emission control. NESHAP regulations require best available technology (BAT) which differs from BACT in the procedure used for its selection. BAT is selected on a nationwide basis considering economic, energy and environmental impacts, whereas BACT is selected on a plant-by-plant basis considering economic, energy and environmental impacts. For this reason, BAT and BACT may not necessarily reflect the same level of control. Therefore, a new VC source undergoing PSD review may be required to implement a level of control (i.e., BACT) that is more stringent than the BAT required by the VC NESHAP.

The primary purpose of BACT is to minimize consumption of increments (i.e., allowable growth within an attainment area) and thus expand the area's potential for future growth by addressing the interrelated impacts of energy availability, economy and environment. BACT determinations are made on a case-by-case basis, and the results form the basis for control strategy decisions. A BACT application may exempt a regulated pollutant from PSD review; for example, a company requesting a permit to construct an EDC/VC and PVC plant on the same site calculated potential hydrocarbon emissions to be approximately 5,000 tons per year thus making the source subject to PSD review (actual quantities of VC emissions were not determined). However, after application of BACT, the hydrocarbon emissions, including VC, were reduced to less than 50 tons per year which resulted in an exemption from PSD review. The BACT determination required more stringent control of specific VC emission point sources within the plant to levels less than those required by the VC NESHAP (Winkler, 1980). In another example an EDC/VC plant was allowed to discharge approximately 80 tons per year of VC from the oxy vent under NESHAP. However, the plant chose to incrementally remove 79 tons per year rather than go through PSD review (Brittain, 1980).

The BACT process involves four steps. The first, pollutant applicability, has already been discussed. The second step is determining the emissions unit applicability for the source. All applicable emissions units must be analyzed. A chemical complex producing EDC, VC and PVC provides a good example. Each chemical and polymer is made in

separate processing equipment with each piece of equipment containing several emission units. Emissions from all of the units must be summed for the entire complex which then constitutes one source. Fugitive emissions are included in determining quantities of emissions from each unit. Secondary pollutants (i.e., those emissions associated with a source but not emitted from the source itself) are also included if they cause a potential air quality standard or increment violation.

The third step in BACT review is to identify sensitive concerns (i.e., local air quality concerns and potential environmental impacts). These concerns should be quantifiable, if possible, so that various control alternatives can be compared. This step also encourages public involvement.

The last step is to select alternative control strategies. A base case is first established in order to rank the alternatives and consider them quantitatively. The base case can be considered the case that would be applied in the absence of the BACT decisionmaking process. The choice of the base case is dictated by existing regulations such as New Source Performance Standards (NSPS) or NESHAP requirements. Selection of alternatives is usually based on technical feasibility -- previously demonstrated technology. Innovative technology can be selected also and PSD allows special consideration for its use.

With the creation and analysis of the base case, alternative control strategies affording greater degrees of continuous emission reduction than the base case are ranked in order of control efficiency. The applicant then conducts an economic, energy and economic impact analysis for each alternative control strategy. Upon completion of these analyses, the information will be available to perform the final evaluations that will lead to proposal of BACT.

The other analyses required after the BACT analysis are an air quality analysis and an additional impact analysis, both of which rely on the BACT results. The air quality analysis must demonstrate that NAAQS or PSD increments will not be violated. This is done for each regulated pollutant and is accomplished by projecting the air quality that would exist when the new construction or modification is operating. Dispersion modeling is used to project this air quality. The modeling

takes into consideration the impact area, other sources in the areas, and existing ambient concentrations. The complexity of the analysis depends on location, and in some cases, ambient monitoring will be required. Finally, the additional analysis considers the impact on soils, vegetation, and visibility in the affected area from the increased emissions.

The applicant now has conducted the required analyses and based on the results proposes BACT to the reviewing agency that has responsibility for approval. The reviewing agency's determination is made on a case-by-case basis and the emission rates proposed as BACT may not necessarily be the rate ultimately specified in the PSD permit.

7.2.3 NESHAP Delegation to States

Section 112(d)(1) of the CAA allows each state to develop and submit to the Administrator a procedure for implementing and enforcing emission standards for hazardous air pollutants for sources in their state. If the Administrator finds the state procedure adequate, he shall delegate to the state the authority under the CAA to implement and enforce the NESHAP standards. Currently, those states that have received NESHAP delegation that contain VC sources are Texas, Georgia, and California. The state program must be as least as stringent as the Federal VC NESHAP. The state can also develop a program that is more stringent. California has developed a more progressive program that exemplifies the effect that NESHAP delegation can have on reducing VC emissions below those levels required by the Federal VC NESHAP.

The California Air Resources Board (CARB) was delegated NESHAP authority and, in response, adopted a state ambient air quality standard (AAQS) for VC of 10 parts per billion (ppb). CARB chose the 10 ppb level as the state AAQS because it was the lowest detectable limit for VC at that time. Responsibility for implementing the standard was then delegated to the local Districts (county-wide areas) within California. The Districts' mandate is to attain and maintain the AAQS's adopted by California, although the Districts' rules and regulations apply specifically to the sources within their jurisdiction.

All of the five VC sources in California are located in the South Coast Air Quality Management District (SCAQMD). In response to the

10 ppb AAQS, SCAQMD adopted the Federal NESHAP (Rule 1005) as their authority for enforcement of the AAQS and proposed a resolution adopting Rule 1005.1 as their program for controlling VC emissions to 10 ppb. Some of the major differences between Rule 1005.1 and the Federal NESHAP will be discussed in the following subsections.

Ambient monitoring. Designated plants, or those plants subject to Rule 1005.1, are not allowed to discharge VC in quantities that result in ambient concentrations greater than 10 ppb, 24-hour average, measured at any point beyond the property line of the plant where people reside and work. Sources are required to operate up to eight air monitoring stations in the vicinity of the plant to ensure that the 10 ppb level is being attained. These stations are selected and approved based on meteorological data, other available monitoring data, and location of populations around the plant. Meteorological data must also be monitored at these stations. Records of all the data must be maintained and monthly summaries submitted to SCAQMD. A plant can reduce the number of required stations if no violations occur in any period of 6 consecutive months. This exemption becomes void if a significant violation occurs. Minor, nonperiodic and infrequent breakdowns may be overlooked.

Primary control device. All equipment containing more than 10 ppm VC is required to be vented to the primary control device. The control device must then be operated at an efficiency to limit total emissions from the stack to less than 50 grams per hour. Selection of the emission limit was based on worst case modeling indicating that this level of emissions would maintain the 10 ppb AAQS. The 50 gram per hour limit sets a ceiling on growth (which the VC NESHAP 10 ppm limit does not; plants can continue to grow and discharge larger quantities of VC under the 10 ppm Federal standard).

Bubble concept. Rule 1005.1 allows a source to "bubble" or group their emissions to the degree that the 50 gram per hour limit is maintained. If a source requests this method of emissions reduction, all original construction and operation permits must be submitted to SCAQMD and new permits filed for approval. SCAQMD reissues these permits specifying emission levels or any other conditions necessary to ensure all emission limits are met.

Reactor opening loss (ROL). ROL emissions have been reduced to a 10 ppm concentration rather than the Federal standard of 0.02 gram VC per kilogram of PVC produced.

Operational Requirements. All vent valves and relief devices (other than emergency relief valves) upstream of stripping must be vented to a receiving vessel. Off-specification polymer batches must be discharged to a sealed container or stripped to required levels. Failure of a rupture disc preceding an emergency relief valve is a violation unless vented to control equipment.

Management plan. A management plan must be submitted for the reduction of VC emissions. The plan should include, but is not limited to,

- A plan and schedule to locate and identify all emissions sources that may cause the AAQS to be exceeded;
- An outline of employee training programs for preventing emissions;
- A method for screening operating data to identify operators most often responsible for excessive emissions; and
- An outline of a special training program or other methods to eliminate excessive emissions.

Leak detection. A leak is the detection of VC from any location, other than a stack vent or designed equipment opening, from which VC exceeds the background level of 10 ppm (measured 5 centimeters from source). All equipment containing or using VC shall be free of leaks. Equipment is to be inspected on a regular basis and records kept – all leaks are to be eliminated within 24 hours. Any leak detected during a SCAQMD inspection is a violation.

New or modified plants. The builder must demonstrate that the ambient air quality will not exceed the 10 ppb AAQS as a result of any emission from a new or modified source.

Relief valve discharges. Designated plants must install and operate pressure indicating and recording instruments (or approved equivalents) monitoring the discharge of emergency relief valves and manual vent valves. Data from these instruments must be summarized monthly and submitted to SCAQMD.

Current status of Rule 1005.1. The above subsections represent a summary of the major differences between the Federal NESHAP and the SCAQMD Rule 1005.1. Rule 1005.1 is currently being challenged in court by Stauffer Chemical and the B.F. Goodrich Chemical Group on the basis that the Rule is unconstitutional.

7.3 RESOURCE CONSERVATION AND RECOVERY ACT (RCRA)

RCRA was established in 1976 for the protection of public health and welfare by supplying guidelines to protect the quality of groundwater, surface water, and ambient air from contamination by solid waste. Draft regulations were issued in 1978 and final regulations in May 1980. These regulations control hazardous wastes from "cradle-to-grave" or from the point of generation through transportation, storage and ultimate disposal. This will be accomplished by a manifest system. If the generator produces hazardous wastes in sufficient quantities (greater than 1,000 kilograms per calendar month, except for some highly toxic wastes with lower limits of 1 kilogram per calendar month), he is responsible for their disposal. On-site disposal will require a permit with strict requirements for siting, operating, and monitoring the facility. Otherwise, the waste must be disposed of in a facility with a permit subject to the same strict requirements. The generator remains responsible for off-site disposal.

RCRA will probably have more of an effect on EDC/VC plants than PVC plants. The following EDC/VC processes have been identified as sources of hazardous wastes (EPA, 1979b, p. 181), 1) heavy ends from distillation of VC in production of VC from EDC, 2) heavy ends from distillation of EDC in VC production, and 3) heavy ends from distillation of EDC in EDC production. PVC sludge is not designated as a hazardous waste.

These solid wastes have been specifically listed as hazardous but it will still be the responsibility of the generator to show that other solid wastes originating from his facility are not hazardous. VC has been identified as a pollutant that could cause a solid waste to be classified hazardous (EPA, 1979b, p. 175). Also, surface impoundments, utilized by EDC/VC and PVC plants to collect waste streams, represent disposal sites and may require upgrading to meet RCRA standards of performance (Hanrahan, 1979, p. 23).

One of the more common methods being proposed for disposal of hazardous wastes is incineration. RCRA has extensive permit requirements for direct land disposal plus long term liabilities for generators using this method. However, incineration disposes of wastes without pretreatment and without incurring the long term liabilities of the manifest system. EDC/VC plants or PVC plants incinerating their hazardous wastes will be required to obtain a permit to operate the incinerator under RCRA.

7.4 TOXIC SUBSTANCES CONTROL ACT (TSCA)

TSCA was enacted in 1976 and provides EPA with the authority to secure information on all new and existing chemical substances and to control the substances determined to be hazardous to public health and the environment. Basically, TSCA was instituted to control the commerce of toxic products and the regulations provide EPA with powers that do not exist under any other Federal toxics-related laws. The other environmental laws (e.g., Clean Air Act, Clean Water Act, RCRA) are concerned with the control and disposition of gaseous, liquid and solid wastes and byproducts. OSHA focuses directly on worker exposure problems. However, TSCA deals with chemicals and products throughout their life cycle – manufacturing, distribution, use, and disposal (EPA, 1979b).

EPA will control the chemicals by requiring submission of a Premanufacture Notification (PMN) before marketing a new substance not listed in the TSCA 1979 Inventory of Toxic Substances. The PMN contains extensive background information including test data and literature predicting the effect that substances may have on workers, the environment, and consumer populations. Exceptions to TSCA are foods, drugs and pesticides that must be registered with specific agencies (e.g., FDA for foods and drugs, and EPA for pesticides). Any chemicals in the 1979 Inventory that are released to the environment by discharge must be listed in any state permits (to construct and operate), RCRA permits, and National Pollutant Discharge Elimination System (NPDES) permits under the Clean Water Act.

EDC, VC and many polymers of VC are already listed in the Inventory, and public health and environmental effects have been well established for these substances. A PMN is not required unless the "old" or listed

substance is used in a significantly new way (as determined by EPA). However, any new chemicals used in polymer development (e.g., new copolymers containing VC) will require a PMN prior to marketing.

7.5 CLEAN WATER ACT

Section 307 of the Clean Water Act required the EPA to publish a list of toxic pollutants and authorized EPA to promulgate effluent standards for those pollutants. In addition to these listed toxic pollutants, amendments to the Clean Water Act in 1977 required that "Consent Decree Pollutants" be added to the list of toxic pollutants if effluent limits failed to achieve water quality criteria (EPA, 1979b). VC is one of these "Consent Decree Pollutants" for which effluent guidelines were developed (see Federal Register, Nov. 28, 1980; 45 FR 79318). These effluent limitations are listed on, and enforced through, the discharge permit required under the National Pollutant Discharge Elimination System (NPDES).

Section 311 entitled "Oil and Hazardous Substance Liability," authorizes EPA to promulgate Hazardous Spill Regulations. Under these regulations EPA designated as hazardous those substances which, when discharged, present an imminent and substantial danger to the public health or welfare. An additional 28 chemicals have been added to the existing list of 271 hazardous substances published in 1978 — ethylene dichloride (EDC) used to produce VC and vinylidene chloride (used as a comonomer with VC) are on the proposed list (EPA, 1979b). Any spill consisting of these chemicals would result in a penalty, which is determined on a case-by-case basis. Sources in compliance with effluent standards established for these chemicals in other sections of the Clean Water Act are exempt from these requirements.

7.6 SAFE DRINKING WATER ACT

The Safe Drinking Water Act of 1974 was established to ensure that the public is provided with safe drinking water. This protection of public health is accomplished by EPA through the adoption of National Interim Primary Drinking Water Regulations that specify maximum levels for certain toxic contaminants in public drinking water. Secondary drinking water regulations have been proposed as guidelines to the states to ensure non-health related qualities of drinking water.

As a guideline, a list of chemicals indicative of industrial pollution has been published by EPA — VC is one of these indicators (EPA, 1979b). In addition, the EPA Office of Drinking Water, Criteria and Standards Division, has drafted a criteria document that would be used to establish a drinking water standard for VC.

7.7 HAZARDOUS MATERIALS TRANSPORTATION ACT

The Department of Transportation (DOT) under the Hazardous Materials Transportation Act of 1974 has promulgated final regulations on the transport of hazardous wastes and hazardous substances. VC, EDC, and several comonomers are subject to these regulations. The principal objective of this rule, as it pertains to the use of identification numbers for the regulated substances, is to improve the efficiency of civil emergency personnel (such as firemen and policemen) in the identification of hazardous materials, and to facilitate the accurate transmission of information to and from the scenes of accidents involving hazardous materials.

7.8 OCCUPATIONAL SAFETY AND HEALTH ACT

OSHA recently published a request for information on VC and PVC in the Federal Register on December 18, 1979 (44 FR 74928). This request was for voluntary submission of data and information that could be used as part of a review of the current OSHA VC standard. OSHA is concerned primarily with PVC dust and that the dust might cause pneumoconiosis. OSHA is investigating to determine whether the disease is caused by residual levels of VC in the dust or by the actual dust itself. The progress of this investigation has not been determined to date.

7.9 SUPERFUND LEGISLATION

The Comprehensive Environmental Response, Compensation and Liability Act of 1980 (Superfund) was recently signed into law to further the control of hazardous substances in the environment. The purpose of superfund is to:

- establish a federal cause of action against those responsible for the release of a hazardous substance into the environment;
- create a $1.6 billion trust fund to be used for cleaning up hazardous substances released into the environment or for taking action to prevent a threatened release; and

- create a $200 million fund for surveillance, care and maintenance of RCRA-closed hazardous substance disposal sites, and for any damages or environmental cleanup costs associated with such a site.

The $1.6 billion cleanup fund will be created from $1.38 billion in industry taxes and $0.22 billion in government revenues. The $200 million surveillance, care and maintenance fund will be created from industry taxes. These taxes will be on crude petroleum products, chemicals produced, and hazardous wastes generated. Regulations for implementing the superfund will be promulgated in the near future.

7.10 FOOD AND DRUG ADMINISTRATION REGULATIONS

The Food and Drug Administration (FDA) establishes requirements for PVC resins fabricated into products that come into human contact (e.g., beverage containers, baby bottle nipples, blood bags, pharmaceutical products, and food wrap). A processor producing these resins must meet requirements specifying operational procedures, resin characteristics (e.g., clarity, purity), and residual levels of VC (RVC). The FDA puts restrictions on all process steps from polymerization through fabrication. These resins are usually small-batch specialty resins that are stripped under controlled conditions because of their heat sensitivity. Also, reactors must be maintained differently (e.g., cleaning requirements are specified) and frequency of reactor opening is dictated.

7.11 OTHER STATE AND LOCAL REGULATIONS

The state regulations having the greatest impact on reducing VC emission are those mentioned previously under the Clean Air Act. Prior to construction or modification of a source and subsequent operation, companies will be required to obtain permits to construct and operate. It is through these permits that states will set limitations and conditions for emission reduction in nonattainment areas. These limitations may require further reduction of VC emissions below NESHAP limits, either through a reduction in hydrocarbons or VC specifically.

7.11 REFERENCES FOR CHAPTER 7

Brittain, Martin. 1980. NESHAP Coordinator, EPA Region VI. Meeting Report. July 23, 1980.

Environmental Protection Agency. 1979(a). "National Emission Standards for Identifying, Assessing and Regulating Airborne Substances Posing a Risk of Cancer," Proposed Rules, Federal Register, Vol. 44, No. 197. October 10, 1979(a).

Environmental Protection Agency. 1979(b). A Handbook of Key Federal Regulations and Criteria for Multimedia Environmental Control. EPA-600/7-79-175. August 1979(b).

Environmental Protection Agency. 1975. Standard Support and Environmental Impact Statement: Emission Standard for Vinyl Chloride, EPA-450/2-75-009. October 1975.

Hanrahan, David. 1979. "Hazardous Wastes: Current Problems and Near-Term Solutions," Technology Review. November 1979.

Holbrook, W.C. 1980. Director Toxicology and Environmental Affairs, B.F. Goodrich Chemical Division. Meeting Report: B.F. Goodrich, General Tire and TRW representatives. October 30, 1980.

Winkler, Joe. 1980. Technical Support Section, EPA Region VI. Preliminary Determination for Formosa Plastics Company, PSD-TX-226. February 22, 1980.

APPENDIX A

VINYL CHLORIDE NATIONAL EMISSIONS STANDARD FOR HAZARDOUS AIR POLLUTANTS

Title 40—Protection of Environment

CHAPTER I—ENVIRONMENTAL PROTECTION AGENCY

SUBCHAPTER C—AIR PROGRAMS

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Appendix A—Compliance Status Information.
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Method 101—Reference method for determination of particulate and gaseous mercury emissions from stationary sources (air streams).
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Method 103—Beryllium screening method.
Method 104—Reference method for determination of beryllium emissions from stationary sources.
Method 105—Method for determination of mercury in wastewater treatment plant sewage sludges. [7]
Method 106—Determination of vinyl chloride from stationary sources. [28]
Method 107—Determination of vinyl chloride of inprocess wastewater samples, and vinyl chloride content of polyvinyl chloride resin, slurry, wet cake, and latex samples. [28]

AUTHORITY: Sec. 112, 301(a) of the Clean Air Act as amended (42 U.S.C. 7412, 7601(a)), unless otherwise noted. [28, 49 FR]

Subpart A—General Provisions

§ 61.01 Applicability.

The provisions of this part apply to the owner or operator of any stationary source for which a standard is prescribed under this part.

§ 61.02 Definitions.

As used in this part, all terms not defined herein shall have the meaning given them in the act:

(a) "Act" means the Clean Air Act (42 U.S.C. 1857 et seq.).

(b) "Administrator" means the Administrator of the Environmental Protection Agency or his authorized representative.

(c) "Alternative method" means any method of sampling and analyzing for an air pollutant which is not a reference method or an equivalent method but which has been demonstrated to the Administrator's satisfaction to produce, in specific cases, results adequate for his determination of compliance.[2]

(d) "Commenced" means that an owner or operator has undertaken a continuous program of construction or modification or that an owner or operator has entered into a contractual obligation to undertake and complete, within a reasonable time, a continuous program of construction or modification.

(e) "Compliance schedule" means the date or dates by which a source or category of sources is required to comply with the standards of this part and with any steps toward such compliance which are set forth in a waiver of compliance under § 61.11.

(f) "Construction" means fabrication, erection, or installation of a stationary source.

(g) "Effective date" is the date of promulgation in the FEDERAL REGISTER of an applicable standard or other regulation under this part.

(h) "Equivalent method" means any method of sampling and analyzing for an air pollutant which has been demonstrated to the Administrator's satisfaction to have a consistent and quantitatively known relationship to the reference method, under specified conditions.

(i) "Existing source" means any stationary source which is not a new source.

(j) "Modification" means any physical change in, or change in the method of operation of, a stationary source which increases the amount of any hazardous air pollutant emitted by such source or which results in the emission of any hazardous air pollutant not previously emitted, except that:

(1) Routine maintenance, repair, and replacement shall not be considered physical changes, and

(2) The following shall not be considered a change in the method of operation:

(i) An increase in the production rate, if such increase does not exceed the operating design capacity of the stationary source;

(ii) An increase in hours of operation.

(k) "New source" means any stationary source, the construction or modification of which is commenced after the publication in the FEDERAL REGISTER of proposed national emission standards for hazardous air pollutants which will be applicable to such source.

(l) "Owner or operator" means any person who owns, leases, operates, controls, or supervises a stationary source.

(m) "Reference method" means any method of sampling and analyzing for an air pollutant, as described in Appendix B to this part.

(n) "Startup" means the setting in operation of a stationary source for any purpose.

(o) "Standard" means a national emission standard for a hazardous air pollutant proposed or promulgated under this part.

(p) "Stationary source" means any building, structure, facility, or installation which emits or may emit any air pollutant which has been designated as hazardous by the Administrator.

§ 61.03 Units and abbreviations.[42]

Used in this part are abbreviations and symbols of units of measure. These are defined as follows:

(a) System International (SI) units of measure:

A = ampere
g = gram
Hz = hertz
J = joule
K = degree Kelvin
kg = kilogram
m = meter
m^3 = cubic meter
mg = milligram = 10^{-3} gram
mm = millimeter = 10^{-3} meter
Mg = megagram = 10^6 gram
mol = mole
N = newton
ng = nanogram = 10^{-9} gram
nm = nanometer = 10^{-9} meter
Pa = pascal
s = second
V = volt
W = watt
Ω = ohm
μg = microgram = 10^{-6} gram

(b) Other units of measure:

°C = degree Celsius (centigrade)
cfm = cubic feet per minute
cc = cubic centimeter
d = day
°F = degree Fahrenheit
ft^2 = square feet
ft^3 = cubic feet
gal = gallon
in = inch
in Hg = inches of mercury
in H_2O = inches of water
l = liter
lb = pound
lpm = liter per minute
min = minute
ml = milliliter = 10^{-3} liter
oz = ounces
psig = pounds per square inch gage
°R = degree Rankine
μl = microliter = 10^{-6} liter
v/v = volume per volume
yd^2 = square yards
yr = year

(c) Chemical nomenclature:

Be = beryllium
Hg = mercury
H_2O = water

(d) Miscellaneous:

act = actual
avg = average
I.D. = inside diameter
M = molar
N = normal
O.D. = outside diameter
% = percent
std = standard

(Sections 112 and 301(a) of the Clean Air Act, as amended [42 U.S.C. 1857c-7, 1857g(a)].)

§ 61.04 Address.[4]

(a) All requests, reports, applications, submittals, and other communications to the Administrator pursuant to this part shall be submitted in duplicate and addressed to the appropriate Regional Office of the Environmental Protection Agency, to the attention of the Director, Enforcement Division. The regional offices are as follows:

Region I (Connecticut, Maine, New Hampshire, Massachusetts, Rhode Island, Vermont), John F. Kennedy Federal Building, Boston, Massachusetts 02203.

Region II (New York, New Jersey, Puerto Rico, Virgin Islands), Federal Office Building, 26 Federal Plaza (Foley Square), New York, N.Y. 10007.

Region III (Delaware, District of Columbia, Pennsylvania, Maryland, Virginia, West Virginia), Curtis Building, Sixth and Walnut Streets, Philadelphia, Pennsylvania 19106.

Region IV (Alabama, Florida, Georgia, Mississippi, Kentucky, North Carolina, South Carolina, Tennessee), Suite 300, 1421 Peachtree Street, Atlanta, Georgia 30309.

Region V (Illinois, Indiana, Minnesota, Michigan, Ohio, Wisconsin), 230 South Dearborn Street, Chicago, Illinois 60604.[43]

Region VI (Arkansas, Louisiana, New Mexico, Oklahoma, Texas), 1600 Patterson Street, Dallas, Texas 75201.

Region VII (Iowa, Kansas, Missouri, Nebraska), 1735 Baltimore Street, Kansas City, Missouri 64108.

Region VIII (Colorado, Montana, North Dakota, South Dakota, Utah, Wyoming), 1860 Lincoln Tower, 1860 Lincoln Street, Denver, Colorado 80203.

Region IX (Arizona, California, Hawaii, Nevada, Guam, American Samoa), 100 California Street, San Francisco, California 94111.

Region X (Washington, Oregon, Idaho, Alaska), 1200 Sixth Avenue, Seattle, Washington 98101.

(b) Section 112(d) directs the Administrator to delegate to each State, when appropriate, the authority to implement and enforce the national emission standards for hazardous air pollutants for stationary sources located in such State. All information required to be submitted to EPA under paragraph (a) of this section, must also be submitted to the appropriate State Agency of any State to which this authority has been delegated (provided, that each specific delegation may exempt sources from a certain federal or State reporting requirement). The appropriate mailing address for those States whose delegation request has been approved is as follows:

(A) [Reserved]

(B) State of Alabama, Air Pollution Control Division, Air Pollution Control Commission 645 S. McDonough Street, Montgomery, Alabama 36104.[23]

(C) [Reserved]

(D) Arizona:

Pima County Air Pollution Control District, 151 West Congress Street, Tucson AZ 85701.[30]

(E) [Reserved]

(F) California 5, 6, 15, 20, 21, 24, 28, 31

Bay Area Air Pollution Control District, 939 Ellis Street, San Francisco, CA 94109.

Del Norte County Air Pollution Control District, Courthouse, Crescent City, CA 95531.

Fresno County Air Pollution Control District, 315 S. Cedar Avenue, Fresno, CA 93702.

Humboldt County Air Pollution Control District, 5600 S. Broadway, Eureka, CA 95501.

Kern County Air Pollution Control District, 1700 Flower Street (P.O. Box 997) Bakersfield, CA 93302.

Madera County Air Pollution Control District, 133 W. Yosemite Avenue, Madera, CA 93637.

Mendocino County Air Pollution Control District, County Courthouse, Ukiah, CA 95482.

Monterey Bay Unified Air Pollution Control District, 420 Church Street (P.O. Box 487), Salinas, CA 93901.

Northern Sonoma County Air Pollution Control District, 3313 Chanate Road, Santa Rosa, CA 95404

Sacramento County Air Pollution Control District, 3701 Branch Center Road, Sacramento, CA 95827.

San Diego County Air Pollution Control District, 9150 Chesapeake Drive, San Diego, CA 92123.

San Joaquin County Air Pollution Control District, 1601 E. Hazelton Street (P.O. Box 2009), Stockton, CA 95201.

Santa Barbara Air Pollution Control District, 4440 Calle Real, Santa Barbara, CA 93110.

Stanislaus County Air Pollution Control District, 830 Scenic Drive, Modesto, CA 95350.

Trinity County Air Pollution Control District, Box AJ, Weaverville, CA 96093

Ventura County Air Pollution Control District, 625 E. Santa Clara Street, Ventura, CA 93001.

(G) State of Colorado, Colorado Air Pollution Control Division, 4210 East 11th Avenue, Denver, Colorado 80220.[9]

(H) State of Connecticut, Department of Environmental Protection, State Office Building, Hartford, Connecticut 06115.[14]

(I) State of Delaware (for fossil fuel-fired steam generators; incinerators; nitric acid plants; asphalt concrete plants; storage vessels for petroleum liquids; and sewage treatment plants only): Delaware Department of Natural Resources and Environmental Control, Edward Tatnall Building, Dover, Del. 19901.[46]

(J)-(K) [Reserved]

(L) State of Georgia, Environmental Protection Division, Department of Natural Resources, 270 Washington Street, S.W., Atlanta, Georgia 30334.[19]

(M)-(O) [Reserved]

(P) State of Indiana, Indiana Air Pollution Control Board, 1330 West Michigan Street, Indianapolis, Indiana 46206.[20]

(Q)-(R) [Reserved]

(S) Division of Air Pollution Control, Department for Natural Resources and Environmental Protection, U.S. 127, Frankfort, Ky. 40601.[45]

(T) [reserved].

(U) State of Maine, Department of Environmental Protection, State House, Augusta, Maine 04330.[11]

(V) [Reserved]

(W) Massachusetts Department of Environmental Quality Engineering, Division of Air Quality Control, 600 Washington Street, Boston, Massachusetts 02111.[17]

(X) State of Michigan, Air Pollution Control Division, Michigan Department of Natural Resources, Stevens T. Mason Building, 8th Floor, Lansing, Michigan 48926.[12]

(Y) Minnesota Pollution Control Agency, Division of Air Quality, 1935 West County Road B-2, Roseville, Minn. 55113.[44]

(Z) [Reserved]

(AA) [Reserved]

(BB) State of Montana, Department of Health and Environmental Sciences, Cogswell Building, Helena, Mont. 59601.[21]

(CC)-(DD) [reserved].

(EE) New Hampshire Air Pollution Control Agency, Department of Health and Welfare, State Laboratory Building, Hazen Drive, Concord, New Hampshire 03301.[17]

(FF)—State of New Jersey: New Jersey Department of Environmental Protection, John Fitch Plaza, P.O. Box 2807, Trenton, New Jersey 08625.[37]

(GG) [Reserved]

(HH) New York: New York State Department of Environmental Conservation, 50 Wolf Road, Albany, New York 12233, attention: Division of Air Resources.[8]

(II) North Carolina Environmental Management Commission, Department of Natural and Economic Resources, Division of Environmental Management, P.O. Box 27687, Raleigh, North Carolina 27611. Attention: Air Quality Section.[32]

(JJ) State of North Dakota, State Department of Health, State Capitol, Bismarck, North Dakota 58501.[27]

(KK)-(LL) [Reserved]

(MM) State of Oregon, Department of Environmental Quality, 1234 SW Morrison Street, Portland, Oregon 97205.[34]

(NN) (a) Commonwealth of Pennsylvania (except for City of Philadelphia and Allegheny County) Pennsylvania Department of Environmental Resources, Bureau of Air Quality and Noise Control, Post Office Box 2063, Harrisburg, Pennsylvania 17120.

(b) City of Philadelphia, Philadelphia Department of Public Health Air Management Services, 801 Arch Street, Philadelphia, Pennsylvania 19107.[33]

(OO) [Reserved]

(PP) State of South Carolina, Office of Environmental Quality Control, Department of Health and Environmental Control, 2600 Bull Street, Columbia, South Carolina 29201.[39]

(QQ)-(TT) [Reserved]

(UU) State of Vermont, Agency of Environmental Protection, Box 489, Montpelier, Vermont 05602.[43]

(VV) Commonwealth of Virginia, Virginia State Air Pollution Control Board, Room 1106, Ninth Street Office Building, Richmond, Virginia 23219.[13]

(WW) (1) Washington: State of Washington, Department of Ecology, Olympia, Washington 98504.

(2) Northwest Air Pollution Authority, 207 Pioneer Building, Second and Pine Streets, Mount Vernon, Washington 98273.

(3) Puget Sound Air Pollution Control Agency, 410 West Harrison Street, Seattle, Washington 98119.

(4) Spokane County Air Pollution Control Authority, North 811 Jefferson, Spokane, Washington 99201.

(5) Yakima County Clean Air Authority, County Courthouse, Yakima, Washington 98901.[16]

(6) Olympic Air Pollution Control Authority, 120 East State Avenue, Olympia, Washington 98501.

(7) Southwest Air Pollution Control Authority, Suite 7801 N. NE Hazel Dell Avenue, Vancouver, Washington 98665.[15]

(XX) [Reserved]

(YY) Wisconsin—Wisconsin Department of Natural Resources, P.O. Box 7921, Madison, Wisconsin 53707.[37]

(ZZ) [Reserved]

(AAA) [Reserved]

(BBB)—Commonwealth of Puerto Rico Commonwealth of Puerto Rico Environmental Quality Board, P.O Box 11786 Santurce, P.R 00910.[42]

(CCC) U.S. Virgin Islands: U.S. Virgin Islands Department of Conservation and Cultural Affairs, P.O. Box 578, Charlotte Amalie, St. Thomas, U.S. Virgin Islands 00801.[22]

(Secs. 101, 110, 111, 112 and 301 of the Clean Air Act, as amended, 42 U.S.C. 1857, 1857c-5, 6, 7 and 1857g.)

§ 61.05 Prohibited activities.

(a) After the effective date of any standard prescribed under this part, no owner or operator shall construct or modify any stationary source subject to such standard without first obtaining written approval of the Administrator in accordance with this subpart, except under an exemption granted by the President under section 112(c)(2) of the act. Sources, the construction or modification of which commenced after the publication date of the standards proposed to be applicable to such source, are subject to this prohibition.

(b) After the effective date of any standard prescribed under this part, no owner or operator shall operate any new source in violation of such standard except under an exemption granted by the President under section 112(c)(2) of the act.

(c) Ninety days after the effective date of any standard prescribed under this part, no owner or operator shall operate any existing stationary source in violation of such standard, except under a waiver granted by the Administrator in accordance with this subpart or under an exemption granted by the President under section 112(c)(2) of the act.

(d) No owner or operator subject to the provisions of this part shall fail to report, revise reports, or report source test results as required under this part.

§ 61.06 Determination of construction or modification.

Upon written application by an owner or operator, the Administrator will make a determination of whether actions taken or intended to be taken by such owner or operator constitute construction or modification or the commencement thereof within the meaning of this part. The Administrator will within 30 days of receipt of sufficient information to evaluate an application, notify the owner or operator of his determination.

§ 61.07 Application for approval of construction or modification.

(a) The owner or operator of any new source to which a standard prescribed under this part is applicable shall, prior to the date on which construction or modification is planned to commence, or within 30 days after the effective date in the case of a new source that already has commenced construction or modification and has not begun operation, submit to the Administrator an application for approval of such construction or modification. A separate application shall be submitted for each stationary source.

(b) Each application shall include:

(1) The name and address of the applicant.

(2) The location or proposed location of the source.

(3) Technical information describing the proposed nature, size, design, operating design capacity, and method of operation of the source, including a description of any equipment to be used for control of emissions. Such technical information shall include calculations of emission estimates in sufficient detail to permit assessment of the validity of such calculations.

§ 61.08 Approval by Administrator.

(a) The Administrator will, within 90 days of receipt of sufficient information to evaluate an application under § 61.07, notify the owner or operator of approval or intention to deny approval of construction or modification.

(b) If the Administrator determines that a stationary source for which an application pursuant to § 61.07 was submitted will, if properly operated, not cause emissions in violation of a standard, he will approve the construction or modification of such source.

(c) Prior to denying any application for approval of construction or modification pursuant to this section, the Administrator will notify the owner or operator making such application of the Administrator's intention to issue such denial, together with:

(1) Notice of the information and findings on which such intended denial is based, and

(2) Notice of opportunity for such owner or operator to present, within such time limit as the Administrator shall specify, additional information or arguments to the Administrator prior to final action on such application.

(d) A final determination to deny any application for approval will be in writing and will set forth the specific grounds on which such denial is based. Such final determination will be made within 60 days of presentation of additional information or arguments, or 90 days after the final date specified for presentation, if no presentation is made.

(e) Neither the submission of an application for approval nor the Administrator's granting of approval to construct or modify shall:

(1) Relieve an owner or operator of legal responsibility for compliance with any applicable provision of this part or of any other applicable Federal, State, or local requirement, or

(2) Prevent the Administrator from implementing or enforcing this part or taking any other action under the act.

§ 61.09 Notification of startup.

(a) Any owner or operator of a source which has an initial startup after the effective date of a standard prescribed under this part shall furnish the Administrator written notification as follows:

(1) A notification of the anticipated date of initial startup of the source not more than 60 days nor less than 30 days prior to such date.

(2) A notification of the actual date of initial startup of the source within 15 days after such date.

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)).

§ 61.10 Source reporting and waiver request.

(a) The owner or operator of any existing source, or any new source to which a standard prescribed under this part is applicable which had an initial startup which preceded the effective date of a standard prescribed under this part shall, within 90 days after the effective date, provide the following information in writing to the Administrator:

(1) Name and address of the owner or operator.

(2) The location of the source.

(3) The type of hazardous pollutants emitted by the stationary source.

(4) A brief description of the nature, size, design, and method of operation of the stationary source including the operating design capacity of such source. Identify each point of emission for each hazardous pollutant.

(5) The average weight per month of the hazardous materials being processed by the source, over the last 12 months preceding the date of the report.

(6) A description of the existing control equipment for each emission point.

(i) Primary control device(s) for each hazardous pollutant.

(ii) Secondary control device(s) for each hazardous pollutant.

(iii) Estimated control efficiency (percent) for each control device.

(7) A statement by the owner or operator of the source as to whether he can comply with the standards prescribed in this part within 90 days of the effective date.

(b) The owner or operator of an existing source unable to operate in compliance with any standard prescribed under this part may request a waiver of compliance with such standard for a period not exceeding 2 years from the effective date. Any request shall be in writing and shall include the following information:

(1) A description of the controls to be installed to comply with the standard.

(2) A compliance schedule, including the date each step toward compliance will be reached. Such list shall include as a minimum the following dates:

(i) Date by which contracts for emission control systems or process modifications will be awarded, or date by which orders will be issued for the purchase of component parts to accomplish emission control or process modification;

(ii) Date of initiation of onsite construction or installation of emission control equipment or process change;

(iii) Date by which onsite construction or installation of emission control equipment or process modification is to be completed; and

(iv) Date by which final compliance is

to be achieved.

(3) A description of interim emission control steps which will be taken during the waiver period.

(c) Changes in the information provided under paragraph (a) of this section shall be provided to the Administrator within 30 days after such change, except that if changes will result from modification of the source, as defined in § 61.02 (j), the provisions of § 61.07 and § 61.08 are applicable.

(d) The format for reporting under this section is included as Appendix A of this part. Advice on reporting the status of compliance may be obtained from the Administrator.

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)).

§ 61.11 Waiver of compliance.

(a) Based on the information provided in any request under § 61.10, or other information, the Administrator may grant a waiver of compliance with a standard for a period not exceeding 2 years from the effective date of such standard.

(b) Such waiver will be in writing and will:

(1) Identify the stationary source covered.

(2) Specify the termination date of the waiver. The waiver may be terminated at an earlier date if the conditions specified under paragraph (b)(3) of this section are not met.

(3) Specify dates by which steps toward compliance are to be taken; and impose such additional conditions as the Administrator determines to be necessary to assure installation of the necessary controls within the waiver period, and to assure protection of the health of persons during the waiver period.

(c) Prior to denying any request for a waiver pursuant to this section, the Administrator will notify the owner or operator making such request of the Administrator's intention to issue such denial, together with:

(1) Notice of the information and findings on which such intended denial is based, and

(2) Notice of opportunity for such owner or operator to present, within such time limit as the Administrator specifies, additional information or arguments to the Administrator prior to final action on such request.

(d) A final determination to deny any request for a waiver will be in writing and will set forth the specific grounds on which such denial is based. Such final determination will be made within 60 days after presentation of additional information or arguments, or 60 days after the final date specified for such presentation, if no presentation is made.

(e) The granting of a waiver under this section shall not abrogate the Administrator's authority under section 114 of the act.

§ 61.12 Emission tests and monitoring.

(a) Emission tests and monitoring shall be conducted and reported as set forth in this part and Appendix B to this part.

(b) The owner or operator of a new source subject to this part, and at the or operator of an existing source subject to this part, shall provide or cause to be provided, emission testing facilities as follows:

(1) Sampling ports adequate for test methods applicable to such source.

(2) Safe sampling platform(s).

(3) Safe access to sampling platform(s).

(4) Utilities for sampling and testing equipment.

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)).

§ 61.13 Waiver of emission tests.

(a) Emission tests may be waived upon written application to the Administrator if, in his judgment, the source is meeting the standard, or if the source is operating under a waiver of compliance or has requested a waiver of compliance.

(b) If application for waiver of the emission test is made, such application shall accompany the information required by § 61.10. The appropriate form is contained in Appendix A to this part.

(c) Approval of any waiver granted pursuant to this section shall not abrogate the Administrator's authority under the act or in any way prohibit the Administrator from later canceling such waiver. Such cancellation will be made only after notice is given to the owner or operator of the source.

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)).

§ 61.14 Source test and analytical methods.

(a) Methods 101, 102, and 104 in Appendix B to this part shall be used for all source tests required under this part, unless an equivalent method or an alternative method has been approved by the Administrator.

(b) Method 103 in Appendix B to this part is hereby approved by the Administrator as an alternative method for source subject to § 61.23(a) and § 61.43 (b).

(c) The Administrator may, after notice to the owner or operator, withdraw approval of an alternative method granted under paragraphs (a), (b) or (d) of this section. Where the test results using an alternative method do not adequately indicate whether a source is in compliance with a standard, the Administrator may require the use of the reference method or its equivalent.

(d) Method 106 in Appendix B to this part is hereby approved by the Administrator as an alternative method for sources subject to § 61.53(b).

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)).

§ 61.15 Availability of information.[2]

The availability to the public of information provided to, or otherwise obtained by, the Administrator under this part shall be governed by Part 2 of this chapter.

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)).

§ 61.16 State authority.

(a) The provisions of this part shall not be construed in any manner to preclude any State or political subdivision thereof from:

(1) Adopting and enforcing any emission limiting regulation applicable to a stationary source, provided that such emission limiting regulation is not less stringent than the standards prescribed under this part.

(2) Requiring the owner or operator of a stationary source, other than a stationary source owned or operated by the United States, to obtain permits, licenses, or approvals prior to initiating construction, modification, or operation of such source.

(Sec. 114, Clean Air Act as amended (42 U.S.C. 7414)).

§ 61.17 Circumvention.[7]

No owner or operator subject to the provisions of this part shall build, erect, install, or use any article, machine, equipment, process, or method, the use of which conceals an emission which would otherwise constitute a violation of an applicable standard. Such concealment includes, but is not limited to, the use of gaseous diluents to achieve compliance with a visible emissions standard, and the piecemeal carrying out of an operation to avoid coverage by a standard that applies only to operations larger than a specified size.

Subpart F—National Emission Standard for Vinyl Chloride [34]

§ 61.60 Applicability.

(a) This subpart applies to plants which produce:

(1) Ethylene dichloride by reaction of oxygen and hydrogen chloride with ethylene.

(2) Vinyl chloride by any process, and/or

(3) One or more polymers containing any fraction of polymerized vinyl chloride.

(b) This subpart does not apply to equipment used in research and development if the reactor used to polymerize the vinyl chloride processed in the equipment has a capacity of no more than 0.19 m³ (50 gal).

(c) Sections of this subpart other than §§ 61.61; 61.64 (a)(1), (b), (c), and (d); 61.67; 61.68; 61.69; 61.70; and 61.71 do not apply to equipment used in research and development if the reactor used to polymerize the vinyl chloride processed in the equipment has a capacity of greater than 0.19 m³ (50 gal) and no more than 4.67 m³ (1180 gal).[35]

§ 61.61 Definitions.

Terms used in this subpart are defined in the Act, in Subpart A of this part, or in this section as follows:

(a) "Ethylene dichloride plant" includes any plant which produces ethylene dichloride by reaction of oxygen and hydrogen chloride with ethylene.

(b) "Vinyl chloride plant" includes any plant which produces vinyl chloride by any process.

(c) "Polyvinyl chloride plant" includes any plant where vinyl chloride alone or in combination with other materials is polymerized.

(d) "Slip gauge" means a gauge which has a probe that moves through the gas/liquid interface in a storage or transfer vessel and indicates the level of vinyl chloride in the vessel by the physical state of the material the gauge discharges.

(e) "Type of resin" means the broad classification of resin referring to the basic manufacturing process for producing that resin, including, but not limited to, the suspension, dispersion, latex, bulk, and solution processes.

(f) "Grade of resin" means the subdivision of resin classification which describes it as a unique resin, i.e., the most exact description of a resin with no further subdivision.

(g) "Dispersion resin" means a resin manufactured in such away as to form fluid dispersions when dispersed in a plasticizer or plasticizer/diluent mixtures.

(h) "Latex resin" means a resin which is produced by a polymerization process which initiates from free radical catalyst sites and is subundried.

(i) "Bulk resin" means a resin which is produced by a polymerization process in which no water is used.

(j) "Inprocess wastewater" means any water which, during manufacturing or processing, comes into direct contact with vinyl chloride or polyvinyl chloride or results from the production or use of any raw material, intermediate product, finished product, by-product, or waste product containing vinyl chloride or polyvinyl chloride but which has not been discharged to a wastewater treatment process or discharged untreated as wastewater.

(k) "Wastewater treatment process" includes any process which modifies characteristics such as BOD, COD, TSS, and pH, usually for the purpose of meeting effluent guidelines and standards; it does not include any process the purpose of which is to remove vinyl chloride from water to meet requirements of this subpart.

(l) "In vinyl chloride service" means that a piece of equipment contains or contacts either a liquid that is at least 10 percent by weight vinyl chloride or a gas that is at least 10 percent by volume vinyl chloride.

(m) "Standard operating procedure" means a formal written procedure officially adopted by the plant owner or operator and available on a routine basis to those persons responsible for carrying out the procedure.

(n) "Run" means the net period of time during which an emission sample is collected.

(o) "Ethylene dichloride purification" includes any part of the process of ethylene dichloride production which follows ethylene dichloride formation and in which finished ethylene dichloride is produced.

(p) "Vinyl chloride purification" includes any part of the process of vinyl chloride production which follows vinyl chloride formation and in which finished vinyl chloride is produced.

(q) "Reactor" includes any vessel in which vinyl chloride is partially or totally polymerized into polyvinyl chloride.

(r) "Reactor opening loss" means the emissions of vinyl chloride occurring when a reactor is vented to the atmosphere for any purpose other than an emergency relief discharge as defined in § 61.65(a).

(s) "Stripper" includes any vessel in which residual vinyl chloride is removed from polyvinyl chloride resin, except bulk resin, in the slurry form by the use of heat and/or vacuum. In the case of bulk resin, stripper includes any vessel which is used to remove residual vinyl chloride from polyvinyl chloride resin immediately following the polymerization step in the plant process flow.

(t) "Standard temperature" means a temperature of 20° C (68° F).[36]

(u) "Standard pressure" means a pressure of 760 mm of Hg (29.92 in. of Hg).[36]

§ 61.62 Emission standard for ethylene dichloride plants.[36]

(a) Ethylene dichloride purification: The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from any equipment used in ethylene dichloride purification is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b)(6)(i) before being opened.

(b) Oxychlorination reactor: Except as provided in § 61.65(a), emissions of vinyl chloride to the atmosphere from each oxychlorination reactor are not to exceed 0.2 g/kg (0.0002 lb/lb) of the 100 percent ethylene dichloride product from the oxychlorination process.

§ 61.63 Emission standard for vinyl chloride plants.

An owner or operator of a vinyl chloride plant shall comply with the requirements of this section and § 61.65.

(a) Vinyl chloride formation and purification: The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from any equipment used in vinyl chloride formation and/or purification is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b)(6)(i) before being opened.

§ 61.64 Emission standard for polyvinyl chloride plants.

An owner or operator of a polyvinyl chloride plant shall comply with the requirements of this section and § 61.65.

(a) *Reactor.* The following requirements apply to reactors:

(1) The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each reactor is not to exceed 10 ppm, except as provided in paragraph (a)(2) of this section and § 61.65(a).

(2) The reactor opening loss from each reactor is not to exceed 0.02 g vinyl chloride/kg (0.00002 lb vinyl chloride/lb) of polyvinyl chloride product, with the product determined on a dry solids basis. This requirement applies to any vessel which is used as a reactor or as both a reactor and a stripper. In the bulk process, the product means the gross product of prepolymerization and postpolymerization.

(3) Manual vent valve discharge: Except for an emergency manual vent valve discharge, there is to be no discharge to the atmosphere from any manual vent valve on a polyvinyl chloride reactor in vinyl chloride service. An emergency manual vent valve discharge means a discharge to the atmosphere which could not have been avoided by taking measures to prevent the discharge. Within 10

days of any discharge to the atmosphere from any manual vent valve, the owner or operator of the source from which the discharge occurs shall submit to the Administrator a report in writing containing information on the source, nature and cause of the discharge, the date and time of the discharge, the approximate total vinyl chloride loss during the discharge, the method used for determining the vinyl chloride loss, the action that was taken to prevent the discharge, and measures adopted to prevent future discharges.

(b) *Stripper.* The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each stripper is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b)(6)(i) before being opened.

(c) *Mixing, weighing, and holding containers.* The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each mixing, weighing, or holding container in vinyl chloride service which precedes the stripper (or the reactor if the plant has no stripper) in the plant process flow is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b)(6)(i) before being opened.

(d) *Monomer recovery system.* The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each monomer recovery system is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b)(6)(i) before being opened.

(e) *Sources following the stripper(s).* The following requirements apply to emissions of vinyl chloride to the atmosphere from the combination of all sources following the stripper(s) [or the reactor(s) if the plant has no stripper(s)] in the plant process flow including but not limited to, centrifuges, concentrators, blend tanks, filters, dryers, conveyor air discharges, baggers, storage containers, and inprocess wastewater:

(1) In polyvinyl chloride plants using stripping technology to control vinyl chloride emissions, the weighted average residual vinyl chloride concentration in all grades of polyvinyl chloride resin processed through the stripping operation on each calendar day, measured immediately after the stripping operation is completed, may not exceed:

(i) 2000 ppm for polyvinyl chloride dispersion resins, excluding latex resins;

(ii) 400 ppm for all other polyvinyl chloride resins, including latex resins, averaged separately for each type of resin; or

(2) In polyvinyl chloride plants controlling vinyl chloride emissions with technology other than stripping or in addition to stripping, emissions of vinyl chloride to the atmosphere may not exceed:

(i) 2 g/kg (0.002 lb/lb) product from the stripper(s) [or reactor(s) if the plant has no stripper(s)] for dispersion polyvinyl chloride resins, excluding latex resins, with the product determined on a dry solids basis;

(ii) 0.4 g/kg (0.0004 lb/lb) product from the strippers [or reactor(s) if the plant has no stripper(s)] for all other polyvinyl chloride resins, including latex resins, with the product determined on a dry solids basis.

§ 61.65 Emission standard for ethylene dichloride, vinyl chloride and polyvinyl chloride plants.

An owner or operator of an ethylene dichloride, vinyl chloride, and/or polyvinyl chloride plant shall comply with the requirements of this section.

(a) *Relief valve discharge.* Except for an emergency relief discharge, there is to be no discharge to the atmosphere from any relief valve on any equipment in vinyl chloride service. An emergency relief discharge means a discharge which could not have been avoided by taking measures to prevent the discharge. Within 10 days of any relief valve discharge, the owner or operator of the source from which the relief valve discharge occurs shall submit to the Administrator a report in writing containing information on the source, nature and cause of the discharge, the date and time of the discharge, the approximate total vinyl chloride loss during the discharge, the method used for determining the vinyl chloride loss, the action that was taken to prevent the discharge, and measures adopted to prevent future discharges.

(b) *Fugitive emission sources.* (1) *Loading and unloading lines:* Vinyl chloride emissions from loading and unloading lines in vinyl chloride service which are opened to the atmosphere after each loading or unloading operation are to be minimized as follows: [3]

(i) After each loading or unloading operation and before opening a loading or unloading line to the atmosphere, the quantity of vinyl chloride in all parts of each loading or unloading line that are to be opened to the atmosphere is to be reduced so that the parts combined contain no greater than 0.0038 m^3 (0.13 ft^3) of vinyl chloride, at standard temperature and pressure; and

(ii) Any vinyl chloride removed from a loading or unloading line in accordance with paragraph (b)(1)(i) of this section is to be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm, or equivalent as provided in § 61.66.

(2) *Slip gauges.* During loading or unloading operations, the vinyl chloride emissions from each slip gauge in vinyl chloride service are to be minimized by ducting any vinyl chloride discharged from the slip gauge through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm, or equivalent as provided in § 61.66.

(3) Leakage from pump, compressor, and agitator seals:

(i) *Rotating pumps.* Vinyl chloride emissions from seals on all rotating pumps in vinyl chloride service are to be minimized by installing sealless pumps, pumps with double mechanical seals, or equivalent as provided in § 61.66. If double mechanical seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the pump; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(ii) *Reciprocating pumps.* Vinyl chloride emissions from seals on all reciprocating pumps in vinyl chloride service are to be minimized by installing double outboard seals, or equivalent as provided in § 61.66. If double outboard seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the pump; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(iii) *Rotating compressor.* Vinyl chloride emissions from seals on all rotating compressors in vinyl chloride service are to be minimized by installing compressors with double mechanical seals, or equivalent as provided in § 61.66. If double mechanical seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the compressor; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(iv) *Reciprocating compressors.* Vinyl chloride emissions from seals on all reciprocating compressors in vinyl chloride service are to be minimized by installing double outboard seals, or equivalent as provided in § 61.66. If double outboard seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the compressor; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(v) *Agitator.* Vinyl chloride emissions from seals on all agitators in vinyl chloride service are to be minimized by in-

stalling agitators with double mechanical seals, or equivalent as provided in § 61.64. If double mechanical seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the agitated vessel; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(4) *Leakage from relief valves.* Vinyl chloride emissions due to leakage from each relief valve on equipment in vinyl chloride service are to be minimized by installing a rupture disk between the equipment and the relief valve, by connecting the relief valve discharge to a process line or recovery system, or equivalent as provided in § 61.66.

(5) *Manual venting of gases.* Except as provided in § 61.64(a)(2), all gases which are manually vented from equipment in vinyl chloride service are to be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(6) *Opening of equipment.* Vinyl chloride emissions from opening of equipment (including loading or unloading lines that are not opened to the atmosphere after each loading or unloading operation) are to be minimized as follows:

(i) Before opening any equipment for any reason, the quantity of vinyl chloride is to be reduced so that the equipment contains no more than 2.6 percent by volume vinyl chloride or 0.0068 m^3 (26 gal) of vinyl chloride, whichever is larger, at standard temperature and pressure; and

(ii) Any vinyl chloride removed from the equipment in accordance with paragraph (b)(6)(i) of this section is to be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm, or equivalent as provided in § 61.66.

(7) *Samples.* Unused portions of samples containing at least 10 percent by weight vinyl chloride are to be returned to the process, and sampling techniques are to be such that sample containers in vinyl chloride service are purged into a closed process system.

(8) *Leak detection and elimination.* Vinyl chloride emissions due to leaks from equipment in vinyl chloride service are to be minimized by instituting and implementing a formal leak detection and elimination program. The owner or operator shall submit a description of the program to the Administrator for approval. The program is to be submitted within 45 days of the effective date of these regulations, unless a waiver of compliance is granted under § 61.11. If a waiver of compliance is granted, the program is to be submitted on a date scheduled by the Administrator. Approval of a program will be granted by the Administrator provided he finds:

(i) It includes a reliable and accurate vinyl chloride monitoring system for detection of major leaks and identification of the general area of the plant where a leak is located. A vinyl chloride monitoring system means a device which obtains air samples from one or more points on a continuous sequential basis and analyzes the samples with gas chromatography or, if the owner or operator assumes that all hydrocarbons measured are vinyl chloride, with infrared spectrophotometry, flame ion detection, or an equivalent or alternative method.

(ii) It includes a reliable and accurate portable hydrocarbon detector to be used routinely to find small leaks and to pinpoint the major leaks indicated by the vinyl chloride monitoring system. A portable hydrocarbon detector means a device which measures hydrocarbons with a sensitivity of at least 10 ppm and is of such design and size that it can be used to measure emissions from localized points.

(iii) It provides for an acceptable calibration and maintenance schedule for the vinyl chloride monitoring system and portable hydrocarbon detector. For the vinyl chloride monitoring system, a daily span check is to be conducted with a concentration of vinyl chloride equal to the concentration defined as a leak according to paragraph (b)(8)(vi) of this section. The calibration is to be done with either:

(A) A calibration gas mixture prepared from the gases specified in sections 5.2.1 and 5.2.2 of Test Method 106 and in accordance with section 7.1 of Test Method 106, or[36]

(B) A calibration gas cylinder standard containing the appropriate concentration of vinyl chloride. The gas composition of the calibration gas cylinder standard is to have been certified by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration does not change greater than ±5 percent from the certified value. The date of gas cylinder preparation, certified vinyl chloride concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the manufacturer to the buyer. If a gas chromatograph is used as the vinyl chloride monitoring system, these gas mixtures may be directly used to prepare a chromatograph calibration curve as described in section 7.3 of Test Method 106. The requirements in section 5.2.1.1 and 5.2.2.2 of Test Method 106 for certification of cylinder standards and for establishment and verification of calibration standards are to be followed.[37]

(iv) The location and number of points to be monitored and the frequency of monitoring provided for in the program are acceptable when they are compared with the number of pieces of equipment in vinyl chloride service and the size and physical layout of the plant.

(v) It contains an acceptable plan of action to be taken when a leak is detected.

(vi) It contains a definition of leak which is acceptable when compared with the background concentrations of vinyl chloride in the areas of the plant to be monitored by the vinyl chloride monitoring system. Measurements of background concentrations of vinyl chloride in the areas of the plant to be monitored by the vinyl chloride monitoring system are to be included with the description of the program. The definition of leak for a given plant may vary among the different areas within the plant and is also to change over time as background concentrations in the plant are reduced.

(9) *Inprocess wastewater.* Vinyl chloride emissions to the atmosphere from inprocess wastewater are to be reduced as follows:

(i) The concentration of vinyl chloride in each inprocess wastewater stream containing greater than 10 ppm vinyl chloride measured immediately as it leaves a piece of equipment and before being mixed with any other inprocess wastewater stream is to be reduced to no more than 10 ppm by weight before being mixed with any other inprocess wastewater stream which contains less than 10 ppm vinyl chloride; before being exposed to the atmosphere; before being discharged to a wastewater treatment process; or before being discharged untreated as a wastewater. This paragraph does apply to water which is used to displace vinyl chloride from equipment before it is opened to the atmosphere in accordance with § 61.64(a)(3) or paragraph (b)(6) of this section, but does not apply to water which is used to wash out equipment after the equipment has already been opened to the atmosphere in accordance with § 61.64(a)(1) or paragraph (b)(6) of this section.[38]

(ii) Any vinyl chloride removed from the inprocess wastewater in accordance with paragraph (b)(9)(i) of this section is to be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm, or equivalent as provided in § 61.66.

(c) The requirements in paragraphs (b)(1), (b)(2), (b)(5), (b)(6), (b)(7) and (b)(8) of this section are to be incorporated into a standard operating procedure, and made available upon request for inspection by the Administrator. The standard operating procedure is to include provisions for measuring the vinyl chloride in equipment ≥4.75 m^3 (1,256 gal) in volume for which an emission limit is prescribed in § 61.65(b)(6)(i) prior to opening the equipment and using Test Method 106, a portable hydrocarbon detector, or an equivalent or alternative method. The method of measurement is to meet the requirements in § 61.67(g)(5)(i)(A) or (g)((5)(i)(B).[39]

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)).[40]

§ 61.66 Equivalent equipment and procedures.

Upon written application from an owner or operator, the Administrator may approve use of equipment or procedures which have been demonstrated to his satisfaction to be equivalent in terms of reducing vinyl chloride emissions to the atmosphere to those prescribed for compliance with a specific paragraph of this subpart. For an existing source, any request for using an equivalent method as the initial measure of control is to be submitted to the Administrator within 30 days of the effective date. For a new source, any request for using an equivalent method is to be submitted to the Administrator with the application for approval of construction or modification required by § 61.07.

§ 61.67 Emission tests.

(a) Unless a waiver of emission testing is obtained under § 61.13, the owner or operator of a source to which this subpart applies shall test emissions from the source.

(1) Within 90 days of the effective date in the case of an existing source or a new source which has an initial startup date preceding the effective date, or

(2) Within 90 days of startup in the case of a new source, initial startup of which occurs after the effective date.

(b) The owner or operator shall provide the Administrator at least 30 days prior notice of an emission test to afford the Administrator the opportunity to have an observer present during the test.

(c) Any emission test is to be conducted while the equipment being tested is operating at the maximum production rate at which the equipment will be operated and under other relevant conditions as may be specified by the Administrator based on representative performance of the source.

(d) [Reserved][38]

(e) When at all possible, each sample is to be analyzed within 24 hours, but in no case in excess of 72 hours of sample collection. Vinyl chloride emissions are to be determined within 30 days after the emission test. The owner or operator shall report the determinations to the Administrator by a registered letter dispatched before the close of the next business day following the determination.[38]

(f) The owner or operator shall retain at the plant and make available, upon request, for inspection by the Administrator, for a minimum of 2 years records of emission test results and other data needed to determine emissions.

(g) Unless otherwise specified, the owner or operator shall use test Test Methods in Appendix B to this part for each test as required by paragraphs (g)(1), (g)(2), (g)(3), (g)(4), and (g)(5) of this section, unless an equivalent method or an alternative method has been approved by the Administrator. If the Administrator finds reasonable grounds to dispute the results obtained by an equivalent or alternative method, he may require the use of a reference method. If the results of the reference and equivalent or alternative methods do not agree, the results obtained by the reference method prevail, and the Administrator may notify the owner or operator that approval of the method previously considered to be equivalent or alternative is withdrawn.

(1) Test Method 106 is to be used to determine the vinyl chloride emissions from any source for which an emission limit is prescribed in §§ 61.62(a) or (b) § 61.63(a), or §§ 61.64(a)(1), (b), (c), or (d), or from any control system to which reactor emissions are required to be ducted in § 61.64(a)(2) or to which fugitive emissions are required to be ducted in § 61.65(b)(1)(ii), (b)(2), (b)(5), (b)(6)(ii), or (b)(9)(ii).

(i) For each run, one sample is to be collected. The sampling site is to be at least two stack or duct diameters downstream and one half diameter upstream from any flow disturbance such as a bend, expansion, contraction, or visible flame. For a rectangular cross section an equivalent diameter is to be determined from the following equation:

$$\text{equivalent diameter} = 2\frac{(\text{length})\ (\text{width})}{\text{length} + \text{width}}$$

The sampling point in the duct is to be at the centroid of the cross section. The sample is to be extracted at a rate proportional to the gas velocity at the sampling point. The sample is to be taken over a minimum of one hour, and is to contain a minimum volume of 60 liters corrected to standard conditions.

(ii) Each emission test is to consist of three runs. For the purpose of determining emissions, the average of results of all runs is to apply. The average is to be computed on a time weighted basis.[38]

(iii) For gas streams containing more than 10 percent oxygen the concentration of vinyl chloride as determined by Test Method 106 is to be corrected to 10 percent oxygen (dry basis) for determination of emissions by using the following equation:

$$C_{a\ corrected} = C_a\frac{10.9}{20.9 - \text{percent } O_2}$$

where:

$C_{a\ corrected}$ = The concentration of vinyl chloride in the exhaust gases, corrected to 10-percent oxygen.

C_a = The concentration of vinyl chloride as measured by Test Method 106.

20.9 = Percent oxygen in the ambient air at standard conditions.

10.9 = Percent oxygen in the ambient air at standard conditions, minus the 10.0-percent oxygen to which the correction is being made.

Percent O_2 = Percent oxygen in the exhaust gas as measured by Reference Method 3 in Appendix A of Part 60 of this chapter.[38]

(iv) For those emission sources where the emission limit is prescribed in terms of mass rather than concentration, mass emissions in kg/100 kg product are to be determined by using the following equation:

$$C_{a1} = \frac{[C_a(2.60)\,Q\ 10^{-6}]\ [100]}{Z}$$

where:

C_{a1} = kg vinyl chloride/100 kg product.

C_a = The concentration of vinyl chloride as measured by Test Method 106.

2.60 = Density of vinyl chloride at one atmosphere and 20° C in kg/m³.

Q = Volumetric flow rate in m³/hr as determined by Reference Method 2 of Appendix A to Part 60 of this chapter.

10^{-6} = Conversion factor for ppm.

Z = Production rate (kg/hr).[38]

(2) Test Method 107 is to be used to determine the concentration of vinyl chloride in each inprocess wastewater stream for which an emission limit is prescribed in § 61.65(b)(9)(i).

(3) Where a stripping operation is used to attain the emission limit in § 61.64(e), emissions are to be determined using Test Method 107 as follows:

(i) The number of strippers and samples and the types and grades of resin to be sampled are to be determined by the Administrator for each individual plant at the time of the test based on the plant's operation.

(ii) Each sample is to be taken immediately following the stripping operation.

(iii) The corresponding quantity of material processed by each stripper is to be determined on a dry solids basis and by a method submitted to and approved by the Administrator.

(iv) At the prior request of the Administrator, the owner or operator shall provide duplicates of the samples required in paragraph (g)(3)(i) of this section.

(4) Where control technology other than or in addition to a stripping operation is used to attain the emission limit in § 61.64(e), emissions are to be determined as follows:

(i) Test Method 106 is to be used to determine atmospheric emissions from all of the process equipment simultaneously. The requirements of paragraph (g)(1) of this section are to be met.

(ii) Test Method 107 is to be used to determine the concentration of vinyl chloride in each inprocess wastewater stream subject to the emission limit prescribed in § 61.64(e). The mass of vinyl chloride in kg/100 kg product in each in process wastewater stream is to be determined by using the following equation:

$$C_{a1} = \frac{[C_a R\ 10^{-6}]\ [100]}{Z}$$

where:

C_{a1} = kg vinyl chloride/100 kg product.

C_a = the concentration of vinyl chloride as measured by Test Method 107.

R = water flow rate in l/hr, determined in accordance with a method which has been submitted to and approved by the Administrator.

10^{-6} = Conversion factor for ppm.

Z = Production rate (kg/hr), determined in accordance with a method which has been submitted and approved by the Administrator.

(5) The reactor opening loss for which an emission limit is prescribed in § 61.64(b)(2) is to be determined. The number of reactors for which the determination

is to be made is to be specified by the Administrator for each individual plant at the time of the determination based on the plant's operation. For a reactor that is also used as a stripper, the determination may be made immediately following the stripping operation.

(i) Except as provided in paragraph (g)(5)(ii) of this section, the reactor opening loss is to be determined using the following equation:

$$C = \frac{W\ (2.60)\ (10^{-6})\ (Cb)}{YZ}$$

where:

C = kg vinyl chloride emissions/kg product.
W = Capacity of the reactor in m^3.
2.60 = Density of vinyl chloride at one atmosphere and 25° C in kg/m^3.
10^{-6} = Conversion factor for ppm.
Cb = ppm by volume vinyl chloride as determined by Test Method 106 or a portable hydrocarbon detector which measures hydrocarbons with a sensitivity of at least 10 ppm.
Y = Number of batches since the reactor was last opened to the atmosphere.
Z = Average kg of polyvinyl chloride produced per batch in the number of batches since the reactor was last opened to the atmosphere.

(A) If Method 106 is used to determine the concentration of vinyl chloride (Cb), the sample is to be withdrawn at a constant rate with a probe of sufficient length to reach the vessel bottom from the manhole. Samples are to be taken for 5 minutes within 6 inches of the vessel bottom, 5 minutes near the vessel center, and 5 minutes near the vessel top.

(B) If a portable hydrocarbon detector is used to determine the concentration of vinyl chloride (Cb), a probe of sufficient length to reach the vessel bottom from the manhole is to be used to make the measurements. One measurement will be made within 6 inches of the vessel bottom, one near the vessel center and one near the vessel top. Measurements are to be made at each location until the reading is stabilized. All hydrocarbons measured are to be assumed to be vinyl chloride.

(C) The production rate of polyvinyl chloride (Z) is to be determined by a method submitted to and approved by the Administrator.

(ii) A calculation based on the number of evacuations, the vacuum involved, and the volume of gas in the reactor is hereby approved by the Administrator as an alternative method for determining reactor opening loss for postpolymerization reactors in the manufacture of bulk resins.

Clean Air Act as amended (42 U.S.C. 7414(1), 7607)

§ 61.68 Emission monitoring.

(a) A vinyl chloride monitoring system is to be used to monitor on a continuous basis the emissions from the sources for which emission limits are prescribed in § 61.62(a) and (b), § 61.63(a), and § 61.64(a)(1), (b), (c), and (d), and for any control system to which reactor emissions are required to be ducted in § 61.64(a)(2) or to which fugitive emissions are required to be ducted in § 61.66 (b)(1)(ii), and (b)(2), (b)(5), (b)(6)(ii), and (b)(9)(ii).[30]

(b) The vinyl chloride monitoring system(s) used to meet the requirement in paragraph (a) of this section is to be a device which obtains air samples from one or more points on a continuous sequential basis and analyzes the samples with gas chromotography or, if the owner or operator assumes that all hydrocarbons measured are vinyl chloride, with infrared spectrophotometry, flame ion detection, or an equivalent or alternative method. The vinyl chloride monitoring system used to meet the requirements in § 61.65(b)(8)(i) may be used to meet the requirements of this section.

(c) A daily span check is to be conducted for each vinyl chloride monitoring system used. For all of the emission sources listed in paragraph (a) of this section, except the one for which an emission limit is prescribed in § 61.62(b), the daily span check is to be conducted with a concentration of vinyl chloride equal to 10 ppm. For the emission source for which an emission limit is prescribed in § 61.62(b), the daily span check is to be conducted with a concentration of vinyl chloride which is determined to be equivalent to the emission limit for that source based on the emission test required by § 61.67. The calibration is to be done with either:

(1) A calibration gas mixture prepared from the gases specified in sections 5.2.1 and 5.2.2 of Test Method 106 and in accordance with section 7.1 of Test Method 106, or[31]

(2) A calibration gas cylinder standard containing the appropriate concentration of vinyl chloride. The gas composition of the calibration gas cylinder standard is to have been certified by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration does not change greater than ±5 percent from the certified value. The date of gas cylinder preparation, certified vinyl chloride concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the manufacturer to the buyer. If a gas chromatograph is used as the vinyl chloride monitoring system, these gas mixtures may be directly used to prepare a chromatograph calibration curve as described in section 7.3 of Test Method 106. The requirements in sections 5.2.3.1 and 5.2.3.2 of Test Method 106 for certification of cylinder standards and for establishment and verification of calibration standards are to be followed.[32]

Clean Air Act as amended (42 U.S.C. 7414(1), 7607)

§ 61.69 Initial report.

(a) An owner or operator of any source to which this subpart applies shall submit a statement in writing notifying the Administrator that the equipment and procedural specifications in § 61.66 (b)(1), (b)(2), (b)(3), (b)(4), (b)(5), (b)(6), (b)(7), and (b)(8) are being implemented.

(b)(1) In the case of an existing source or a new source which has an initial startup date preceding the effective date, the statement is to be submitted within 90 days of the effective date, unless a waiver of compliance is granted under § 61.11, along with the information required under § 61.10. If a waiver of compliance is granted, the statement is to be submitted on a date scheduled by the Administrator.

(2) In the case of a new source which did not have an initial startup date preceding the effective date, the statement is to be submitted within 90 days of the initial startup date.

(c) The statement is to contain the following information:

(1) A list of the equipment installed for compliance.

(2) A description of the physical and functional characteristics of each piece of equipment.

(3) A description of the methods which have been incorporated into the standard operating procedures for measuring or calculating the emissions for which emission limits are prescribed in § 61.65 (b)(1)(i) and (b)(6)(i).

(4) A statement that each piece of equipment is installed and that each piece of equipment and each procedure is being used.

Clean Air Act as amended (42 U.S.C. 7414(1), 7607)

§ 61.70 Semiannual report.

(a) The owner or operator of any source to which this subpart applies shall submit to the Administrator on September 15 and March 15 of each year a report in writing containing the information required by this section. The first semiannual report is to be submitted following the first full 6 month reporting period after the initial report is submitted.[33]

(b)(1) In the case of an existing source or a new source which has an initial startup date preceding the effective date, the first report is to be submitted within 180 days of the effective date, unless a waiver of compliance is granted under § 61.11. If a waiver of compliance is granted, the first report is to be submitted on a date scheduled by the Administrator.

(2) In the case of a new source which did not have an initial startup date preceding the effective date, the first report is to be submitted within 180 days of the initial startup date.

(c) Unless otherwise specified, the owner or operator shall use the Test Methods in Appendix B to this part to conduct emission tests as required by paragraphs (c)(2) and (c)(3) of this section, unless an equivalent or an alternative method has been approved by the Administrator. If the Administrator finds reasonable grounds to dispute the results obtained by an equivalent or alternative method, he may require the use

of a reference method. If the results of the reference and equivalent or alternative methods do not agree, the results obtained by the reference method prevail, and the Administrator may notify the owner or operator that approval of the method previously considered to be equivalent or alternative is withdrawn.

(i) The owner or operator shall include in the report a record of any emissions which averaged over any hour period (commencing on the hour) are in excess of the emission limits prescribed in §§ 61.62(a) or (b), § 61.63(a), or § 61.64(a)(1), (b), (c), or (d), or for any control system to which reactor emissions are required to be ducted in § 61.64(a)(2) or to which fugitive emissions are required to be ducted in § 61.66 (b)(1)(ii), (b)(2), (b)(6), (b)(6)(ii), or (b)(6)(iii). The emissions are to be measured in accordance with § 61.68.

(2) In polyvinyl chloride plants for which a stripping operation is used to attain the emission level prescribed in § 61.64(e), the owner or operator shall include in the report a record of the vinyl chloride content in the polyvinyl chloride resin. Test Method 107 is to be used to determine vinyl chloride content as follows:

(i) If batch stripping is used, one representative sample of polyvinyl chloride resin is to be taken from each batch of each grade of resin immediately following the completion of the stripping operation, and identified by resin type and grade and the date and time the batch is completed. The corresponding quantity of material processed in each stripper batch is to be recorded and identified by resin type and grade and the date and time the batch is completed.[38]

(ii) If continuous stripping is used, one representative sample of polyvinyl chloride resin is to be taken for each grade of resin processed or at intervals of 8 hours for each grade of resin which is being processed, whichever is more frequent. The sample is to be taken as the resin flows out of the stripper and identified by resin type and grade and the date and time the sample was taken. The corresponding quantity of material processed by each stripper over the time period represented by the sample during the eight hour period, is to be recorded and identified by resin type and grade and the date and time it represents.

(iii) The quantity of material processed by the stripper is to be determined on a dry solids basis and by a method submitted to and approved by the Administrator.

(iv) At the prior request of the Administrator, the owner or operator shall provide duplicates of the samples required in paragraphs (e)(2)(i) and (e)(2)(ii) of this section.

(v) The report to the Administrator by the owner or operator is to include the vinyl chloride content found in each sample required by paragraphs (e)(2)(i) and (e)(2)(ii) of this section, averaged separately for each type of resin, over each calendar day and weighted according to the quantity of each grade of resin processed by the stripper(s) that calendar day, according to the following equation:

$$A_{T_i} = \frac{\sum_{j=1}^{n} P_{e_j} M_{e_j}}{Q_{T_i}} = \frac{P_{e_1} M_{e_1} + P_{e_2} M_{e_2} + \cdots + P_{e_n} M_{e_n}}{Q_{T_i}}$$

where:

A = 24-hour average concentration of type T_i resin in ppm (dry weight basis).
Q = Total production of type T_i resin over the 24-hour period, in kg.
T_i = Type of resin: $i = 1, 2 \ldots m$ where m is total number of resin types produced during the 24-hour period.
M = Concentration of vinyl chloride in one sample of grade G_j resin, in ppm.
P = Production of grade G_j resin represented by the sample, in kg.
G_j = Grade of resin: e.g., G_1, G_2, and G_n.
n = Total number of grades of resin produced during the 24-hour period.[38]

(vi) The owner or operator shall retain at the source and make available for inspection by the Administrator for a minimum of 2 years records of all data needed to furnish the information required by paragraph (c)(2)(v) of this section. The records are to contain the following information:

(A) The vinyl chloride content found in all the samples required in paragraphs (c)(2)(i) and (c)(2)(ii) of this section, identified by the resin type and grade and the time and date of the sample, and

(B) The corresponding quantity of polyvinyl chloride resin processed by the stripper(s), identified by the resin type and grade and the time and date it represents.

(3) The owner or operator shall include in the report a record of the emissions from each reactor opening for which an emission limit is prescribed in § 61.64(a)(2). Emissions are to be determined in accordance with § 61.67(g)(5), except that emissions for each reactor are to be determined. For a reactor that is also used as a stripper, the determination may be made immediately following the stripping operation.

Secs. 114 of the Clean Air Act as amended (42 U.S.C. 7414)).[38] [47]

§ 61.71 Recordkeeping.

(a) The owner or operator of any source to which this subpart applies shall retain the following information at the source and make it available for inspection by the Administrator for a minimum of two years:

(1) A record of the leaks detected by the vinyl chloride monitoring system, as required by § 61.65(b)(5), including the concentrations of vinyl chloride measured, analyzed, and recorded by the vinyl chloride detector, the location of each measurement and the date and approximate time of each measurement.

(2) A record of the leaks detected during routine monitoring with the portable hydrocarbon detector and the action taken to repair the leaks, as required by § 61.65(b)(5), including a brief statement explaining the location and cause of each leak detected with the portable hydrocarbon detector, the date and time of the leak, and any action taken to eliminate that leak.[38]

(3) A record of emissions measured in accordance with § 61.68.[38]

(4) A daily operating record for each polyvinyl chloride reactor, including pressure and temperature.[38]

Secs. 114 of the Clean Air Act as amended (42 U.S.C. 7414)).[38] [47]

38 FR 8826, 4/6/73 (1)

as amended

41 FR 46560, 10/21/76 (28)
41 FR 53017, 12/3/76 (30)
42 FR 29005, 6/7/77 (38)
42 FR 41424, 8/17/77 (40)
43 FR 8800, 3/3/78 (47)

APPENDIX A

National Emission Standards for Hazardous Air Pollutants

Compliance Status Information

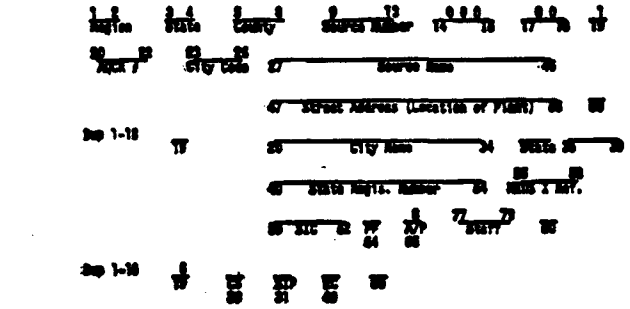
I. SOURCE REPORT

INSTRUCTIONS: Owners or operators of sources of hazardous pollutants subject to the National Emission Standards for Hazardous Air Pollutants are required to submit the information contained in Section I to the appropriate U.S. Environmental Protection Agency Regional Office prior to 90 days after the effective date of any standards or amendments which require the submission of such information.

A list of regional offices is provided in §61.04.

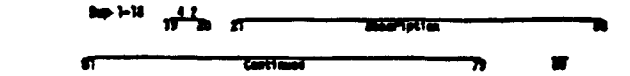
A. SOURCE INFORMATION

1. Identification/Location - Indicate the name and address of each source.

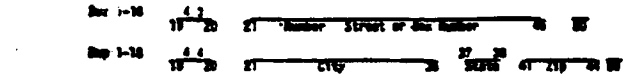


2. Contact - Indicate the name and telephone number of the owner or operator or other responsible official whom EPA may contact concerning this report.

3. Source Description - Briefly state the nature of the source (e.g., "chlor-alkali plant" or "uranium dryer").



4. Alternative Mailing Address - Indicate an alternative mailing address if correspondence is to be directed to a location different than that specified above.



5. Compliance Status - The emissions from this source ___ can ___ cannot meet the emission limitations contained in the National Emission Standards on or prior to 90 days after the effective date of any standards or amendments which require the submission of such information.

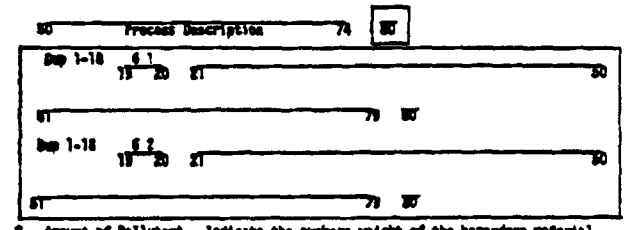
_____
Signature of Owner, Operator or Other Responsible Official

NOTE: If the emissions from the source will exceed these limits set by the National Emission Standards for Hazardous Air Pollutants, the source will be in violation and subject to Federal enforcement actions unless granted a waiver of compliance by the Administrator of the U.S. Environmental Protection Agency. The information needed for such waivers is listed in Section II of this form.

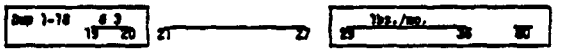
8. PROCESS INFORMATION. Part B should be completed separately for each point of emission for each hazardous pollutant. (Sources subject to 61.22(i) may omit number 4, below.)

A. Pollutant Emitted - Indicate the type of hazardous pollutant emitted by the process. Indicate "AS" for asbestos, "BE" for beryllium, or "HG" for mercury.

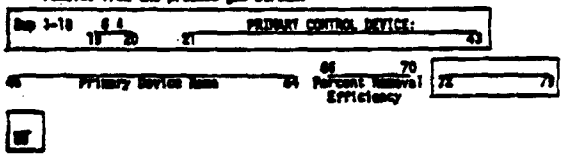
B. Process Description - Provide a brief description of each process (e.g., "hydrogen and box" in a mercury chlor-alkali plant, "grinding machine" in a beryllium machine shop). Use additional sheets if necessary.



C. Amount of Pollutant - Indicate the average weight of the hazardous material named in Item I which enters the process in pounds per month (based on the previous twelve months of operation).



D. Control Devices
a. Indicate the type of pollution control devices, if any, used to reduce the emissions from the process (e.g., venturi scrubber, baghouse, wet cyclone) and the estimated percent of the pollutant which the device removes from the process gas stream.



II. WAIVER REQUESTS

A. WAIVER OF COMPLIANCE. Owners or operators of sources unable to operate in compliance with the National Emission Standards for Hazardous Air Pollutants prior to 90 days after the effective date of any standards or amendments which require the submission of such information may request a waiver of compliance from the Administrator of the U.S. Environmental Protection Agency for the time period necessary to install appropriate control devices or make modifications to achieve compliance. The Administrator may grant a waiver of compliance with the standard for a period not exceeding two years from the effective date of the hazardous pollutant standards, if he finds that such period is necessary for the installation of controls and that steps will be taken during the period of the waiver to assure that the health of persons will be protected from imminent endangerment.

The report information provided in Section I must accompany this application. Applications should be sent to the appropriate EPA regional office.

1. Processes Involved - Indicate the process or processes emitting hazardous pollutants to which emission controls are to be applied.

2. Controls

   a. Describe the proposed type of control device to be added or modification to be made to the process to reduce the emissions of hazardous pollutants to an acceptable level. (Use additional sheets if necessary.)

   b. Describe the measures that will be taken during the waiver period to assure that the health of persons will be protected from imminent endangerment. (Use additional sheets if necessary.)

3. Increments of Progress - Specify the dates by which the following increments of progress will be met.

   - Date by which contracts for emission control systems or process modifications will be awarded; or date by which orders will be issued for the purchase of the component parts to accomplish emission control or process modification.

Rep 1-16 017 17–19 20–24 25–60 61 MO/DY/YR 66 67

   - Date of initiation of on-site construction or installation of emission control equipment or process change.

Rep 1-16 027 17–19 20–24 25–60 61 MO/DY/YR 66 67

   - Date by which on-site construction or installation of emission control equipment or process modification is to be completed.

Rep 1-16 037 17–19 20–24 25–60 61 MO/DY/YR 66 67

   - Date by which final compliance is to be achieved.

Rep 1-16 047 17–19 20–24 25–60 61 MO/DY/YR 66 67

B. WAIVER OF EMISSION TESTS. A waiver of emission testing may be granted to owners or operators of sources of beryllium or mercury pollutants if, in the judgment of the Administrator of the Environmental Protection Agency the emissions from the source comply with the appropriate standard or if the owners or operators of the source have requested a waiver of compliance or have been granted a waiver of compliance.

This application should accompany the report information provided in Section I.

1. Reason - State the reasons for requesting a waiver of emission testing. If the reason stated is that the emissions from the source are within the prescribed limits, documentation of this condition must be attached.

_____

_____

_____ _____

Date Signature of the owner or operator

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)).

Method 106—Determination of Vinyl Chloride from Stationary Sources

Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling, as there are many details that are beyond the scope of this presentation. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. Principle and Applicability.

1.1 An integrated bag sample of stack gas containing vinyl chloride (chloroethene) is subjected to chromatographic analysis, using a flame ionization detector.[38]

1.2 The method is applicable to the measurement of vinyl chloride in stack gases from ethylene dichloride, vinyl chloride and polyvinyl chloride manufacturing processes, except where the vinyl chloride is contained in particulate matter.

2. Range and Sensitivity.

The lower limit of detection will vary according to the chromatograph used. Values reported include 1×10^{-7} mg and 4×10^{-4} mg.

3. *Interferences.* Acetaldehyde, which can occur in some vinyl chloride sources, will interfere with the vinyl chloride peak from the Chromosorb 102[1] column. See sections 4.3.3 and 6.4. If resolution of the vinyl chloride peak is still not satisfactory for a particular sample, then chromatograph parameters can be further altered with prior approval of the Administrator. If alteration of the chromatograph parameters fails to resolve the vinyl chloride peak, then supplemental confirmation of the vinyl chloride peak through an absolute analytical techniques, such as mass spectroscopy, must be performed.[39]

4. Apparatus.

4.1 *Sampling* (Figure 106-1).[38]

4.1.1 Probe—Stainless steel, Pyrex glass, or Teflon tubing according to stack temperature, each equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample line—Teflon, 6.4 mm outside diameter, of sufficient length to connect probe to bag. A new unused piece is employed for each series of bag samples that constitutes an emission test.

4.1.3 Male (2) and female (2) stainless steel quick-connects, with ball checks (one pair without) located as shown in Figure 106-1.[38]

4.1.4 Tedlar bags, 100 liter capacity—To contain sample. Teflon bags are not acceptable. Aluminized Mylar bags may be used, provided that the samples are analyzed within 24 hours of collection.

4.1.5 Rigid leakproof containers for 4.1.4, with covering to protect contents from sunlight.

4.1.6 Needle valve—To adjust sample flow rate.

4.1.7 Pump—Leak-free. Minimum capacity 2 liters per minute.

4.1.8 Charcoal tube—To prevent admission of vinyl chloride to atmosphere in vicinity of sampler.

4.1.9 Flow meter—For observing sample flow rate; capable of measuring a flow range from 0.10 to 1.00 liter per minute.

4.1.10 *Connecting tubing.* Teflon, 6.4 mm outside diameter, to assemble sample train (Figure 106-1).[38]

4.1.11 Pitot tube—Type S (or equivalent), attached to the probe so that the sampling flow rate can be regulated proportional to the stack gas velocity.

4.2 Sample recovery.

4.2.1 Tubing—Teflon, 6.4 mm outside diameter, to connect bag to gas chromatograph sample loop. A new unused piece is employed for each series of bag samples that constitutes an emission test, and is to be discarded upon conclusion of analysis of those bags.

4.3 Analysis.

4.3.1 Gas chromatograph—With flame ionization detector, potentiometric strip chart recorder and 1.0 to 5.0 ml heated sampling loop in automatic sample valve.

4.3.2 *Chromatographic column.* Stainless steel, 2 m×3.3 mm, containing 80/100 mesh Chromosorb 102. A secondary column of GE SF-96, 20 percent on 60/80 mesh AW Chromosorb P, stainless steel, 2 m×3.3 mm or Porepak T, 80/100 mesh, stainless steel, 1 m×3.3 mm is required if acetaldehyde is present. If used, a secondary column is placed after the Chromosorb 102 column. The combined columns should then be operated at 120° C.[38]

4.3.3 Flow meters (2)—Rotameter type, 0 to 100 ml/min capacity, with flow control valves.

4.3.4 Gas regulators—For required gas cylinders.

4.3.5 Thermometer—Accurate to one degree centigrade, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer—Accurate to 5 mm Hg, to measure atmospheric pressure around gas chromatograph during sample analysis.

4.3.7 Pump—Leak-free. Minimum capacity 100 ml/min.

4.4 Calibration.

4.4.1 Tubing—Teflon, 6.4 mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar bags—Sixteen-inch square size, separate bag marked for each calibration concentration.

4.4.3 Syringe—0.5 ml, gas tight.

4.4.4 Syringe—50-ml, gas tight.

4.4.5 Flow meter—Rotameter type, 0 to 1000 ml/min range accurate to ±1%, to meter nitrogen in preparation of standard gas mixtures.

4.4.6 Stop watch—Of known accuracy, to time gas flow in preparation of standard gas mixtures.

5. Reagents. It is necessary that all reagents be of chromatographic grade.

5.1 Analysis.

5.1.1 Helium gas or nitrogen gas—Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen gas—Zero grade.

5.1.3 Oxygen gas, or Air, as required by the detector—Zero grade.

5.2 *Calibration.* Use one of the following options: either 5.2.1 and 5.2.3, or 5.2.2.[38]

5.2.1 *Vinyl chloride, 99.9+ percent.* Pure vinyl chloride gas certified by the manufacturer to contain a minimum of 99.9 percent vinyl chloride for use in the preparation of standard gas mixtures in Section 7.1. If the gas manufacturer maintains a bulk cylinder supply of 99.9+ percent vinyl chloride, the certification analysis may have been performed on this supply rather than on each gas cylinder prepared from this bulk supply. The date of gas cylinder preparation and the certified analysis must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer.[38]

5.2.2 *Nitrogen gas.* Zero grade, for preparation of standard gas mixtures.[38]

5.2.3 *Cylinder standards* (3). Gas mixture standards (50, 10, and 5 ppm vinyl chloride in nitrogen cylinders) for which the gas composition has been certified by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration does not change greater than ±5 percent from the certified value. The date of gas cylinder preparation, certified vinyl chloride concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer. These gas mixture standards may be directly used to prepare a chromatograph calibration curve as described in section 7.3.[38]

5.2.3.1 *Cylinder standards certification.* The concentration of vinyl chloride in nitrogen in each cylinder must have been certified by the manufacturer by a direct analysis of each cylinder using an analytical procedure that the manufacturer had calibrated on the day of cylinder analysis. The calibration of the analytical procedure shall, as a minimum, have utilized a three-point calibration curve. It is recommended that the manufacturer maintain two calibration standards and use these standards in the following way: (1) A high concentration standard (between 50 and 100 ppm) for preparation of a calibration curve by an appropriate dilution technique; (2) a low concentration standard (between 5 and 10 ppm) for verification of the dilution technique used.[38]

5.2.3.2 *Establishment and verification of calibration standards.* The concentration of each calibration standard must have been established by the manufacturer using reliable procedures. Additionally, each calibration standard must have been verified by the manufacturer by one of the following procedures, and the agreement between the initially determined concentration value and the verification concentration value must be within ± 5 percent: (1) verification value determined by comparison with a calibrated vinyl chloride permeation tube, (2) verification value determined by comparison with a gas mixture prepared in accordance with the procedure described in section 7.1 and using 99.9+ percent vinyl chloride, or (3) verification value obtained by having the calibration standard analyzed by the National Bureau of Standards. All calibration standards must be renewed on a time interval consistent with the shelf life of the cylinder standards sold.[38]

6. Procedure.

6.1 Sampling. Assemble the sample train as in Figure 106-1. Perform a bag leak check according to Section 7.4. Observe that all connections between the bag and the probe are tight. Place the end of the probe at the centroid of the stack and start the pump with the needle valve adjusted to yield a flow of 0.5 lpm. After a period of time sufficient to purge the line several times has elapsed, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate proportional to the stack velocity. Direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

6.2 *Sample storage.* Sample bags must be kept out of direct sunlight. When at all possible analysis is to be performed within 24 hours, but in no case in excess of 72 hours of sample collection.[38]

6.3 Sample recovery. With a piece of Teflon tubing identified for that bag, connect a

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[1] Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

bag inlet valve to the gas chromatograph sample valve. Switch the valve to withdraw gas from the bag through the sample loop. Plumb the equipment on the sample gas passes from the sample valve to the leak-free pump, and then to a charcoal tube, followed by a 0–100 ml/min rotameter with flow control valve.

6.4 Analysis. Set the column temperature to 100° C, the detector temperature to 150° C, and the sample loop temperature to 70° C. When optimum hydrogen and oxygen flow rates have been determined verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 40 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for thirty seconds at the rate of 100 ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed and the attenuator setting. Record the laboratory pressure. From the chart, select the peak having the retention time corresponding to vinyl chloride, as determined in Section 7.2. Measure the peak area, A_m, by use of a disc integrator or a planimeter. Measure the peak height, H_m. Record A_m, H_m, and the retention time. Repeat the injection at least two times or until two consecutive vinyl chloride peaks do not vary in area more than 5%. The average value for these two areas will be used to compute the bag concentration.[3]

Compare the ratio of H_m to A_m for the vinyl chloride sample with the same ratio for the standard peak which is closest in height. As a guideline, if these ratios differ by more than 10%, the vinyl chloride peak may not be pure (possibly acetaldehyde is present) and the secondary column should be employed (see Section 4.1.2).

6.5 Measure the ambient temperature and barometric pressure near the bag. (Assume the relative humidity to be 100 percent.) From a water saturation vapor pressure table, determine and record the water vapor content of the bag.[3]

7. Calibration and Standards.

7.1 *Preparation of vinyl chloride standard gas mixtures.* Evacuate a nitrogen-flush mylar Tedlar bag that has passed a leak check (described in Section 7.6) and sweep in 5 liters of nitrogen. While the bag is filling, use the 0.5 ml syringe to inject 250 μl of 99.9+ percent vinyl chloride through the wall of the bag. Upon withdrawing the syringe needle, immediately cover the resulting hole with a piece of adhesive tape. The bag now contains a vinyl chloride concentration of 50 ppm. In a like manner use the other syringes to prepare gas mixtures having 10 and 5 ppm vinyl chloride concentrations. Place each bag on a smooth surface and alternately depress opposite sides of the bag 50 times to further mix the gases. These gas mixture standards may be used for 14 days from the date of preparation, after which time preparation of new gas mixtures is required. (Caution.—Contamination may be a problem when a bag is reused if the new gas mixture standard contains a lower concentration than the previous gas mixture standard did.)[3]

7.2 Determination of vinyl chloride retention time. This section can be performed simultaneously with Section 7.3. Establish chromatograph conditions identical with those in Section 6.3, above. Set attenuator to X 1 position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed and the attenuator setting. Record peaks and detector responses that occur in the absence of vinyl chloride. Maintain conditions. With the equipment plumbing arranged identically to Section 6.3, flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the vinyl chloride calibration mixtures and activate the sample valve. Record the injection time. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This quantity, divided by the chart speed, is defined as the retention time record.

7.3 *Preparation of chromatograph calibration curve.* Make a gas chromatographic measurement of each gas mixture standard (described in section 6.2.3 or 7.1) using conditions identical with those listed in sections 6.3 and 6.4. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with each standard gas mixture and activate the sample valve. Record C_c, the concentration of vinyl chloride injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate A_c, the peak area multiplied by the attenuator setting. Repeat until two injection areas are within 5 percent, then plot these points v. C_c. When the other concentrations have been plotted, draw a smooth curve through the points. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.[3]

7.4 Bag leak checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks as follows. To leak check, connect a water manometer and pressurize the bag to 6–10 cm H_2O (2–4 in H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. Also check the rigid container for leaks in this manner.

(Note: An alternative leak check method is to pressurize the bag to 6–10 cm H_2O or 2–4 in. H_2O and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in-line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

8. Calculations.

8.1 Determine the sample peak area as follows:

$$A_c = A_m A_f$$

Equation 106–1

where:
A_c = The sample peak area.
A_m = The measured peak area.
A_f = The attenuation factor.

8.2 Vinyl chloride concentrations. From the calibration curve described in Section 7.3, above, select the value of C, that corresponds to A_c, the sample peak area. Calculate C_v as follows:

$$C_v = \frac{C_c P_r T_s}{P_s T_r (1 - B_{ws})}$$

Equation 106–2

Where:
B_{ws} = The water vapor content of the bag sample, as analyzed.
C_v = The concentration of vinyl chloride in the bag sample in ppm.
C_c = The concentration of vinyl chloride indicated by the gas chromatograph, in ppm.
P_r = The reference pressure, the laboratory pressure recorded during calibration, mm Hg.
T_s = The sample loop temperature, or the absolute temperature of the sample at the time of analysis, °K.
P_s = The laboratory pressure at time of analysis, mm Hg.
T_r = The reference temperature, the sample loop temperature recorded during calibration, °K.

9. References.

1. Brown, D. W., Loy, E. W. and Stephenson, M. E. "Vinyl Chloride Monitoring Near the B. F. Goodrich Chemical Company in Louisville, Kentucky." Region IV, U.S. Environmental Protection Agency, Surveillance and Analysis Division, Athens, Georgia, June 24, 1974.

2. "Evaluation of A Collection and Analytical Procedure for Vinyl Chloride in Air," by G. D. Clayton and Associates, December 13, 1974. EPA Contract No. 68-02-1408, Task Order No. 2. EPA Report #N. 75-VCL-1.

3. "Standardization of Stationary Source Emission Method for Vinyl Chloride," by Midwest Research Institute, 1976. EPA Contract No. 68-02-1098, Task Order No. 7.

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)).

Method 107—Determination of Vinyl Chloride Content of Inprocess Wastewater Samples, and Vinyl Chloride Content of Polyvinyl Chloride Resin, Slurry, Wet Cake, and Latex Samples

Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with sampling, as there are many details that are beyond the scope of this presentation. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. Principle and Applicability.

1.1 The basis for this method relates to the vapor equilibrium which is established between RVCM, PVC, resin, water, and air in a closed system. It has been demonstrated that the RVCM in a PVC resin will equilibrate in a closed vessel quite rapidly, provided that the temperature of the PVC resin is maintained above the glass transition temperature of that specific resin.

1.2 This procedure is suitable for determining the vinyl choride monomer (VCM) content of inprocess wastewater samples, and the residual vinyl chloride monomer (RVCM) content of polyvinyl chloride (PVC) resins, wet cake, slurry, and latex samples. It cannot be used for polymer in fused forms, such as sheet or cubes. If a resolution of the vinyl chloride peak is not satisfactory for a particular sample, then chromatograph parameters may be altered provided that the precision and reproducibility of the analysis of vinyl chloride cylinder standards are not impaired. If there is reason to believe that some other hydrocarbon with an identical retention time is present in the sample, then supplemental confirmation of the vinyl chloride peak through an absolute analytical technique, such as mass spectroscopy, should be performed.[36]

2. Range and Sensitivity.

The lower limit of detection of vinyl chloride will vary according to the chromatograph used. Values reported include 1×10^{-7} mg and 4×10^{-7} mg. With proper calibration, the upper limit may be extended as needed.

3. Precision and Reproducibility.

An interlaboratory comparison between seven laboratories of three resin samples, each split into three parts, yielded a standard deviation of 2.63 % for a sample with a mean of 2.00 ppm, 4.10 % for a sample with a mean of 1.00 ppm, and 5.39 % for a sample with a mean of 62.66 ppm.

4. Safety.

Do not release vinyl chloride to the laboratory atmosphere during preparation of standards. Venting or purging with VCM/air mixtures must be held to a minimum. When they are required, the vapor must be routed to outside air. Vinyl chloride, even at low ppm levels, must never be vented inside the laboratory. After vials have been analyzed, the pressure within the vial must be vented prior to removal from the instrument turntable. Vials must be vented into an activated charcoal tube using a hypodermic needle to prevent release of vinyl chloride into the laboratory atmosphere. The charcoal must be replaced prior to vinyl chloride breakthrough.

5. Apparatus.

5.1 Sampling.

5.1.1 Bottles—60 ml (2 oz), with vented lined screw on tops, for PVC samples.

5.1.2 Vials—20 ml Hypo-vials,[1] sealed with Teflon faced Tuf-Bond discs for water samples.

5.1.3 Electrical tape—or equivalent, to prevent loosening of bottle tops.

5.2 Sample recovery.

5.2.1 Vials—With seals and caps, Perkin-Elmer Corporation No. 109-0118, or equivalent.

5.2.2 Analytical balance—Capable of weighing to ±0.001 gram.

5.2.3 Syringes, 100 μl—Precision Series "A" No. 010025, or equivalent.

5.2.4 Vial Sealer, Perkin-Elmer No. 109-0106 or equivalent.

5.3 Analysis.

5.3.1 Gas chromatograph—Perkin-Elmer Corporation Model F-40 head-space analyzer, No. 109-0001, or equivalent.

5.3.2 *Chromatographic column.* Stainless steel, 2 m × 3.2 mm, containing 0.4 percent Carbowax 1500 on Carbopak A, Perkin-Elmer Corporation No. 109-0123, or equivalent. Carbopak C can be used in place of Carbopak A. If methanol and/or acetaldehyde is present in the sample, a pair of Poropak Q columns in series (1 m × 3.2 mm followed by 2 m × 3.2 mm) with provision for backflush of the first column has been shown to provide adequate separation of vinyl chloride.[36]

5.3.3 Thermometer—0 to 100° C, accurate to ±0.1° C, Perkin-Elmer No. 109-0109 or equivalent.

5.3.4 Sample tray thermostat system—Perkin-Elmer No. 109-0103, or equivalent.

5.3.5 Septa—Sandwich type, for automatic dosing, 13 mm, Perkin-Elmer No. 109-1008, or equivalent.

5.3.6 Integrator - recorder — Hewlett - Packard Model 3380A, or equivalent.

5.3.7 Filter drier assembly (3)—Perkin-Elmer No. 2230117, or equivalent.

5.3.8 Soap film flowmeter—Hewlett Packard No. 0101-0112, or equivalent.

5.4 Calibration.

5.4.1 Regulators—for required gas cylinders.

6. Reagents.

6.1 Analysis.

6.1.1 Hydrogen gas—zero grade.

6.1.2 Nitrogen gas—zero grade.

6.1.3 Air—zero grade.

6.2 *Calibration.*

6.2.1 *Cylinder standards* (4). Gas mixture standards (80, 200, 2,000, and 4,000 ppm vinyl chloride in nitrogen cylinders) for which the gas composition has been certified by the manufacturer. Lower concentration standards should be obtained if lower concentrations of vinyl chloride samples are expected, as the intent is to bracket the sample concentrations with standards. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration does not change greater than ±5 percent from the certified value. The date of gas cylinder preparation, certified vinyl chloride concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the manufacturer to the buyer.[36]

6.2.1.1 *Cylinder standards certification.* The concentration of vinyl chloride in nitrogen in each cylinder must have been certified by the manufacturer by a direct analysis of each cylinder using an analytical procedure that the manufacturer had calibrated on the day of cylinder analysis. The calibration of the analytical procedure shall, as a minimum, have utilized a three-point calibration curve. It is recommended that the manufacturer maintain two calibration standards and use these standards in the following way: (1) A high concentration standard (between 4,000 and 8,000 ppm) for preparation of a calibration curve by an appropriate dilution technique; (2) a low concentration standard (between 50 and 500 ppm); for verification of the dilution technique used.[36]

6.2.1.2 *Establishment and verification of calibration standards.* The concentration of each calibration standard must have been established by the manufacturer using reliable procedures. Additionally, each calibration standard must have been verified by the manufacturer by one of the following procedures, and the agreement between the initially determined concentration value and the verification concentration value must be within ±5 percent: (1) Verification value determined by comparison with a gas mixture standard generated in a similar manner to the procedure described in section 7.1 of Method 106 for preparing gas mixture standards using 99.9+ percent vinyl chloride, or (2) verification value obtained by having the calibration standard analyzed by the National Bureau of Standards. All calibration standards must be renewed on a time interval consistent with the shelf life of the cylinder standards sold.[36]

7. Procedure.

7.1 Sampling.

7.1.1 PVC sampling—Allow the resin or slurry to flow from a tap on the tank or silo until the tap line has been well purged. Extend a 60 ml sample bottle under the tap, fill, and immediately tightly cap the bottle. Wrap electrical tape around the cap and bottle to prevent the top from loosening. Place an identifying label on each bottle, and record the date, time, and sample location both on the bottles and in a log book.

7.1.2 Water sampling—Prior to use, the 20 ml vials (without the discs) must be capped with aluminum foil and muffled at 400°C for at least one hour to destroy or remove any organic matter that could interfere with analysis. At the sampling location fill the vials bubble-free, to overflowing so that a convex meniscus forms at the top. The excess water is displaced as the sealing disc is carefully placed, Teflon side down, on the opening of the vial. Place the aluminum seal over the disc and the neck of the vial and crimp into place. Affix an identifying label on the bottle, and record the date, time, and sample location both on the vials and in a log book. All samples must be kept refrigerated until analyzed.

7.2 Sample recovery. Samples must be run within 24 hours.

7.2.1 Resin samples—The weight of the resin used must be between 0.1 and 4.5 grams. An exact weight must be obtained (±0.001 gram) for each sample. In the case of suspension resins a volumetric cup can be prepared which will hold the required amount of sample. The sample bottle is opened, and the cup volume of resin is added to the tared sample vial (including septum and aluminum cap). The vial is immediately sealed and the exact sample weight is then obtained. Report this value on the data sheet as it is required for calculation of RVCM. In the case of relatively dry resin samples (water content <0.2 weight %), 100 μl of distilled water must be injected into the vial, after sealing and weighing, using a 100 μl syringe. In the case of dispersion resins, the cup cannot be used. The sample is instead weighed approximately in an aluminum dish, transferred to the tared vial and weighed accurately in the vial. The sample is then placed in the Perkin-Elmer head space analyzer (or equivalent) and conditioned for one hour at 90°C.

NOTE: Some aluminum vial caps have a center section which must be removed prior to placing into sample tray. If not removed,

[1] Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

serious damage to the injection needle will occur.

7.2.2 Suspension resin slurry and wet cake samples—Slurry must be filtered using a small Buchner funnel with vacuum to yield wet cake. The filtering process must be continued only as long as a steady stream of water is exiting from the funnel. Excessive filtration time could result in some loss of VCM. The wet cake sample (0.10 to 4.5 grams) is added to a tared vial (including septum and aluminum cap) and immediately sealed. Sample weight is then determined to 3 decimal places. The sample is then placed in the Perkin-Elmer head space analyzer (or equivalent) and conditioned for one hour at 90°C. A sample of wet cake is used to determine TS (total solids). This is required for calculating the RVCM.

7.2.3 Dispersion resin slurry samples.—This material should not be filtered. Sample must be thoroughly mixed. Using a tared vial (including septum and aluminum cap) add approximately 8 drops (0.25 to 0.35 grams) of slurry or latex using a medicine dropper. This should be done immediately after mixing. Seal the vial as soon as possible. Determine sample weight accurate to 0.001 grams. Total sample weight must not exceed 0.50 grams. Condition the vial for one hour at 90°C in the analyzer. Determine the TS on the slurry sample (Section 7.3.5).

7.2.4 Inprocess wastewater samples—Using a tared vial (including septum and aluminum cap) quickly add approximately 1 cc of water using a medicine dropper. Seal the vial as soon as possible. Determine sample weight accurate to 0.001 gram. Condition the vial for two hours at 90°C in the analyzer.

7.3 Analysis.

7.3.1 Preparation of gas chromatograph—Install the chromatographic column and condition overnight at 150°C. Do not connect the exit end of the column to the detector while conditioning.

7.3.1.1 Flow rate adjustments—Adjust flow rates as follows:

a. Nitrogen carrier gas—Set regulator on cylinder to read 80 psig. Set regulator on chromatograph to 1.3 kg/cm². Normal flows at this pressure should be 25 to 40 cc/minute. Check with bubble flow meter.

b. Burner air supply—Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to supply air to burner at a rate between 250 and 300 cc/minute. Check with bubble flowmeter.

c. Hydrogen supply—Set regulator on cylinder to read 30 psig. Set regulator on chromatograph to supply approximately 25±5 cc/minute. Optimize hydrogen flow to yield the most sensitive detector response without extinguishing the flame. Check flow with bubble meter and record this flow.

7.3.1.2 Temperature adjustments—Set temperatures as follows:

a. Oven (chromatographic column), 80° C.

b. Heating line, 140° C.

c. Injection block, 140° C.

d. Sample chamber, water temperature, 90° C±1.0° C.

7.3.1.3 Ignition of flame ionization detector—Ignite the detector according to the manufacturer's instructions.

7.3.1.4 Amplifier balance—Balance the amplifier according to the manufacturer's instructions.

7.3.2 Programming the chromatograph—Program the chromatograph as follows:

a. *L*—Heating time—The normal setting is 3 seconds.

b. A—Analysis time—The normal setting is 0 minutes. Certain types of samples contain high boiling materials which can cause interference with the vinyl chloride peak on subsequent analyses. In these cases the analysis time must be adjusted to eliminate the interference. An automated backflush system can also be used to solve this problem.

c. B—Flushing—The normal setting is 0.3 minutes.

d. W—Stabilization time. The normal setting is 0.3 minutes.[36]

e. K—Number of analyses per sample—The normal setting is 1.

7.3.3 Preparation of sample turntable—Before placing any sample into turntable, be certain that the center section of the aluminum cap has been removed. The numbered sample bottles should be placed in the corresponding numbered positions in the turntable. Insert samples in the following order:

Positions 1 & 2—Old 2000 ppm standards for conditioning. These are necessary only after the analyzer has not been used for 24 hours or longer.

Position 3—50 ppm standard, freshly prepared.

Position 4—500 ppm standard, freshly prepared.

Position 5—2000 ppm standard, freshly prepared.

Position 6—4000 ppm standard, freshly prepared.

Position 7—Sample No. 7 (This is the first sample of the day, but is given as 7 to be consistent with the turntable and the integrator printout.)

After all samples have been positioned, insert the second set of 50, 500, 2000, and 4000 ppm standards. Samples, including standards must be conditioned in the bath of 90° C for 1 hour (not to exceed 5 hours).

7.3.4 Start chromatograph program—When all samples, including standards, have been conditioned at 90° C for 1 hour, start the analysis program according to the manufacturers' instructions. These instructions must be carefully followed when starting and stopping program to prevent damage to the dosing assembly.

7.3.5 Determination of total solids (TS).

For wet cake, slurry, resin solution, and PVC latex samples, determine TS for each sample by accurately weighing approximately 2 to 4 grams of sample in an aluminum pan before and after placing in a draft oven (105 to 110° C). Samples must be dried to constant weight. After first weighing return the pan to the oven for a short period of time and then reweigh to verify complete dryness. TS is then calculated as the final sample weight divided by initial sample weight.

8. Calibration.

Calibration is to be performed each eight-hour period when the instrument is used. Each day, prior to running samples, the column should be conditioned by running two of the previous days 2000 ppm standards.

8.1 Preparation of Standards.

Calibration standards are prepared by filling the vials with the vinyl chloride/nitrogen standards, rapidly seating the septum and sealing with the aluminum cap. Use a stainless steel line from the cylinder to the vial. Do not use rubber or tygon tubing. The sample line from the cylinder must be purged (into hood) for several minutes prior to filling vials. After purging, reduce the flow rate to approximately 500–1000 cc/min. Place end of tubing into vial (near bottom), and after one minute slowly remove tubing. Place septum in vial as soon as possible to minimize mixing air with sample. After the standard vials are sealed, inject 100 μl of distilled water.

8.2 Preparation of chromatograph calibration curve.

Prepare two 50 ppm, two 500 ppm, two 2000 ppm, and two 4000 ppm standard samples. Run the calibration samples in exactly the same manner as regular samples. Plot A_i, the integrator area counts for each standard sample vs C_i, the concentration of vinyl chloride in each standard sample. Draw a line of best fit through the points.

9. Calculations.

9.1 Response factor.

From the calibration curve described in Section 8.2, above, select the value of C_i that corresponds to A_i for each sample. Compute the response factor, R_i, for each sample, as follows:

$$R_i = \frac{A_i}{C_i} \quad \text{Equation 107-1}$$

9.2 Residual vinyl chloride monomer concentration, or vinyl chloride monomer concentration.

Calculate C_{vw} as follows:

$$C_{vw} = \frac{A_i P_o}{R_i T_i}\left(\frac{M_v V_v}{m_s R} + K T_i\right)$$

Equation 107-2

where:

C_{vw} = Concentration of vinyl chloride in the sample, in ppm.

P_o = Laboratory atmosphere pressure, mm Hg.

T_i = Room temperature, °K.

M_v = Molecular weight of VCM (62.5).

V_v = Volume of vapor phase (vial volume less sample volume).

m_s = Weight of sample, grams.

R = Gas constant [62.360 (cc-mm-mole-degrees Kelvin)].

K = Henry's Law constant. For VCM in PVC at 90° C, $K = 6.48 \times 10^{-6} = K_p$. For VCM in 1 cc (approximate) wastewater sample at 90° C, $K = 5.0 \times 10^{-6} = K_w$.

T_i = Equilibration temperature °K.

If the following conditions are met, Equation 107-2 can be simplified as follows:

1. T_i = 22° C (295° K).
2. T_i = 90° (363° K).
3. P_o = 760 mm Hg.
4. $V_v = V_v - \frac{m_s}{1.4} = 23.5 - \frac{m_s}{1.4}$

Where

V_v = Vial volume, cc (23.5).

5. Sample contains less than 0.5 percent water.

$$C_{vw} = \frac{A_i}{R_i}\left(4.197 \times 10^{-4} + \frac{5.988 \times 10^{-3}}{m_s}\right) \quad \text{Equation 107-3}$$

The following general equation can be used for any sample which contains VCM, PVC and water.

$$C_{vw} = \frac{A_i P_o}{R_i T_i} \times \left[\frac{M_v V_v}{R m_s} + K_p (TS) T_i + K_w (1 - TS) T_i\right]$$

Equation 107-4

where:

TS = Total solids.

NOTE: K_v must be determined for samples with a vapor volume to liquid volume ratio other than 22.5 to 1. This ratio can be obtained by adjusting the sample weight through giving consideration to the total solids and density of the PVC.

Results calculated using Equation 107-4 represent concentration based on the total sample. To obtain results based on dry PVC content, divide by TS.

For a 1-cc wastewater sample (that is, 22.5 to 1 vapor volume to liquid volume ratio), K_v is 8.0×10^{-4}. Thus, Equation 107-4 can be simplified to the following:

$$C_{vc} = \frac{A_s}{K_s}\left[\frac{5.988 \times 10^{-1}}{m_s} + (2.066 \times 10^{-1})\right] \qquad \text{Equation 107-5}$$

(Secs. 112 and 301(a) of the Clean Air Act, 42 U.S.C. 1857c-7 and 1857g(a).)[39]

10. References.

a. Residual Vinyl Chloride Monomer Content of Polyvinyl Chloride Resins and Wet Cake Samples, B. F. Goodrich Chemical Co. Standard Test Procedure No. 1005-T. B. F. Goodrich Technical Center, Avon Lake, Ohio. January 30, 1975.

b. Berens, A. R., "The Solubility of Vinyl Chloride in Polyvinyl Chloride," ACS-Division of Polymer Chemistry, Polymer Preprints *15* (2): 197, 1974.

c. Berens, A. R., "The Diffusion of Vinyl Chloride in Polyvinyl Chloride," ACS-Division of Polymer Chemistry, Polymer Preprints *15* (2): 203, 1974.

d. Berens, A. R., L. B. Crider, C. J. Tomasek and J. M. Whitney, Analysis for Vinyl Chloride in PVC Powders by Head-Space Gas Chromatography," to be published.

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)). [40 FR 59547]

APPENDIX B

REGIONAL EPA AND INDUSTRIAL CONTACTS

Table B-1. REGIONAL EPA AND INDUSTRIAL CONTACTS

Region/Company/Division	Date of meeting	Place	Contact	Purpose of meeting
EPA/DSSE	6-19-80	Washington,DC	Rich Biondi	Obtain input from DSSE personnel as to areas of concern to be incorporated into the VC Review Study
Region I (Boston)	8-13-80	Boston	Cathy McNair	Discuss the VC Review Study and obtain input from the Region to the review study's areas of concern.
Region II (New York)	8-12-80	New York	Michael Pucci	Discuss the VC Review Study and obtain input from the Region to the review study's areas of concern.
Region III (Philadelphia)	9-16-80	Philadelphia	Jean Thompson	Discuss the VC Review Study and obtain input from the Region to the review study's areas of concern.

(continued)

Table B-1. Continued

Region/Company/Division	Date of meeting	Place	Contact	Purpose of meeting
Region IV (Atlanta)	8-3-80	Atlanta	Wayne Aronson	Discuss the VC Review Study and obtain input from the Region to the review study's areas of concern.
Region V (Chicago)	8-19-80	Chicago	Bruce Varner	Discuss the VC Review Study and obtain input from the Region to the review study's areas of concern.
Region VI (Dallas)	7-23-80 10-27-80	Dallas	Martin Brittain	Discuss the VC Review Study and obtain input from the Region to the review study's areas of concern.
South Coast Air Quality Monitoring Division (SCAQMD)	10-28-80	El Monte, CA	Doug Newton	(Region IX has designated authority to SCAQMD) Discuss VC Review Study; discuss SCAQMD's Rule 1005.1 which supercedes the VC NESHAP.
Society of the Plastics Industry	7-31-80	EPA, Durham, NC	Robert Laundrie	Discuss the scope of the VC Review Study.

(continued)

Table B-1. Continued

Region/Company/Division	Date of meeting	Place	Contact	Purpose of meeting
Conoco Chemical Company	8-7-80	Lake Charles, LA	Joseph Ledvina	Become familiar with new and existing air pollution control techniques currently being used to control VC emissions; discuss plant processes.
Conoco Chemical Company	10-17-80	TRW, RTP	Joseph Ledvina	Become familiar with new and existing air pollution control techniques currently being used to control VC emissions; discuss containment devices.
Diamond Shamrock Corp.	8-6-80	Deer Park, TX	Alex Evins	Become familiar with new and existing air pollution control techniques currently being used to control VC emissions; discuss plant processes.

(continued)

Table B-1. Continued

Region/Company/Division	Date of meeting	Place	Contact	Purpose of meeting
Diamond Shamrock Corporation	8-6-80	Independence,TX	Alex Evins	Become familiar with new and existing air pollution control techniques currently being used to control VC emissions: discuss plant processes.
Dow Chemical Company	8-5-80	Oyster Creek, TX	Robert Oubre	Become familiar with new and existing air pollution control techniques currently being used to control VC emissions; discuss plant processes.
Dow Chemical Company	9-11-80	Midland, MI	Robert Ammons	Become familiar with new and existing air pollution control techniques currently being used to control VC emissions; discuss plant processes.
General Tire & Rubber Co.	9-10-80	Astabula, OH	Robert Laundrie	Become familiar with new and existing air pollution control techniques currently being used to control VC emissions; discuss plant processes.

(continued)

Table B-1. Continued

Region/Company/Division	Date of meeting	Place	Contact	Purpose of meeting
B. F. Goodrich Chemical Div.	8-20-80	Henry, ILL.	W. C. Holbrook	Become familiar with new and existing air pollution control techniques currently being used to control VC emissions; discuss plant processes.
B. F. Goodrich Chemical Div.	9-17-80	Pedricktown, NJ	W. C. Holbrook	Become familiar with new and existing air pollution control techniques currently being used to control VC emissions; discuss plant processes.
B. F. Goodrich Chemical Div.	10-30-80	Cleveland, OH	W. C. Holbrook	Become familiar with new and existing air pollution control techniques currently being used to control VC emissions; discuss SCAQMD Rule 1005.1.
Great American Chemical Corp.	8-13-80	Fitchburg, MASS	Russ Mercier	Become familiar with new and existing air pollution control techniques currently being used to control VC emissions; discuss plant processes.

(continued)

Table B-1. Concluded

Region/Company/Division	Date of meeting	Place	Contact	Purpose of meeting
Hooker Chemical Co.	9-15-80	Burlington, NJ	Harold Dubec	Become familiar with new and existing air pollution control techniques currently being used to control VC emissions; discuss plant processes.
Shintech, Inc.	8-5-80	Freeport, TX	John Yonge	Become familiar with new and existing air pollution control techniques currently being used to control VC emissions; discuss plant processes.

APPENDIX C

CURRENT INDUSTRIAL SOURCES

OPERATING ETHYLENE DICHLORIDE/VINYL CHLORIDE PLANTS

Region	Plant	Location	Process
IV	B. F. Goodrich	Calvert City, Kentucky	EDC/VC
VI	Borden Chemical	Geismar, Louisiana	EDC/VC
VI	Conoco Chemical	Westlake, Louisiana	EDC/VC
VI	Diamond Shamrock	Deer Park, Texas*	EDC/VC
VI	Diamond Shamrock	LaPorte, Texas*	EDC/VC
VI	Dow Chemical	Plaquemine, Louisiana*	EDC/VC (2)
VI	Dow Chemical	Oyster Creek, Texas	EDC/VC
VI	Dow Chemical	Freeport, Texas	EDC/VC
VI	Ethyl Corporation	Baton Rouge, Louisiana	EDC/VC
VI	Georgia Pacific	Plaquemine, Louisiana*	EDC/VC
VI	ICI Americas	Baton Rouge, Louisiana	EDC/VC
VI	Monochem, Inc.	Geismar, Louisiana	EDC/VC
VI	PPG Industries	Lake Charles, Louisiana	EDC/VC
VI	Shell Chemical	Norco, Louisiana	EDC/VC
VI	Shell Chemical	Deer Park, Texas	EDC/VC
VI	Vulcan Materials	Geismar, Louisiana	EDC only
IX	Stauffer Chemicals	Long Beach, California	EDC/VC

*Began operation since promulgation of the regulation (October, 1976).

OPERATING POLYVINYL CHLORIDE PLANTS

Region	Plant	Location	Polymerization process
I	Borden, Inc.	Leominster, Mass.	Suspension, latex
I	Great American	Fitchburg, Mass.	Suspension
I	International Materials	New Bedford, Mass.	Suspension*
II	B. F. Goodrich	Pedricktown, N.J.	Suspension, dispersion, bulk
II	Goodyear Tire & Rubber	Niagara Falls, N.Y.	Suspension, dispersion
II	Hooker Chemical	Burlington, N. J.	Bulk
II	Pantasote	Passaic, N. J.	Suspension
II	Tenneco	Burlington, N. J.	Suspension, dispersion
II	Tenneco	Flemington, N. J.	Suspension
II	Union Carbide	Sommerset, N. J.	Latex
III	Diamond Shamrock	Delaware City, Del.	Suspension, dispersion
III	Firestone	Perryville, Md.	Suspension, dispersion
III	Firestone	Pottstown, Pa.	Suspension, dispersion
III	Pantasote	Point Pleasant, W. Va.	Suspension
III	Stauffer	Delaware City, Del.	Suspension, dispersion
IV	Air Products	Calvert City, Ky.	Suspension, latex
IV	Air Products	Pensacola, Fla.	Suspension
IV	B. F. Goodrich	Louisville, Ky.	Suspension, latex
IV	Conoco	Aberdeen, Miss.	Suspension
IV	Union Carbide	Tucker, Georgia	Latex

*Began operation since promulgation of the regulation (October, 1976).

OPERATING POLYVINYL CHLORIDE PLANTS (Continued)

Region	Plant	Location	Polymerization process
V	B. F. Goodrich	Henry, Ill.	Suspension, dispersion
V	B. F. Goodrich	Avon Lake, OH	Suspension, dispersion, latex
V	Borden	Illiopolis, Ill.	Suspension, dispersion
V	Dow	Midland, Mich.	Suspension, dispersion
V	General Tire	Ashtabula, OH	Suspension
VI	B. F. Goodrich	Plaquemine, LA	Bulk
VI	Certainteed	Sulphur, LA	Bulk
VI	Conoco	Ponca City, OK	Suspension *
VI	Conoco	Oklahoma City, OK	Suspension
VI	Diamond Shamrock	Deer Park, TX.	Suspension, dispersion
VI	Ethyl	Baton Rouge, LA	Suspension, dispersion
VI	Firestone	Addis, LA	Suspension *
VI	Georgia Pacific	Plaquemine, LA	Suspension
VI	Shintech	Freeport, TX	Suspension
VI	Tenneco	Pasadena, TX	Suspension
VI	Union Carbide	Texas City, TX	Solution
IX	B. F. Goodrich	Long Beach, CA	Suspension
IX	Stauffer	Long Beach, CA	Suspension
IX	Union Carbide	Torrance, CA	Latex

*Began operation since promulgation of the regulation (October, 1976).