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December 6, 1977

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Re: SPI-PVC Safety Group
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SPI-PVC Health Committee
SPI-PVC Communications Committee
SPI-PVC Lawyers Subcommittee

Gentlemen:

Attached hereto is a letter from Harold Himmelman at Beveridge, Fairbanks & Diamond written to cover the Environmental Protection Agency's Draft Inspection Manual for Vinyl Chloride.

Due to the technical nature and bulk of this document, copies are being supplied at this time only to the listed Voting Representatives and members of the Manufacturing Technology Committee.

Having received this document only late Monday afternoon, we are sending it out without having an opportunity to review it. As always, if before we report to you further about the Manual you have any questions, comments or suggestions with regard to it, please do not hesitate to let us know.

Cordially yours,

Joseph E. Hadley, Jr.

Enclosures

cc: (Without copies of Manual)
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December 5, 1977

BY HAND

Joseph E. Hadley, Jr.
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Dear Joe:

I am enclosing herewith the vinyl chloride field inspection manual which EPA's Division on Stationary Source Enforcement has asked me to distribute to the industry. You will recall from my September 29, 1977 letter that the field inspection manual was originally prepared in draft by Research Triangle Institute. The manual, as you know, will be used by EPA inspectors during on-site visits to VCM, PVC and ethylene dichloride plants.

In addition to regional EPA offices and Research Triangle Park, SPI is the only other party to have received a copy of this draft as of this time. The Division of Stationary Source Enforcement wants all comments on the draft submitted by January 6, 1978. Currently, the Division plans no hearings on the manual and hopes none will be necessary. However, should there be major areas in need of further discussion, there is some possibility that an informal hearing or meeting might be held. EPA hopes to make the field manual final, and to issue it, within two or three months.

Although I am sure that the entire manual will be of extreme interest, I should report that SPI has been especially requested to review Chapters 2 and 3.

Sincerely yours,



Harold Himmelman

HH:cl
Enclosure
cc: John R. Lawrence
Robert Laundrie

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NATIONAL EMISSION STANDARDS
FOR HAZARDOUS AIR POLLUTANTS
INSPECTION MANUAL
for
VINYL CHLORIDE

Prepared by

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Contract No. 68-01-4141
Task No. 2

EPA Project Officer
John R. Busik

Prepared for

U. S. ENVIRONMENTAL PROTECTION AGENCY
Division of Stationary Source Enforcement
Washington, D. C.

November 1977

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ACKNOWLEDGEMENT

This Inspection Manual was prepared by Mr. Michael F. Lamorte of the Research Triangle Institute. Project Officer for the Environmental Protection Agency - Enforcement Division was Mr. John R. Busik. The Task Manager was Mr. Richard Biondi assisted by Ms. Libby Scopino. The author appreciates the many contributions made by Mr. Biondi and Ms. Scopino during the preparation of this Manual. The author also appreciates the assistance of Surveillance and Analysis and of Enforcement Division personnel of District 6 in applying the Inspection Forms under field conditions.

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LIST OF CHEMICAL FORMULAS

<u>Name</u>	<u>Formula</u>
Acetylene	$\text{HC} \equiv \text{CH}$
Chlorine	Cl_2
Ethylene	$\text{CH}_2 = \text{CH}_2$
Ethylene Dichloride	$\text{ClCH}_2 - \text{CH}_2\text{Cl}$
Hydrogen Chloride	HCl
Oxygen	O_2
Polyvinyl Chloride	$\text{-(H}_2\text{C} = \text{CHCl)-}_n$
Vinyl Chloride Monomer	$\text{H}_2\text{C} = \text{CHCl}$
Water	H_2O

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1.0 INTRODUCTION

1.1 BACKGROUND

Pursuant to Section 112 of the Clean Air Act (42-U.S.C. 1857), the Administrator of the U. S. Environmental Protection Agency (EPA) has added vinyl chloride to the list of hazardous air pollutants (40 FR 59477) and established a national emission standard (40 FR 59532) for facilities which manufacture ethylene dichloride, vinyl chloride, and/or polyvinyl chloride. The NESHAPS regulations are applicable to plants producing the following: ethylene dichloride by the reaction of oxygen and hydrogen chloride with ethylene; vinyl chloride by any process; and one or more polymers containing any fraction of polymerized vinyl chloride. The regulations 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 no more than 0.19 m^3 (50 gal). Research and development facilities containing a polymerization reactor capacity greater than 0.19 m^3 (50 gal) but no more than 4.07 m^3 (1100 gal) are exempt from all parts of the regulations except the 10 ppm limit. The proposed emission standards for existing and new plants were advanced in the Federal Register, December 24, 1975 for vinyl chloride in plants manufacturing ethylene dichloride, vinyl chloride, and/or polyvinyl chloride. Final standards (40 FRL 618-1) became effective October 21, 1976 and apply to existing and new plants [1].

EPA decided to regulate vinyl chloride because it has been implicated as the causal agent of angiosarcoma (a rare form of liver cancer) and other serious disorders, both carcinogenic and non-carcinogenic, in people subjected to occupational exposure and in laboratory animals exposed to controlled concentrations of vinyl chloride [2]. Reasonable extrapolations from these findings cause concern that vinyl chloride may cause or contribute to the same or similar disorders at present ambient concentration levels. The purpose of the standard is to set limits of vinyl chloride

emissions from all known process and fugitive emission sources in ethylene dichloride, vinyl chloride, and/or polyvinyl chloride plants to the level which insures a clean, healthy environment. This will have the effect of furthering the protection of public health by minimizing the health risks to people living in the vicinity of these plants and to any additional people who are exposed as a result of new construction [3].

This Inspection Manual contains the guidelines for the benefit of and the standardized procedures to be followed by EPA field inspectors or their designated representatives. In conjunction with the operator's testing and monitoring results and the required recording and record-keeping of these results, the basic enforcement tools are readily available to properly trained field inspectors. The degree to which this portion of the NESHAPS program is successful depends critically on the effectiveness and efficiency with which inspectors conduct field inspections.

1.2 AUTHORITY

Authority for promulgation of the NESHAPS standards and regulations of Air pollutants is contained in Section 112 of the Clean Air Act (42 U.S.C. 1857). It directs the Administrator of the U. S. Environmental Protection Agency to establish emission standards and regulations for hazardous air pollutants (40 FR 59477), to maintain a current listing of these pollutants, and to publish in this listing those pollutants that contribute to producing a hazardous condition to human life and to the environment.

1.3 APPLICABILITY

The applicability of the NESHAPS standards and regulations is specified with respect to the function of the facility, product and process by which the product is produced.

There are no exemptions to the NESHAPS vinyl chloride emission standards and regulations for production plants which employ reactors of any capacity to produce one or more of the following: ethylene dichloride by reaction of oxygen and hydrogen chloride with ethylene; vinyl chloride by any process; and one or more polymers containing any fraction of polymerized vinyl chloride [1].

Equipment employed in research and development of the polymerization of vinyl chloride for which the reactor capacity is not greater than 0.19 m³

(50 gal) is not subject in any way to the vinyl chloride emission standards and regulations [1].

Equipment employed in research and development of the polymerization of vinyl chloride for which the reactor capacity is greater than 0.19 m³ (50 gal) and less than 4.07 m³ (1100 gal) is subject only to the 10 ppm vinyl chloride emission limit into the atmosphere from each reactor, stripper, monomer recovery system, and mixing, weighing, and holding containers [1].

1.4 DEFINITIONS

The definitions of terms used in this Inspection Manual are precise and this precision is required to conduct inspections properly. The terms requiring this precision are defined below [1].

- (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 that 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 that 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 a way as to form fluid dispersions when dispersed in a plasticizer or plasticizer/diluent mixtures.

- (h) "Latex resin" means a resin that is produced by a polymerization process that initiates from free radical catalyst sites and is sold undried.
- (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 and/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 that 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 that 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 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.

2.0 EDC, VC AND PVC INDUSTRIES

Polyvinyl chloride is a polymer employed in the fabrication of literally thousands of consumer and industrial products. The manufacturers of these products purchase the polyvinyl chloride resin from a relatively small number of producers. Polyvinyl chloride is polymerized from the vinyl chloride monomer. In turn vinyl chloride is produced from ethylene dichloride by cracking ethylene dichloride during dehydrochlorination or from the hydrochlorination of acetylene.

In the following brief presentation, the attributes of ethylene dichloride, vinyl chloride, and polyvinyl chloride production facilities are discussed with respect to those considerations that are pertinent to plant inspections.

2.1 ETHYLENE DICHLORIDE (EDC)

The principal process for ethylene dichloride production in the U.S. is oxychlorination which involves the reaction of oxygen and hydrogen chloride with ethylene [4]. This process accounts for 92% of the production in the U.S. [4]. In 1974, there were nine plants using this process to produce 5.05 billion pounds of ethylene dichloride per year [6]. This accounts for 74% of the total used for vinyl chloride production and approximately 77.5% of the 20.4 million pounds per year of vinyl chloride emission [6].

While refined ethylene dichloride is sold for other industrial uses, its major use is for vinyl chloride monomer production. Typically the economics of the industry dictates that an ethylene dichloride plant be in close proximity to a vinyl chloride monomer plant in which case the shipping cost of large, continuous flows of pure ethylene dichloride to a vinyl chloride plant is minimal [4]. This has led to the concentration of these plants in Texas, Louisiana and the northern states [4]. In most

cases, the unconverted ethylene dichloride from the vinyl chloride plant is recycled back with the crude ethylene dichloride [4].

Vinyl chloride emissions occur in an ethylene dichloride plant using the oxychlorination process from three sources: side reactions in the oxychlorination process and dissolved vinyl chloride in recycled hydrogen chloride and in recycled unconverted ethylene dichloride. Physically, the major vinyl chloride emission sources are the EDC reactor, EDC refining and the fugitive emissions that may be present.

2.2 VINYL CHLORIDE (VC)

There are four processes to produce vinyl chloride monomer [6]. There are fifteen plants producing vinyl chloride having a production capacity of 6.8 billion pounds per year [6]. Two plants use the hydrochlorination of acetylene, nine use the chlorination-oxychlorination of ethylene (with oxygen from air) and dehydrochlorination, one uses the same process, except that pure oxygen is used in place of air, and three plants use the direct chlorination of ethylene and dehydrochlorination [6].

The main sources of vinyl chloride emissions in plants using the hydrochlorination of acetylene are reactor condenser vent (continuous), scrubber vent (continuous), heavy ends storage vent (intermittent), and assorted fugitive sources [6].

The sources of emissions from the chlorination-oxychlorination of ethylene and dehydrochlorination processes using oxygen from air or using pure oxygen are the same. The main sources of emissions are those discussed in Section 2.1 and not repeated here, purification system vents (continuous), scrubber vent (continuous), loading area (intermittent), and vinyl chloride emissions from the purification process; but the loss per unit **product** produced is greater from the purification portion of the plant.

The process using direct chlorination and dehydrochlorination is used in vinyl chloride production when the manufacturing facility has other uses for the hydrogen chloride by-product. This process also uses ethylene dichloride in a dehydrochlorination process to produce vinyl chloride from ethylene dichloride.

2.3 POLYVINYL CHLORIDE (PVC)

Polyvinyl chloride is produced by a polymerization process from the vinyl chloride monomer. There are five processes used to polymerize the monomer: suspension polymerization is the most widely used and accounts for 78% of the U.S. plant capacity; dispersion polymerization (i.e., emulsion) accounts for 13%; bulk polymerization for 6% [4]. The latex polyvinyl chloride is produced by dispersion polymerization and is sold and transported in a water suspension; solution polymerization is adaptable to a continuous process for copolymers and is used by one company in the U.S. [4].

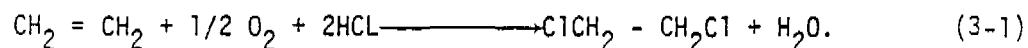
Emissions may occur at any point of the processes, such as storage, reactors, strippers, mixers, weighers, blenders, recovery systems, inprocess wastewater, loading facilities, etc. [6].

3.0 PROCESS FLOW DESCRIPTION AND EMISSION POINT IDENTIFICATION

The manufacturing processes covered in the vinyl chloride emissions Final Standard are discussed in this chapter with the aid of process flow diagrams. The emission points covered in the Standard are listed and keyed on the corresponding flow diagrams for each process.

3.1 ETHYLENE DICHLORIDE--OXYCHLORINATION*

One of the major processes for ethylene dichloride (see Section 3.4) production in the U.S. is oxychlorination which involves the reaction of oxygen and hydrogen chloride with ethylene [4]. The oxygen may be introduced into the process in concentrated form or by an air stream as shown in Figures 3.1(a) and 3.1(b), respectively [6]. The two processes are similar and will be discussed together since the emission sources are identical. The generic reaction equation for the process is given by



This reaction takes place in the reactor, shown in Figures 3.1(a) and 3.1(b), at elevated temperature. The oxychlorination process typically exhibits a 98% conversion to ethylene dichloride per pass from the reaction represented in Eq. (3-1) [6]. The raw materials (ethylene, hydrogen chloride and oxygen/air) are made to pass through a catalyst. In the presence of oxygen, the catalyst concentrates the ethylene and chlorine allowing for the reaction, Eq. (3-1), to take place at a lower temperature. Because the reaction is highly exothermic, a water flow over the reaction tube surface is required to control the temperature in the reactor. The result is that steam evolves at the exit port of the water jacket.

*While this process is usually identified as oxychlorination, it is more precisely an oxyhydrochlorination process.

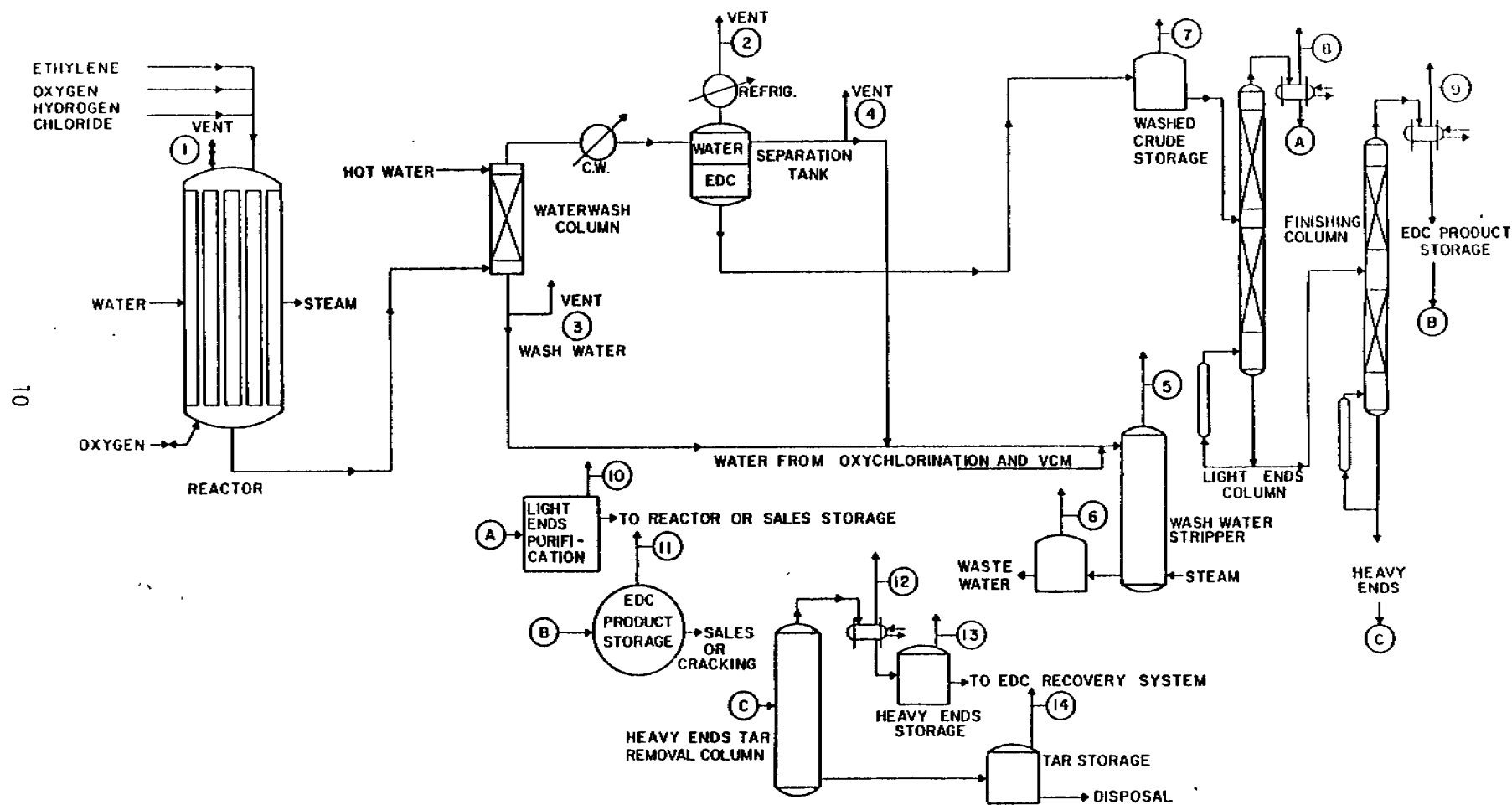


Figure 3.1(a). Ethylene dichloride process flow diagram using oxychlorination which involves the reaction of oxygen and hydrogen chloride with ethylene.

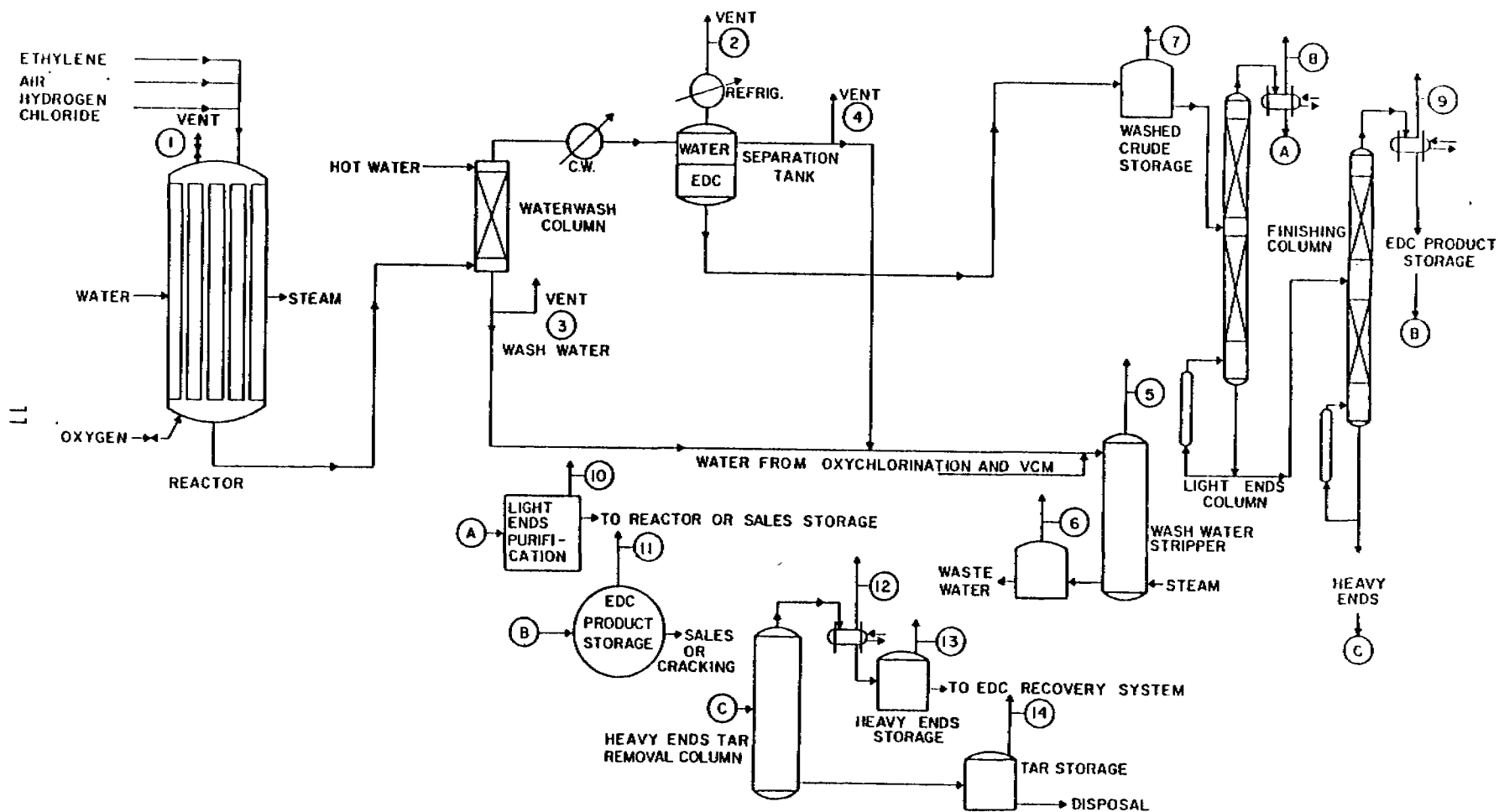


Figure 3.1(b). Ethylene dichloride process flow diagram using oxychlorination which involves the reaction of oxygen present in air and hydrogen chloride with ethylene.

Table 3.1: Most probable emission points identified by the keys in Figures 3.1(a) and 3.1(b) in the oxy-chlorination process for ethylene dichloride.

Position Name	Key	Frequency
Reactor Vent	1	Continuous
Reactor Refrigerator Condenser Vent	2	Continuous
Wastewater from Water Wash Column	3	Continuous
Wastewater from Wash/Crude Storage	4	Continuous
Wash Water Stripper Vent	5	Continuous
Wash Water Stripper Storage Vent	6	Continuous
Wash Crude Product Storage Vent	7	Intermittent
Light-Ends Column Condenser Vent	8	Continuous
Finishing Column Vent	9	Continuous
Light-Ends Purification Column Vent	10	Intermittent
Refined EDC Storage Tank Vent	11	Intermittant
Heavy-Ends, Tar-Removed Column Vent	12	Continuous
Heavy-Ends Storage Tank Vent	13	Intermittent
Tar Storage Tank Vent	14	Intermittent
Fugitive	Entire Plant	Intermittent/ Continuous

The gas stream that exits the reactor contains ethylene dichloride in the form of a gas. In the process represented in Figure 3.1(a) this stream also contains ethylene, hydrogen chloride and oxygen; while that in Figure 3.1(b) is similar except that air rather than oxygen is present. The stream is passed through a hot water wash column to remove impurities from the ethylene dichloride, to maintain its gaseous state, and to introduce water vapor. The ethylene dichloride gas and water vapor stream are passed through a cold water condenser prior to entering the separation tank. The separated, purified ethylene dichloride is then transported to a storage tank [6].

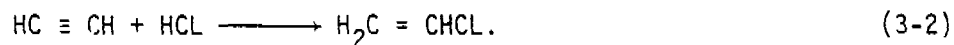
The water from the hot water wash and from the separation tank is passed through a stripping column to separate ethylene dichloride and waste by-products. The separated ethylene dichloride is passed on to the EDC storage tank, while the waste by-products are disposed.

The most probable emission points are listed in Table 3.1 and identified by the keys shown in Figures 3.1(a) and 3.1(b). The emission sources are listed to correspond with operational steps in the generalized hydrochlorination process. Fugitive emission sources (pumps, pump maintenance valves, pressure relief valves, samplers, etc.) are not identified because the locations of these sources are unique for each plant. The emission from any point, whether listed or not, depends on the operating condition (batch or continuous, reaction efficiency, etc.) of the plant at the time of inspection and in some cases on the immediate past history of operating conditions [6].

3.2 VINYL CHLORIDE

3.2.1 Hydrochlorination of acetylene

In this process vinyl chloride monomer is produced by the hydrochlorination of acetylene. The reaction occurs between hydrogen chloride and acetylene at 85-141°C in the reactor shown in Figure 3.2, in the presence of a catalyst, mercuric chloride on activated carbon [6]. The reaction is governed by the equation



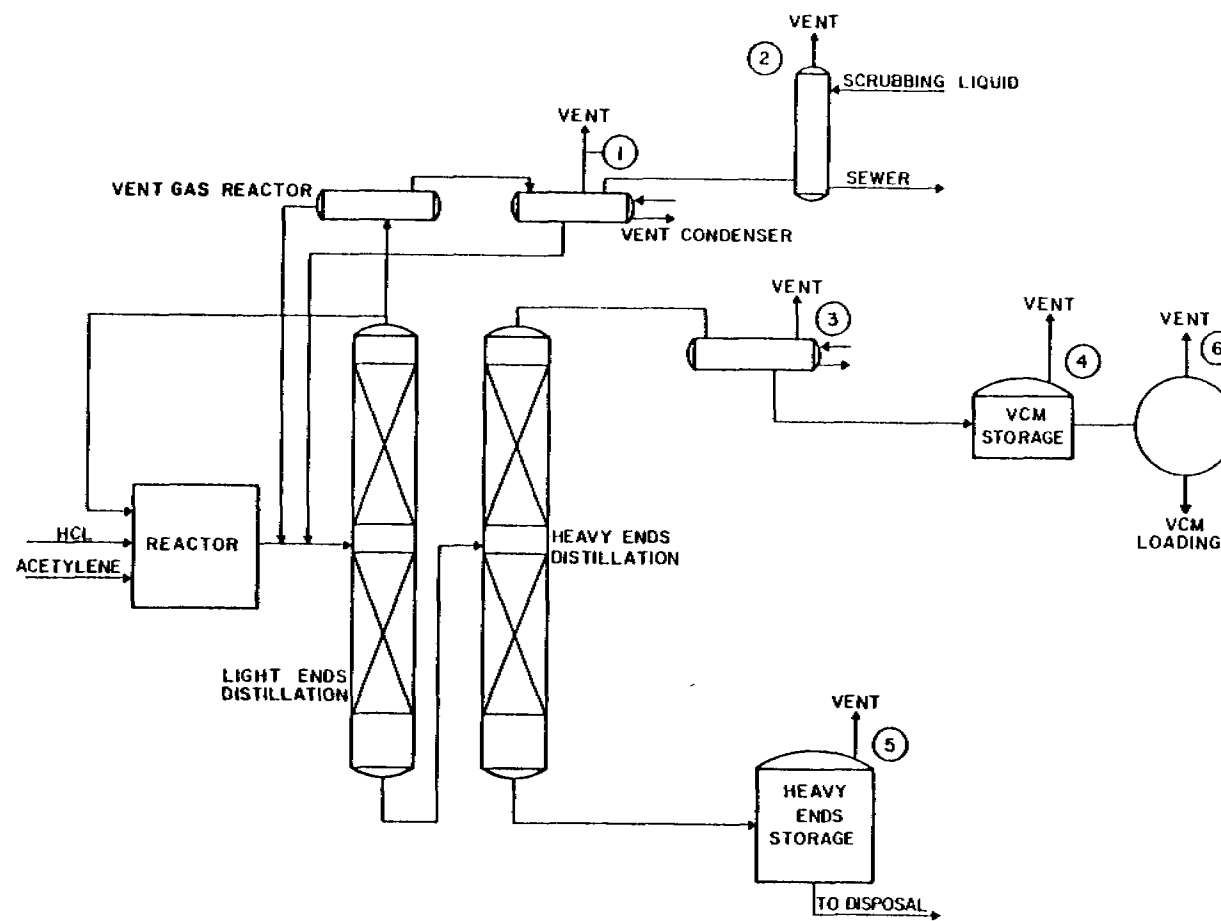


Figure 3.2. Vinyl chloride monomer process flow diagram using hydrochlorination of acetylene.

The reaction typically exhibits a 90% conversion to vinyl chloride per pass. As a result, acetylene and hydrogen chloride gases exit the reactor as well as vinyl chloride. These gases are compressed, cooled and pumped to a purification system consisting of a light-ends distillation column and a heavy-ends distillation column. In the light ends distillation column acetylene is separated and transported back into the reactor for another pass. Other volatile gases are passed to the vent gas reactor and vent condenser. Table 3.2 lists the main products and their boiling point temperatures. This shows that acetylene has the lowest boiling point temperature and is separated easily from the other compounds.

Table 3.2: Hydrochlorination of acetylene product gases and their boiling point temperatures.

Gas	Symbol	Boiling Point Temperature
Acetylene	$\text{HC} \equiv \text{CH}$	- 84°C
Hydrogen Chloride	HCl	+ 110°C
Vinyl Chloride	$\text{H}_2\text{C} = \text{CHCl}$	- 13°C
Ethylene Dichloride	$\text{ClCH}_2 - \text{CH}_2\text{Cl}$	+ 83°C

The reaction represented in Eq. (3-2) is exothermic. Therefore, the heavy-ends that are transported to the heavy-ends distillation column from the light-ends distillation column will contain some polymerized material as well as vinyl chloride monomer. The vinyl chloride is distilled, subsequently liquefied and placed in a storage tank. The heavy-ends are transported to a temporary storage tank and ultimately incinerated.

The most probable emission points are listed in Table 3.3 and identified by the keys shown in Figure 3.2. The emission sources are listed to correspond with operational steps in the generalized hydrochlorination process. Fugitive emission sources (pumps, pump maintenance valves, pressure relief valves, samplers, etc.) are not identified because the locations of these sources are unique for each plant. The emission from any point, whether listed or not, depends on the operating conditions (batch or continuous, reaction efficiency, etc.) of the plant at the time of inspection and in some cases on the immediate past history of operating conditions.

Table 3.3: Most probable emission points identified by the keys in Figure 3.2 in the hydrochlorination of acetylene for vinyl chloride monomer.

Position Name	Key	Frequency
Reactor Condenser Vent	1	Continuous
Scrubber Vent	2	Continuous
VCM Condenser Vent	3	Continuous
VCM Storage Vent	4	Continuous
Heavy-Ends Storage Vent	5	Intermittent*
VCM Loading Vent	6	Intermittent
Fugitive	Entire Plant	Intermittent/Continuous

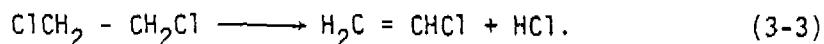
*Intermittent is used in the sense that if the rate of incineration is greater than the rate of storage, emission is probably non-existent. When the reverse is true, emission will be continuous.

3.2.2 Dehydrochlorination of ethylene dichloride

The production of vinyl chloride monomer by dehydrochlorination (removal of hydrogen chloride) involves the thermal dehydrochlorination of dry ethylene dichloride. Thermal dehydrochlorination is sometimes referred to as a cracking process. Vinyl chloride results when ethylene dichloride is placed in a cracking furnace at approximately 510°C [4]. For most efficient operation, the furnace is packed with a catalyst such as pumice or charcoal. Typically, the conversion efficiency per pass is 94 to 97%.

The cracking of ethylene dichloride to obtain vinyl chloride monomer is used exclusively in those processes in which ethylene dichloride is the intermediary crude. This includes the chlorination-oxychlorination of ethylene process using concentrated oxygen or oxygen in air (described in Section 3.1.1) and the direct chlorination of ethylene process (not covered in the Standard). The cracking process is the same regardless of the process used to obtain ethylene dichloride.

The reaction is represented by the equation



In an integrated ethylene dichloride-vinyl chloride plant, where the oxychlorination process is employed to produce ethylene dichloride, the hydrogen chloride by-product in Eq. (3-3) is returned to the ethylene dichloride reactor as an input crude shown in Eq. (3-1) [4,6].

Figure 3.3 shows the process flow diagram [6]. The ethylene dichloride is transported as a liquid (boiling point +83°C, see Table 3.2) and is vaporized completely prior to entering the cracking furnace. The hydrogen chloride is removed in the cracking furnace. The gas flow exiting the cracking furnace consists of mainly vinyl chloride, but also present are ethylene dichloride, hydrogen chloride and other hydrocarbons. The

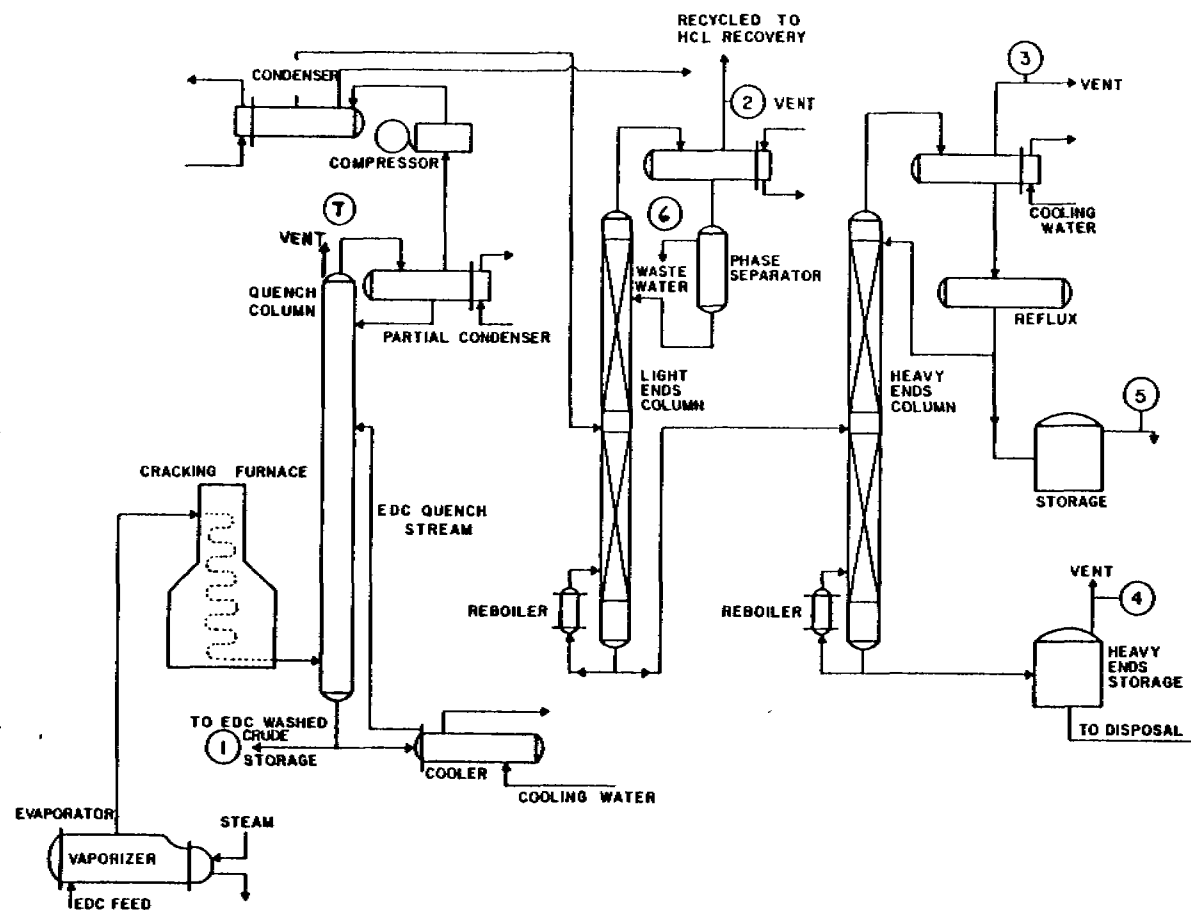


Figure 3.3. Vinyl chloride monomer process flow diagram using dehydrochlorination of ethylene dichloride.

quenching column uses liquid ethylene dichloride to liquify the ethylene dichloride and the hydrogen chloride while the gaseous vinyl chloride passes on to the partial condenser and condenser. Hydrogen chloride gas also flows along with the vinyl chloride since hydrogen chloride is not very soluble in ethylene dichloride at the quenching temperature.

The liquid ethylene dichloride is transported to the washed crude storage in the ethylene dichloride section of the plant and ultimately transported back to the cracking furnace for another pass.

The vinyl chloride and hydrogen chloride gases are cooled, compressed and pumped to a purification system consisting of a light-ends distillation column and a heavy-ends distillation column. In the light-ends column the vinyl chloride is separated from the hydrogen chloride. The hydrogen chloride is recycled to the ethylene dichloride reactor if the oxychlorination process is used. Other volatile by-products are passed to the vent gas reactor.

The reaction represented in Eq. (3-3) is exothermic [6]. Therefore, the heavy-ends and the light-ends distillation columns will contain some polymerized material as well as vinyl chloride monomer. The vinyl chloride is distilled, subsequently liquefied and placed in a storage tank. The heavy ends are transported to a temporary storage tank and ultimately incinerated.

The most probable emission points are listed in Table 3.4 and identified by the keys shown in Figure 3.3. The emission sources are listed to correspond with operational steps in the generalized dehydrochlorination process. Fugitive emission sources (pumps, pump maintenance valves, pressure relief valves, samplers, etc.) are not identified because the location of sources is unique for each plant. The emission from any point, **whether** listed or not, depends on the operating conditions (batch or **continuous**, reaction efficiency, etc.) of the plant at the time of inspection and in some cases on the immediate past history of operating conditions.

3.3 POLYVINYL CHLORIDE

3.3.1 Suspension polymerization

The suspension polymerization process is the most common process for polyvinyl chloride production [4]. The resin produced is sometimes referred

Table 3.4: Most probable emission points identified by the keys in Figure 3.3 in the dehydrochlorination of ethylene dichloride for vinyl chloride monomer.

Position Name	Key	Frequency
Recycling of EDC to Washed Crude Storage	1	Intermittent
Light-ends Distillation Column Vent	2	Intermittent
Heavy-ends Distillation Column Vent	3	Intermittent
Heavy-ends Storage Vent	4	Intermittent
VCM Storage Vent	5	Intermittent
Light-ends Column Waste Water	6	Continuous
Quench Column Vent	7	Continuous
Fugitive	Entire Plant	Intermittent/ Continuous

to as suspension resin. Polymerization of vinyl chloride requires the mixing of weighed amounts of vinyl chloride (weighed amounts of a comonomer where desired to change the polyvinyl chloride properties), catalyst, water and suspending agents (soap) [4]. The raw materials are mixed in a clean glass or stainless steel lined reactor. Air is removed from the reactor by a steam jet or vacuum pump. Reaction temperature is controlled by either cooling or heating, depending on the details of the process used. The reaction is initiated by the catalyst. As the reaction proceeds, polyvinyl chloride is produced in particle form. Agitation is employed to prevent a slurry from agglomerating in the reactor and the suspending agent disperses the vinyl chloride droplets. The polymerization process is allowed to continue until ¹85 to ²90% of the vinyl chloride has polymerized; this requires approximately 6 hours [4]. At this time, the reaction is stopped because the process is not as controllable. If allowed to continue beyond this point, the product becomes increasingly less uniform with respect to molecular weight and, therefore, the physical properties are less uniform. The vinyl chloride residue is in vapor form in the reactor, dissolved in water, and/or trapped in the polyvinyl chloride granules.

Figure 3.4 shows the process flow diagram for suspension polymerization [4]. Vinyl chloride is supplied to the weighing station from the vinyl chloride source (plant or tank car) and from the recovery system. The comonomer (if required) for a batch is weighed in its own weighing station. In addition to the weighed quantities of vinyl chloride monomer and comonomer, the initiator catalyst and suspending agent are transported to the reactor. The polymerization takes place at elevated temperatures and at a pressure in the range of 5.1 to 6.8 atmospheres. ~~The residue from the reactor is transferred to the stripper tank where the vinyl chloride is removed and transported to the vinyl chloride recovery system.~~

The contents of the reactor (polyvinyl chloride granules, gases, water and initiator catalyst) are subjected to a stripping process to remove unreacted vinyl chloride. The stripping process may take place in the reactor or the contents may be transferred to a stripper vessel where stripping takes place. Vinyl chloride is stripped by the application of heat alone or by the application of the combination of heat and vacuum. The vinyl chloride and

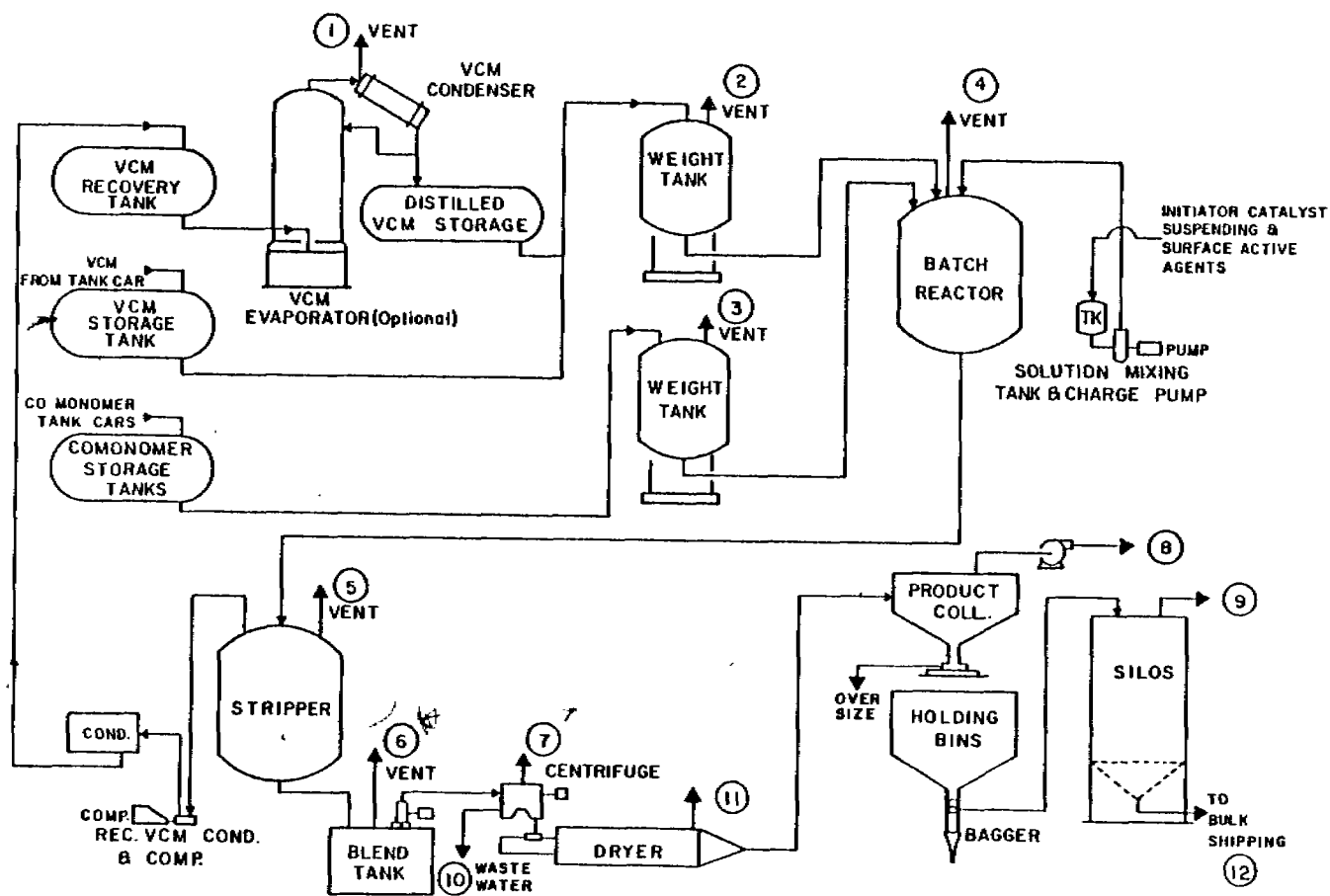


Figure 3.4. Polyvinyl chloride process flow diagram using suspension polymerization.

* = ...

other volitized chemicals driven off are transferred to the recovery system. The vinyl chloride is obtained from the distillation column and passed on to the recovery system storage tank. The other gases are vented, and included will be some vinyl chloride. The remaining slurry is transported to a slurry blend tank where several batches are blended together to obtain a more uniform product [4].

The blended slurry is then pumped to a centrifuge where most of the water is removed. The wet polyvinyl chloride is then dried to remove remaining water and vinyl chloride. The resin is then transferred to storage or bagging stations.

Table 3.5 lists the most probable emission sources for the suspension process with the key referred to Figure 3.4. The Key 1 denotes the recovery system vent through which the noncondensable gases are vented. The venting may take place manually or automatically and may be intermittent or continuous depending on the system design and the pressures employed.

Keys 2 and 3 are the weighing stations for the vinyl chloride monomer and comonomer. High pressure may build up at these stations, in which case the emission will contain vinyl chloride.

2 The reactor emissions, Key 4, may arise when a run-away condition develops and due to residual vinyl chloride vapor will always arise when the reactor manhole is opened for cleaning. A run-away condition typically develops in the event of a power failure, equipment failure and/or operator failure. When this occurs, the reaction for the batch may require a temporary or a complete termination either by automatic pressure valve release or by manual venting [4].

Keys 5, 6 and 7 are all associated with the stripping, blending and drying operations of the polyvinyl chloride slurry. In each of these operations vinyl chloride emissions may occur [4]. Keys 8 and 9 are points where emissions may occur in the storage and bagging of the resins, while Key 10 is the emission point from the waste water treatment process.

3.3.2 Emulsion (i.e., dispersion) polymerization

The emulsion polymerization process uses equipment basically similar to that of the suspension process described in Section 3.3.1 [4]. The resin produced is sometimes called an emulsion resin. Emulsion resins can be polymerized at lower temperatures and at a higher rate than suspension

Table 3.5: Most probable emission points identified by the keys in Figure 3.4 in the suspension polymerization process for polyvinyl chloride.

POSITION NAME	KEY	FREQUENCY
Vinyl Chloride Recovery Vent	1	Intermittent/Continuous
Vinyl Chloride Weighing Tank Vent	2	Intermittent
Comonomer Weighing Tank Vent	3	Intermittent
Reactor Vent and Opening Loss	4	Intermittent
Stripper Vent	5	Intermittent
Slurry Blend Tank Vent	6	Intermittent
Centrifuge Vent	7	Intermittent
Product Collection Vent	8	Intermittent
Silo Vent	9	Continuous
Waste Water	10	Continuous
Dryer Exhaust	11	Intermittent
Bulk Loading	12	Intermittent
Fugitive	Entire Plant	Intermittent/Continuous

resins. However, emulsion resins are also more sensitive to heat and shear stresses. When subjected to either or a combination of heat and shear stresses, the resultant changes in the resin's physical characteristics may make it unsuitable for use. The resin obtained from the emulsion process is of smaller particle size than obtained from the suspension process [4].

The emulsion process flow diagram is shown in Figure 3.5 and the corresponding keyed emission sources are presented in Table 3.6. A study of Figures 3.4 and 3.5 show that the processes are identical in the following ways: batch reactor process; water is used as the suspending medium to suspend liquid vinyl chloride; all process equipment is identical except for the dryer. In addition, the suspension process uses a centrifuge to aid in drying while the emulsion process does not.

In the emulsion process soap and water are used as the emulsifier. The emulsion process differs from the suspension in the following ways: more soap is added to the slurry in the reactor which stabilizes the monomer droplets and results in the absence of agglomerates; a spray dryer is used because it does not produce excessive temperature or shear stresses during the drying, while the rotary, flash, or fluidized bed dryer used in the suspension process may produce these stresses [4].

3.3.3 Latex dispersion polymerization

Latex resins are produced by the emulsion process [4]. The latex resin is polymerized vinyl chloride monomer suspended in water. It is sold and transported in this solution form. The process is identical in almost all ways to the suspension and emulsion processes. It differs in that there is no drying process step and more soap is added in the reactor than for the emulsion or suspension processes [4]. The result is a latex resin which is a colloidal suspension of polyvinyl chloride. The process flow diagram and most probable emission sources are shown in Figure 3.6 and Table 3.7, respectively.

3.3.4 Bulk polymerization

The bulk polymerization process is a batch process and consists of two polymerization steps [4]. In the pre-polymerization reactor there is liquid vinyl chloride in the presence of a polymerization initiator. The reactor is of a similar design to that used in the suspension process. The conversion to polyvinyl chloride from vinyl chloride is in the range 7 to

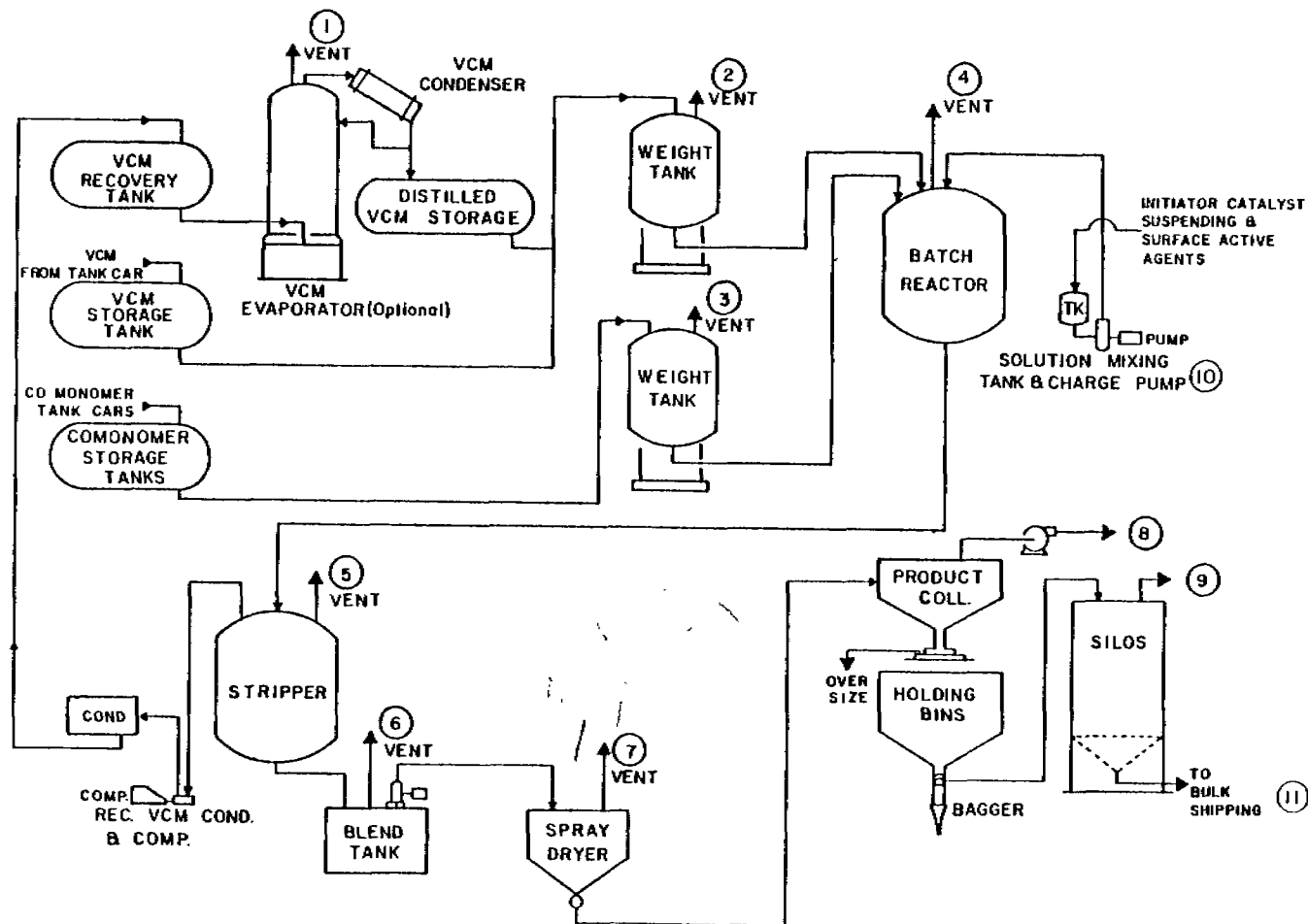


Figure 3.5. Polyvinyl chloride process flow diagram using emulsion (i.e., dispersion) polymerization.

Table 3.6: Most probable emission points identified by the keys in Figure 3.5 in the emulsion (i.e., dispersion) polymerization process for polyvinyl chloride.

POSITION NAME	KEY	FREQUENCY
Vinyl Chloride Recovery Vent	1	Intermittent/Continuous
Vinyl Chloride Weighing Tank Vent	2	Intermittent
Comonomer Weighing Tank Vent	3	Intermittent
Reactor Vent and Opening Loss	4	Intermittent
Stripper Vent	5	Intermittent
Slurry Blend Tank Vent	6	Intermittent
Spray Dryer Vent	7	Intermittent
Product Collection Vent	8	Intermittent
Silo Vent	9	Continuous
Process Water	10	Intermittent
Bulk Loading	11	Intermittent
Fugitive	Entire Plant	Intermittent/Continuous

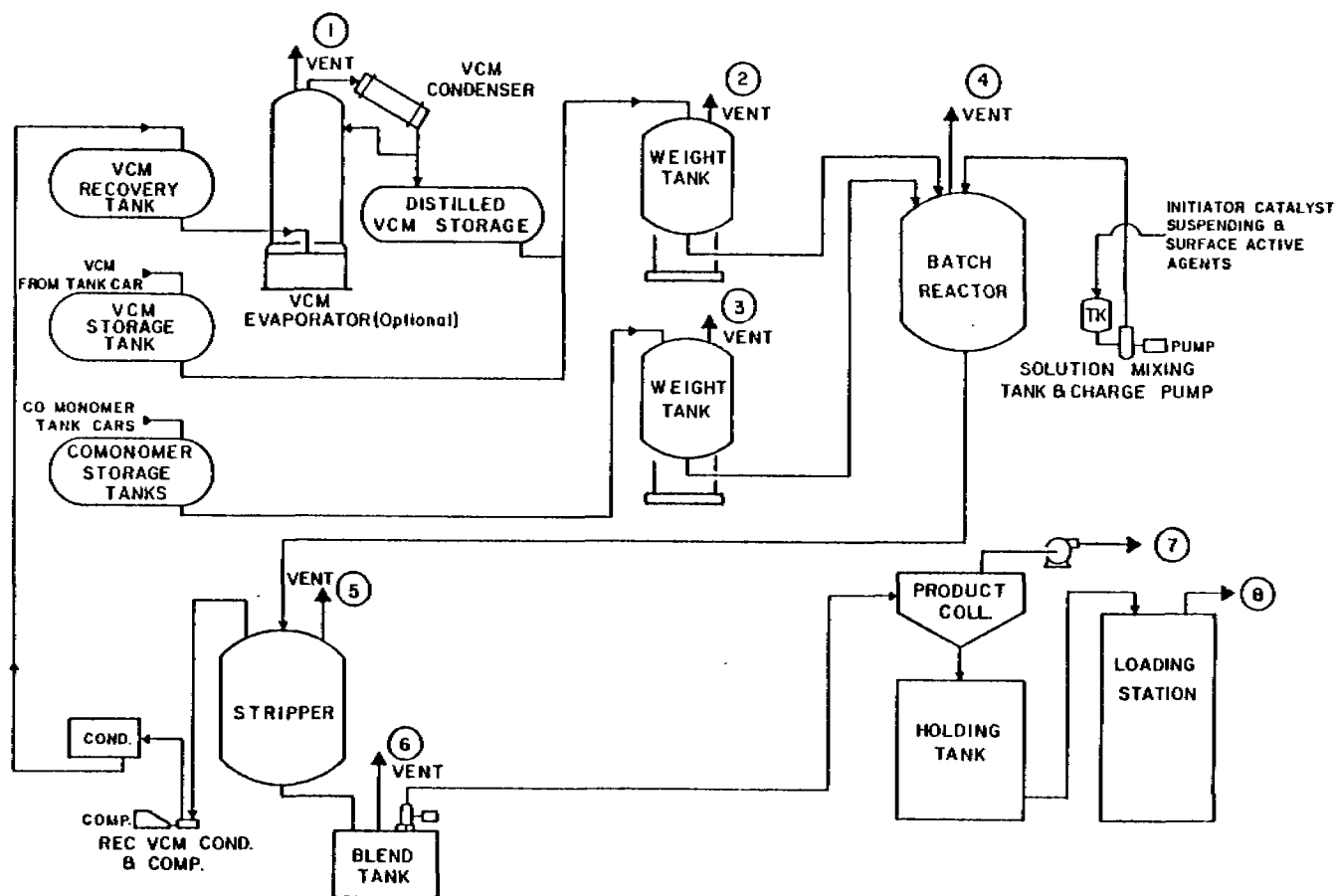


Figure 3.6. Polyvinyl chloride latex process flow diagram using emulsion (i.e., dispersion) polymerization.

Table 3.7: Most probable emission points identified by the keys in Figure 3.6 in the emulsion (i.e. dispersion) polymerization process for polyvinyl chloride latex.

POSITION NAME	KEY	FREQUENCY
Vinyl Chloride Recovery Vent	1	Intermittent/Continuous
Vinyl Chloride Weighing Tank Vent	2	Intermittent
Comonomer Weighing Tank Vent	3	Intermittent
Reactor Vent and Opening Loss	4	Intermittent
Stripper Vent	5	Intermittent
Slurry Blend Tank Vent	6	Intermittent
Product Collection Vent	7	Continuous
Loading Station	8	Continuous
Fugitive	Entire Plant	Intermittent/Continuous

12% [4]. This suspended polyvinyl chloride in liquid vinyl chloride is then transferred to a larger, high pressure, horizontal-type reactor. To this is added more liquid vinyl chloride and initiator. This reactor, sometimes called an autoclave, serves as the post polymerization reactor resulting in a reaction efficiency of approximately 85 to 90% [4]. The post-polymerization reactor is more rugged and the agitation more vigorous than the pre-polymerization reactor [4].

The post-polymerization reactor must be cleaned after each batch; less frequent cleaning is required for the pre-polymerization reactor.

The bulk process is similar in most aspects to the suspension process. Since there is no water or water vapor in the suspension, low temperature (-35°C or -31°F as opposed to 7°C or 44.6°F in the suspension and dispersion) condensers may be employed in the recovery system. Moreover, the drying operation is not needed, and no in-process waste water system is present [4].

The remaining monomer in the post-polymerization vessel may be removed by a number of processes. The monomer may be removed by vacuum alone. Another method is to introduce steam into the autoclave and the steam and released vinyl chloride are removed by vacuum. The steam-vacuum procedure may be repeated as many times as required to meet the emission standard. Those plants using the steam-vacuum process require wastewater stripping to bring the waste water in compliance with the emission standard. Whichever method is used, the recovered monomer is placed in a temporary holding tank and recycled back to the pre-polymerization reactor through a filter [4].

The process flow diagram and the most probable emission points are given in Figure 3.7 and the keyed emission points listed in Table 3.8 [4].

3.3.5 Solvent polymerization

The solvent polymerization product is considered a speciality product and is a small segment of the total PVC industry [5]. However, it serves a large number of important needs that usually involve thin PVC coatings, such as for the food and beverage industries [5]. The early developed process is shown in Figure 3.8 and the more recently developed process is shown in Figure 3.9 [5]. The processes are similar in most aspects, differing

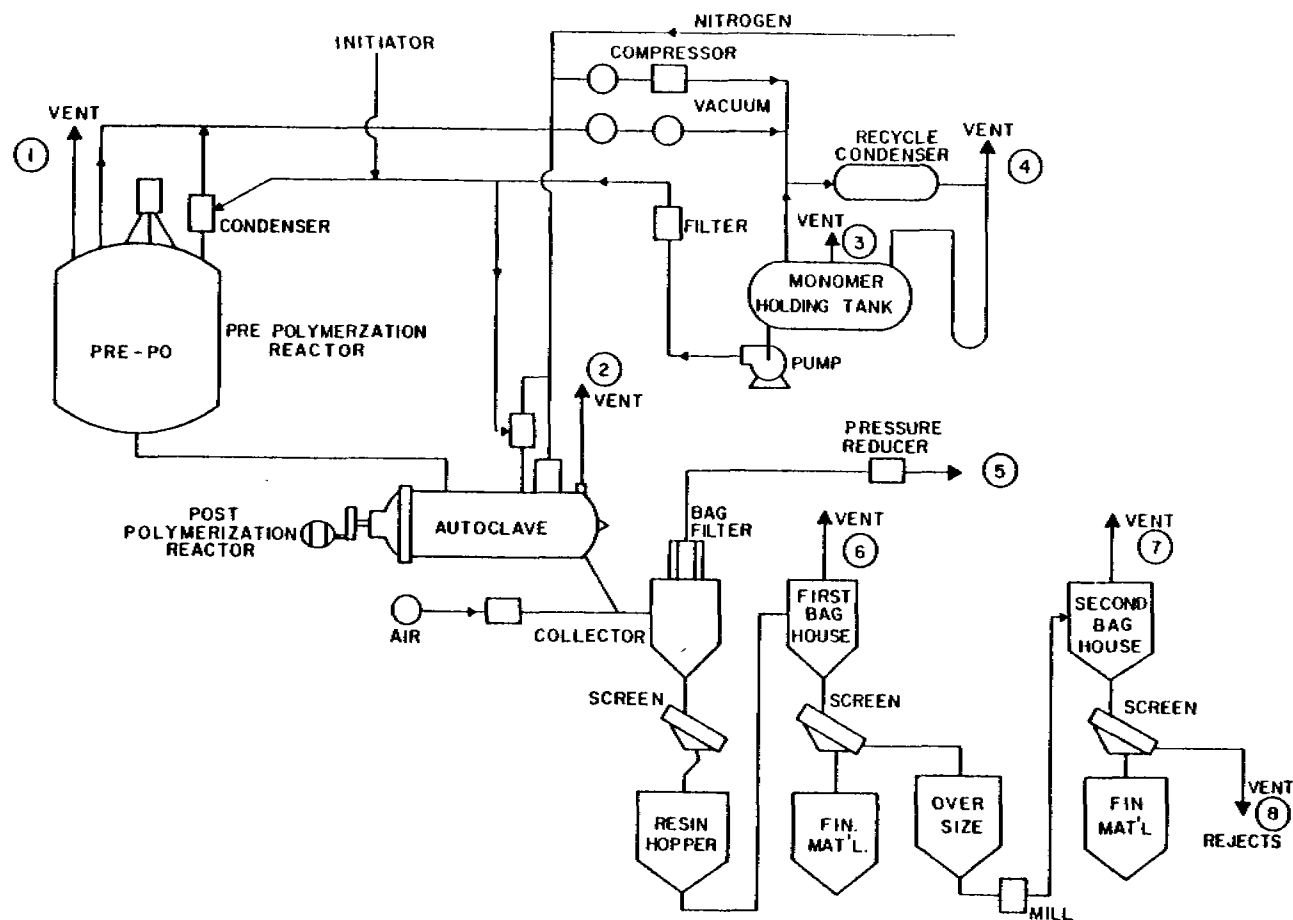


Figure 3.7. Polyvinyl chloride process flow diagram using bulk polymerization.

Table 3.8: Most probable emission points identified by the keys in Figure 3.7 in the bulk polymerization process for polyvinyl chloride resin.

POSITION NAME	KEY	FREQUENCY
Pre-Polymerization Reactor Vent	1	Intermittent
Post-Polymerization Reactor Vent	2	Continuous
Monomer Holding Tank Vent	3	Continuous
Recycle Condenser Vent	4	Continuous
Pressure Reducer Vent	5	Continuous
First Bag House Vent	6	Continuous
Second Bag House Vent	7	Continuous
Reject Vent	8	Continuous
Fugitive	Entire Plant	Intermittent/ Continuous

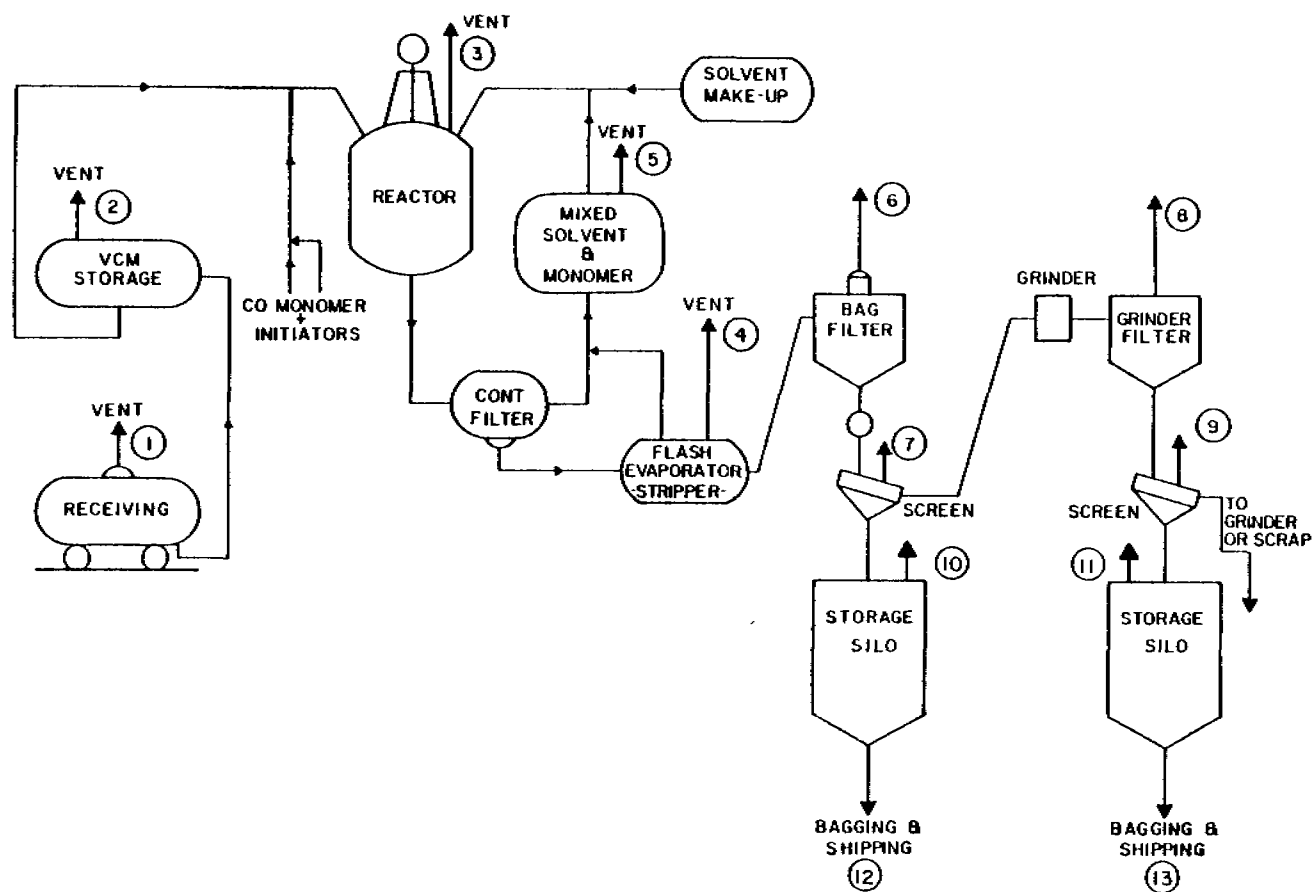


Figure 3.8. Early polyvinyl chloride process flow diagram using solvent polymerization.

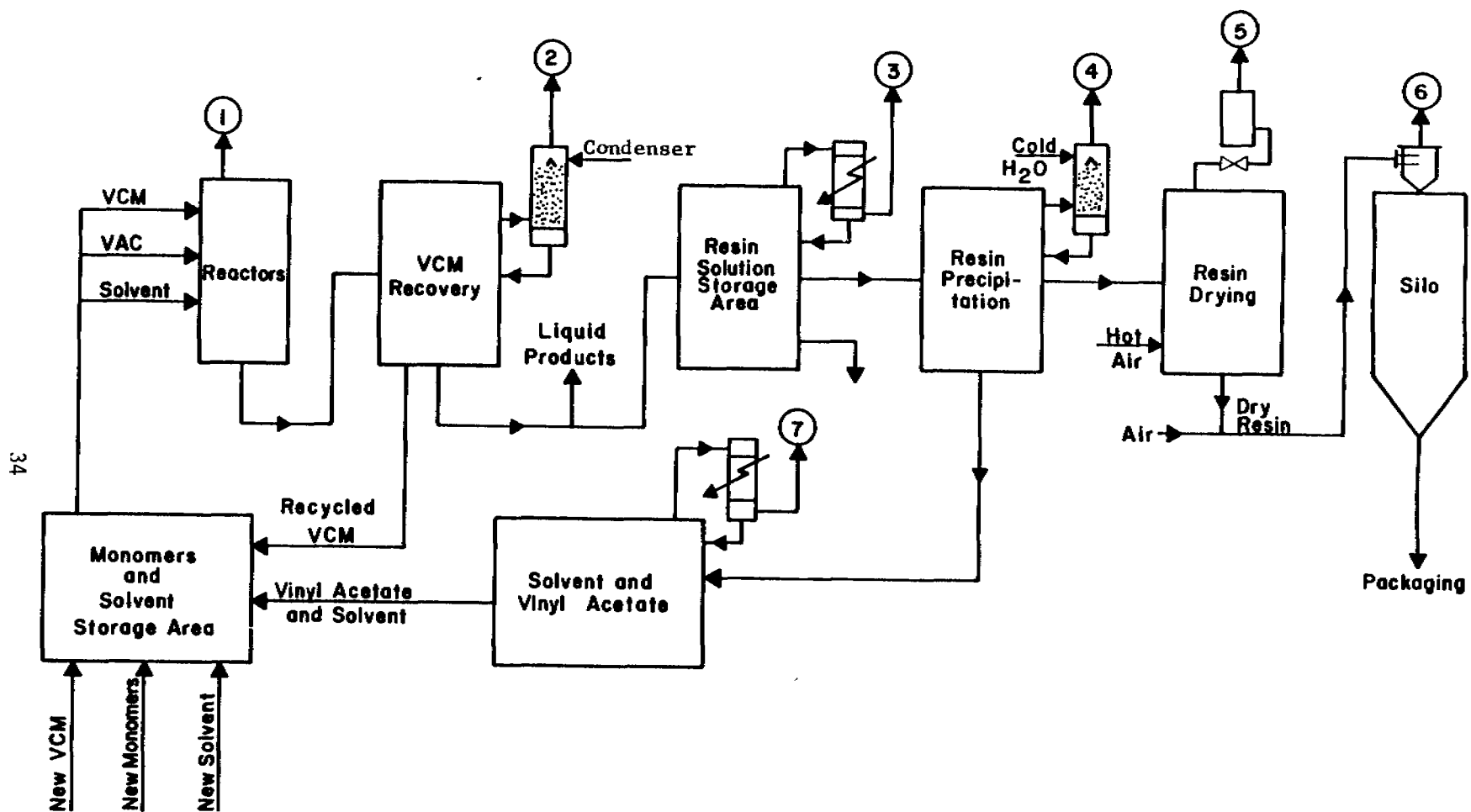


Figure 3.9: More recent polyvinyl chloride process flow diagram using solvent polymerization.

more in the technological developments of recent years than in the basic process operations. The early process is described below followed by the points of difference.

The early process flow diagram is shown in Figure 3.8 and the corresponding source emission points listed in Table 3.9. The emission points in Table 3.10 correspond to the process flow diagram shown in Figure 3.9. The comonomers, initiators and solvents are continuously introduced into the reactor.

The process flow shows that the VCM, comonomer and initiator are introduced into the reactor along with the solvent, usually n-butane [4]. The comonomer is almost always vinyl acetate. The continuous process provides a degree of turbulence among the constituents in the reactor that results in a copolymer conversion efficiency approaching 100%. A continuous copolymer stream is drawn off from the reactor and filtered. The filter cake is passed on to a flash evaporator where it is dried and the monomers recycled. The solvent is drained from the filter and recycled back into the reactor along with the recovered monomers. During any one pass of the solvent stream, some solvent is lost to the process; therefore a solvent make-up stream is also required [4].

Vinyl chloride emissions from the reactor area in a continuous process are relatively lower than from batch processes [4]. There is some evidence to suggest that the vinyl chloride is more easily removed from the resin than in other polymerization processes.

The most important difference between the processes is that the earlier process produced a slurry as a result of polymerization while the later process produces a solution. The stripping operation from solution gives a lower VCM concentration and typically produces less emissions. Moreover, inprocess water comes into contact with the polymerized material after the stripping operation. This avoids the requirement of an inprocess water stripper, and the inprocess water storage and treatment equipment should not give any emissions. Finally, drying is accomplished by means of hot air rather than flash evaporator.

Table 3.9: Most probable emission points identified by the keys in Figure 3.8 in the solvent polymerization process for polyvinyl chloride and copolymers.

POSITION NAME	KEY	FREQUENCY
Receiving Tank Vent	1	Continuous
VCM Storage Vent	2	Continuous
Reactor Vent	3	Continuous
Flash Evaporator (Stripper)	4	Continuous
Solvent and Monomer Recovery	5	Continuous
Bag Filter	6	Continuous
Bag Filter-Screen	7	Continuous
Grinder Filter	8	Continuous
Grinder Filter-Screen	9	Continuous
Storage Silo	10, 11	Continuous
Bulk Loading	12, 13	Intermittent
Fugitive	Entire Plant	Intermittent/ Continuous

Table 3.10: Most probable emission points identified by the keys in Figure 3.9 in the solvent polymerization process for polyvinyl chloride and copolymers.

POSITION NAME	KEY	FREQUENCY
Reactor	1	Continuous
Monomer Condensor	2,3,4	Continuous
Resin Drying	5	Continuous
Silo	6	Continuous
Solvent and Vinyl Acetate Condensor	7	Continuous
Fugitive	Entire Plant	Intermittent/ Continuous

3.4 CLARIFYING NOTE ON THE BALANCED OXYCHLORINATION - DEHYDROCHLORINATION PROCESS

Oxychlorination and direct chlorination are the two major processes used for ethylene dichloride production [4]. EDC plants operate a balanced process which consists of a vinyl chloride plant and a direct chlorination plant operated adjacent to and in coordination with the oxychlorination plant [4]. The Standard covers the oxychlorination, but not the direct chlorination process. However, this strict interpretation is not the intent of the Standard [4]. The Standard promulgated on October 21, 1976 covers any and all portions of any process that receives, transports or processes recovered ethylene dichloride from the oxychlorination plant, even though these processes may also be used for materials from the direct chlorination process.

A block diagram of the balanced process is shown in Figure 3.10. Typically ethylene dichloride refining is common to both the direct chlorination and to the oxychlorination plants. Therefore, the ethylene dichloride crudes are refined through the same equipments. In Figure 3.10 the EDC refining equipment is shown to be part of the EDC oxychlorination plant. The crude produced from the oxychlorination plant may contain vinyl chloride monomer. Therefore, the common receiving point of the monomer and all downstream parts of the direct chlorination plant are subject to the Standard.

That the crude from the oxychlorination plant may contain vinyl chloride arises because of recycled ethylene dichloride and because the recycled hydrogen chloride used is a by-product of the monomer cracking. In Figure 3.10 this is shown by the flow of HCl and EDC from the dehydrochlorination to the oxychlorination reactors and EDC refining, respectively.

While the vinyl chloride monomer is present in small concentrations in HCl after having been subjected to a stripping process and to even lower concentrations if the ethylene dichloride crude is also stripped of the monomer, equipment malfunctions may give rise to significant monomer concentrations in the crude produced in the oxychlorination plant. In the absence of equipment malfunctions, the monomer is easily stripped during the HCl and EDC stripping operations. This is true because the monomer boiling point is -13°C while it is $+110^{\circ}\text{C}$ and $+83^{\circ}\text{C}$ for HCl and EDC, respectively (Table 3.2).

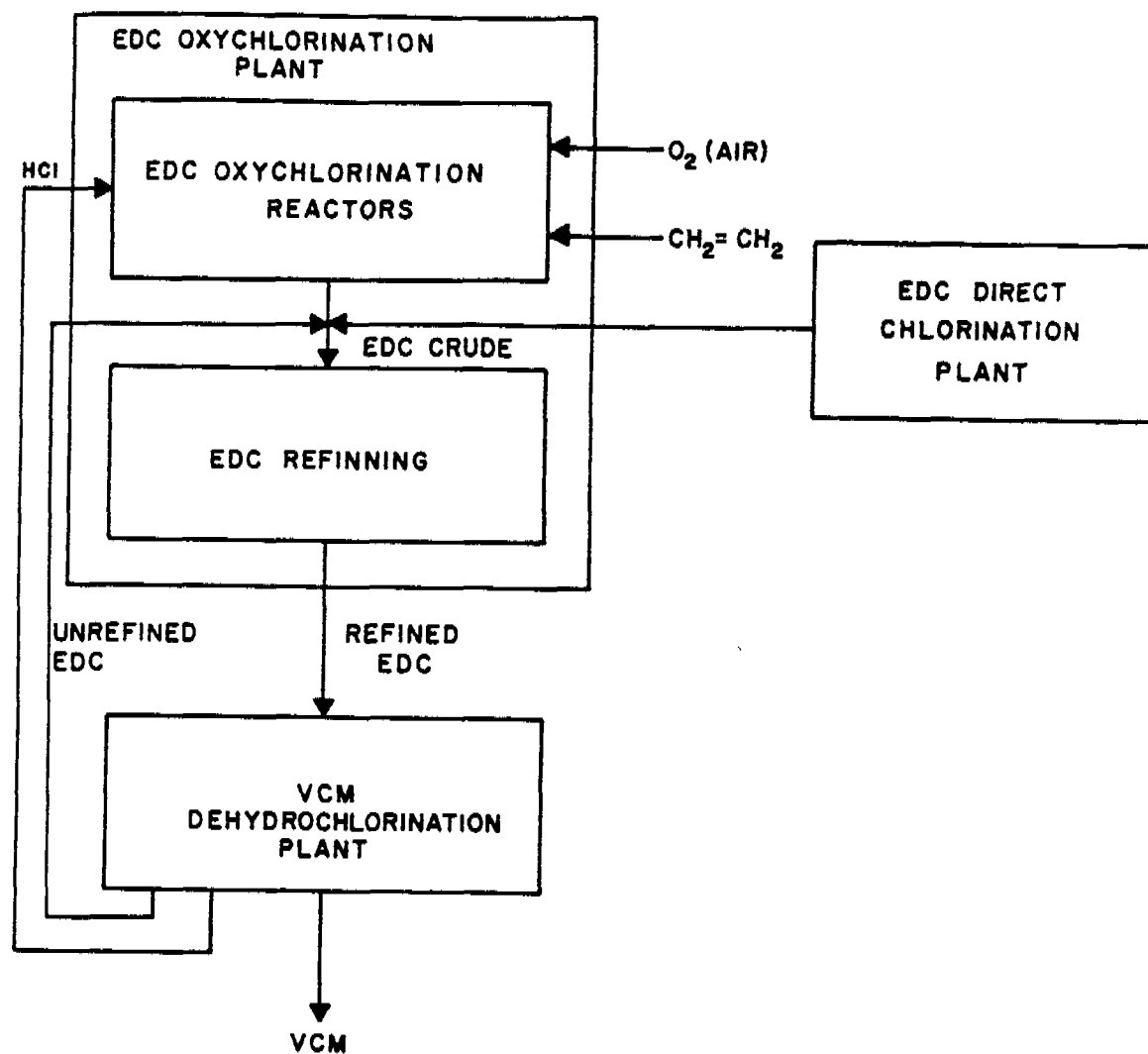


Figure 3.10: Block diagram of a balanced oxychlorination-dehydrochlorination process.

The economics of the PVC industry demands that large producers of EDC employ the balanced oxychlorination - dehydrochlorination type plants [4]. From Eq. (3-3) it is seen that for each vinyl chloride molecule produced in the cracking of EDC, one HCl molecule evolves as a by-product. This forms the HCl stream in Figure 3.10. However, in the oxychlorination reaction, governed by Eq. (3-1), two HCl molecules are required for each EDC molecule produced. The HCl by-product provides at a maximum one-half the EDC required by the cracking furnace. Therefore, the direct chlorination process must supply at least one-half of the EDC required in a balance type plant. Presently, 95% of the EDC annual production rate is produced in balance type plants.

3.5 PHOTOGRAPHS OF EQUIPMENT

The technology employed in the EDC, VC and PVC industries is of a relatively higher technical level than Inspectors normally encounter in other plant inspections subject to the Clean Air Act. In addition, specific processes differ for the same general product class from plant to plant. In many cases, if not in most, the equipments used were constructed according to unique specifications. The operation of the equipments may be different, in which case the materials, size, shape and their placement in the plant may also be different. Typically, the Inspector is not able to draw from experiences gained of previous inspections to the degree that is commonly done in other industries.

To assist the Inspector in conducting complete and efficient plant inspections, photographs of equipments are shown in Figures 3.11 to 3.40 from which VC emissions are more likely to occur. From photographs of general types of equipment such as reactors, strippers, storage vessels, etc., it will be less difficult to determine the function of more specialized equipment types. No attempt has been made to present photographs of different types and sizes of equipments because this would require in excess of 200 photographs. Table 3.11 gives the figure numbers and the equipment category of those selected for reproduction in this Manual.

Table 3.11: Figure number of photographs and corresponding equipment category.

Figure Number	Equipment Category
3.11 to 3.15	Reactors
3.16 to 3.18	Strippers
3.19 to 3.24	Storage Vessels
3.25 and 3.26	Dryers
3.27 to 3.32	Distillation Vessels
3.33 and 3.34	RD/SRV
3.35	Double Mechanical Seal
3.36 and 3.37	Railroad tank car loading and unloading
3.38 to 3.40	Incinerators

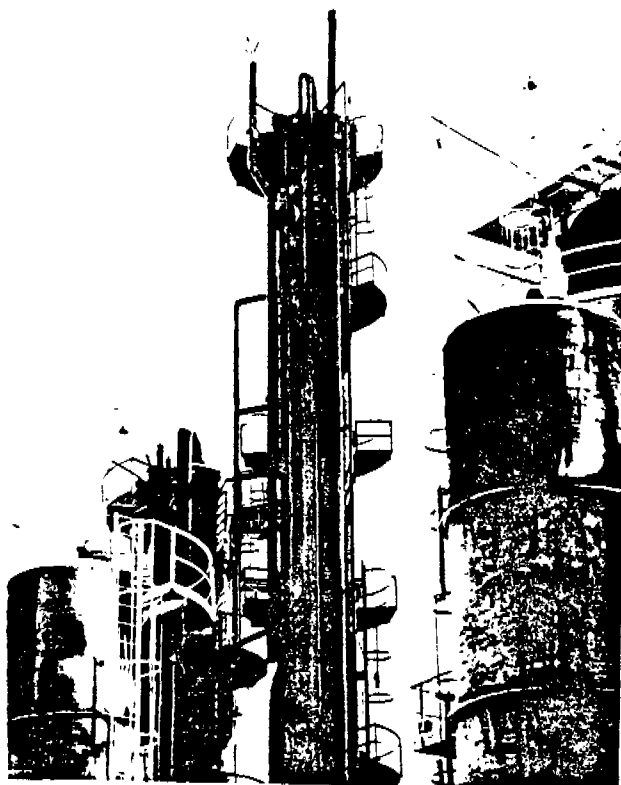


Figure 3.11 Large capacity VC reactor using the oxychlorination process is located in the tall vessel. The oxychlorination manual vent is the open ended pipe, rising above the top of the reactor on the left side.

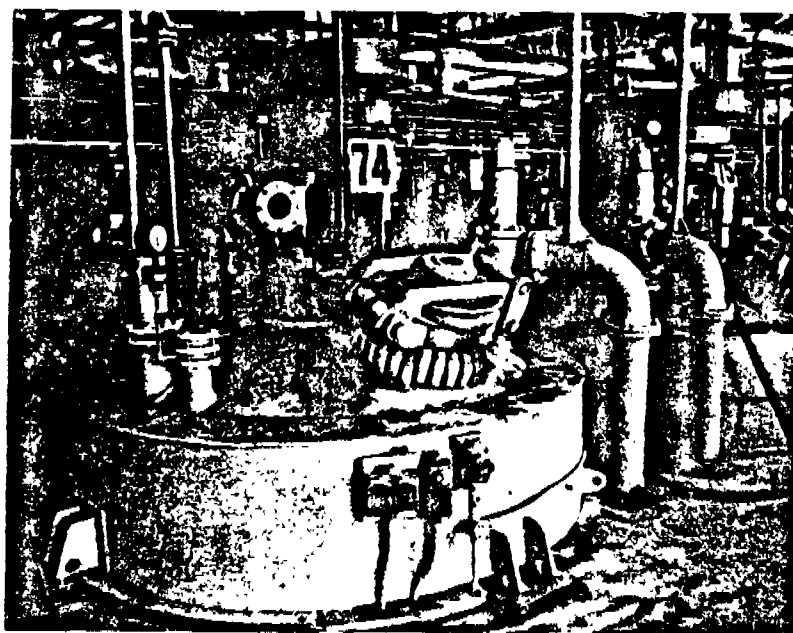


Figure 3.12 The tops of medium capacity, side-by-side PVC reactors using the emulsion process may be seen. Individual RD/SRV and manual vents may also be seen mounted on top of each reactor.

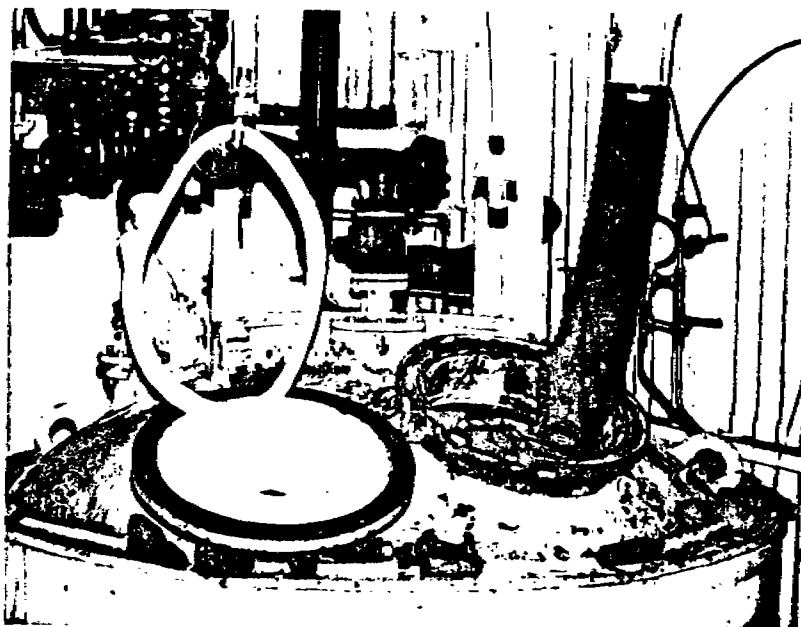


Figure 3.13 Small size PVC reactor with cover removed to clean reactor in preparation for next polymerization run. Prior to removing cover the PVC and water solution were removed and transferred to stripper. "Elephant trunk" is placed through the opening to vent vinyl chloride gas through "trunk" to the recovery system in order to be in compliance with emissions standard reactor opening loss. This type reactor is used in the suspension, emulsion and latex polymerization processes.

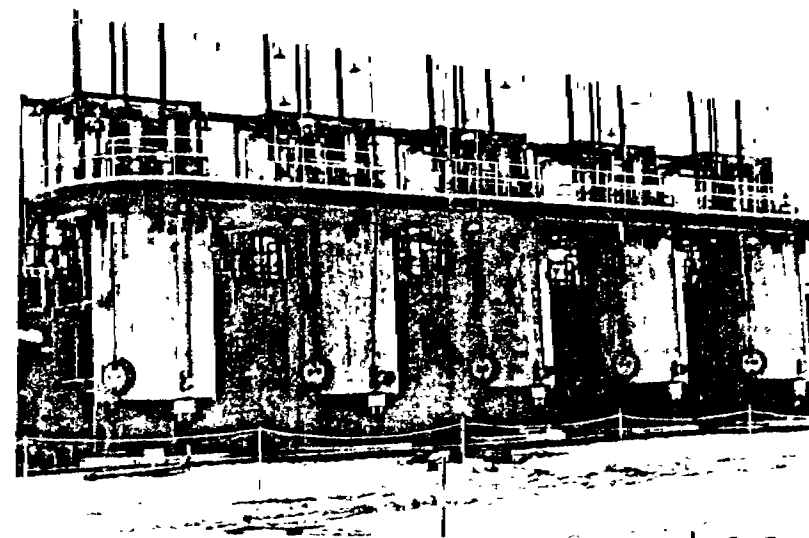


Figure 3.14 Medium capacity side-by-side PVC reactors using solvent process. Individual RD/SRV and manual vents connected to vinyl chloride recovery system may also be seen. Lower portion of reactors comprise the heating elements to raise the contents to the temperature required for polymerization.

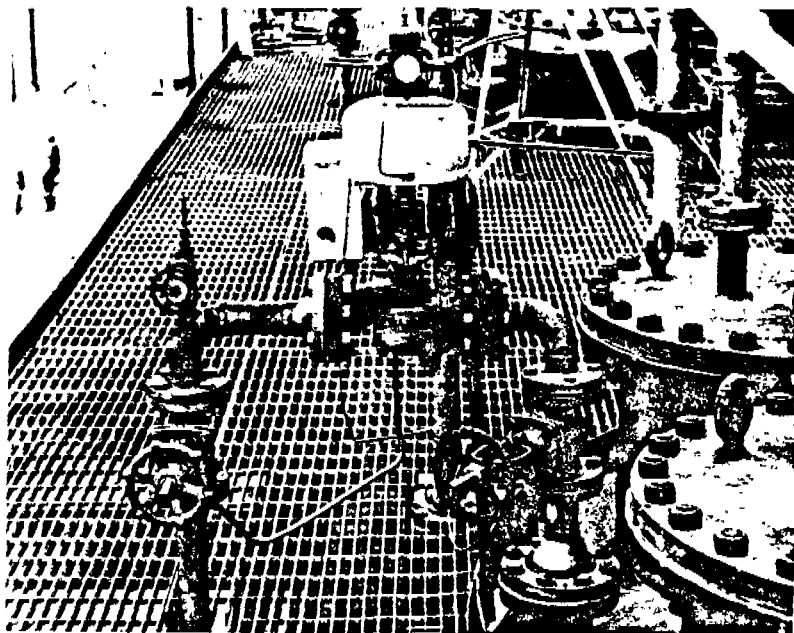


Figure 3.15 The top of medium capacity, side-by-side PVC reactors using solvent process. Foreground shows a motor valve for emergency venting through to the VC monomer recovery system.



Figure 3.16 The top of a small capacity PVC stripper vessel used in the suspension, emulsion and latex processes. The RD/SRV vent is connected to the recovery system.

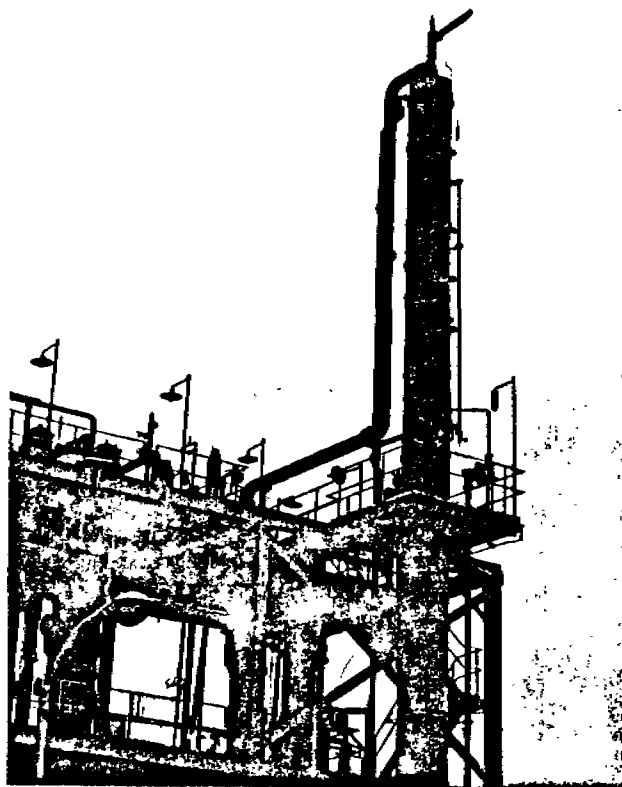


Figure 3.17 A stripper column is shown that removes VC from a PVC-varnish solution resulting from the solvent polymerization process.

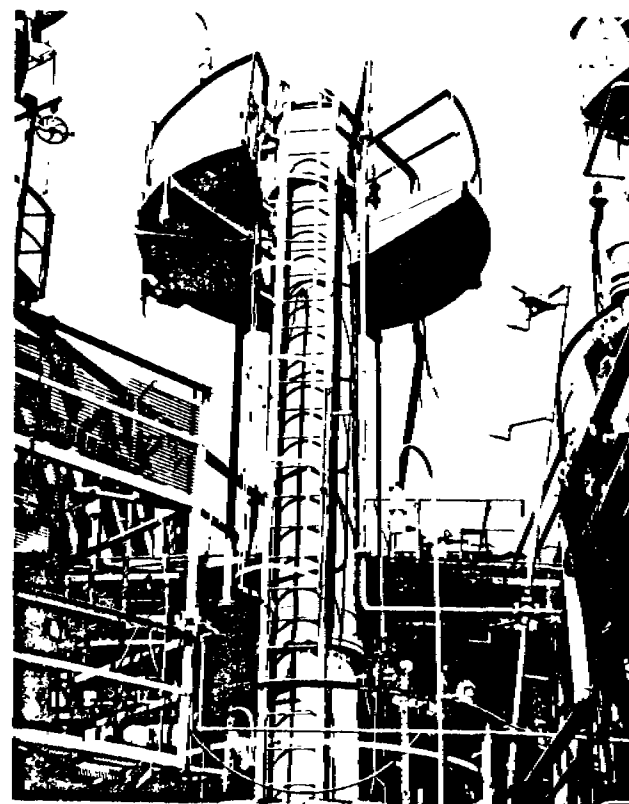


Figure 3.18 A typical wastewater stripper column is shown that may be found in EDC, VC and PVC plants.

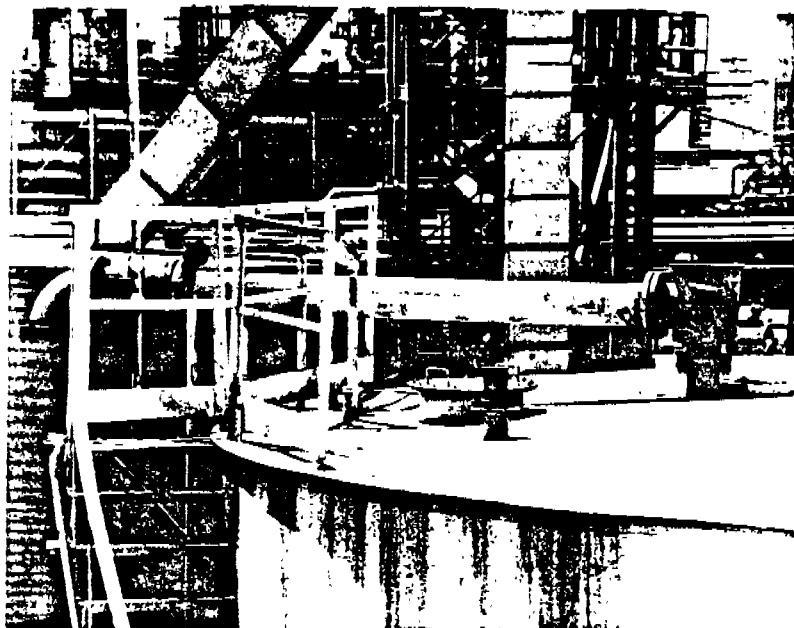


Figure 3.19 The top of an EDC storage tank is shown with its vent.



Figure 3.20 Cylindrical, side-by-side, above ground VC storage tanks are shown. RD/SRV vents may be seen on pipe rack above tanks.

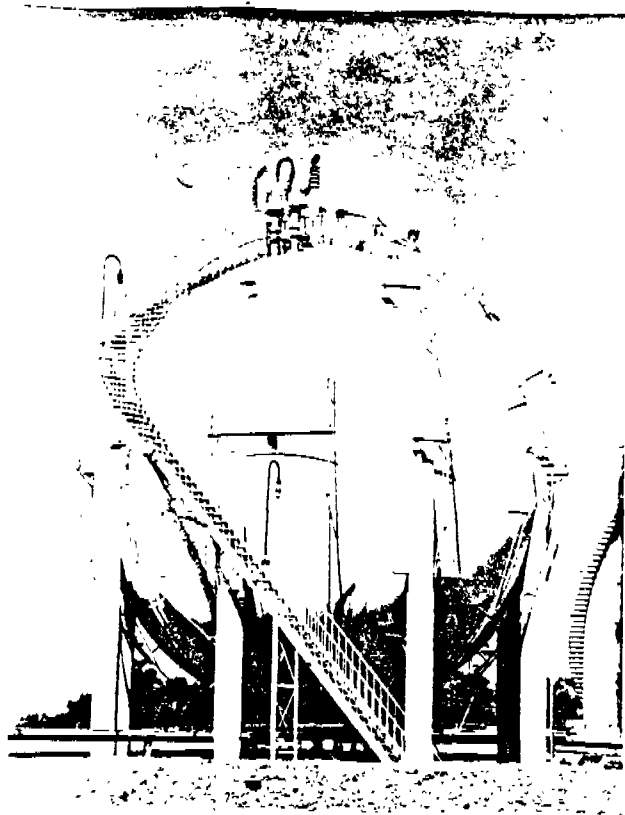


Figure 3.21 Spherical, above ground vinyl chloride storage tanks. RD/SRV vents may be seen perched on top of sphere.



Figure 3.22 Underground VC monomer storage tank area is shown.

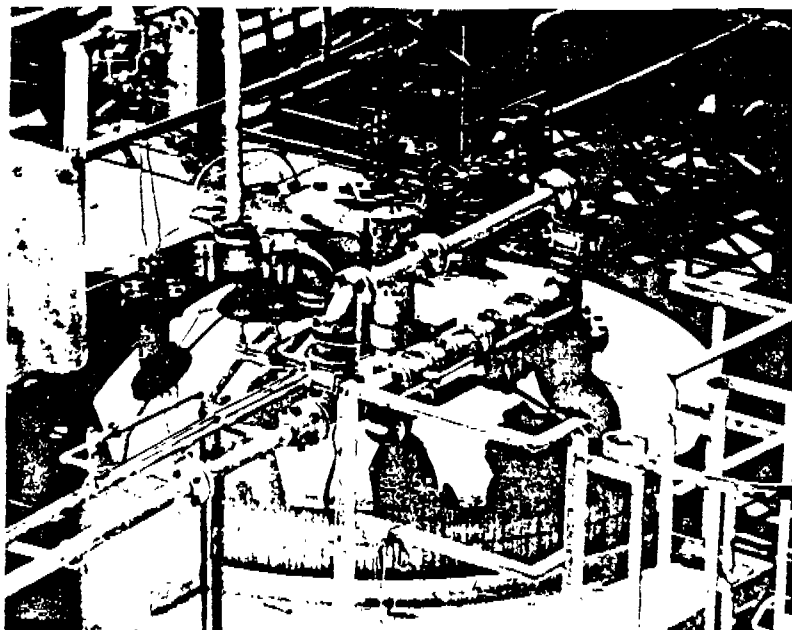


Figure 3.23 Wash water stripper storage tank with its vent mounted at the top of the tank in an EDC-VC plant.

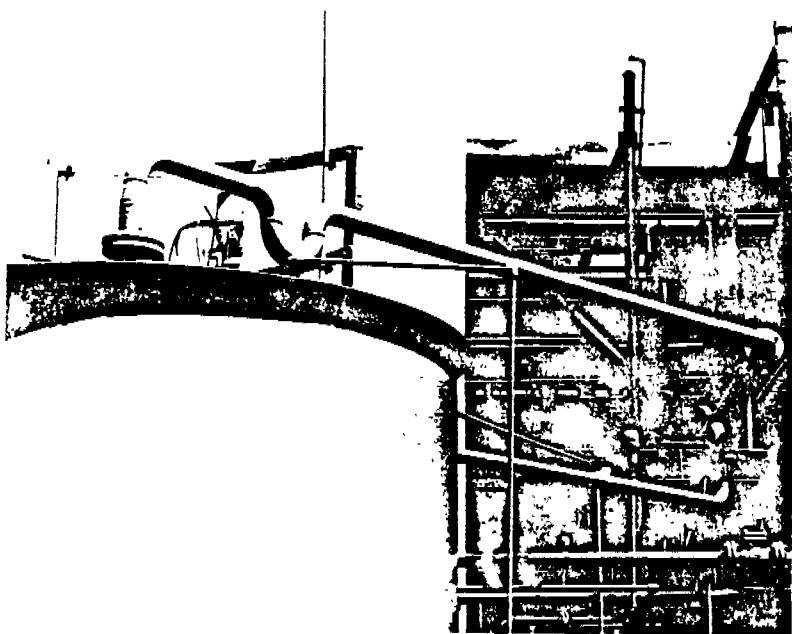


Figure 3.24 Upper portion of tar storage tank shown with its vent connected to recovery system in an EDC plant.

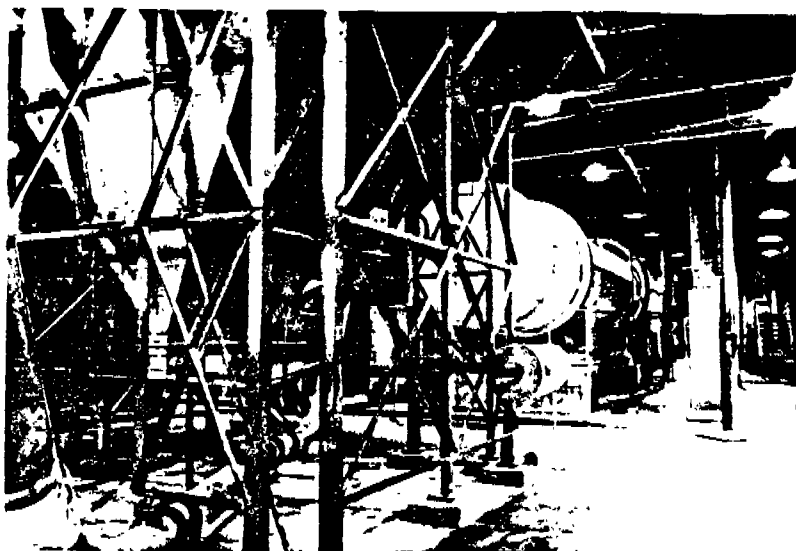


Figure 3.25 PVC suspension resin rotary dryer and dust collector. Drying is accomplished by the application of heat and rotary action.



Figure 3.26 PVC emulsion resin spray drying takes place in the cylindrical building. Large diameter feed pipe, seen at the left of the dryer, carries resin to the top of the dryer. Dust collector is perched at top of dryer.



Figure 3.27 An EDC light ends distillation column is shown with its RD/SRV vent.



Figure 3.28 An EDC heavy ends distillation column is shown.

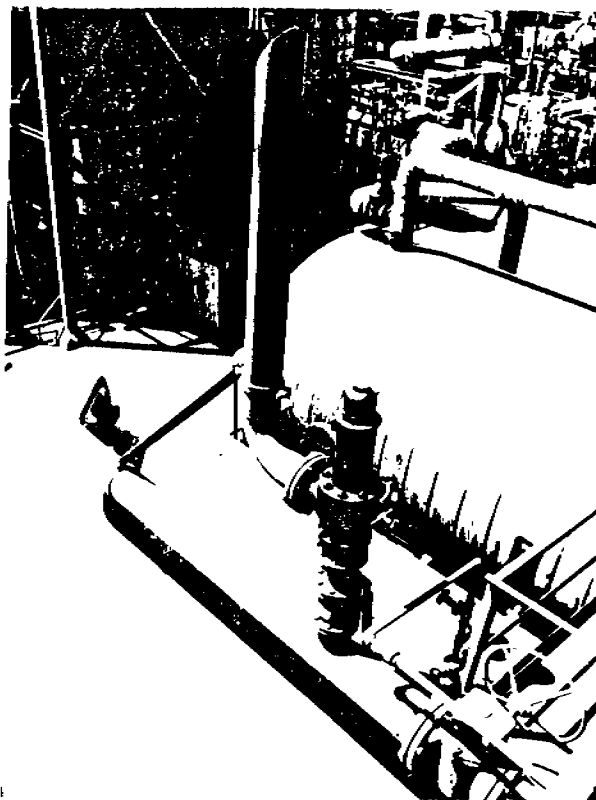


Figure 3.29 The top of an EDC light ends column condenser showing the RD/SRV vent.

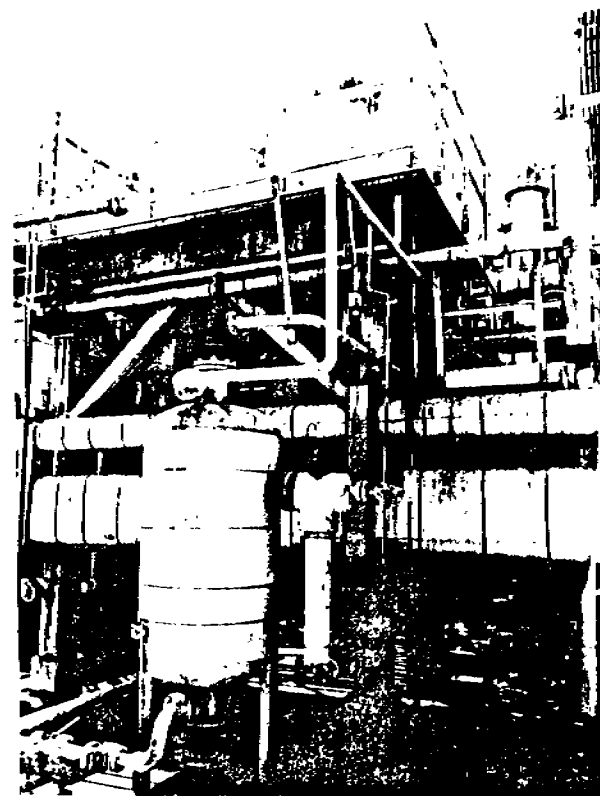


Figure 3.30 In the foreground the light ends dryer regeneration vessel is shown in balanced EDC-VC plant.



Figure 3.31 An EDC finishing column with the RD/SRV and its vent mounted on the top. (In some installations the finishing column performs the function of the light ends distillation column while in others it encompasses the functions of both the light and heavy ends columns.)

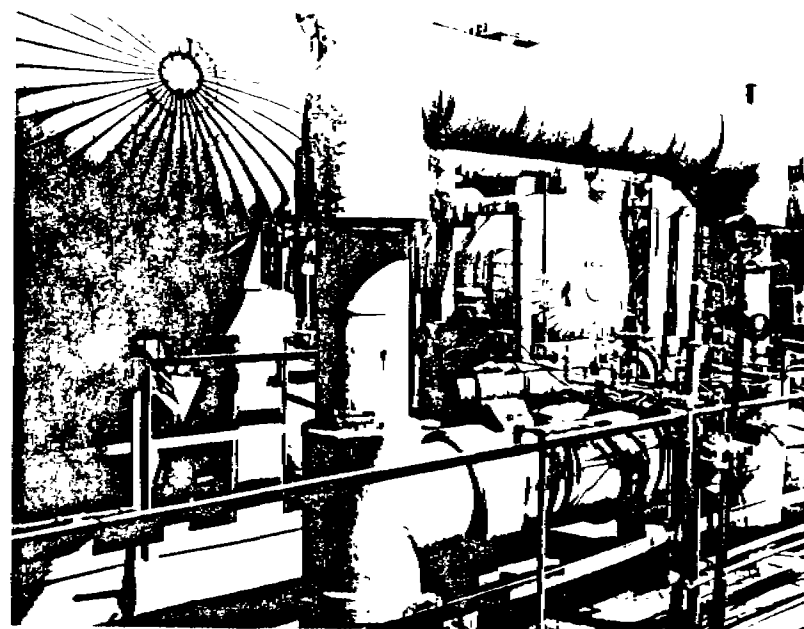


Figure 3.32 Foreground shows the insulated piping connected to the reactor refrigerator condenser vessel in a balanced EDC oxychlorination plant.

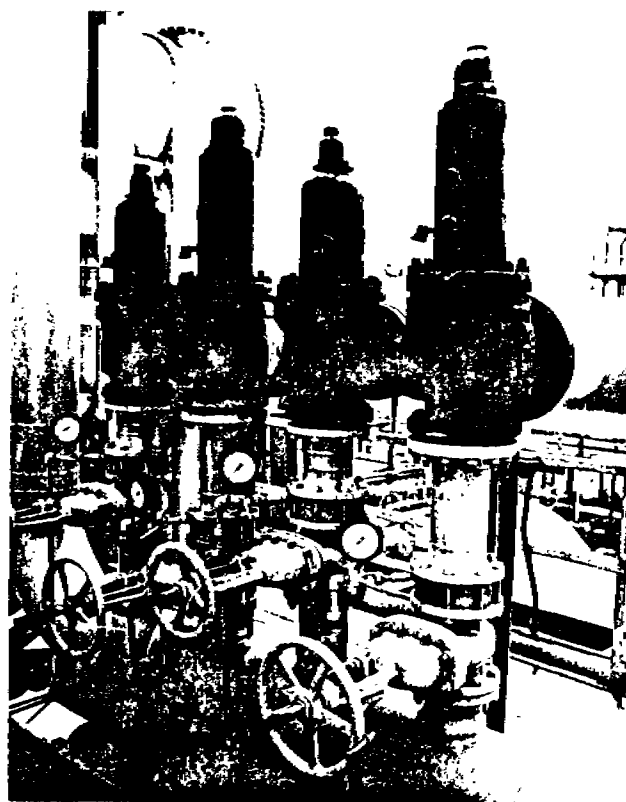


Figure 3.33 Typical RD/SRV assembly with the vents from each connected to a manifold of the recovery system.

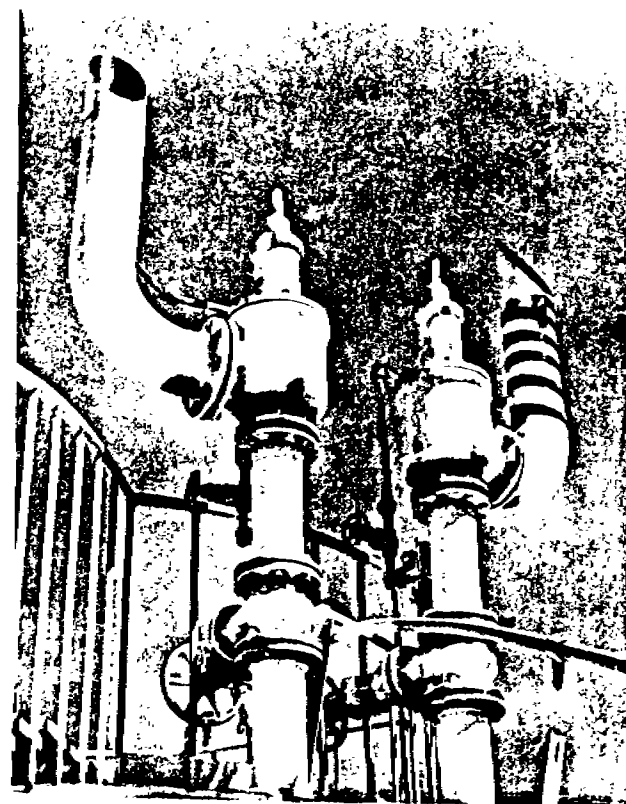


Figure 3.34 Dual RD/SRV vents mounted at top of spherical vinyl chloride storage tank.

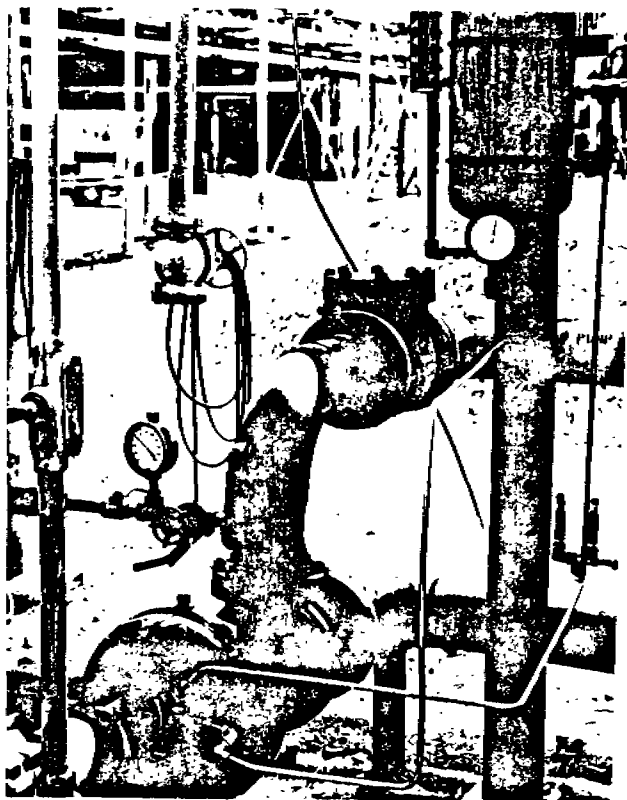


Figure 3.35 Typical pump and double mechanical seal.

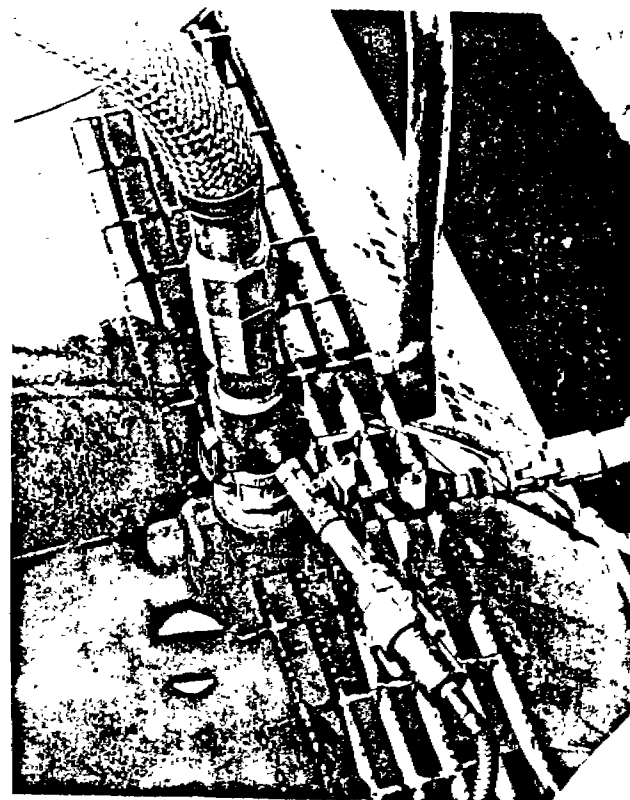


Figure 3.36 Top connections on railroad tank car shown with flexible hose attached for VC loading. Smaller diameter flexible hose in the foreground is connected to recovery system.

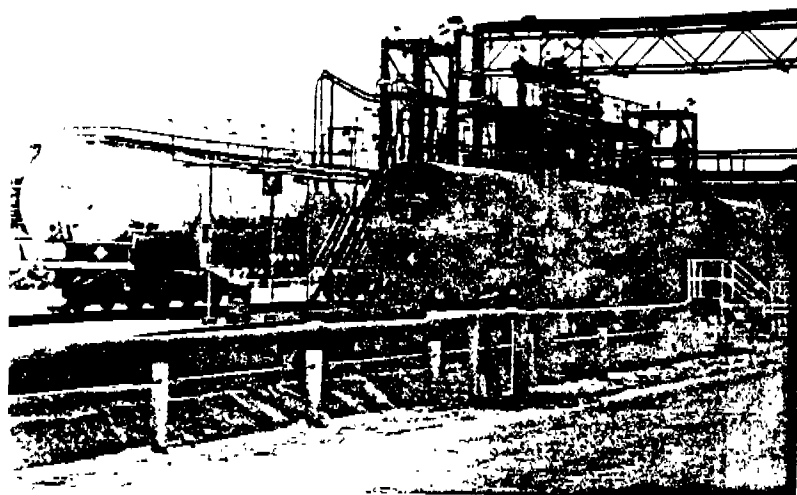


Figure 3.37 Railroad tank car loading platform shown with pipe rack support for flexible hose VC feed and recovery system in VC plant.

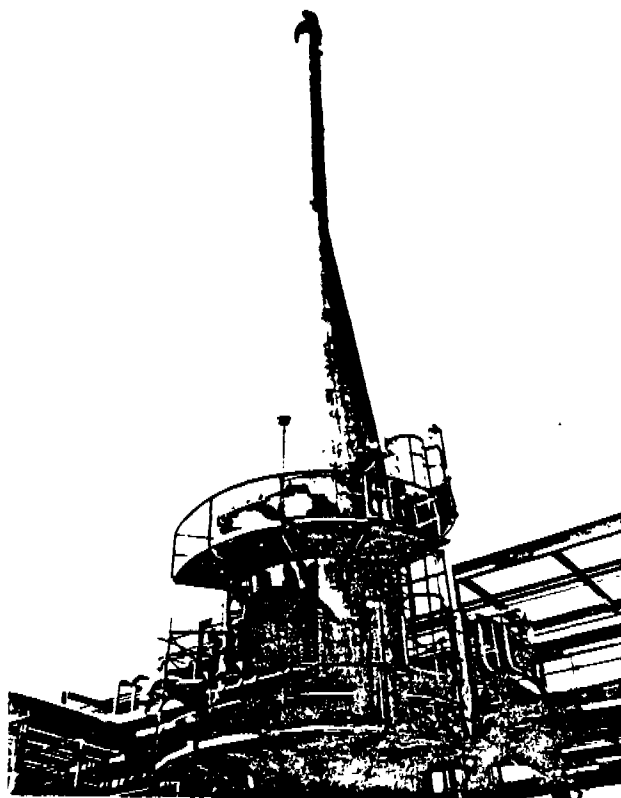


Figure 3.38 Incinerator and scrubber stack showing the steam exhaust stream in an EDC-VC plant.

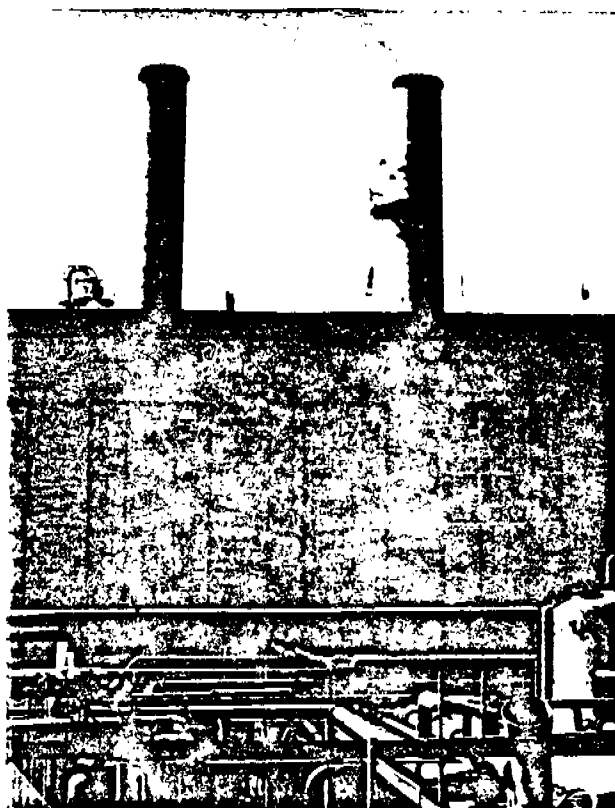


Figure 3.39 Incinerator and stacks of a PVC plant showing the platform (center stack) on which stack samples are taken to determine VC emission concentration.

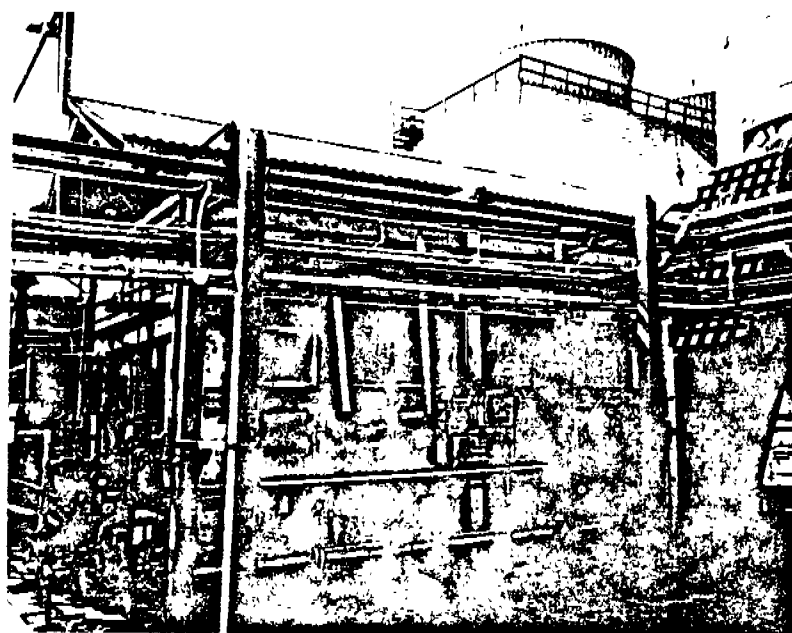


Figure 3.40 Typical incinerator in a VC and PVC plant with bottom portion of stack shown at the right.

4.0 LEAK DETECTION MONITORING INSTRUMENTATION, RECORDS, AND REPORTS

A requirement of the Standard is that an EPA approved leak detection and elimination program be operational. This requirement includes an installed continuous leak detection monitoring system, routine leak detection monitoring with a portable hydrocarbon detector and a leak elimination plan.

The Standard also requires recordkeeping (recording and retention for at least two years) of data relating to leaks detected by one of several ways.

Conducting a meaningful inspection for the determination of compliance of vinyl chloride emissions in typical EDC-VCM-PVC plants presents a number of unique challenges. The first is that the technology used requires a relatively high degree of expertise. The second is that the plant area, from raw materials to finished product shipping, is measured in acres rather than in square feet and may extend from below ground level to several hundred feet above ground. Added to these is the difficulty in making a definitive determination of some equipments with respect to the specific process(es) or function(s) they serve. Therefore, the NESHAPS Inspector needs to resort to complementary methods, in addition to normal inspection procedures, to make a determination of compliance.

To circumvent these unique challenges, a NESHAPS inspection, of necessity, will need to rely on the in-plant continuous monitoring instrumentation and the records obtained therefrom. In this chapter, the typical continuous monitoring system, the resultant records and reports are described and discussed. All are required to be in compliance.

4.1 LEAK DETECTION MONITORING INSTRUMENTATION

The standard promulgated on October 21, 1976 requires that continuous monitoring detection and measurement instrumentation be permanently installed in a plant in which vinyl chloride may be emitted to the atmosphere.

Typically, the instrumentation consists of a vinyl chloride or hydrocarbon measurement instrument, mini-computer, computer program for data acquisition and data reduction, data terminal and assorted 1/4" stainless steel tubing, solenoid valves, vacuum pumps, etc. The measurement instrument may be a gas chromatograph or, if the owner/operator assumes that all hydrocarbons measured are vinyl chloride, an infrared spectrometer or flame ion detector or an equivalent or alternative method.

The monitoring instrumentation is based on area (i.e., volume) sampling. However, some plants will also monitor fugitive emission sources such as pump seals, agitator seals, couplings, etc. The typical instrumentation system uses one measurement instrument with a system of tubing that serves to draw air samples from an area of the plant into the detector air sample chamber where a measurement of vinyl chloride concentration is made. The concentration value is then transmitted to the computer memory to be printed out on the computer terminal at a later time. The time interval between measurements is 1 to 3 minutes. Usually, each monitoring point is measured in sequence ~~and~~ the sequence is ~~unchanging~~. When all points associated with a measurement instrument have been measured for vinyl chloride emissions and transmitted to the computer memory, the computer program provides for each measurement to be printed in tabular form. Each measurement is identified with respect to the time of the measurement and location within the plant. Depending on the computer program, average vinyl chloride emissions for each point on the basis of shift, day, week and month may also be printed out and become a part of the record. In some instances, the data terminal does not print any measurement made unless the vinyl chloride concentration is greater than some defined level, such as 5 ppm. Plants that employ this system will record each measurement for each point on the measurement instrument's printer. It too becomes a part of the required recordkeeping. Usually the concentration is measured at each point at least every 25 minutes. Each plant sets its own threshold level for the purpose of defining a leak. In most cases, two consecutive measurements from the

same monitoring point equal to or greater than the concentration threshold value are used in the definition of a leak. The concentration threshold level is the definition of a leak for the leak detection monitoring system. This definition requires the approval of the EPA Administrator and it is set at a level compared with the vinyl chloride background concentration.

When two consecutive measurements at a point indicate a leak, plant personnel assigned to the "Leak Detection Patrol" investigate with a portable instrument the region of the plant in which the monitoring point is located.

The monitoring system is required to be calibrated daily by one of two methods, described in 61.68(c). Some plants reserve one of the points in the sequence of point measurements for calibration. Thus, the instrument is calibrated in each sequence of measurement.

Some plants may use more than one measurement instrument when a large number of points are being monitored. The number of points under observation by an instrument ranges from 9 to 19, while the total number in a plant ranges from 9 to 76. However, EPA approval is required with respect to the position and minimum number of points.

A schematic of a monitoring system is shown in Figure 4.1 for which there are n-air sample inlets. When a solenoid valve is activated, it allows an air sample to be drawn by a vacuum pump from a point in the plant into the detector air sample chamber. The pump operates continuously, evacuating the manifold of the previous air sample so as not to influence the vinyl chloride concentration measurement of the next air sample. In addition, the volume of the air sample drawn prior to actual measurement is sufficient to effectively purge the detector air sample chamber of any residue from previous air samples.

The ~~switching~~ of the solenoid valves may be accomplished by one of two methods: a mechanical or electronic timer where the sequence is unchanging; a computer-controlled system where the sequence may be changed according to a program. Those installations using timers usually activate one solenoid at any one time. Computer-controlled systems may have sophisticated programs where one or more solenoids may be operated to more quickly assess the emission(s) in one or more plant areas.

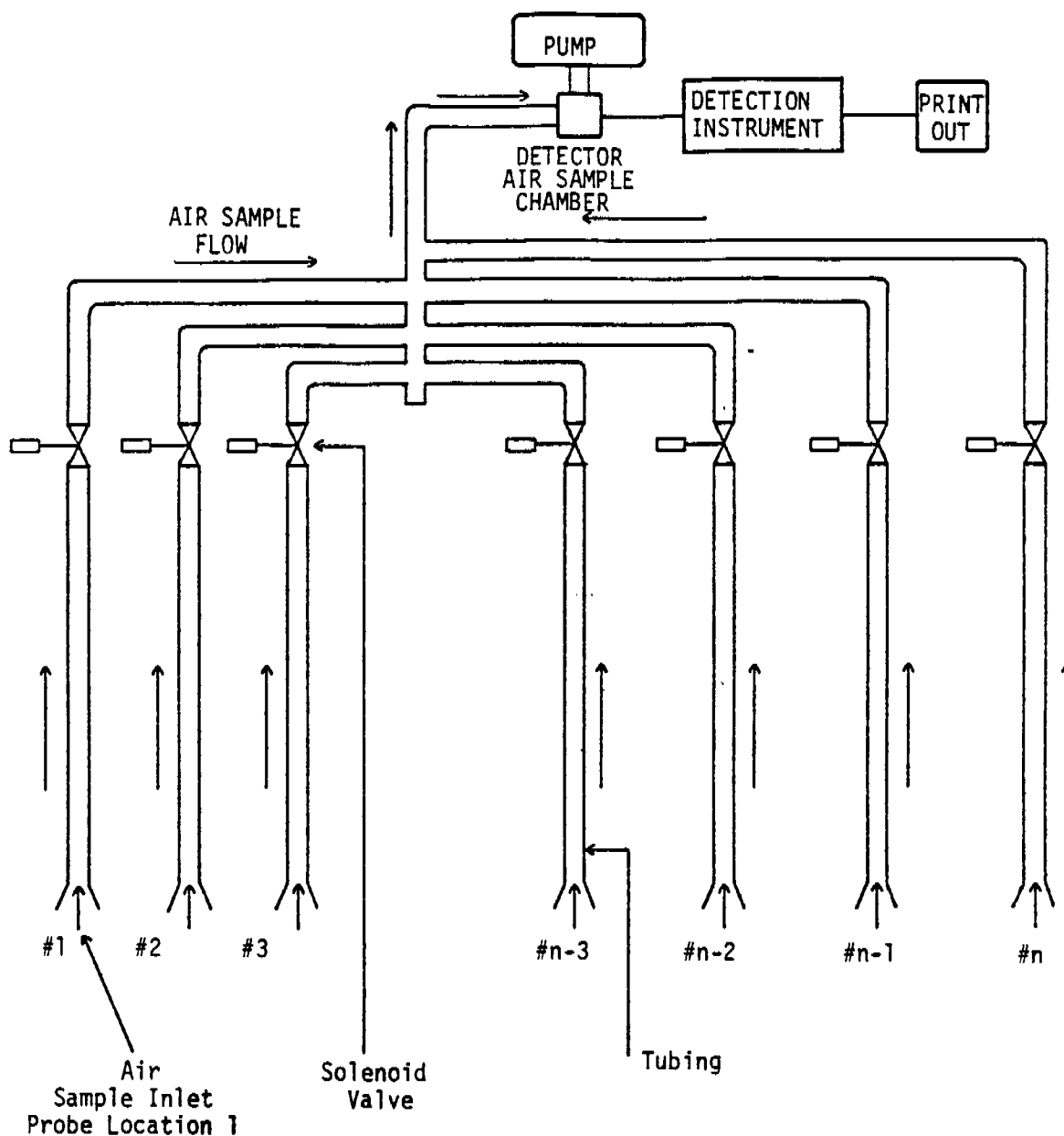


Figure 4.1: Schematic diagram of continuous monitoring system for vinyl chloride emissions.

4.2 LEAK DETECTION MONITORING RECORDKEEPING

The owner/operator is required to record data, retain the records on location for a minimum of two years and to make available, upon request of an EPA representative, those records obtained from the continuous ~~leak~~ leak detection monitoring system.

Specific data of the detected leaks will be recorded and retained which pertain to the location within the plant, vinyl chloride concentration and the date and approximate time of measurement.

4.3 ROUTINE LEAK DETECTION AND RELIEF DISCHARGE RECORDKEEPING

The owner/operator is also required to record data, retain the records on location for a minimum of two years and to make available, upon request of an EPA representative, records obtained of leaks detected during routine monitoring with a portable hydrocarbon detector and for relief discharges from reactors.

Specific data of each leak detected during routine monitoring will be recorded and retained which relate to location within the plant, vinyl chloride concentration, date and time of measurement, cause of each leak, and the action taken to repair or eliminate each leak.

Specific data of each relief discharge from reactors will be recorded and retained which pertain to 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 the measures adopted to prevent future discharges. In addition, a daily operating record for each reactor, including pressures and temperatures, will be recorded and retained.

5.0 INSPECTION PROCEDURES AND INSPECTION FORMS

The plant's compliance with the Standard will be determined through periodic inspections by an EPA representative, in addition to data required in the semi-annual reports on stripping and reactor opening loss and on emission tests. The inspection entails a physical inspection as well as a review and assessment of the plant's records.

In the following presentation, a number of forms have been developed for the purpose of aiding the inspector to make a definitive inspection in the most efficient and expeditious manner. If the forms are used properly, all major facets in the Standard will be covered. In fact, the questions and statements that make up the forms mirror the major facets of the Standard. Moreover, the questions and statements have been couched so that answers and responses may elucidate or reveal non-compliance conditions. Ideally, all questions and statements on all forms will be answered completely during the regular or periodic inspections. However, some plants may excel in complying with one or more sections of the Standard. An inspector having become aware of this fact may elect not to pursue questions and statements relating to that portion of the Standard.

The frequency of the inspections is not recommended in this document, because this is a function of personnel being available on a regular basis. Besides, experienced inspectors are the best judge of the required inspection frequency.

The forms described below are self explanatory and provide a sequence that an inspector may choose to follow during an inspection.

5.1 SUMMARY OF COMPLIANCE STATUS

This form serves to summarize on one page the status of the plant with respect to the major facets of the Standard. The questions and statements serve to determine where emissions occur and at what levels, the emission control devices used for each emission source and the waivers that have

been issued. This form will be most useful to personnel of the Enforcement Division having responsibility to make a determination of compliance.

5.2 CHECKLIST

This form contains 29 question and statements requiring responses. They are grouped under the following categories: General, Leak Detection Monitoring System, Stack Emission Monitoring System, Portable Instrument, Leak Detection and Elimination, Discharges to the Atmosphere, Fugitive Emissions, Reactors and Furnaces, Control Devices, Stack Emissions, Inprocess Wastewater and Reactor Opening Loss. The responses require the inspector, in most cases, to actually view and verify. In the case of instrumentation, there is provision for the inspector to determine the accuracy of the instrumentation and/or system calibration. It is strongly recommended that a calibration be performed on one or more monitoring points of the leak detection monitoring system. In doing so, the inspector automatically checks the integrity of those monitoring points.

It may be more practical for the plant's personnel to provide the responses to No. 23 rather than the inspector. However, the inspector should be present during the time the sample is being prepared and data obtained.

It is strongly recommended that the inspector observe in its entirety the plant's procedure to determine the reactor opening loss.

5.3 ON REVIEW OF RECORDS

Due to the maturity of the PVC industry and the economic environment that results, EDC, VCM and PVC are typically large capacity plants. One plant may cover many acres and extend up to 100 to 200 feet above ground level as well as below ground level. It may be physically impossible for an inspector to inspect all parts of a plant in person. It is strongly recommended that the central point of the inspector's focus be placed on the records that the plant is required to maintain, and particularly the leak detection monitoring system. Therefore, the review and assessment of the plant's records is an important aspect of every inspection. The items in the form provided for the review of records is designed to elucidate compliance at the major or most probable emission points.

5.4 PRE-TEST EQUIPMENT CHECKLIST FOR STACK EMISSION TEST

The stack emission test required in the Standard, Test Method 106, is very clear and precise on the equipment and apparatus to perform the test. This form is designed to ensure that both inspector and plant personnel are reminded of the entire equipment and apparatus list required. It also serves to document alternative or equivalent equipment or procedures.

5.5 EQUIPMENT CHECKLIST FOR VINYL CHLORIDE CONCENTRATION IN INPROCESS WASTEWATER, RESIN, SLURRY, WET CAKE AND LATEX SAMPLES

Test Method 107 is also clear and precise on the equipment and apparatus required to analyze samples in a head space analyzer. This form is designed to aid the inspector and plant personnel in conducting analytical tests that conform with the Standard.

SUMMARY OF COMPLIANCE STATUS
 (SCS)
 NESHAPS INSPECTION FOR VINYL CHLORIDE EMISSIONS COMPLIANCE

Inspection Date _____
 Inspector's Name _____
 Firm's Name _____
 Firm's Address _____

PARAMETER OR ITEM		EMISSION SOURCE STATUS			
Emission Source					
1	Where ducted? Atmosphere or Control Device				
2	Emission Control Device Description				
	In Existence				
	Date to be Installed				
3	Frequency of Emissions Cont./Intermit./Emergency				
4	Applicable Regulations				
5	Emission Standard ppm by vol. or ppm by wt. or gm. per Kg.				
6	Estimated Emissions ppm by vol. or ppm by wt. or gm. per Kg.				
7	Monitoring Requirements				
8	Waiver Applications				
9	Date Waiver Issued				
10	Remarks on Compliance Emissions & Emission Tests				
	Waivers				
	Recordkeeping				

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COLORITE 007358

CHECKLIST

NESHAPS INSPECTION FOR VINYL CHLORIDE EMISSIONS COMPLIANCE

Inspection Date _____

Inspector's Name _____

GENERAL

1. Firm's name _____

2. Firm's address _____

3. Process designation/product identification (check one or more):

EDC: ☐ oxychlorination ☐ balanced ☐ N.A.

VCM: ☐ hydrochlorination ☐ dehydrochlorination ☐ N.A.

PVC: ☐ suspension ☐ dispersion ☐ latex ☐ N.A.

☐ bulk ☐ solution ☐ copolymer _____

4. Rated and average annual reactor/cracking capacity

EDC: Design _____; Normal Max. _____; Actual _____

VCM: Design _____; Normal Max. _____; Actual _____

PVC: Design _____; Normal Max. _____; Actual _____

LEAK DETECTION MONITORING SYSTEM

5. Permanent leak detection monitoring system [61.65(8)(i)]

a) Total number of points monitored: _____

b) Number of measuring instruments: _____; Type(s) _____

c) Time interval to cycle all points: _____

d) Definition of a Leak: _____

e) Lower detection limit (LDL) of instrument _____

f) Measurement sequence: ☐ unchanging ☐ program controlled

g) Data reduction (check one or more)

☐ none ☐ hourly ☐ shift ☐ daily ☐ weekly ☐ monthly

☐ other (specify) _____

6. Calibration of leak detection monitoring system [61.65(8)(iii)]:

- a) List instruments and data from monitor points which were tested for calibration. (Attach sheets if more space is required.)

Date & Time	Location in Plant	Instrum. Iden.	Cal. VCM Concen.	Instrum. VCM Concen.	Percent Deviation	Action Required

- b) Calibration method used (check one or more)

- ☐ None
☐ Paragraph 61.65(8)(iii)(A) - Test Method 106 - 5.2.1, 5.2.3
☐ Paragraph 61.65(8)(iii)(B)
☐ Other _____

STACK EMISSION MONITORING SYSTEM

7. Emission (i.e., stack) monitoring system

- a) List emission (i.e., stack) sources

Location in Plant	Ducted Processes	Continuous or Sampling, Other	Number of Monitoring Points

- b) Lower Detection Limit (LDL) of instrument _____.

8. Calibration of emission monitoring system:

- a) List instruments and data from monitor points which were tested for calibration.

Date & Time	Location in Plant	Instrum. Iden.	Cal. VCM Concen.	Instrum. VCM Concen.	Percent Deviation	Action Required

PORTABLE INSTRUMENT

9. Calibration of portable hydrocarbon detector(s):

- a) List instrument(s) which were tested for calibration

Date & Time	Location in Plant	Instrum. Iden.	Cal. VCM Concen.	Instrum. VCM Concen.	Percent Deviation	Action Required

b) Calibration method used (check one or more)

- ☐ None
- ☐ Paragraph 61.65(7)(iii)(A) - Test Method 106-5.2.1, 5.2.3
- ☐ Paragraph 61.65(7)(iii)(B)
- ☐ Other _____

LEAK DETECTION AND ELIMINATION

10. Leak detection and elimination process [61.65(8)]

- a) What is the frequency of the "Leak Detection Patrol"? _____.
- b) Check typical points and equipment which are required to be routinely checked for leaks by the "Leak Detection Patrol" in the following:

- | | | |
|---|--|---|
| ☐ reactor | ☐ storage - heavy | ☐ control devices |
| ☐ cracking furnace | ☐ storage - water | ☐ pumps |
| ☐ stripper | ☐ light ends col. | ☐ compressors |
| ☐ EDC purification | ☐ heavy ends col. | ☐ agitator(s) |
| ☐ recovery system | ☐ wastewater col. | ☐ loading |
| ☐ mixing | ☐ water wash col. | ☐ unloading |
| ☐ weighing | ☐ water quench col. | ☐ flanges |
| ☐ holding tank | ☐ wash water stripper | ☐ valves |
| ☐ separation tank | ☐ dryer | ☐ filter strainers |
| ☐ blending tank | ☐ condensers | ☐ centrifuges |
| ☐ storage - raw | ☐ RD/SRV | ☐ holding bins |
| ☐ storage - finished | | ☐ silos |
| ☐ Others: _____ | | |

- c) What is the average elapsed time between the determination of a leak by personnel of the "Leak Detection Patrol" and the plant's personnel taking corrective action for the purpose of eliminating the leak?

Small leaks: _____

Large leaks: _____

- d) What is the average elapsed time between the monitoring system alarm becoming activated and the plant's personnel taking corrective action for the purpose of eliminating the leak?

Small leaks: _____

Large leaks: _____

DISCHARGES TO THE ATMOSPHERE

11. Safety relief valves (SRV) and other emergency type (i.e., manual, vents, are: (check one or more)

- ☐ connected to the recovery system through a common header (i.e., manifold)
- ☐ vented to the atmosphere
- ☐ is manual vent ducted to recovery system

12. If a pressure gage is located between rupture disc (RD) and safety relief valve (SRV), list points in the plant where the gage indicates a higher than normal pressure, typically 0 to 5 psig. (Note: While in common use in plants, a pressure gage between RD and SRV is not a requirement of the Standard.) Identify those RD/SRV points which are in PVC plants by check (✓) in column 3.

RD/SRV Identification	Location In Plant	PVC Service	Inspector's Comments

13. List vents, other than emergency types, which are vented to the atmosphere and not connected to a recovery system, and which are suspected of having had short and/or long periods of emissions exceeding the limits specified in Sections 61.62, 61.63, 61.64 and 61.65.

Vent Identification	Location In Plant	Location of Nearest Monitoring Point(s)

FUGITIVE EMISSIONS

14. Investigate and witness the plant's standard operating procedure [61.65(c)] for fugitive emission sources [61.65(b)(1), (b)(2), (b)(5), (b)(6) and (b)(7)] and list any possible deficiencies.

Pertinent Fugitive Emission Source	Location In Plant	Possible Deficiency

15. Are plant personnel following the established standard operating procedures?

☐ Yes ☐ No

16. If the response to the above is "NO", list pertinent fugitive emission source, location in plant and action required where the established standard operating procedure is not being followed.

Pertinent Fugitive Emission Source	Location In Plant	Action Required

17. List equipment, location in plant, identification in the process of any pump, compressor and agitator which is not equipped as seal-less or with a double mechanical seal or which does not duct emissions through a control system.

Equipment	Location In Plant	Identification In Process	Inspector's Comments

18. Incoming raw material received by:

☐ Pipeline ☐ Truck ☐ Rail ☐ Barge

19. Finished product material shipped by:

☐ Pipeline ☐ Truck ☐ Rail ☐ Barge

REACTORS AND FURNACES

20. Give the number of reactors for each capacity.

EDC: Capacity _____ Number _____

PVC: Capacity _____ Number _____

VCM (Hydrochlorination):

Capacity _____ Number _____

21. Give the number of cracking furnaces.

VCM(dehydrochlorination): Capacity _____ Number _____

CONTROL DEVICES

22. List control devices, location in plant, major entering streams, major exiting streams, vent location.

Control Device	Location In Plant	Major Entering Streams	Major Exiting Streams	Vent Location

STACK EMISSIONS

23. List plant's performance specifications of stack emission continuous monitoring instrumentation:

- a) Stack identification _____;
- b) Mean value, _____, calculated from a series of absolute measurements made by using the equipment specifications and procedure of reference Test Method 106 (see APPENDIX A);
- c) Number of measurements used to calculate the mean value _____;
- d) Accuracy, _____ percent of the mean value;
- e) Calibration error, _____ percent of each calibration gas mixture value;
- f) Zero drift (2 hr.), _____ percent of calibration span;
- g) Zero drift (24 hr.), _____ percent of calibration span;
- h) Calibration drift (2 hr.), _____ percent of calibration span;
- i) Calibration drift (24 hr.), _____ percent of calibration span;
- j) Response time, _____ (Time required from the insertion of a known vinyl chloride concentration gas sample into the stack and the stack instrument indicating a value 95% of the known vinyl chloride concentration).

24. If more than one stack was tested, and if the other test data were significantly different from the above data, use attach sheets to provide the information obtained from other stack tests.

25. Were the stack emission tests made under conditions of maximum production rate?

☐ Yes ☐ No

If the response is No, give the percent of maximum production rate under which the stack emission tests were made: _____ percent.

26. Were all stack samples analyzed within 24 hours? ☐ Yes ☐ No

If the response is No, give elapsed time, to the nearest hour, from taking sample to its being analyzed: _____ hours.

27. List deviations or substitutes from reference Test Method 106 equipments materials and procedures which are required in conducting the stack emission tests.

Equipments/Materials/Procedure Identification	Deviation or Substitutes From Test Method 106	Inspector's Comments

INPROCESS WASTEWATER

28. Identify any inprocess wastewater stream and location in plant which is mixed with another water stream prior to the reduction of vinyl chloride concentration to 10 ppm or less.

Inprocess Wastewater Stream Identification	Location In Plant	Identification of Process Step	Inspector's Comments

REACTOR OPENING LOSS

29. Briefly describe the plant's procedure to determine the emission due to opening the reactor.

ON REVIEW OF RECORDS

NESHAPS INSPECTION FOR VINYL CHLORIDE EMISSIONS COMPLIANCE

Review Date _____

Reviewer's Name _____

Firm's Name _____

Firm's Address _____

EMISSION (STACK)

1. Review of hourly ☐yes ☐no average from continuous stack emission.
2. Number of stack emissions (continuous emissions for 1 hour or more) which exceeded limits specified in Sections 61.62, 61.63 and 61.64:

3. Were each of these emissions properly and accurately reported in the appropriate Semi-annual Report?

☐ Yes ☐ No

4. If the response to No. 3 is No, list date, time, emission point location, duration, estimated integrated emission, and the cause or causes of emission. (Attach sheets if more space is required.)

Date & Time	Location In Plant	Duration	Est. Integrated Emission	Cause or Causes	Action Taken

LEAK DETECTION SYSTEM

5. Review of (check one or more) ☐hourly ☐shift ☐daily ☐weekly
☐monthly average from leak detection system.

6. Number of times one or more monitoring points indicated emission levels exceeded the value for the leak definition (See CHECKLIST 5 (d):

7. List date, time, monitoring point location, duration, estimated integrated emission and the cause or causes of emission of those leaks in No. 6. (Attach sheets if more space is required.)

Date & Time	Location In Plant	Duration	Est. Integrated Emission	Cause or Causes	Action Taken

ATMOSPHERIC DISCHARGES

8. Number of emergency discharges to the atmosphere: _____.
9. Were each of those emergency atmospheric discharges properly and accurately reported?
- ☐ Yes ☐ No
10. Were adequate preventative and/or maintenance procedures taken to prevent and minimize emergency atmospheric discharges?
- ☐ Yes ☐ No
11. If the response to either or both No. 9 and No. 10 is No, list date, time, emission point location, duration, estimated integrated emission, and the cause or causes of the improperly and/or inaccurate reporting and the inadequate preventative and/or maintenance procedures relating to the emergency atmospheric discharges. (Attach sheets if more space is required.)

Date & Time	Location in Plant	Duration	Est. Integrated Emission	Cause or Causes	Inspector's Comments

12. Determine from plant records whether temperature, pressure, flow rate(s) and/or other process variables and/or if equipment failures (i.e., reduced flow rate of cooling water, defective temperature controller, etc.) gave rise to the necessity of the emergency discharge(s) from PVC reactors. List the date, time, location in plant and the condition(s) which appear to have produced the need for an emergency discharge(s).

Date & Time	Location In Plant	Conditions

13. List the dates and time when similar or equivalent conditions existed as in No. 12 and for which an emergency discharge was not reported.

Date & Time	Location In Plant	Conditions

14. Review the leak detection records of those monitoring points nearest the location(s) and down stream in No. 13 on those dates and times where conditions existed which appear to give rise to the necessity of emergency discharge. List date, time, location in plant and the emission levels of the nearest monitoring points.

Date & Time	Location In Plant	Emission Level of Monitoring Points			

15. List the date, time, location in plant from the tabulation in No. 14 where the owner/operator appears not to be in compliance with the NESHAPS vinyl chloride standard and its amendments.

Date & Time	Location In Plant	Inspector's Comments

REACTOR OPENING LOSS

16. Review analytical records of vinyl chloride concentration in polyvinyl chloride to determine "reactor opening loss" of reactors (and stripper where applicable), prepolymerization and post polymerization vessels. List date, vessel identification, and batch identification where emissions exceeded standard.

Date	Vessel Identification	Batch Identification	Inspector's Comments

RESIN, SLURRY, WET CAKE AND LATEX SAMPLING

17. Review analytical records of vinyl chloride concentration in polyvinyl chloride resin, slurry, wet cake and latex to determine the weighed average residual vinyl chloride concentration in all grades of polyvinyl chloride resin processed through the stripping operation on each calendar day. List date, vessel identification, and batch identification where emissions exceeded standard.

Date	Vessel Identification	Batch Identification	Inspector's Comments

RECORDKEEPING

18. Review and assess the recordkeeping as required in the standard in the listing below, and comment on each with respect to completeness, form and ease of reference.

Record	Inspector's Comments
Stack emission monitoring	
Leak detection monitoring	
Leaks detected by "Leak Detection Patrol"	
Stack emission tests	
Reactor opening emissions	
Inprocess waste water emissions	
Resin, slurry, wet cake and latex emissions	

PRE-TEST
EQUIPMENT CHECKLIST FOR STACK EMISSION TEST
(TEST METHOD 106)

NESHAPS INSPECTION FOR VINYL CHLORIDE EMISSIONS COMPLIANCE

Pre-Test Meeting Date _____

Inspector's Name _____

Firm's Name _____

Firm's Address _____

1. Probe

a) Is probe made of stainless steel, pyrex glass, or teflon tubing?

b) What is temperature of stack? _____

c) Does probe have glass wool plug? ☐ Yes ☐ No

2. Sample line

a) Is sample line made of teflon? ☐ Yes ☐ No

b) Is a new unused piece used for each series of bag samples? ☐ Yes ☐ No

3. Quick connects

a) Are 2 male and 2 female connects used? ☐ Yes ☐ No

b) Are they made of stainless steel? ☐ Yes ☐ No

c) Does the pair for the bag have ball checks? ☐ Yes ☐ No

d) Are they assembled as required? ☐ Yes ☐ No

4. Rigid container

a) Is container leak proof? ☐ Yes ☐ No ☐ Unknown

b) Does it have a cover to protect contents from sunlight? ☐ Yes ☐ No

5. Sampling bags

a) What material are bags made of? _____

b) Are bags of 100 liter capacity? ☐ Yes ☐ No ☐ Unknown

6. Needle valve

Will needle valve allow proper adjustment of sample flow? ☐ Yes ☐ No

7. Vacuum pump

a) Is pump of the leak-free type? ☐ Yes ☐ No

b) Does pump have a minimum capacity of 2 liters per minute? ☐ Yes ☐ No

8. Charcoal tube

Does a charcoal tube follow pump to prevent admission of vinyl chloride to atmosphere? ☐ Yes ☐ No

9. Flow meter

Does the flow meter have a capability of measuring flow range from 0.10 to 1.00 liter per minute? ☐ Yes ☐ No

10. Pitot tube and manometer

a) What type of pitot tube is used? _____

b) Is pitot tube attached to probe? ☐ Yes ☐ No

c) Will an inclined manometer be used? ☐ Yes ☐ No

11. List substitutes for equipments and materials required in Test Method 106 in conducting stack emission tests.

Equipment/Materials Identification	Substitute	Inspector's Comments

12. Is plant in compliance with Test Method 106? ☐ Yes ☐ No
13. If the response is No, list action items which must be completed prior to Test date in order to conduct stack emission tests:

Action Item 1: _____

2: _____

3: _____

14. Test Date: _____

EQUIPMENT CHECKLIST FOR VINYL
CHLORIDE IN INPROCESS WASTEWATER,
RESIN, SLURRY, WET CAKE AND LATEX SAMPLES
(TEST METHOD 107)

NESHAPS INSPECTION FOR VINYL CHLORIDE EMISSIONS COMPLIANCE

Inspection Date _____

Inspector's Name _____

Firm's Name _____

Firm's Address _____

1. Sample bottles

a) Are the sample bottles of 60 ml (2oz) capacity?

☐ Yes ☐ No

b) Do the bottles have waxed lined screw on top?

☐ Yes ☐ No

c) Do the bottles have electrical tape or equivalent to prevent loosening of bottle tops?

☐ Yes ☐ No

2. Vials

a) Are vials of 50 ml capacity?

☐ Yes ☐ No

b) Are they equipped with sealed Teflon faced Tuf-Bond discs for water samples?

☐ Yes ☐ No

c) Are they equipped with seals and caps, Perkin-Elmer Corporation No. 105-0118 or equivalent?

☐ Yes ☐ No ☐ Unknown

3. Analytical balance

a) Is it capable of weighing reproducibility to ± 0.001 gram?

☐ Yes ☐ No ☐ Unknown

b) What is the weighing span in the region of weight that is used in Test Method 107? _____

4. Syringe

a) Is its capacity 100 μ l? ☐ Yes ☐ No ☐ Unknown

b) Is the model Precision Series "A" No. 010025 or equivalent?

☐ Yes ☐ No ☐ Unknown

5. Vial Sealer

a) Is the Model, Perkin-Elmer No. 105-0106 or equivalent?

☐ Yes ☐ No ☐ Unknown

6. Gas Chromatograph

a) Is the Model, Perkin-Elmer Model F-40 head space analyzer No. 104-0001 or equivalent?

☐ Yes ☐ No ☐ Unknown

b) List substitutes used for the following:

2 m x 3.2 mm stainless steel column; _____

contains 0.4% carbowax on carbopak A (or Carbopak B)
Perkin-Elmer No. 105-0133 or equivalent: _____

7. Thermometer

a) Range 0 to 100°C, with accuracy $\pm$ 0.1°C, Perkin-Elmer No. 105-0109 or equivalent.

☐ Yes ☐ No

8. Sample Tray Thermostat System

a) Perkin-Elmer No. 105-0103 or equivalent.

☐ Yes ☐ No

9. Septa

a) Sandwich type, for automatic dosing, 13 mm, Perkin-Elmer No. 105-1008 or equivalent.

☐ Yes ☐ No

10. Integrator - Recorder

a) Hewlett-Packard Model 3380A or equivalent. ☐ Yes ☐ No

11. Filter dryer assembly

a) Perkin-Elmer No. 2230117 or equivalent. ☐ Yes ☐ No

12. Soap Film Flowmeter

a) Hewlett-Packard No. 0101-0113 or equivalent.

☐ Yes ☐ No

APPENDIX A: MEAN VALUE CALCULATION

The mean value calculated from the reference method (Test Method 106) test data measurements is used as a norm to assess the stack emission continuous monitoring instrumentation.

The mean value of the data set is calculated according to the following expression

$$\bar{X} = \frac{1}{n} \sum_{i=1}^n X_i \quad (A-1)$$

where

X_i = The i^{th} absolute measurement obtained from reference Test Method 106,

$\sum_{i=1}^n$ = Sum of the n - absolute measurements,

n = Number of absolute measurements,

$\bar{X}$ = Mean value.

APPENDIX B
NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR
POLLUTANTS

Standard For Vinyl Chloride

federal register

THURSDAY, OCTOBER 21, 1976



PART II:

ENVIRONMENTAL PROTECTION AGENCY

NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS

Standard For Vinyl Chloride

Title 40—Protection of Environment

CHAPTER I—ENVIRONMENTAL
PROTECTION AGENCY

SUBCHAPTER C—AIR PROGRAMS

[FRL 618-1]

PART 61—NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS

Standard for Vinyl Chloride

On December 24, 1975, under section 112 of the Clean Air Act, as amended (42 U.S.C. 1857), the Environmental Protection Agency (EPA) added vinyl chloride to the list of hazardous air pollutants (40 FR 59477) and proposed a national emission standard for it (40 FR 59532). The standard covers plants which manufacture ethylene dichloride, vinyl chloride, and/or polyvinyl chloride.

EPA decided to regulate vinyl chloride because it has been implicated as the causal agent of angiosarcoma and other serious disorders, both carcinogenic and noncarcinogenic, in people with occupational exposure and in animals with experimental exposure to vinyl chloride. Reasonable extrapolations from these findings cause concern that vinyl chloride may cause or contribute to the same or similar disorders at present ambient air levels. The purpose of the standard is to minimize vinyl chloride emissions from all known process and fugitive emission sources in ethylene dichloride-vinyl chloride and polyvinyl chloride plants to the level attainable with best available control technology. This will have the effect of furthering the protection of public health by minimizing the health risks to the people living in the vicinity of these plants and to any additional people who are exposed as a result of new construction.

Interested parties participated in the rulemaking by sending comments to EPA. The comments have been carefully considered, and where determined by the Administrator to be appropriate, changes have been made to the regulation as promulgated.

SUMMARY OF THE STANDARD

In ethylene dichloride-vinyl chloride plants, the standard limits vinyl chloride emissions from the ethylene dichloride and vinyl chloride formation and purification processes to 10 ppm. For the oxychlorination process, vinyl chloride emissions are limited to 0.2 g/kg of ethylene dichloride product.

In polyvinyl chloride plants, the standard limits vinyl chloride emissions from equipment preceding and including the stripper in the plant process flow to 10 ppm. Emissions from equipment following the stripper are to be controlled by stripping dispersion resins to 2000 ppm and other resins to 400 ppm, or by using equivalent controls. Vinyl chloride emissions from reactor opening are to be reduced to 0.02 g/kg polyvinyl chloride product.

In both ethylene dichloride-vinyl chloride and polyvinyl chloride plants, relief valve discharges and manual venting of gases are prohibited except under emergency conditions. Fugitive emissions

are required to be captured and controlled.

HEALTH AND ENVIRONMENTAL IMPACTS

EPA prepared a document entitled the *Quantitative Risk Assessment for Community Exposure to Vinyl Chloride* which estimates the risk from vinyl chloride exposure to populations living in the vicinity of vinyl chloride-emitting plants before and after implementation of controls to meet the standard. There are no dose-response data for the concentrations of vinyl chloride found in the ambient air. Therefore, assessments of risk at ambient levels of exposure were extrapolated from dose-response data from higher levels of exposure using both a linear model and a log-probit model. Extrapolations made with each of these models entailed using different sets of assumptions. Because different assumptions can be made in extrapolating to low doses, the health risks are reported in ranges.

It was estimated that 4.6 million people live within 5 miles of ethylene dichloride-vinyl chloride and polyvinyl chloride plants and that the average exposure around these plants before installation of controls to meet the standard is 17 parts per billion. The exposure levels for uncontrolled plants were calculated based on estimated 1974 emission levels. Using the linear dose-response model, EPA found that the rate of initiation of liver angiosarcoma among people living around uncontrolled plants is expected to range from less than one to ten cases of liver angiosarcoma per year of exposure to vinyl chloride. The log-probit model gave predictions that are 0.1 to 0.01 times this rate. This wide range is an indication of the uncertainties in extrapolation to low doses. Due to the long latency time observed in cancer cases resulting from vinyl chloride exposure, increases initiated by exposure this year will not be diagnosed until the 1990's or later. Vinyl chloride is also estimated to produce an equal number of primary cancers at other sites, for a total of somewhere between less than one and twenty cases of cancer per year of exposure among residents around plants. The number of these effects is expected to be reduced at least in proportion to the reduction in the ambient annual average vinyl chloride concentration, which is expected to be 5 percent of the uncontrolled levels after the standard is implemented.

Changes in the standard since proposal do not affect the level of control required. Thus, the environmental impact of the promulgated standard is, with one exception, the same as that described in Chapter 6 of Volume I of the *Standard Support and Environmental Impact Statement*. According to data submitted by the Society of Plastics Industry, Inc. (SPI), the impact on water consumption in the draft environmental impact statement was overstated. In estimating the impact on water consumption, EPA based its estimates on worst case conditions. That is, EPA assumed that those control systems with the

greatest water usage would be employed and that there would be no recycling of water. There is no regulation which would require water recycling. According to SPI, the control system utilizing the most water will not be used generally by the industry and economic factors will cause plants to recycle much of the water. Therefore, according to SPI the impact of the standard on water consumption will be negligible.

The environmental impacts of the promulgated standard may be summarized as follows: The primary environmental impacts of the standard are beneficial and will consist of vinyl chloride emission reductions of approximately 94 percent at ethylene dichloride-vinyl chloride plants and 95 percent at polyvinyl chloride plants. Percentage numbers for both source categories are based on an estimated 90 percent reduction in fugitive emissions and 1974 emission levels.

The potential secondary environmental impacts of the standard are either insignificant or will be minimized without additional action, except for one adverse impact. Hydrogen chloride is already emitted by process equipment at ethylene dichloride-vinyl chloride plants and by other petrochemical plants in the complexes where ethylene dichloride-vinyl chloride plants are typically located. An incinerator used to attain the standard at an ethylene dichloride-vinyl chloride plant could increase hydrogen chloride emissions by several fold. Typically, however, due to the corrosion problems which would otherwise occur both on plant property and in the community, plants use scrubbers to control already existing hydrogen chloride emissions. Hydrogen chloride emissions resulting from control of vinyl chloride emissions are expected to be controlled for the same reason. If even a moderately efficient scrubber (95 percent control) were used to control the hydrogen chloride emissions resulting from incineration of vinyl chloride emissions, the increase in hydrogen chloride emissions from a typical ethylene dichloride-vinyl chloride plant due to the standard would be reduced to 35 percent. However, EPA plans to further evaluate the need to control hydrogen chloride emissions, since diffusion model results indicate that under "worst-case" meteorological conditions, the hydrogen chloride emissions from the process equipment and the incinerator combined would cause maximum ambient concentrations of hydrogen chloride in the vicinity of ethylene dichloride-vinyl chloride plants to be in the same range or somewhat higher than existing foreign standards and National Academy of Sciences (NAS) guidelines for public exposure.

ECONOMIC IMPACT

In accordance with Executive Order 11821 and OMB circular A-107, EPA carefully evaluated the economic and inflationary impact of the proposed standard and alternative control levels and certified this in the preamble to the proposed standard. These impacts are

discussed in Chapter 7 of Volume I of the *Standard Support and Environmental Impact Statement*. Comments on the proposed standard have resulted in only one major change in the economic impact analysis. EPA estimated that there would be four plant closures as a result of the promulgated standard. Of the four plants identified as possible closure candidates, one has given notice that it no longer produces polyvinyl chloride and the other three have indicated that they do not intend to close as a result of the standard.

The economic impacts of the promulgated standard may be summarized as follows: The total capital cost for existing plants to meet the standard is estimated to be \$198 million, of which \$15 million is for ethylene dichloride-vinyl chloride plants and \$183 million is for polyvinyl chloride plants. EPA estimates that these plants will have to spend \$70 million per year to maintain the required emission levels. In addition, the total capital cost for existing plants to meet the EPA's 1983 water effluent guideline limitations is expected to be \$83 million and the total annualized operation cost is \$17 million. The costs to the industry of meeting the OSHA standard cannot be quantified at this time, but they are expected to overlap to some degree with the costs to meet EPA's fugitive emission regulations. The costs of meeting the fugitive emission regulations are included in the total costs cited above for meeting the promulgated regulation. Broken out separately, the capital cost of meeting the fugitive emission regulations is \$37 million and the annualized cost is \$25 million.

The standard is not expected to deter construction of new ethylene dichloride-vinyl chloride plants or most types of new polyvinyl chloride plants. For one type of polyvinyl chloride plant (dispersion process) that represents 13 percent of the industry production, the standard would significantly deter the construction of smaller plants.

It is estimated that the price of polyvinyl chloride resins will rise by approximately 7.3 percent in order to maintain precontrol profitability and also to recover the total annualized control costs necessitated by the standard at ethylene dichloride-vinyl chloride plants and polyvinyl chloride plants. This increase is estimated to translate into a maximum consumer price increase in goods fabricated from polyvinyl chloride resins of approximately 3.3 percent. Recovery of effluent annualized costs plus maintenance of precontrol profitability is estimated to add approximately 2 percent to polyvinyl chloride resin prices and result in an additional maximum consumer price increase of 1 percent.

PUBLIC PARTICIPATION

During the public comment period, 50 comment letters on the proposed standard were received. There were 24 from industry; 3 from environmental groups; 15 from Federal, State, and local agencies; and 8 from individual citizens. As required by section 112(b) (1) (B) of the

Act, a public hearing was held on the proposed standard on February 3, 1978, in Washington, D.C. Presentations were made by the Environmental Defense Fund, the Society of the Plastics Industry, Inc., Dow Chemical Company, Diamond Shamrock Corporation, and Air Products and Chemicals, Inc. Copies of the comment letters received, the public hearing record, and a summary of the comments with EPA's responses are available for public inspection and copying at the EPA Public Information Reference Unit, Room 2922 (EPA Library), 401 M Street, SW., Washington, D.C. In addition, copies of the comment summary and Agency responses may be obtained upon written request from the Public Information Center, (PM-215), Environmental Protection Agency, 401 M Street, SW., Washington, D.C. 20460 (specify *Standard Support and Environmental Impact Statement, Emission Standard for Vinyl Chloride, Volume II*).

SIGNIFICANT COMMENTS AND CHANGES TO THE PROPOSED REGULATION

(1) *Decision to list vinyl chloride as a hazardous air pollutant.* In general, the commenters did not contest EPA's decision to list vinyl chloride as a hazardous air pollutant. However, three commenters (two companies and one Federal agency) argued that EPA placed undue emphasis on factors suggesting that vinyl chloride presented a health risk and ignored factors suggesting that no significant risk was involved. Under section 112, however, EPA could remove vinyl chloride from the list of hazardous air pollutants only if information were presented to EPA that shows that vinyl chloride is clearly not a hazardous air pollutant. As discussed more fully in the comment summary, the commenters did not provide conclusive evidence that vinyl chloride is not a hazardous air pollutant which causes or contributes to death or serious illness, nor did they conclusively prove that the health risk factors emphasized by EPA were insignificant.

Several other commenters agreed with EPA's decision to list vinyl chloride as a hazardous air pollutant, but argued that EPA had overstated the health problem, the emission levels, and the projected ambient air concentrations around uncontrolled plants. With regard to the alleged overstated health problem, the commenters stated, for example, that the U.S. worker EPA discussed as having been exposed to vinyl chloride levels lower than those usually encountered in polyvinyl chloride production has been dropped from the National Institute of Occupational Safety and Health's listing of workers with angiosarcoma. EPA agrees that there are questions concerning the level of exposure and in some cases the pathology of these cases not involved directly in polyvinyl chloride and vinyl chloride production. These uncertainties are stated in the appropriate footnotes of the *Scientific and Technical Assessment Report on Vinyl Chloride and Polyvinyl Chloride (STAR)* where the angiosarcoma cases are listed. However, in spite of these uncertainties, in view of

the possible exposure patterns, these cases cannot be ignored in the evaluation of the potential public health problems.

With regard to the alleged overstated emission levels, the uncontrolled emission levels reported by EPA were based on 1974 data. This qualification was stated wherever emission data were presented. EPA recognizes that emissions have been reduced since that time, and stated this in the preamble to the proposed standard. EPA decided not to gather more recent data on emission levels, because these emission levels are expected to change, and gathering the data would take considerable time both on the part of EPA and on the part of industry. Since the purpose of the standard is to minimize emissions, these more current data would not affect the standard itself. The 1974 emission levels were also used in diffusion modeling to project maximum ambient air concentrations around uncontrolled plants. These maximum air concentrations would probably be lower if 1976 emission levels were used. This would reduce the relative impact of the standard below that described in the *Standard Support and Environmental Impact Statement*, but would not affect the basis of the standard itself.

(2) *Approach for regulating Vinyl Chloride Under Section 112.* Two approaches other than using best available control technology were suggested by the commenters for regulating vinyl chloride under section 112. The first was to ban polyvinyl chloride products for which substitutes are currently available and to gradually phase out other polyvinyl chloride products as substitutes are developed.

In the preamble to the proposed standard EPA specified its reasons for not setting a zero emission limit for vinyl chloride, as follows: (1) There are beneficial uses of vinyl chloride products for which desirable substitutes are not readily available; (2) there are potentially adverse health and environmental impacts from substitutes which have not been thoroughly studied; (3) there are a number of employees, particularly in the fabrication industries, who would become at least temporarily unemployed; and (4) control technology is available which is capable of substantially reducing emissions of vinyl chloride into the atmosphere.

EPA agrees that substitutes do exist or could be manufactured for most polyvinyl chloride uses. However, in general, these substitutes do not have some of the more desirable characteristics of polyvinyl chloride, such as nonflammability. If vinyl chloride and polyvinyl chloride were banned, other substitutes with these more desirable characteristics would likely be developed. There is a risk that these substitutes would also have adverse health or environmental effects. Since control measures are available which can reduce vinyl chloride emissions by 90 percent or more, it does not seem prudent to reduce emissions by the remaining percentage and take the risk of introducing new untested chemicals into the environment.

Another approach suggested by the commenters was to base the standard for each individual emission point on cost versus benefit. Several of the fugitive emission sources were named specifically as ones for which the costs of control were substantially higher than the benefits. Although EPA did determine a cost-benefit ratio for the controls required for a number of emission points, EPA does not believe such a ratio is an appropriate basis on which to set a standard. Section 111 of the Clean Air Act provides for the development of standards based on best control technology (considering costs). Even under section 111, however, standards are not based on a fine balancing of costs versus benefits. Instead, costs are considered in terms of the affordability of the control technology required to achieve a given emission level and the economic impact of possible standards on the industry in question. Unlike section 111, section 112 does not explicitly provide for consideration of costs, so it would clearly be inappropriate to consider costs to a greater extent under section 112 than would be done under section 111. As discussed in the preamble to the proposed standard for vinyl chloride, EPA believes costs may be considered under section 112, but only to a very limited extent; i.e., to assure that the costs of control technology are not grossly disproportionate to the amount of emission reduction achieved. In comparison with other emission points, the costs of controlling the fugitive emission sources mentioned by the commenters are relatively small compared with the amount of emission reduction achieved.

Several commenters recommended adding to the regulation a provision for excess emissions during startup, shutdown, and malfunction. EPA considered this comment, and decided that this addition is not necessary for the vinyl chloride standard. Startup and shutdown of the process has essentially no effect on emissions to the atmosphere for polyvinyl chloride production, and technology exists to avoid excess emissions during startup and shutdown at ethylene dichloride/vinyl chloride plants. We do not believe plants should be allowed to emit excess emissions during malfunctions, and therefore are requiring them to shut down immediately.

(3) *Selection of source categories.* In the preamble to the proposed standard, EPA recognized that some small research and development facilities may exist where the emissions of vinyl chloride are insignificant and covering these facilities under the standard would be unnecessary and inappropriate. However, EPA did not have sufficient information available to clearly define which facilities should be excluded from the standard, and encouraged interested parties to submit such information during the comment period. Based on the information submitted, EPA decided to exempt polyvinyl chloride reactors and associated equipment from applicability of all parts of the standard if the reactors are used in a research and development and have a

capacity of no more than 0.19 m³ (50 gal). Reactors in this size range can generally be found in a laboratory, whereas the larger reactors are typically pilot scale facilities. Emissions from laboratory scale equipment are relatively small, and application of the controls required by the standard would be expensive and impractical. EPA also decided to exempt research and development facilities containing reactors greater than 0.19 m³ (50 gal) and no more than 4.07 m³ (1100 gal) in capacity from all parts of the standard except the 10 ppm limit for reactors, strippers, monomer recovery systems, and mixing, weighing and holding containers. EPA decided not to require these facilities to meet other parts of the standard because of the technical problems involved in doing so. For example, the standard for reactor opening is based in part on reducing the frequency of opening the reactor. Research and development reactors have to be opened after every batch for thorough cleaning. Also, stripping technology is developed individually for each resin in research and development equipment. Therefore, attainment of the stripping limitations in the research and development equipment would not always be possible. The 4.07 m³ (1100 gal) figure was selected as an upper cut-off point because there are no commercial reactors smaller than this.

(4) *Emission limits.* The only major change in the emission limits between proposal and promulgation is the addition of a provision for emergency manual venting of vinyl chloride from reactors to the atmosphere. The proposed standard prohibited all manual venting to the atmosphere. In the preamble to the proposed standard, EPA invited interested persons to comment on whether permitting manual venting to the atmosphere could result in overall lower emissions. There are several methods available for preventing relief discharges from reactors, one of which is manual venting of part of the reactor contents for purposes of cooling and reduction in pressure within the reactor. The higher the temperature and pressure within the reactor, the greater the amount of vinyl chloride which has to be removed to bring the reactor under control. Manual venting can be done at a lower pressure than the pressure required to open the relief valve. For this reason manual venting can result in lower emissions than would occur by allowing the reactor to discharge through the relief valve. Furthermore, a manual vent valve is under the control of an operator and can be closed. A relief valve may become clogged with resin and not close. The result would be loss of all the reactor contents.

The contents of a reactor can be manually vented to a gasholder or other holding vessel. However, in some cases, such as during severe weather conditions, several reactors may be out of control at one time. There would be insufficient holding capacity under these conditions to manually vent the contents of all the reactors to a gasholder. Therefore, when all other measures to prevent relief valve discharges have been exhausted, manual

venting will be permitted as a last resort before the relief valve opens. The same notification procedures are required for manual venting to the atmosphere as are required for relief discharges.

There are several changes in the numerical emission limits in the promulgated standard. Except for the standard for reactor opening loss, these changes simply involve conversion to the International System of Units (SI). There was an error involved in the original calculation used to derive the standard for reactor opening. Correcting this error doubles the allowable emissions. It is emphasized that the change in this standard is a correction, and not a change in the intent for the degree of control required.

The proposed standard required the installation of a rupture disc beneath each relief valve to prevent leakage from the relief valve. A provision has been added to the promulgated standard so that a rupture disc is not required if the relief valve is tied into a process line or recovery system. In this case, any leakage from the relief valve would be contained.

The regulation for obtaining vinyl chloride samples has been changed to an operating procedure. The proposed standard stated that there were to be no emissions from taking the samples. Several commenters pointed out that the use of the word "no" would make this regulation impractical to enforce. Therefore, the promulgated standard specifies the operating procedure which EPA originally intended to be used to control this source. This revision is only a change in wording and does not represent a change in the level of the standard.

The regulation for taking samples has also been revised to apply only to samples containing at least 10 percent by weight vinyl chloride. This is consistent with the other parts of the standard which apply to equipment "in vinyl chloride service." "In vinyl chloride service" distinguishes between situations where vinyl chloride is clearly involved and situations where vinyl chloride is a minor component or contaminant, and as defined in promulgated § 61.61(1) 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.

The proposed standard required a vinyl chloride monitoring system for continuously measuring vinyl chloride levels both within the plant (for leak detection) and within stacks. The proposed standard did not outline required specifications for the monitoring system, except that it was to analyze the samples with gas chromatography, or if all hydrocarbons were assumed to be vinyl chloride, with infrared spectrophotometry, flame ion detection, or equivalent. It required that each plant submit a description of its monitoring system to EPA, so that EPA could determine whether it was acceptable or not. Comments were received indicating a need for EPA to specify some criteria for judging the acceptability of monitoring systems. The accuracy of the monitor-

ing system would be related to the frequency of calibration. Therefore, EPA has included in the promulgated standard requirements for the frequency of calibration and procedures to be carried out in the calibration of the monitoring instruments.

The portable hydrocarbon detector required by the proposed standard was required to have a sensitivity of 5 ppm. Comments were received indicating that instruments in this sensitivity range are delicate and require continuing maintenance. The portable hydrocarbon detector is required for leak detection and for measuring vinyl chloride concentrations inside the equipment before opening it. A 5 ppm sensitivity is not needed in either case, and the required sensitivity has been changed to 10 ppm in the promulgated standard.

The proposed standard contained a single regulation for compressors. The promulgated standard has separate regulations for rotating and reciprocating compressors. This is consistent with having separate regulations for rotating and reciprocating pumps in both the proposed and promulgated standards.

Section 61.68 of the proposed standard provided for the use of equivalent methods of control which have been approved by EPA. The promulgated standard requires that the plant owner or operator submit a request for determination of equivalency within 30 days of the promulgation date if the alternative control method is intended as the initial means of control. The purpose of this is to provide time for EPA to evaluate the method before the plant has to be in compliance (for existing sources, 90 days after the promulgation date). EPA also suggests that this request for determination of equivalency be accompanied by a request for waiver of compliance pursuant to section 112(e)(1)(B)(ii) of the Act. The request for a waiver for compliance should provide for the case where EPA determines that a method is not equivalent and the plant needs to purchase other equipment. In no case will the waiver of compliance be extended beyond two years from the date of promulgation.

There are several wording clarifications which have been made in the promulgated standard. The definition for "in vinyl chloride service" (§ 60.61(1)) has been clarified by stating that it means equipment that contacts vinyl chloride as well as equipment that contains vinyl chloride. This would include such equipment as agitators.

Words have been added in §§ 61.62, 61.63, and 61.64 to clarify that the 10 ppm emission limits do not have to be met when equipment has already been opened in compliance with the regulation for opening of equipment. Equipment that has met the opening of equipment regulation can contain more than 10 ppm vinyl chloride and would be in violation of the standard if this statement were not included.

The requirements for stripping polyvinyl chloride resins to specified levels have been revised in §§ 61.64(e), 61.67

(g)(3)(ii), and 61.70(c)(2)(i) so that measurement of the vinyl chloride levels in the resins is to be made immediately after stripping is completed rather than as the resin is being transferred out of the stripper. This allows a plant to carry out operations in a stripper after stripping has been completed but before it is transferred out of the stripper. This is consistent with the original intent of the standard.

The regulation for loading and unloading lines in § 61.65(b)(1) has been revised to clarify that it applies only to lines that are disconnected after each loading or unloading operation. Permanently installed pipelines that are opened infrequently for inspection or maintenance, for example, are covered by the opening of equipment regulation rather than the loading and unloading line regulation.

The regulation for improper wastewater in the proposed standard could have been misinterpreted to require individual treatment of wastewater streams. Section 61.65(b)(9)(i) of the promulgated standard clarifies that wastewater streams that are required to be treated (i.e., those containing greater than 10 ppm vinyl chloride) can be combined to be treated. However, wastewater streams that contain greater than 10 ppm vinyl chloride cannot be combined with wastewater streams that contain less than 10 ppm vinyl chloride before treatment; i.e., dilution cannot be used to meet the standard.

The commenters recommended several changes in the emission limits which have not been incorporated into the promulgated standard. These are discussed in the following paragraphs.

It was recommended that the requirement for double mechanical seals on pumps, compressors, and agitators be removed because the single seals currently used on this equipment have small emissions and are more reliable than double mechanical seals. EPA is aware that each fugitive emission source, such as one pump, taken by itself causes relatively small emissions. Fugitive emissions considered as a whole are a significant source of emissions, however, and the intent of the standard is to reduce these. Double mechanical seal pumps are commonly used in the industry for emission reduction. Sealless pumps or equivalent systems are available as options to double mechanical seals.

The commenters recommended increasing the averaging time for the 10 ppm limits and the emission limits for reactor opening and stripping to 30 days. Some of the commenters apparently thought that the 10 ppm limits had to be met on an instantaneous basis. However, since the performance test for determining compliance consists of three runs for a minimum of an hour each, the averaging time for the 10 ppm limit is at least three hours. Increasing the averaging time to 30 days for any of the emission limits would permit higher peak emission levels. EPA has determined that this is neither desirable nor necessary.

Some commenters requested that the stripping levels for dispersion resins be

made the same as for other resins and others requested that they be made less stringent. EPA decided not to make the standard for stripping dispersion resins the same as for other resins because there is sufficient evidence to indicate that these resins are more difficult to strip than other resins. With regard to making the stripping levels for dispersion resins less stringent, only one of the eight manufacturers of dispersion resins specifically commented that the dispersion resin standard should be made less stringent. Only two of several grades of dispersion resins made by this company cannot meet the 2,000 ppm limit. The proposed standard takes into consideration that some resins are more difficult to strip than others by providing for averaging among different resins.

(5) *Testing, reporting, and record-keeping.* There are several relatively minor changes in the testing, reporting, and recordkeeping requirements. A provision has been added to § 61.67 which requires that stack gas samples taken with Test Method 106 are to be analyzed within 24 hours. This is consistent with the requirements in the proposed Test Method 106. The promulgated standard also specifies that in averaging the results of the three runs required by Test Method 106, a time-weighted average is to be used.

One commenter requested that the oxygen content and moisture content be specified for the 10 ppm concentration standards. The proposed standard specified that the vinyl chloride concentration is to be corrected to 10 percent oxygen (wet basis) if combustion is used as the control measure. In the promulgated standard, this requirement has been expanded to all control measures.

A provision has been added to the promulgated standard which states that if a reactor is also used as a stripper, the reactor opening emissions may be determined immediately following the stripping operation. If a reactor is also used as a stripper, the resin is in the reactor when it is opened. This means that vinyl chloride in the resin which has already been stripped to acceptable levels can escape from the resin and become part of the reactor opening loss. It is EPA's intent that once a resin has been stripped to the required levels, that additional controls are not required. Under the new provision, vinyl chloride escaping from the resin after it has been stripped to acceptable levels is not counted as part of the reactor opening loss.

A section requiring continuous monitoring of stack emissions has been added to the promulgated standard. The continuous monitoring of stack emissions was required in the proposed standard. The addition of a specific paragraph for emission monitoring serves only to clarify the requirement.

The standard has been revised so that the initial report requires a "description" rather than a "detailed description" of the equipment used to control fugitive emissions. Several commenters pointed out that a detailed description would contain proprietary information. EPA agrees that a detailed description in the

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initial report is unnecessary. If additional information is needed, EPA can obtain it under section 114 of the Act and the plant can request confidential treatment in accordance with 40 CFR Part 2 for information it believes to be proprietary.

The proposed standard required that a semiannual report be submitted every 130 days. The promulgated standard specifies dates for the submittal of the reports. It also specifies that the first semiannual report does not have to be submitted until at least six months after the initial report is submitted.

The standard has been revised to eliminate the requirement to record the cause of any leak detected by the vinyl chloride detector, the action taken to repair the leak, and the amount of time required to repair the leak. EPA is concerned only that leaks are detected and repaired. That this has been done can be established by looking at the strip chart record of measurements made by the vinyl chloride detector. These records are still required for the portable hydrocarbon detector however.

Several commentators recommended that the companies be allowed an extra two weeks to submit to EPA data from the initial performance test. They also recommended that they submit the data by regular mail rather than registered mail. EPA has not adopted either of these recommendations. A source is supposed to be in compliance with the standard within 90 days of the promulgation of the standard. The standard requires that the emission tests be done within the 90 day period, and permits an extra 30 days for determination of results. The purpose of using registered mail is to document the fact that emission data have been sent and received. This way if the results are lost in the mail, there will be no question that they were sent.

(6) *Test method.* Test Method 106 has been changed to recognize that on a gas chromatograph equipped with a Chromosorb 102 column, acetaldehyde may interfere with the vinyl chloride peak. When a sample is expected to contain acetaldehyde, a secondary column as described in section 4.3.2 must be employed. Mass spectroscopy or another absolute analytical technique is required to confirm the vinyl chloride peak obtained with the gas chromatograph, only if peak resolution with the secondary column is not successful.

In section 4.1.4, aluminum Mylar bags can be substituted for Tedlar bags. EPA now has data to allow this substitution, provided that the samples are analyzed within 24 hours of collection.

In section 5.1.3 of Test Method 106 the requirement to use "oxygen gas" has been replaced with "oxygen gas or air, as required by the detector." Several commentators stated that most gas chromatographs are designed to use hydrogen and air for their flame detectors. When used in this way, they are capable of detecting 0.5 ppm vinyl chloride in air. This is sensitive enough for monitoring the 10 ppm emission limits stipulated in the standard.

In section 6.4 of Test Method 106 the requirement for an automatic integrator has been replaced with a requirement for a disc integrator or planimeter for measuring peak area. This change is in response to a comment which states that automatic integrators are unnecessarily elaborate and expensive.

A new section 6.5 has been added to Test Method 106 which requires determination of the water vapor content of the sampling bag by measuring the ambient temperature and pressure near the bag. The vinyl chloride concentration of the bag can then be reported on a dry basis. A provision for checking the rigid container for leaks has been added to section 7.4 of Test Method 106.

The only change in Test Method 107 is the provision in Section 5.3.2 for use of Carbotek C as well as Carbotek A.

AUTHORITY: Section 113 of the Clean Air Act as added by sec. 4(a) of Pub. L. 91-604, 84 Stat. 1685 (42 U.S.C. 1857e-7); Section 114 of the Clean Air Act, as added by sec. 4(a) of Pub. L. 91-604, 84 Stat. 1687, and amended by Pub. L. 93-319, sec. 6(a)(4), 88 Stat. 269 (42 U.S.C. 1857e-8); Section 301(a) of the Clean Air Act, as amended by sec. 15(c)(2) of Pub. L. 91-604, 84 Stat. 1713 (42 U.S.C. 1857g(a)).

Dated: October 12, 1976.

JOHN QUARLES,
Acting Administrator.

Part 61 of Chapter I, Title 40 of the Code of Federal Regulations is amended as follows: The table of sections for Part 61 is amended by adding a list of sections for new Subpart F and Part 61 is amended by adding a new Subpart F reading as follows:

Subpart F—National Emission Standard for Vinyl Chloride

- Sec. 61.60 Applicability.
- 61.61 Definitions.
- 61.62 Emission standard for ethylene dichloride plants.
- 61.63 Emission standard for vinyl chloride plants.
- 61.64 Emission standard for polyvinyl chloride plants.
- 61.65 Emission standard for ethylene dichloride, vinyl chloride and polyvinyl chloride plants.
- 61.66 Equivalent equipment and procedures.
- 61.67 Emission tests.
- 61.68 Emission monitoring.
- 61.69 Initial report.
- 61.70 Semiannual report.
- 61.71 Recordkeeping.

AUTHORITY: Section 113 of the Clean Air Act as added by sec. 4(a) of Pub. L. 91-604, 84 Stat. 1685 (42 U.S.C. 1857e-7); section 114 of the Clean Air Act, as added by sec. 4(a) of Pub. L. 91-604, 84 Stat. 1687, and amended by Pub. L. 93-319, sec. 6(a)(4), 88 Stat. 269 (42 U.S.C. 1857e-8); section 301(a) of the Clean Air Act, as amended by sec. 15(c)(2) of Pub. L. 91-604, 84 Stat. 1713 (42 U.S.C. 1857g(a)).

Subpart F—National Emission Standard for Vinyl Chloride

§ 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 § 61.64(a)(1), (b), (c), and (d) 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 4.07 m³ (1100 gal).

§ 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 sold undried.

(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.

§ 61.62 Emission standard for ethylene dichloride plants.

An owner or operator of an ethylene dichloride plant shall comply with the requirements of this section and § 61.65.

(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) 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 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) 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) 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) 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) 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 which are opened to the atmosphere after each loading or unloading operation are to be minimized as follows:

(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 0.0033 m³ (0.13 ft³) 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 emission 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 installing agitators 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 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)(3), 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 chlo-

ride is to be reduced so that the equipment contains no more than 2.0 percent by volume vinyl chloride or 0.0950 m³ (25 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)(3)(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 5.2.3 of Test Method 106, or

(B) A calibration gas cylinder containing the appropriate concentration of vinyl chloride. If a calibration gas cylinder is used, the analysis must be traceable to the National Bureau of Standards or to a gravimetrically calibrated vinyl chloride permeation tube.

(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. The 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)(2) 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)(3) or paragraph (b)(6) of this section.

(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 $\geq 4.75 \text{ m}^3$ 01250 gal in volume for which an emission limit is prescribed in § 61.65(b)(8).

(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).

§ 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) 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.

(e) All samples are to be analyzed within 24 hours, and 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.

(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 50 liters corrected to standard conditions.

(ii) 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 for determination of emissions by using the following equation:

$$C_c(\text{corrected}) = C_s \frac{10.9}{20.9 - \text{percent } O_2}$$

where:

$C_c(\text{corrected})$ = The concentration of vinyl chloride in the exhaust gases, corrected to 10 percent oxygen.

C_s = 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 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.

(iii) For those emission sources where the emission limit is prescribed in terms of mass rather than concentration, mass

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emissions in kg/100 kg product are to be determined by using the following equation:

$$C_{xx} = \frac{[C_s (2.60) Q 10^{-4}] (100)}{Z}$$

where:

C_{xx} = kg vinyl chloride/100 kg product.
 C_s = 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.
 10⁻⁴ = Conversion factor for ppm.
 Z = Production rate (kg/hr).

(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:

$$C_{xx} = \frac{[C_s R 10^{-4}] (100)}{Z}$$

where:

C_{xx} = kg vinyl chloride/100 kg product.
 C_s = 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.
 10⁻⁴ = 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 (a) (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:

$$C = \frac{W (2.60) (10^{-4}) (Cb)}{YZ}$$

where:

C = kg vinyl chloride emission/kg product.
 W = Capacity of the reactor in m³.
 2.60 = Density of vinyl chloride at one atmosphere and 20°C in kg/m³.
 10⁻⁴ = 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.

§ 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 emission are required to be ducted in § 61.65(b) (1) (ii), and (b) (2), (b) (5), (b) (6) (ii), and (b) (9) (ii).

(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 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. 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 § 67.67. The calibration is to be done with either:

(1) A calibration gas mixture prepared from the gases specified in sections 5.2.1 and 5.2.3 of Test Method 106, or

(2) A calibration gas cylinder containing the appropriate concentration of vinyl chloride. If a calibration gas cylinder is used, the analysis must be traceable to the National Bureau of Standards or to a gravimetrically calibrated vinyl chloride permeation tube.

§ 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 § 61.65 (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.

§ 61.70 Semiannual report.

(a) (2) is to be determined. The number source to which this subpart applies shall submit to the Administrator on Septem-

her 15 and March 15 of each year a report in writing containing the information required by this section. The first semi-annual report is to be submitted following the first full 6 month reporting period after the initial report is submitted.

(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.

(1) 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 § 61.65 (b) (1) (II), (b) (2), (b) (5), (b) (6) (II), or (b) (9) (II). 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, 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.

(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 (c) (2) (i) and (c) (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 all the samples required in paragraphs (c) (2) (i) and (c) (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:

$$A = \frac{\sum_{i=1}^n P_i M_i}{Q_T}$$

$$A = \frac{P_1 M_1 + P_2 M_2 + \dots + P_n M_n}{Q_T}$$

A = 24-hour average concentration of type T, resin in ppm.

Q = Total production of type T, resin over the 24-hour period, in kg.

T_i = Type of resin; i = 1, 2, ..., n where n is total number of resin types produced during the 24-hour period.

M = Concentration of vinyl chloride in one sample of grade G_i resin, in ppm.

P = Production of grade G_i resin represented by the sample, in kg.

G_i = Grade of resin, e.g., G₁, G₂, and G₃.

n = Total number of grades of resin produced during the 24-hour period.

(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.

§ 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) (8), including the concentrations of vinyl chloride as 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) (8), 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 measured in accordance with § 61.68.

(3) For the relief discharges from reactors subject to the provisions of § 61.65(a), a daily operating record for each reactor, including pressures and temperatures.

2. Appendix B is amended by adding Test Methods 106 and 107 as follows:

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 (chloroethylene) is subjected to chromatographic analysis, using a flame ionization detector.

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^{-3} mg and 4×10^{-3} mg.

3. Interferences.

Acetaldehyde, which can occur in some vinyl chloride sources, will interfere with the vinyl chloride peak from the Chromosorb 102 column. See sections 4.3.2 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 technique, such as mass spectroscopy, must be performed.

4. Apparatus.

4.1 Sampling (Figure 1).

4.1.1 Probe—Stainless steel, Pyrex glass, or Teflon tubing according to stack temper-

sture, 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 1.

4.1.4 Tedlar bags, 100 liter capacity—To contain sample. Tedlar 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.

4.1.5 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 1).

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, 2.0 x 3.2 mm, containing 80/100 mesh Chromosorb 102. A secondary column of GE SP-90, 20% on 80/80 mesh AW Chromosorb P, stainless steel, 2.0 m x 3.2 mm, will be required if acetaldehyde is present. If used, the SP-90 column is placed after the Chromosorb 102 column. The combined columns should then be operated at 110°C.

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.

Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

4.4.5 Flow meter—Rotameter type, 0 to 1000 ml/min range accurate to $\pm 1\%$, 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.

5.2.1 Vinyl chloride, 99.9+ %—For preparation of standard gas mixtures.

5.2.2 Calibration cylinders (3), optional—One each of 50, 10 and 5 ppm vinyl chloride in nitrogen with certified analysis. Analysis must be traceable to NBS (National Bureau of Standards) or to a gravimetrically calibrated vinyl chloride permeation tube.

5.2.3 Nitrogen gas—Zero grade, for preparation of standard gas mixtures.

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 of sample collection.

6.3 Sample recovery. With a piece of Teflon tubing identified for that bag, connect a 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 so 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_v , by use of H_v , and a disc integrator or a planimeter. Measure the peak height, H_v . Record A_v 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.

Compare the ratio of H_v to A_v 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 4.3.2).

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 the record and water vapor content of the bag.

7. Calibration and Standards.

7.1 Preparation of vinyl chloride standard gas mixtures. Evacuate a sixteen-inch square Tedlar bag that has passed a leak check (described in Section 7.4) and meter in 5.0 liters of nitrogen. While the bag is filling, use the 0.5 ml syringe to inject 250 μ l of 99.9+ % vinyl chloride through the wall of the bag. Upon withdrawing the syringe needle, immediately cover the resulting hole with a piece of adhesive tape. This gives a concentration of 50 ppm of vinyl chloride. In a like manner use the other syringe to prepare dilutions 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.

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 standard gas mixture (described in Section 7.1) using conditions identical with those listed in Section 6.3 above. 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_v , the concentrations 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_v , the peak area multi-

plied by the attenuator setting. Repeat until two injection areas are within 5%, then plot those points vs C_0 . 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.

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 5-10 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 5-10 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 right container, place a rotameter in-line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register any flow when the bag appears to be empty indicates a leak.

8. Calculations

8.1 Determine the sample peak area as follows:

$$A_s = A_m \cdot A$$

Equation 104-1

where

A_s —The sample peak area.

A_m —The measured peak area.

A —The attenuation factor.

8.2 Vinyl chloride concentrations. From the calibration curve described in Section 7.3, above, select the value of C_0 that corresponds to A_s , the sample peak area. Calculate C_0 as follows:

$$C_0 = \frac{C_p \cdot T_0}{P_0 \cdot T_0 (1 - B_{v_0})}$$

Equation 104-2

Where:

B_{v_0} —The water vapor content of the bag sample, as analyzed.

C_0 —The concentration of vinyl chloride in the bag sample in ppm.

C_p —The concentration of vinyl chloride indicated by the gas chromatograph, in ppm.

P_0 —The reference pressure, the laboratory pressure recorded during calibration, mm Hg.

T_0 —The sample bag temperature on the absolute scale at the time of analysis, $^{\circ}K$.

P —The laboratory pressure at time of analysis, mm Hg.

T —The reference temperature, the sample bag temperature recorded during calibration, $^{\circ}K$.

9. References

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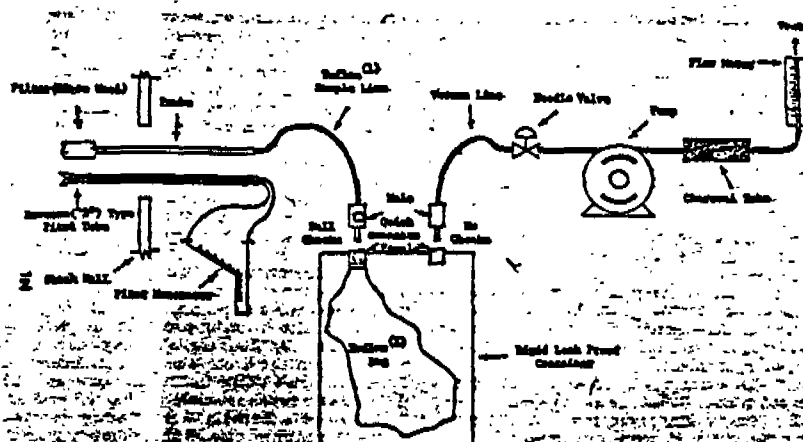


Figure 104-3. Suggested bag sampling method.

104-3. Suggested bag sampling method. Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

METHOD 107—DETERMINATION OF VINYL CHLORIDE CONCENTRATIONS OF INPROCESS WASTEWATER SAMPLES, AND VINYL CHLORIDE CONCENTRATIONS OF POLYVINYL CHLORIDE RESINS, SLURRY, WAX, CAKE, AND LATHE SAMPLES

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 EVCM, PVC, resin, water, and air in a closed system. It has been demonstrated that the EVCM 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 chloride 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 form, 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 with prior approval of the Administrator. 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.

2. Range and Sensitivity

The lower limit of detection of vinyl chloride will vary according to the chromatograph used. Values reported include 1×10^{-6}

mg and 4×10^{-4} 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 2.53% for a sample with a mean of 2.09 ppm, 4.16% for a sample with a mean of 1.66 ppm, and 5.23% 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—50 ml (3 oz), with waxed lined screw on tops, for PVC samples.

5.1.2 Vials—50 ml Hypo-vials, 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. 106-0118, or equivalent.

5.2.2 Analytical balance—Capable of weighing to ± 0.001 gram.

5.2.3 Syringe, 100 μ l—Precision Series "A" No. 010025, or equivalent.

¹ Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

RULES AND REGULATIONS

5.2.4 Vial Sealer, Perkin-Elmer No. 108-0106 or equivalent.

5.3 Analysis.

5.3.1 Gas chromatograph—Perkin-Elmer Corporation Model P-40 head-space analyzer, No. 104-0001, or equivalent.

5.3.2 Chromatographic column—Stainless steel, 2 m x 3.2 mm, containing 0.4% Carbowax 1500 on Carbowax A, Perkin-Elmer Corporation No. 108-0133, or equivalent. Carbowax C can be used in place of Carbowax A.

5.3.3 Thermometer—0 to 100° C, accurate to $\pm 0.1^\circ$ C, Perkin-Elmer No. 105-0106 or equivalent.

5.3.4 Sample tray thermostat system—Perkin-Elmer No. 105-0103, or equivalent.

5.3.5 Septa—Sandwich type, for automatic dosing, 13 mm, Perkin-Elmer No. 108-1008, 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. 0101-0113, 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 Standard cylinders (4)—one each of 50, 500, 2000, and 4000 ppm vinyl chloride in nitrogen, with certified analysis.

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. Extract 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 50 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 0.3 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 < 0.3 weight %), 100 μ l of distilled water must be injected into the vial, after

sealing and weighing, using a 100 μ l 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, 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 gram. 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 In-process 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 50 psig. Set regulator on chromatograph to 1.5 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.

3. Hydrogen supply—Set regulator on cylinder to read 30 psig. Set regulator on chromatograph to supply approximately 35 $\pm$ 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), 50° C.

b. Dosing line, 140° C.

c. Injection block, 140° C.

d. Sample chamber, water temperature, 90° C $\pm 1.0^\circ$ C.

7.3.1.3 Ignition of flame ionization detec-

tor—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. I—Dosing time—The normal setting is 2 seconds.

b. A—Analysis time—The normal setting is 8 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 0.2 minutes.

d. W—Stabilization time—The normal setting is 0.5 minutes.

e. X—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 manufacturer's 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 3 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 vial. 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_s , the integrator area counts for each standard sample vs C_s , 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_s that corresponds to A_s for each sample. Compute the response factor, R_s , for each sample, as follows:

$$R_s = \frac{A_s}{C_s} \quad \text{Equation 107-1}$$

9.2 Residual vinyl chloride monomer concentration, or vinyl chloride monomer concentration.

Calculate C_{res} as follows:

$$C_{res} = \frac{A_s P_s}{R_s T_1} \left(\frac{M_s V_s}{m_s} + K T_1 \right) \quad \text{Equation 107-2}$$

where:

- C_{res} = Concentration of vinyl chloride in the sample, in ppm.
- P_s = Laboratory atmosphere pressure, mm Hg.
- T_1 = Room temperature, °K.
- M_s = Molecular weight of VCM (62.5).
- V_s = Volume of vapor phase (vial volume less sample volume).
- m_s = Weight of sample, grams.
- R = Gas constant (82.05).
- K = Henry's Law constant for VCM in PVC at 25°C, $K = 4.53 \times 10^{-4}$; for VCM in 1 cc (approximate) wastewater sample at 25°C, $K = 4.5 \times 10^{-4}$.
- T_1 = Equilibrium temperature, °K.

If the following conditions are met, Equation 107-2 can be simplified as follows:

1. $T_1 = 25^\circ \text{C}$ (298° K).
2. $T_2 = 25^\circ \text{C}$ (298° K).
3. $P_s = 760$ mm. Hg.

$$\text{4. } V_s = V - \frac{m_s}{\rho_s} = 22.5 - \frac{1m}{1}$$

where:

V_s = Vial volume, cc (22.5).

5. Sample contains less than 0.5% water.

$$C_{res} = \frac{A_s}{R_s} \left(\frac{4.197 \times 10^{-3}}{m_s} + \frac{5.988 \times 10^{-4}}{m_s} \right)$$

Equation 107-3

The following general equation can be used for any sample which contains VCM, PVC and/or water.

$$C_{res} = \frac{A_s P_s}{R_s T_1} \times \left[\frac{M_s V_s}{R m_s} + K_s (TS) T_1 + K_w (1-TS) T_1 \right]$$

Equation 107-4

where:

T_1 = Total solids.

Note: K_w must be determined.

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 (approximate) wastewater sample, Equation 107-4 can be simplified to the following:

$$C_{res} = \frac{A_s}{R_s} \left[\frac{5.988 \times 10^{-3}}{m_s} + (2.066 \times 10^{-4}) \right]$$

Equation 107-5

10. References.

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[FR Doc. 75-30646 Filed 10-20-75; 8:48 am]

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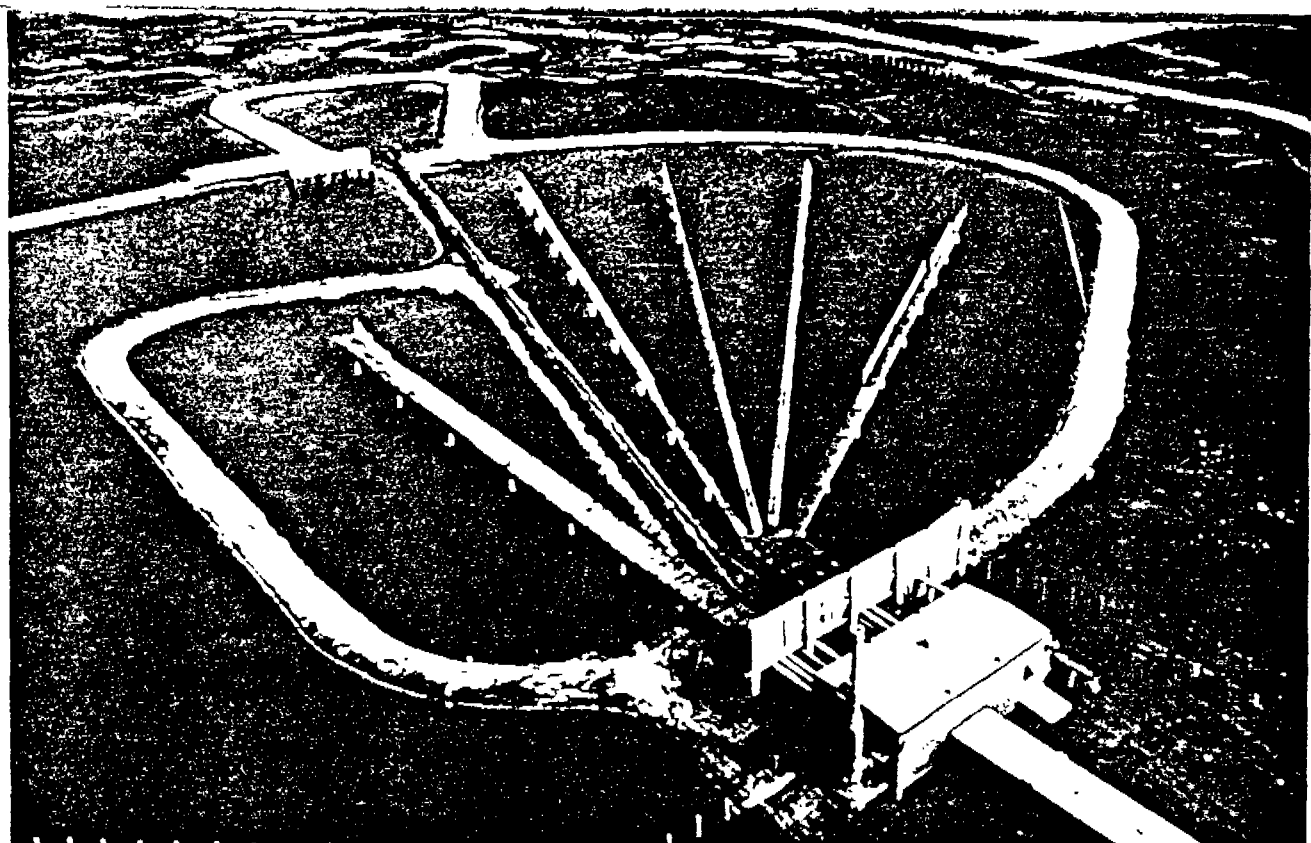
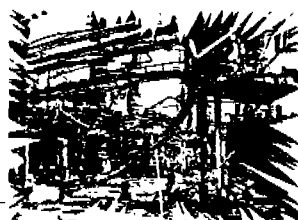


Figure 1. An Alaskan flare that provides smokeless burning without using smoke suppressants.



PLANT LOSS PREVENTION

Environmental Factors Vs. Flare Application

People living near a plant often view a flare as a tremendous waste of their irreplaceable energy resources rather than as the safety device it actually is.

R. Schwartz and M. Keller, John Zink Co., Tulsa, Okla.

Prior to the development of the first successful smokeless flare in the 1950s, (1) the people who designed this equipment were mostly concerned with obtaining positive ignition, and gave little or no thought to the results of the ensuing combustion. That first smokeless design, as remarkable a technical breakthrough as it was for its time, now pales in comparison to the equipment used to meet current environmental regulations.

Today's flare system designer must not only cope with

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smokeless requirements, but must also investigate the total environmental impact including thermal radiation, noise production, ground level concentration of combustion products, visible light, and in some instances the aesthetics of the design. Meeting the increasingly stringent environmental requirements has necessitated large research and development expenditures by the John Zink Co.

The flare system's most dramatic impact on the environment is its potential for production of very large

flames and enormous clouds of smoke. Such emissions can be seen from many miles and can quickly attract the attention of neighbors, public authorities, and environmentalists. Current environmental requirements force the plant designer to route more of the vented gases into the flare system, resulting in larger flare sizes even though the capacity of the attached plant may be the same as previous designs. In addition, the use of larger components in plant design has increased the amount of gas that must be handled smokelessly by the flare.

Normally, the flare designer's first environmental consideration is whether the waste gas will produce smoke. Considerable research into this question indicates the weight ratio of hydrogen to carbon of the waste gas is one of the key factors. (2) However, it has been found that identical H/C ratios will in one case produce smoke, and in another burn without smoke production. Careful investigation of the data has shown that instantaneous H/C ratios in the combustion zone may greatly exceed the average, due to the lack of mixing of waste gases. This observation is supported by flow studies which show tur-

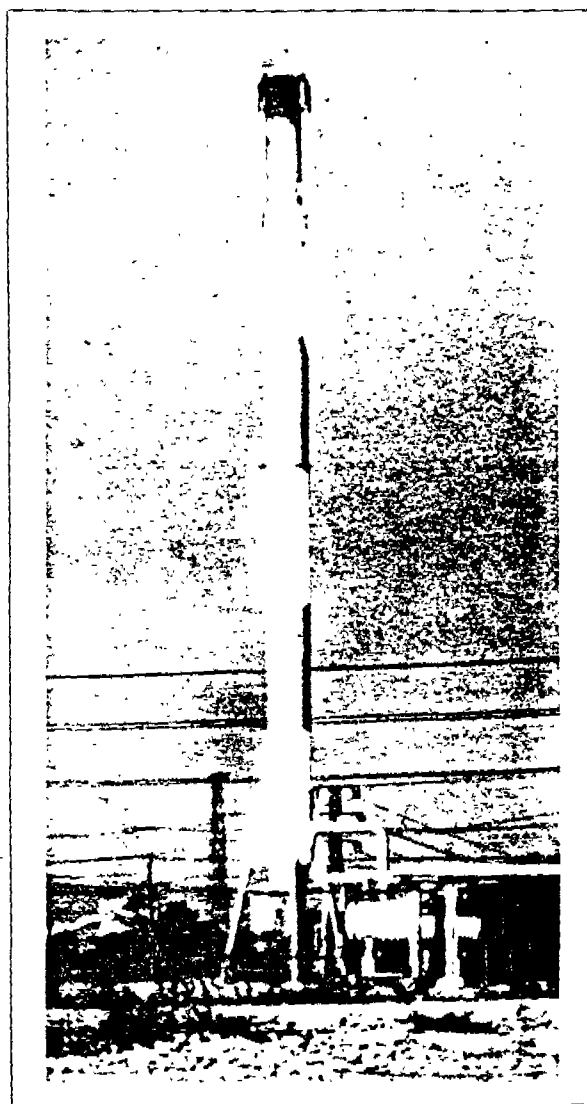


Figure 2. An air-assisted flare installation in the Midwest.

bulent flow, with Reynolds numbers as high as 50,000, failed to promote mixing of gases. (3, 4)

Presence of the liquid phase of hydrocarbons in the relief vapor can also render H/C ratio predictions invalid. Liquid droplets as small as 15 microns can negate smokeless equipment operation, with larger particles producing even greater consequences in the form of fallout of burning liquid particles in addition to unwanted smoke production. Careful consideration must be given to knock-out drum design and location.

The traditional approach to smoke suppression is the injection of steam into the combustion zone. However, there is not total agreement as to the chemistry or physical phenomenon associated with this injection. Since black smoke is clearly an indication of unburned carbon escaping from the combustion zone, the carbon must be completely burned or chemically combined to prevent its escape. Steam injection leads to two endothermic reactions that offset the desired end; the water gas shift ($C + H_2O = CO + H_2$), and steam reforming chemistry ($C_xH_y + H_2O = XCO + ZH_2$). Regardless of which reaction dominates, the end result is the elimination of smoke.

Other factors that also lead to the success of steam injection allow the use of smoke suppressants other than steam. These factors include the eduction of air into the combustion zone, and turbulent mixing, which increases reaction rates and elevates reaction temperatures. These two factors make possible the use of high pressure gas, air, or other smoke suppressants, but with overall lower efficiencies in terms of pounds of suppressant to pounds of hydrocarbons as a result of the loss of the aforementioned chemical reactions.

Another apparent factor is the total kinetic energy in the combustion zone, exclusive of chemical energy release from the combustion process. Such energy levels can be created from high velocity discharge and/or from adding additional energy from a secondary source. The total energy required is a function of gas composition, burner design, quantity of gas being burned and other factors. Extensive experience is required with gases of similar composition to accurately predict the required energy level.

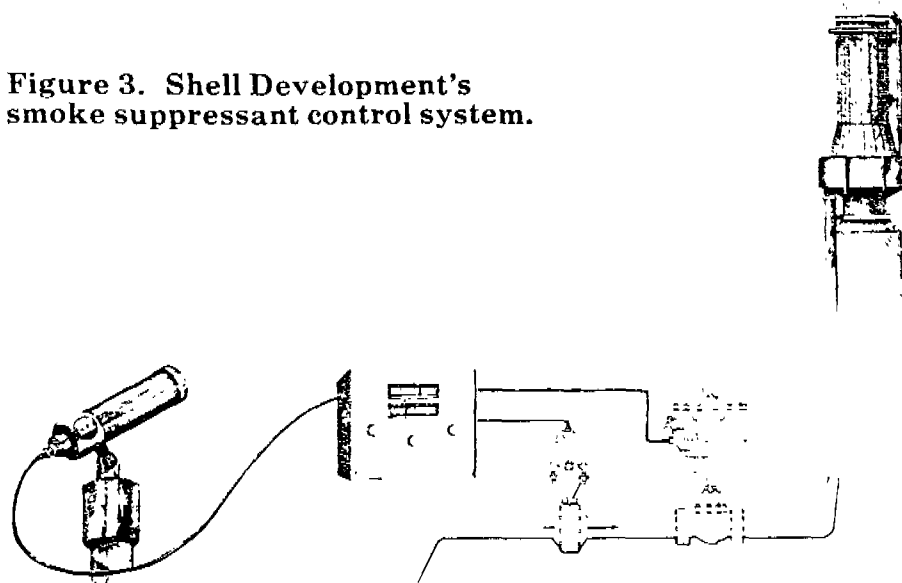
While most smokeless designs use some suppressant to obtain smokeless burning it is possible to achieve smokeless burning without a suppressant as long as a satisfactory energy level can be produced. Pioneer work in the Zink test facilities has produced a proprietary method for maintaining energy levels under virtually infinite turndown ratios. Designs obtaining smokeless burning without suppressants are operationally successful in capacities up to several million lb./hr., Figure 1.

Where a secondary energy source is required, the most common choice is low pressure air. When properly utilized, the low-pressure air can boost kinetic energy to the smokeless burning level, as well as provide primary to the combustion process. Additional advantages of type of flare, Figure 2, dozens of which are in successful operation, are their lower overall installation and operating costs.

Smoke suppressant control

Response time lag in application of steam is a problem that plagues flares old and new. Application of a smoke suppressant was a strictly manual operation. This operation leads to at least three problems: 1) smoking prior to operator response over steaming of the flare and 2) noise that occurs before operator reduction; and 3) waste of steam to gas flow cessation.

Figure 3. Shell Development's smoke suppressant control system.



Numerous attempts have been made to automate the application of smoke suppressant. Some of the problems in automatic control design have been:

1. Sensitivity to low velocities.
2. Ability to withstand high velocities and impact loads.
3. High maintenance due to fouling.
4. Reaction to varying combustion characteristics.
5. Lag time.
6. Ability to install and maintain the device during flare operation.

A remarkable breakthrough in the design of smoke suppressant control has been made by the Shell Development Co. (5) This entirely new concept utilizes a grade-level optical sensor to detect, in a sense, a combined measure of flow, composition and suppressant effectiveness. Burning characteristic changes such as variations in H/C ratio that cannot be effectively detected by velocity and/or density measurement are readily recognized by this new system, Figure 3. The new system eliminates all of the design problems listed above.

Accurate prediction of thermal radiation is becoming increasingly important with larger plants and correspondingly larger flare relief loads. Ever increasing "emergency" vent rates, and economically unfeasible flare heights, have made it more important that cooperative studies between the user and manufacturer be employed to determine flare height.

Several methods have been proposed for calculating flare heights. The overriding consensus of the authors of these methods is that flares, like any combustion process, cannot simply be scaled up from correspondingly small tests. Numerous large-scale tests have been used to develop a proprietary computer program for radiation prediction. Among the factors that are considered are quantity of gas to be burned, composition, smoke suppression method, flare burner design, and ambient conditions.

The question of what constitutes an acceptable radiation level is equally important in determining flare heights. The John Zink research facilities have been used to determine the physiological limits of a person wearing nor-

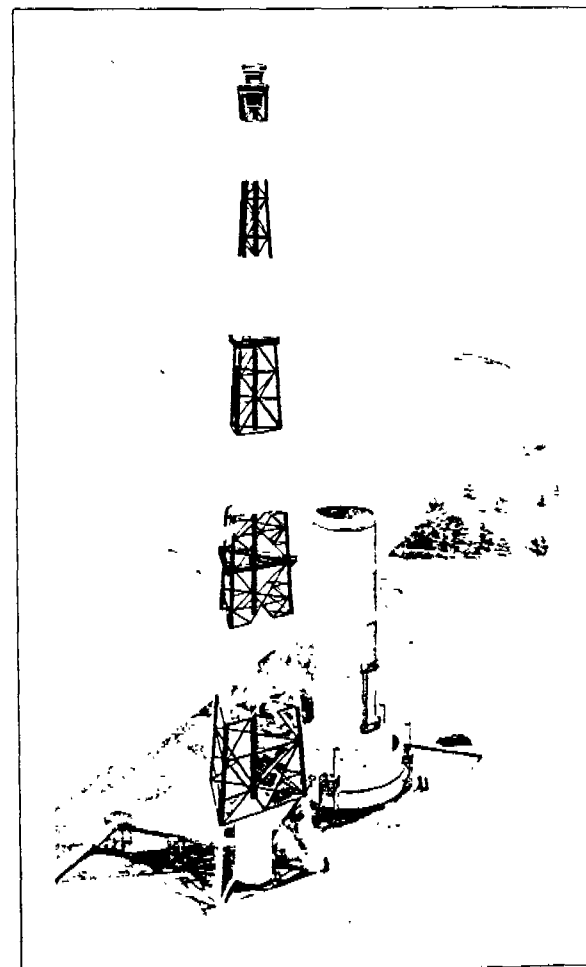


Figure 4. A combination low level and elevated flare system.

mal plant clothing, i.e., hard hat, long-sleeve shirts, and gloves.

This "human testing" has disclosed that radiant impact levels of 1,500 B.t.u./hr./sq. ft. can be tolerated for an indefinite period of time by an active worker. An impact level of 1,650 B.t.u./hr./sq. ft. requires limiting of exposure time to five minutes or less or the use of additional clothing. Impact levels as high as 3,000 B.t.u./hr./sq. ft. were tested. Limited over-exposure resulted in skin reaction similar to a mild sunburn.

Many neighbor complaints are caused by flaring noise. Noise control is a social as well as a legal responsibility. Flaring noise can be attributed mainly to two sources—smoke suppressant injection and combustion. Careful orifice design (6) can greatly reduce the suppressant injection noise on steam flares. However, in practice the minimum size of suppressant orifices is limited due to plugging by line scale, etc. Additional gains in suppressant noise reduction have been made by improving the efficiency of suppressant usage and by the use of the highly responsive optical smoke suppressant control previously discussed.

Combustion noise is related to energy release. Smokeless burning results in an obvious increase in the energy released and the potential for greater combustion noise generation. Therefore, it is inevitable that open smokeless flaring will result in some combustion noise.

In chemical plant applications, where gases other than hydrocarbons are being flared, careful considerations must be given to design. In this case there is no substitute for experience with a similar application. Open burning is dependent on the combustion process being sufficiently exothermic to maintain ignition. Flares burning in the open air transfer a tremendous amount of heat away from the flame and as the temperature levels depress the combustion process can cease.

The amount of energy—Low Heating Value (LHV)—necessary to maintain ignition varies. There is no fixed value for the minimum level required, however, experience allows prediction of the minimum LHV. In cases where the waste gas does not contain sufficient energy to support combustion, it is necessary to make use of special endothermic flare designs.

Flaring of gases such as chlorinated hydrocarbons, phosgene, and sulfur compounds require additional consideration. Burning of chlorine containing compounds will result in production of HCl, and sulfur compounds produce SO₂ and SO₃, all of which have legal threshold concentration limits. Flares, unlike oxidizers and furnaces, do not adapt themselves to post combustion removal of these contaminants; therefore, the approach has been to design sufficient stack heights to provide an allowable ground level concentration.

Ground level concentration

The prediction of ground level concentration is a developing area with several approaches available. Dispersion models such as the Pasquill-Gifford (7, 8) method and plume riser models such as Briggs method (9) seem to lend themselves to flare applications, providing one recognizes the exothermic characteristics of the flare. However, also to be noted is the fact that Briggs method is based on measurements from stacks, not flares. A modified approach has been offered by Peters. (10) If Peters method is used, one must remember to reduce the heat release by an appropriate level due to radiation transfer from the flame, and if appropriate, due to smoke.

Visible light and noise from an elevated flare can be an extremely sensitive problem with the neighbors of a process plant. Although elimination of light is not a legal

responsibility in many areas of the U.S. at this time, it is in several foreign countries. The light of an elevated flare focuses attention on the process plant, leading to many complaints that might otherwise go unregistered. In addition, with today's energy conscious environment, neighbors often view the flare as a tremendous waste of their irreplaceable energy resources rather than as the safety device it actually is. Plants have the responsibility of limiting flaring activity by tightening operating procedures and practices. However, this tightening of procedures cannot completely eliminate some day to day flaring. The alternative to visible flaring is a low-level enclosed burning system. In addition to providing a hidden flame, there is the equally important benefit of noise reduction. Full load noise levels of less than 70 dBA adjacent to the flare have been obtained.

For most plants it is desirable to use a flare system that combines a low level flare with an elevated flare, Figure 4. Day-to-day and startup flaring loads are burned in the low level flare while infrequent high volume emergency loads are handled by both low level and elevated flares. When properly designed such combined systems can prevent visible flaring for virtually all of the plant's operating time. Elimination of light and noise as a focal point is a proven public relations asset to the plant operator. (11)

Today's designer of flaring systems is faced with increased public awareness of the flare's impact on the environment. Equipment selection and system design require careful consideration of safety and environmental aspects. Improved communication and early cooperation between flare manufacturer and plant designer is essential to successful flare system design. #

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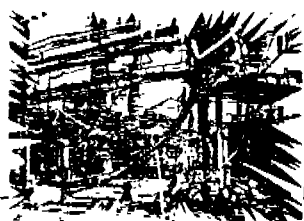
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PLANT LOSS PREVENTION

A Survey of Vapor Cloud Incidents

Trends toward plants with larger capacities, and higher pressures and operating temperatures make understanding how to prevent vapor cloud explosions imperative.

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Table 1. Valuation factors for petroleum equipment.

Year	Factor	Year	Factor
1976.....	1.00	1958.....	2.16
1975.....	1.06	1957.....	2.22
1974.....	1.18	1956.....	2.40
1973.....	1.38	1955.....	2.62
1972.....	1.44	1954.....	2.70
1971.....	1.49	1953.....	2.74
1970.....	1.60	1952.....	2.78
1969.....	1.71	1951.....	2.78
1968.....	1.79	1950.....	2.97
1967.....	1.87	1949.....	3.06
1966.....	1.95	1948.....	3.06
1965.....	2.01	1947.....	3.35
1964.....	2.04	1946.....	4.05
1963.....	2.06	1945.....	4.89
1962.....	2.07	1944.....	4.93
1961.....	2.10	1943.....	5.10
1960.....	2.10	1942.....	5.18
1959.....	2.13	1941.....	5.59
		1940.....	5.98

Vapor cloud explosions have in recent years been the predominant cause of the largest losses in the chemical and petrochemical industry. Because of trends toward plants of larger capacity, higher pressures, higher temperatures and greater inventory holdup, these losses have been increasing both in frequency and severity.

Obviously, as a major insurer of chemical and petrochemical properties, our company has a great interest in vapor cloud losses. We have been gathering data on vapor cloud incidents for about two years in order that methods may be developed for:

1. Reducing the number and severity of these losses.
2. Estimation of loss potential from incidents of this type.
3. Analysis of the cause of these losses to aid in educating our own engineers and our insureds.

In an earlier work (1) concerned with vapor cloud incidents, no differentiation was attempted between the following types of incidents involving large releases of flammable materials:

1. Confined explosions.
2. Boiling liquid expanding vapor explosions (BLEVE's).

Table 2. Type of facility for incidents where overpressures were created.

	Number	%
Industrial.....	32.....	75
Transportation	8.....	18
Other	3.....	7
Total.....	43.....	100

Table 3. Type of industrial plant for incidents where overpressures were created.

Type of Plant	Total Number of Incidents		Number Incidents with \$ Data Available		Corrected Property Damage Loss		Average Corrected Loss, \$ million
	No.	%	No.	%	\$ million	%	
Petrochemical.....	24	75.0	19	70.4	285.3	60.9	15.02
Refinery.....	8	25.0	8	29.6	183.4	39.1	22.92
Totals.....	32	100.0	27	100.0	468.7	100.0	

Table 4. Source of spill material for industrial incidents where overpressures were created.

Source of Spill Material	Total Number of Incidents		Number Incidents with \$ Data Available		Corrected Property Damage Loss		Average Corrected Loss, \$ million
	No.	%	No.	%	\$ million	%	
From Process Equipment.....	24	75	21	78	329.4	70	15.7
From Storage Tanks.....	4	13	4	15	130.0	28	32.5
From Transportation							
Vehicles within Plants.....	3	9	2	7	9.3	2	4.6
Unknown.....	1	3	0	0	—	—	—
Total.....	32	100	27	100	468.7	100	17.4

3. Open-air, unconfined vapor cloud explosions.

The survey by Industrial Risk Insurers was concerned with only the third category. We were careful to exclude a number of notable losses (for example, the several polyvinyl chloride plant explosions) which were in the other two categories.

Also included in the survey were incidents involving large clouds that upon ignition did not create noticeable overpressures and incidents where large clouds did not ignite. (See Appendices A, B, and C.) Since large-cloud fires that do not create overpressures and large clouds that do not ignite do not receive the same degree of publicity that the vapor cloud explosions receive, these lists are not considered to be as complete as the listing of vapor cloud explosions.

For a number of years Industrial Risk Insurers has been using a calculation method to estimate the potential for probable loss in plants where a vapor cloud hazard exists that uses the following criteria:

1. The maximum credible spill is equal to the contents of the largest process vessel or train of vessels not readily isolated. Storage vessels and major supply or fuel pipelines are not considered.

2. The amount of material vaporized for hot flashing liquids is equal to a ratio of the superheat of the material ($C_p \Delta T$) to the heat of vaporization (ΔH_v). Materials with a boiling point below 70°F are assumed to vaporize 100%.

3. The explosive yield is equal to 2% of the theoretical heat of combustion potential in the cloud and is expressed as an equivalent quantity of TNT using a heat of combustion of 2,000 B.t.u./lb. for TNT.

4. A maximum peak overpressure from the explosion is 5 lb./sq. in.

5. Damage to the plant is estimated from published data sources. (2,3)

While we realize that this is a simplistic approach, we feel it is necessary because factors such as wind velocity and direction, weather conditions, degree of confinement, spill rate, and operator response are unknown prior to the incident. Our calculation method, therefore, assumes conditions approaching those encountered with explosively dispersed clouds.

Data sources

Information on the incidents surveyed were gathered from published sources and from private communications. The latter include internal Industrial Risk Insurers loss reports and information supplied by numerous individuals in industry and insurance organizations.

Published sources many times do not contain sufficient data to analyze adequately the cause and effect of a vapor cloud incident. Many of these published sources appeared many years ago, before the possibility of an open air fireball explosion was considered. In addition, they were often written to explain the cause of the incident and do not include information on explosion effects and size of spill. Private communication sources at times gave additional information to supplement published sources.

The information in this survey is the best available to Industrial Risk Insurers at this time. Some of this information is only a best estimate. If other organizations or individuals have additional or more complete or correct information, we would be happy to receive it. We intend to update this survey on a regular basis.

Table 5. Mode of release for incidents where overpressures were created.

Mode of Release	All Incidents		Industrial Incidents		Transportation Incidents		Other Incidents	
	No.	%	No.	%	No.	%	No.	%
Vessel Failures.....	13	30.2	7	21.9	5	62.5	1	33.3
Piping, Valves, or Fittings Failures.....	26	60.5	23	71.9	3	37.5	0	0
Release from Venting Facilities.....	3	7.0	1	3.1	0	0	2	67.7
Unknown.....	1	2.3	1	3.1	0	0	0	0
Total.....	43	100.0	32	100.0	8	100.0	3	100.0

The incident tabulations contained in the vapor cloud survey in the appendices are in three parts: 1) overpressures created; 2) ignition—no overpressures; and 3) no ignition.

Each tabulation is arranged chronologically. As the incidents were gathered, a random number was assigned which is shown as the code number. This number is retained for ease in future updating of the survey. This number is also used as a key to the data sources listing that follows the tabulations.

The loss figures are for property damage only. The actual amount of the loss at the time of incident and the amount of the loss if it had occurred in 1976 are given. Valuation factors used are given in Table 1. These are standard factors used by Industrial Risk Insurers for petroleum and petrochemical plant equipment.

In the "available data" column of the appendices are given, where possible, information on the following: 1) cause of the incident, 2) spill source, 3) amount of material

spilled, 4) size of cloud, 5) location and nature of ignition source, 6) wind conditions, 7) equivalent quantity of TNT, and 8) explosive yield or efficiency factor.

The amount of the material spilled was in some cases given by the data source and in other cases was calculated from spill source data (size of opening, pressure, and time) or cloud size using previously published calculation methods. (4, 5) The TNT equivalent was, in some cases, given by the data source. In others it was calculated from information on the explosive effects by previously published calculation methods and data sources. (2, 3)

Where both the amount of material spilled and the TNT equivalent could be determined, a yield or efficiency factor was calculated utilizing a ratio of the heat of combustion of the material to the heat of combustion of TNT.

Glass breakage data usually is a poor indicator of overpressures from vapor cloud explosions since this damage occurs in a range of 0.5 to 1 lb./sq. in. and the correlation

Table 6. Selected industrial incidents.

Code No.	Year	Material	ΔH_c B.t.u./lb.	Weight of Material in Cloud, lb.	Total B.t.u.'s	Actual Loss, \$ million	Corrected Loss to 1976, \$ million
61	1954	Acrolein	11,830	40,000	4.73×10^8	2	5.4
3	1961	Cyclohexane	18,676	8,500	1.59×10^8	0.7	1.47
76	1962	Ethylene Oxide	11,482	38,000	4.36×10^8	8	16.56
18	1964	Ethylene	20,276	200 to 500	$\begin{Bmatrix} 4 \times 10^6 \\ \text{to} \\ 1 \times 10^7 \end{Bmatrix}$	3.2	6.5
4	1965	Ethyl Chloride	8,246	38,000	3.13×10^8	0.9	1.8
62	1966	Methane	21,502	600	1.2×10^7	4.8	9.4
17	1966	Butadiene	19,200	850	1.6×10^7	0.016	0.03
6	1967	Isobutylene	19,367	20,000	3.87×10^8	17.5	32.7
13	1968	$\leq C_9$	19,000	100,000 to 200,000	$\begin{Bmatrix} 1.9 \times 10^9 \\ \text{to} \\ 3.8 \times 10^9 \end{Bmatrix}$	28	50
40	1969	Naphtha + H_2	19,000	50,000	9.5×10^8	3.5	6
77	1970	$> C_{10} + H_2$	19,000	250,000	4.75×10^9	30	48
19	1971	Ethylene	20,276	8,000	1.62×10^8	2.6	3.9
32	1971	Ethylene	20,276	1,000	2.0×10^7	6.1	9.1
22	1971	Butadiene	19,200	27,000	5.18×10^8	0.245	0.365
9	1974	Cyclohexane	18,676	120,000	2.2×10^9	70	82.6
8	1974	$\geq C_5$ (Unsaturated)	19,000	16,800	3.192×10^8	13.2	15.6
60	1975	Ethylene	20,276	12,000	2.4×10^8	40	42.8
74	1975	H_2	51,571	665	3.4×10^7	2.75	2.91

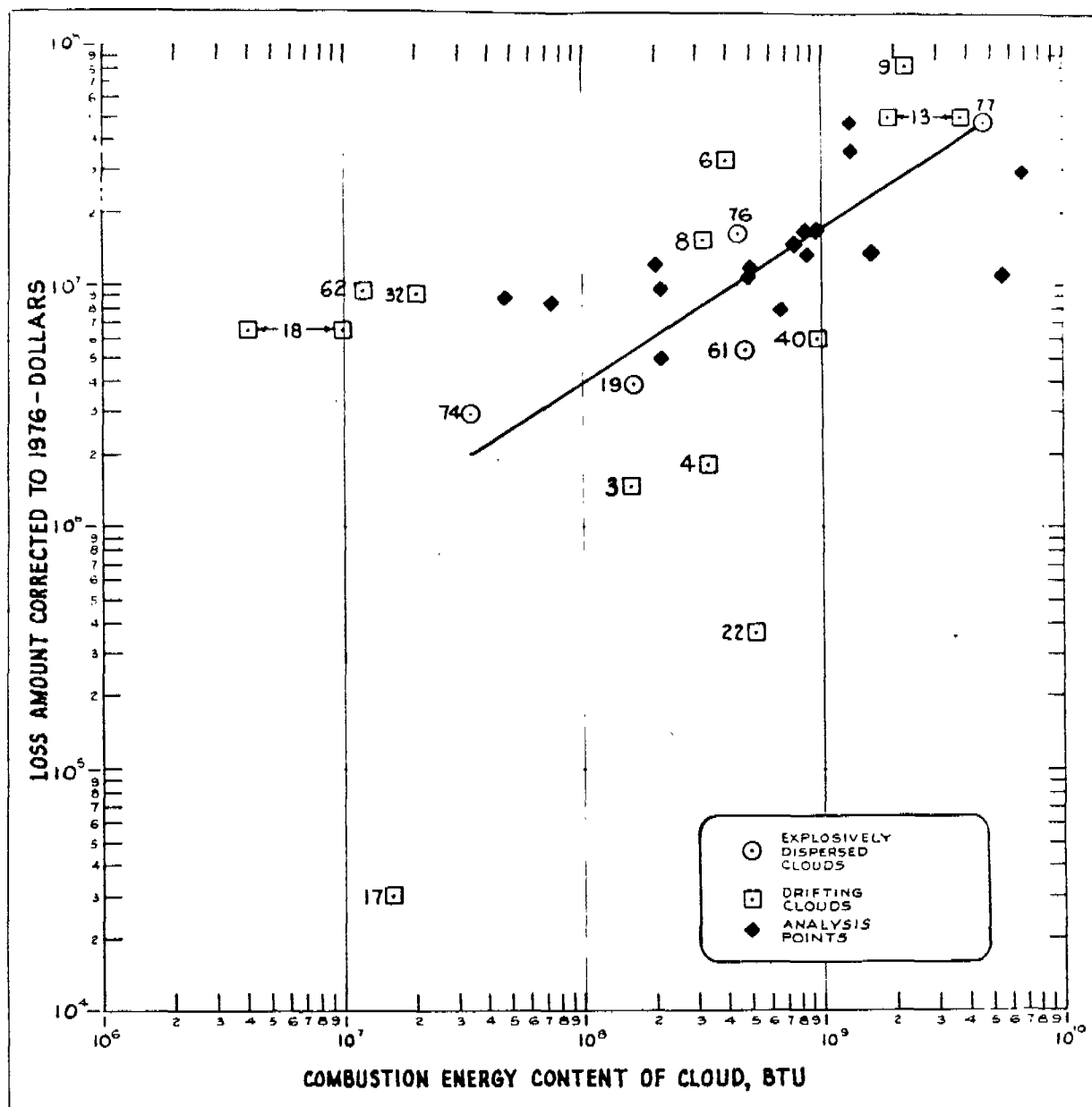


Figure 1. Amount of loss as a function of cloud energy content explosively dispersed vs. drifting clouds.

to TNT explosive effects is less accurate at low overpressures. (6) Where glass breakage was used to calculate the TNT equivalent, this fact is indicated.

Overpressure incidents

Since the incidents where overpressures were created are of more immediate concern and most likely are more complete, the conclusions that follow are only from that tabulation. The other two tabulations are presented for information only.

Type of facility. Table 2 is a breakdown of the type of facility involved in the incidents where overpressures were created (industrial, transportation and others). Where the incident involved transportation vehicles but occurred within an industrial plant, the incident is included in the

industrial category.

Type of industrial plant. Table 3 indicates the type of industrial plant where the 32 industrial losses occurred (petrochemical or refinery) and an average corrected loss amount where loss amount data is available. Note that while only 25% of the losses occurred in refineries, the average property damage loss was \$22.92 million, compared to \$15.02 million in petrochemical plants.

Source of spill. Table 4 shows the source of the spilled material in industrial plants. While 75% of the incidents and 70% of the corrected loss amount were due to spills from process vessels, the average corrected loss amount was only \$15.7 million compared to \$32.5 million for incidents caused by spills from storage tanks. Because of the greater quantities of materials usually found in storage tanks compared to process equipment, a greater average

Table 7. Estimated losses using Industrial Risk Insurers' calculation method.

Material Spilled	ΔH_c B.t.u./lb.	Weight of Material Spilled, lb.	Total B.t.u.'s	Property Damage Loss Estimate, \$ million
Propylene & Propane	19,750	342,000	6.8×10^9	29.6
Benzene	17,446	322,000	5.6×10^9	11.2
Ethylene Oxide	12,024	56,000	6.7×10^8	8.0
Propylene	19,683	46,000	9.1×10^8	17.0
Ethylene	20,276	66,000	1.3×10^9	33.2
Propylene	19,683	66,000	1.3×10^9	47.8
C ₄	19,484	39,000	7.6×10^8	15.2
Butadiene	20,200	42,000	8.5×10^8	13.5
Butadiene	20,200	10,400	2.1×10^8	5.0
Vinyl Chloride	8,239	9,000	7.4×10^7	8.5
Ethyl Chloride	8,822	180,000	1.6×10^9	13.8
Ethylene Oxide	12,024	70,000	8.4×10^8	16.4
Cyclo-hexane	18,846	26,000	4.9×10^8	11.8
Vinyl Chloride	8,239	24,000	2.0×10^8	12.3
Vinyl Chloride	8,239	61,000	5.0×10^8	12.0
Vinyl Chloride	8,239	26,000	2.1×10^8	9.8
Monochlorobenzene	11,754	4,000	4.7×10^7	9.0

loss amount is expected.

Mode of release. The mode of the release leading to incidents where overpressures were created is summarized in Table 5. For industrial plants, the largest number of incidents were caused by failure of piping, valves, or fittings. As would be expected, the largest number of transportation incidents were due to vessel failure, reflecting the number of tank car derailments with consequent puncture of the container.

Loss amount and heat content of cloud. Table 6 is a listing of 18 selected industrial incidents where overpressures were developed. Included in this list are incidents where both loss amount and spill quantity information were available. The heat of combustion for the material spilled is used to obtain a total heat content of the cloud.

The data from Table 6 is presented in Figure 1, in which clouds produced by catastrophic vessel failure (explosive dispersal) are compared to drifting clouds. Note that there is reasonable correlation for the explosively dispersed clouds, but a wide variance for the drifting clouds. This is to be expected since explosively dispersed clouds would be less affected by partial confinement, winds, ambient temperature, humidity, and topographic features.

Note that nine of the drifting cloud incidents fall above and five fall below the line drawn through the explosively dispersed cloud points. This would suggest that explosively dispersed clouds do not represent the most severe condition.

The various factors affecting drifting clouds would tend to cause them to be more severe or less severe than the explosively dispersed clouds. For example, incident code numbers 18 and 32 were small leaks in polyethylene plants where surrounding buildings gave a degree of confinement to the explosion. Therefore, a small leak was able to produce a loss of significant magnitude. Incident code number 9 was a large spill from a large pipe with almost immediate ignition. Dispersion of this cloud would approach explosive dispersion, but because of the congestion in the plant there was a degree of confinement.

Loss potential. Table 7 is a listing of 17 probable maximum loss estimates for plants where a vapor cloud hazard exists insured by Industrial Risk Insurers. These represent

a random sampling of our chemical and petrochemical risks. The estimates were made using the calculation method previously summarized.

The points from Table 7 are plotted in Figure 1. Note that these points show less deviation from the "explosive dispersal line" than do the drifting cloud points. This correlation would indicate that the calculation method described predicts the explosively dispersed vapor cloud which, in turn, is not the "worst case," but approximates an average condition.

While it is conceded that the spread of points in Figure 1 indicates a data deviation that makes questionable any conclusions reached, the data is the best available, at least to the author. The conclusions are at best generalities and should be viewed as such. It is only through thorough analysis of each incident, both large and small, that an understanding of the factors affecting the probability that a vapor cloud explosion will occur and that it will be severe if it does occur can be determined.

I urge those who have information on additional incidents and additional information on incidents included in this survey to forward it to the author. Confidentiality of the source will be strictly observed.

Data submissions should include, if possible, the following:

1. Date and location of incident.
2. The type of process.
3. Material spilled.
4. Size, height, and shape of cloud.
5. Amount of material spilled.
6. Source of spill.
7. Size of spill opening.
8. Pressure and temperature of materials in process.
9. Weather conditions (wind, temperature, humidity).
10. Overpressure effects (description of damage, preferably with photographs).
11. Amount of property damage loss.

In conclusion

There are many factors that affect the development of a vapor cloud and the explosive forces, if an explosion oc-

curs. The data presented in this article are insufficient to reach any firm conclusions concerning these factors. Generally, it may be shown that explosively dispersed vapor cloud explosions produce property damage that is a function of the amount of material dispersed. Drifting-cloud vapor-cloud explosions do not show any consistency. The vapor cloud loss estimation material used by Industrial Risk Insurers predicts an explosively dispersed cloud and is reasonably consistent with the actual incidents in the study. The explosively dispersed cloud is not the most severe nor, for that matter, the least severe incident, but is rather an average incident.

Acknowledgment

I would like to thank the many people in the chemical, petrochemical, and oil industries who contributed much of the information presented in this survey. Without their

valuable assistance, this survey would be far less definitive. #

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Appendix A. Vapor cloud survey, overpressures created.

Code	Year	Location	Type of Process	Material Released	Actual Property Loss, \$ million	Property Loss Corrected to 1976, \$ million	Killed/Injured	Available Data
65	1921	England	—	Hydrogen	?	?	1/?	Break-up of Dirigible ZR-2 over Hull, England released hydrogen which ignited. Windows broken within 2 mi. Blast heard 5 mi. Tremors felt 50 mi.
25	1948	Germany	—	Dimethylether	?	?	Many	Rail car filled "bubble-full." Car overheated in sun. No relief valves. Car rupture explosively dispersed car contents forming vapor cloud which exploded.
61	1954	West Virginia	—	Acrolein	2	5.4	0	6,000 gal. of acrolein explosively dispersed into a vapor cloud when tank car ruptured. Acrolein was contaminated causing polymerization which overtaxed car relief vent.
37	1954	Portland, Ore.	—	LPG	0.33	0.89	?	400 ft. diameter cloud formed from broken safety relief valve stem on tank car. Two storage tanks 60 ft. away distorted indicating 3.5 to 7 lb./sq. in. overpressure.
42	1955	California	Gasoline Plant	Butane	0.4	1.0	?	Rupture of 6 in. line at 500 lb./sq. in. in a gasoline plant led to explosion and fire that destroyed all outside processing equipment including towers, pressure vessels and piping.
33	1956	New York	Polyethylene	Ethylene	?	?	?	40,000 cu. ft. at STP released from polyethylene reactor vent at 20,000 lb./sq. in. Aerial explosion created 1/2 lb./sq. in. overpressures.
44	1958	Oklahoma	Refinery	Propane	0.1	0.2	0/1	Flexible coupling failure. Ignition at boiler. Blew employee into ditch.
47	1959	Georgia	—	LPG	?	?	23/?	Train wreck punctured tank car. Rural area. NFPA report states there was an explosion.
3	1961	Texas	Cyclohexane Oxidation	Cyclohexane	0.7	1.5	1/0	Valve failed at reactor bottom releasing 6,000 gal. spill. Cloud contained 8,500 lb. of vapor. Control room failed. Estimate overpressure of 2 lb. sq. in. at 100 ft. from point of spill.
76	1962	Kentucky	Ethyl Amines	Ethylene Oxide	8	16.6	1/9	Day tank containing 6,500 gal. of ethylene oxide became contaminated with ammonia. Tank ruptured, explosively dispersing ethylene oxide into air. Cloud immediately ignited creating explosive forces equivalent to 18 tons of TNT as evidenced by damage.
48	1962	New York	—	Propane	0.2	0.4	10/17	Truck accident ruptured 6,876 gal. tank. Cloud 400 to 600 ft. in diameter, 80 ft. high exploded. Low overpressures created.
1	1963	Louisiana	Ethylene	Methane or Ethylene	3.9	8.0	0	Sight glass or metering station failure. Explosion of cloud resulted in 1 ton TNT equivalent. Ensuing fire of long duration.
63	1964	Nevada	—	Hydrogen	?	?	0	Venting experiment accidentally resulted in ignition of 200 lb. of hydrogen. Explosive force estimated to be 60 lb. of TNT.
18	1964	Texas	Polyethylene	Ethylene	3.2	6.5	2/17	Failure of 3/8 in. compression fitting on 1,000 to 2,500 lb./sq. in. ethylene line in pipe trench resulted in spill of 200 to 500 lb. Explosion equaled 0.12 to 0.30 tons of TNT. Explosion in courtyard between buildings giving partial confinement.
7	1965	Louisiana	Ethylene	Propane	3.2	6.4	0/12	Vented cold liquid into carbon steel flare header.

Continued on page 60

Appendix A. Vapor cloud survey, overpressures created. (continued)

Code	Year	Location	Type of Process	Material Released	Actual Property Loss, \$ million	Property Loss Corrected to 1976, \$ million	Killed/Injured	Available Data
4	1965	Louisiana	Ethylene Hydrochlorination	Ethyl Chloride	0.9	1.8	0	Rupture of recycle line on reactor led to spill of 6,000 gal. prior to ignition. Explosive force of 0.15 to 0.20 tons of TNT was estimated.
62	1966	West Germany	Ethylene	Methane	4.8	9.4	3/83	Ignition occurred within seconds after pipe failure. Logical source of ignition 200 ft. from leak. 600 lb. of methane released. Explosion equivalent to two to three tons of TNT.
17	1966	Louisiana	Synthetic Rubber	Butadiene	0.016	0.03	3/2	Valve on reactor bottom opened accidentally on air failure. Ignition source 50 ft. from point of spill. Spill about 200 gal. prior to ignition. Overpressures of 0.5 to 1 lb./sq. in. were estimated.
6	1967	Louisiana	Refinery-Alkylation Unit	Isobutylene	35	65	7/?	Failure of 10 in. gate valve bonnet on line led to release of about 20,000 lb. of isobutylene. Explosive force of 12 tons of TNT estimated from glass breakage which would give a 10% yield.
13	1968	The Netherlands	Refinery	C ₉ or lighter Hydrocarbons	28	50	2/75	Breaking of water-oil emulsion in slop-oil tank caused tank froth-over and failure. 50 to 100 tons of hydrocarbons formed huge cloud.
40	1969	England	Refinery-Cyclic Hydroformer	Naptha + H ₂	3.5	6.0	?	Failure of 16 in. vapor line at 250 lb./sq. in. led to formation of large cloud with ignition within 10 sec. Estimate 50,000 lb. spilled.
24	1970	Missouri	—	Propane	?	?	?	122,000 lbs. at 942 lb./sq. in. spill from a pipeline rupture. Cloud 1500 ft. long, and 10 to 20 ft. high detonated (according to U.S. Bureau of Mines) with a force equivalent to 50 to 75 tons of TNT.
77	1970	New Jersey	Refinery, H-oil Unit	C ₁₀ Hydrocarbons + H ₂	30	48	0/4	Failure of reactor operating at 2500 lb./sq. in. due to localized overheating caused large cloud of about 250,000 lb. which, upon ignition, created widespread explosion damage and fires. Overpressures were highly directional. Peripheral damage indicates an explosive yield of up to 50 tons of TNT. A yield factor of about 4% is indicated.
19	1971	Louisiana	Ethylene	Ethylene	2.6	3.9	0/8	Failure of truck tanker with frozen relief valve at about 400 lb./sq. in. released about 8,000 lb. of ethylene. The equivalent of about 1/2 ton of TNT did widespread damage to light construction components.
32	1971	Texas	Polyethylene	Ethylene	8.8	13.1	3/7	Release of about 1,000 lb. of ethylene from 1/2 in. pipe connection to larger pipe. Three explosions occurred. Some confinement from building walls around an alleyway.
22	1971	Texas	Butadiene	Butadiene	0.16	0.24	1/6	Failure of pump, 12 mi./hr. wind caused cloud to drift 600 ft. before ignition from unknown source 8-10 min. after release. Estimate a spill of 27,000 lb. Explosion damage consisted of broken windows, displaced cooling tower internals and cement asbestos siding.
23	1972	Illinois	—	LPG 94% Propylene	7.5	10.8	0/230	118,000 lb. of propylene released when rail cars collided in humping operation in switchyard. Rolling car created an elongated vapor cloud covering about 5 acres. Two explosion centers were identified. U.S. Dept. of Transportation states that the explosion may have been a detonation.
15	1972	Brazil	Refinery	Butane	8.4	12.1	37/53	Frozen open water draw-off valve on bottom of storage sphere resulted in cloud which exploded.
49	1973	Japan	Ethylene	Ethylene	16	22	1/?	Excessive pressure and temperature from process upset caused valve flange to fail.
52	1973	Japan	VCM	Vinyl Chloride	?	?	1/23	Broken valve yoke caused 1,100 ton spill creating 53,000 cu. ft. cloud.
68	1974	Florida	—	Propane	1.0	1.2	0/0	Hose from 9,000 gal. tanker failed causing 40 ft. high vapor cloud. Explosion destroyed two warehouses, crushed cars and broke windows in four block area.
9	1974	England	Cyclohexane Oxidation	Cyclohexane	70	83	28/100	Poorly constructed and installed 20 in. temporary pipe failed releasing 60 tons of materials at 311°F. and 136 lb./sq. in. Ignition in 25 to 35 sec. created 20 to 30 lb./sq. in. overpressures. Explosive force estimated to be equivalent to 15 tons of TNT.
59	1974	Illinois	—	Isobutane	18.4	21.7	7/356	Accident created 22 in. x 26 in. hole in end of 30,000 gal. rail car releasing contents. Ignition of the 1/2 x 3/4 in. cloud was 8 to 10 min. after the collision. Based on damage, the apparent yield of the explosion was between 200 and 400 tons of TNT. An unusually high conversion factor (25 to 50%) is indicated.
38	1974	Mississippi	—	Butane	?	?	0/24	Overfilling of salt dome storage well created a cloud 1.25 mi. in diameter. Two explosions occurred. The second was 800 to 1,000 ft. above grade and

Appendix A. Vapor cloud survey, overpressures created. (continued)

Code	Year	Location	Type of Process	Material Released	Actual Property Loss, \$ million	Property Loss Corrected to 1976, \$ million	Killed/Injured	Available Data
57	1974	England	Polyethylene	Ethylene	?	?	0/2	was the most severe. Glass breakage to 7 mi., houses damaged to 900 feet.
54	1974	Texas	—	Butadiene	13.3	15.7	1/235	Leak from flange joint or broken thermowell in high pressure piping caused spill of 2,000 to 6,000 lb. in about 30 min. Windows broken in 200 yd. radius. Roofs and ceilings in four buildings damaged. Electrical breakers tripped in process areas and boiler house. Part of gas confined in open top barricaded area.
8	1974	Texas	Isoprene Unit	C ₅ Hydrocarbons	13.2	15.6	2/9	Humping accident in railyard resulted in puncture of 34,000 gal. tank car. Amount of spill in 2 to 3 min. before ignition not known. Ignition by locomotive 600 ft. away. Estimate 2 to 3 lb./sq. in. overpressure at 1,000 ft. from point of rupture.
11	1975	Belgium	Polyethylene Plant	Ethylene	26.5	28.1	6/13	Piping failure led to spill of 16,800 lb. Explosion knocked out deluge systems and electrical feed to fire pumps. Most damage from ensuing fire. Maximum overpressure estimated from damage was 3.5 lb./sq. in. at 120 ft. Explosive equivalent of 1 ton of TNT was estimated giving a yield factor of 1%.
60	1975	Holland	Ethylene	Propylene	40	42.8	14/104	Fatigue failure of a vent connection on a compressor suction line let ethylene escape which formed a gas cloud in an open area that ignited from an unknown source. Highly directional pressure waves caused widespread structural damage.
70	1975	Germany	Refinery-Cyclic Hydroformer	Naptha + H ₂	1	1.1	0/4	Failure of level controller on column caused cold liquid to pass out of relief valve and into carbon steel flare header which cracked. Cloud of 12,000 lb. ignited at furnace 150 ft. away.
74	1975	Calif.	Hydrogen	Hydrogen	2.75	2.91	0/2	Failure of carbon steel line due to hydrogen attack. Slight area explosion after release of hydrocarbons in cyclic hydroformer.
79	1975 or 1976	Czechoslovakia	Ethylene	Light Hydrocarbons	?	?	14/?	Crack in tank caused tank failure releasing 665 lb. of gaseous hydrogen to atmosphere. Cloud exploded with an apparent center 30 ft. above grade and an energy release equivalent of 20 to 40 lb. of TNT.
51	1976	Texas	Ethyl Alcohol	Ethylene	18	18	1/15	Extensive damage. No other details available.
								Line failure at 2,000 lb./sq. in. led to ethylene release with subsequent vapor cloud explosion.

Appendix B. Vapor cloud survey, no pressures.

Code	Year	Location	Type of Process	Material Released	Actual Property Loss, \$ million	Property Loss Corrected to 1976, \$ million	Killed/Injured	Available Data
20	1943	California	—	Butane	?	?	5/?	Bottom connection on 4,300 gal. tank failed creating 1/4 mi. diameter cloud.
36	1945	New Jersey	Refinery	Crude Oil	0.10	?	0/2	Failure of cast iron valve on 31,000 bbl. tank created cloud which was ignited at highway 209 ft. away.
26	1954	Tenn.	Pesticides	Isopropyl Alcohol	0.25	0.68	?	Vapor cloud formed from unknown leak source. Vinyl chloride cylinders ruptured from overheating creating loud noises.
43	1957	Quebec, Canada	—	Butane	3.2	7.1	1/?	Overfilling of storage sphere created 1,200 ft. diameter cloud. Storage spheres subsequently ruptured causing some explosion damage.
46	1958	Michigan	Refinery	Butane	0.5	1.1	1/?	Overpressure of 21,000 gal. tank caused failure of tank. Cloud ignited 350 ft. from source.
45	1958	California	Refinery	Oil Froth	9	19.4	2/18	Water in 50,000 bbl. oil tank caused frothing and tank overflow. Amount of vapor formation from froth not known.
50	1965	Texas	?	Butane	?	?	?	Removal of wrong blind flange led to spill of unknown quantity which was ignited by heater 60 ft. from spill point.
71	1966	France	Refinery	C ₃ Hydrocarbons	?	?	45/?	Frozen open water draw-off valve on bottom of storage sphere resulted in cloud which was ignited by vehicle 300 ft. away. Sphere subsequently ruptured.

Continued on page 62

Appendix B. Vapor cloud survey, no overpressures. (continued)

Code	Year	Location	Type of Process	Material Released	Actual Property Loss, \$ million	Property Loss Corrected to 1976, \$ million	Killed/Injured	Available Data
41	1966	Pennsylvania	Refinery	Cumene, Benzene, Propane	?	?	None	Materials discharged at 500 lb./sq in. from rupture of 6 in. pump discharge pipe. Cloud was wind affected.
72	1968	Texas	Isopropyl Alcohol	C ₃ Hydrocarbons & acid mixture	2	3.6	1/2	Cloud formed when 10 in. spool piece split longitudinally was ignited at furnace 180 ft. away.
27	1968	Louisiana	VCM Plant	Vinyl Chloride	0.83	1.48	None	Casing joint or seal failure on pump created cloud which was ignited at furnace 100 ft. from point of failure. Cloud less than 3 ft. high in most areas.
58	1969	England	Cyclohexane Oxidation	Cyclohexane	?	?	2/23	A low cloud formed from 4 tons, which was released at 100 lb./sq. in. and 300°F. from an improperly blinded pipe. Ignition was by a diesel engine which overspeeded located 100 ft. from spill point. Cloud covered an area 250 ft. x 150 ft.
35	1972	Texas	—	Crude Oil	?	?	1/2	Split in 6 in. pipeline ran for 4-1/2 hr. before ignition. Scorched area 1,800 ft. long. About 332,000 gal. of material contained 98% C ₅ or lighter hydrocarbons at 530 lb./sq. in. gauge was released.
14	1972	Montana	Alkylation	Butane	2.3	3.3	1/1	Leak from partly open 6 in. flange was ignited at furnace 100 ft. away. Resulting fire caused vessel to rupture which created minor overpressures.
2	1974	Louisiana	Ethylene	Propylene	2.6	3.1	0/0	Power failure led to failure of expansion joint releasing about 10,000 gal. prior to ignition at furnaces. One deluge system between spill point and ignition source tripped by steam leak prior to ignition.
64	1976	Texas	—	Natural Gas Liquids	0.05	0.05	1/4	Cross country pipeline failure led to cloud which ignited and destroyed farmhouse.
16	1976	Puerto Rico	—	C ₅ Hydrocarbons	?	?	1/2	Tank overpressure led to release of vapor or mist which was 10 to 25 ft. high. Ignition was at a furnace 450 ft. from the tank. Scorched area was

Appendix C. Vapor cloud survey, no ignition.

Code	Year	Location	Type of Process	Material Released	Actual Property Loss, \$ million	Property Loss Corrected to 1976, \$ million	Killed/Injured	Available Data
34	1951	Illinois	?	Butane	—	—	—	about 800 ft. diameter. Cloud was consumed in 10 to 30 sec.
67	1967	Texas	?	Ethylene	—	—	—	9,500 gal. of butane released from ruptured bottom discharge pipe on tank due to freezing of collected water. Excess flow valve failed to operate.
5	1970	Louisiana	VCM Plant	Vinyl Chloride & Ethylene Dichloride	—	—	—	Pilot on 16 in. flare failed allowing release of 4,000 lb. in a 100 ft. deep cloud. Wind was 12-15 mi./hr.
10	1971	Florida	Cyclohexane Oxidation	Cyclohexane	—	—	—	Cloud of 150 ft. diameter formed when packing on ball valve blew out. Waterspray manually actuated. Wind blew cloud away from possible ignition sources.
21	1972	Delaware	PVC Plant	Vinyl Chloride	—	—	—	Failure of a 4 in. weld connection to an 8 in. pipe released 75,000 lb. of material. Cloud was 2,000 ft. long, 1,200 ft. wide and 100 ft. high. Material reached and burned in boilers but did not ignite. A number of other possible ignition sources were passed without ignition. Numerous waterspray systems were actuated manually.
69	1975	Louisiana	Synthetic Rubber	Butadiene	—	—	—	Failure of 3 in. gasket on reactor top released 1,800 gal. Waterspray was actuated by vapor detectors.
73	1975	Louisiana	—	Propane	—	—	—	Approximately 1,000 gal. of material discharged as a gas from a hole in 2 in. nozzle on the top of a storage tank. Waterspray tripped manually.
								Overpressure caused split in 6 in. underground line from storage well releasing 600,000 lb. Cloud was 30 to 40 ft. high and vapor was noted 1 mi. downwind.

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