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National Emission Standards for Hazardous Air Pollutants Inspection Manual for Vinyl Chloride

NATIONAL EMISSION STANDARDS
FOR HAZARDOUS AIR POLLUTANTS
INSPECTION MANUAL
for
V I N Y L C H L O R I D E

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LIST OF CHEMICAL FORMULAS

Name	Formula
Acetylene	$HC \equiv CH$
Chlorine	Cl_2
Ethylene	$CH_2 = CH_2$
Ethylene Dichloride	$ClCH_2 - CH_2Cl$
Hydrogen Chloride	HCl
Oxygen	O_2
Polyvinyl Chloride	$\left(H_2C = CHCl \right)_n$
Vinyl Chloride Monomer	$H_2C = CHCl$
Water	H_2O

LIST OF ABBREVIATIONS

BOD	Biological oxygen demand
COD	Chemical oxygen demand
EDC	Ethylene dichloride
EPA	U.S. Environmental Protection Agency
Eq.	Equation
FR	U.S. Federal Register
HCL	Hydrogen chloride
NESHAP	National Emission Standards for Hazardous Air Pollutants
PVC	Polyvinyl chloride
RD	Rupture disc
SOP	Standard operating procedure
SRV	Safety relief valve
TSS	Total suspended solids
VAC	Vinyl acetate comonomer
VC	Vinyl chloride
VCM	Vinyl chloride monomer

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 National Emission Standards for Hazardous Air Pollutants (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 (41-FR-October 21, 1976, pages 46560-46573) 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. 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 recordkeeping 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), and to maintain a current listing of these pollutants.

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 emissions 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 m^3

(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 m^3 (50 gal) and less than 4.07 m^3 (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 (SOP)" 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]. In 1974, there were nine plants using this process to produce 5.05 billion pounds of ethylene dichloride per year [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.

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 Figure 3.1 [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

$$CH_2 = CH_2 + 1/2\ O_2 + 2HCL \longrightarrow ClCH_2 - CH_2Cl + H_2O. \qquad (3\text{-}1)$$

This reaction takes place in the reactor, shown in Figure 3.1, at elevated temperature. The oxychlorination process typically exhibits a 98% conversion of hydrogen chloride 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.

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

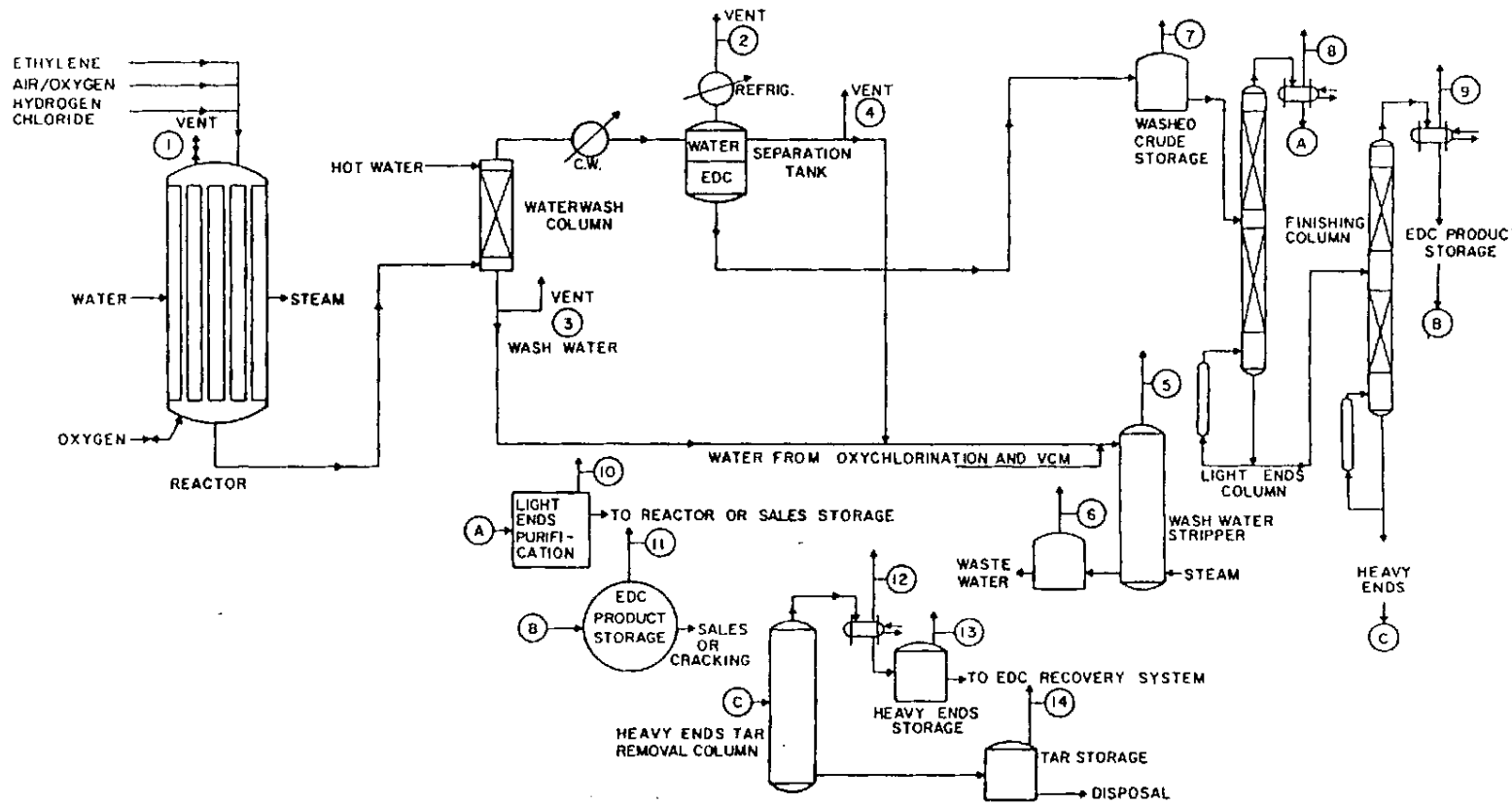

Figure 3.1. Ethylene Dichloride process flow diagram using oxychlordination which involves the reaction of oxygen and hydrogen chloride with ehtylene.

Table 3.1: The potential emission points identified by the keys in Figure 3.1 in the oxychlorination process for ethylene dichloride.

Position Name	Key	Frequency
Reactor Vent	1	Intermittent
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 this stream also contains ethylene, hydrogen chloride and air or pure oxygen. The stream is passed through a hot water wash column to remove impurities from the ethylene dichloride, and to maintain its gaseous state. 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 potential emission points are listed in Table 3.1 and identified by the keys shown in Figure 3.1. 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

$$HC \equiv CH + HCL \longrightarrow H_2C = CHCL. \qquad (3\text{-}2)$$

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

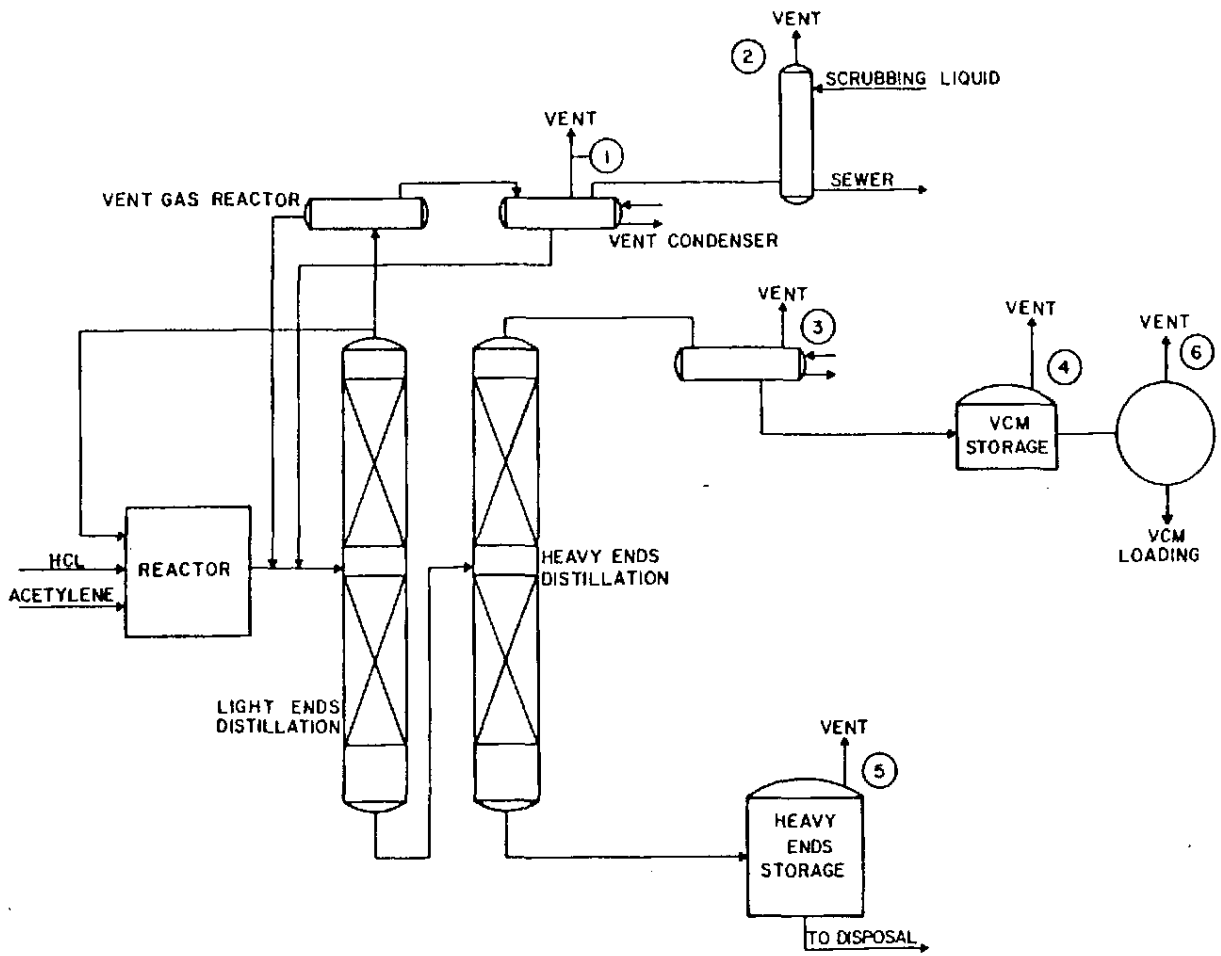

Figure 3.2. Vinyl chloride monomer process flow diagram using hydrochlorination of acetylene.

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	$HC \equiv CH$	- 84°C
Hydrogen Chloride	HCl	- 85°C
Vinyl Chloride	$H_2C = CHCl$	- 13°C
Ethylene Dichloride	$ClCH_2 - CH_2Cl$	+ 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 potential 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: The potential 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 intermittent. 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 reaction is represented by the equation

$$ClCH_2 - CH_2Cl \longrightarrow H_2C = CHCl + HCl. \qquad (3\text{-}3)$$

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 generated 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 quenching column uses liquid ethylene dichloride to liquify the ethylene dichloride in the mixture while the gaseous vinyl chloride passes on to the partial condenser and condenser.

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.

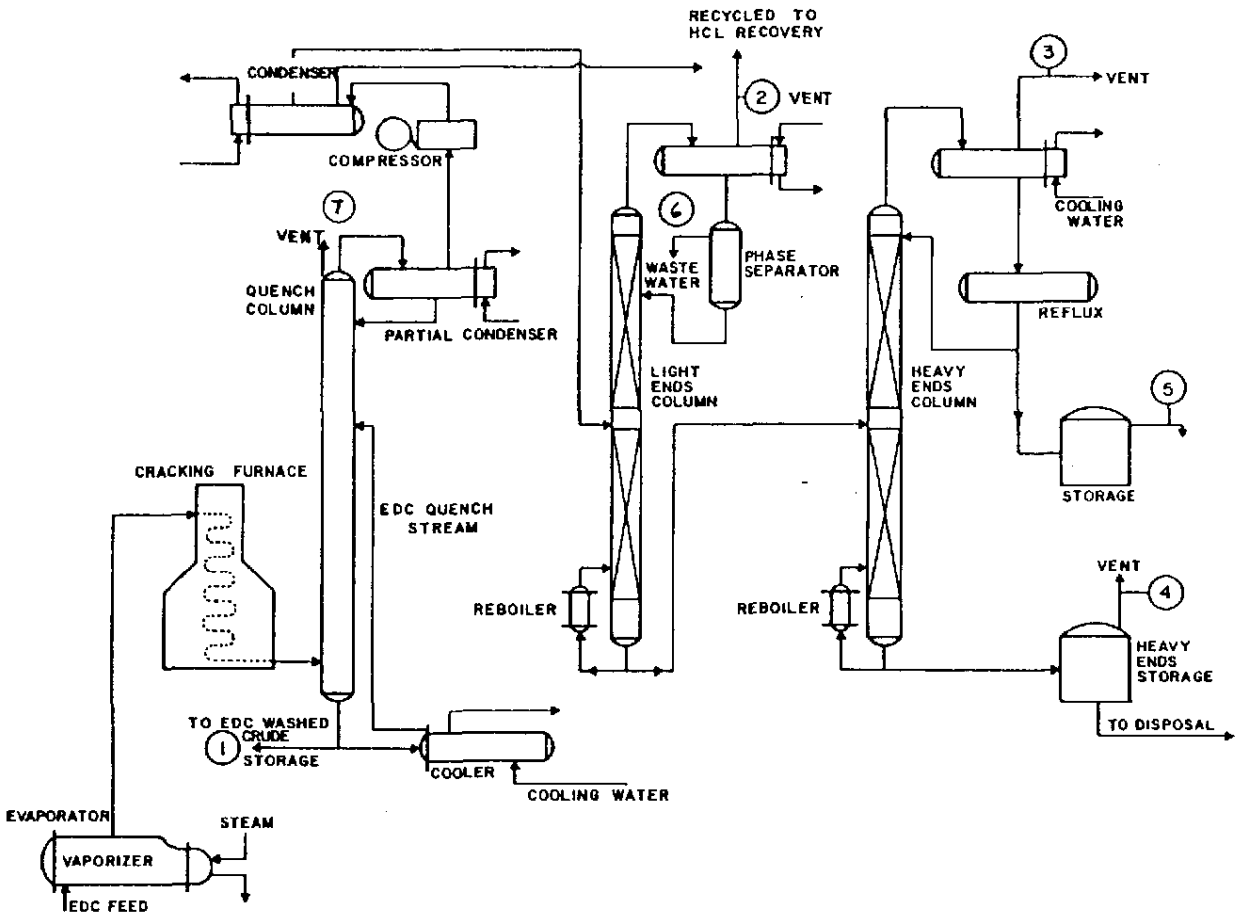

Figure 3.3. Vinyl chloride monomer process flow diagram using dehydrochlorination of ethylene dichloride.

The potential 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 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 [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 85 to 90% of the vinyl chloride has polymerized; this requires approximately 6 hours [4]. 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

Table 3.4: The potential 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

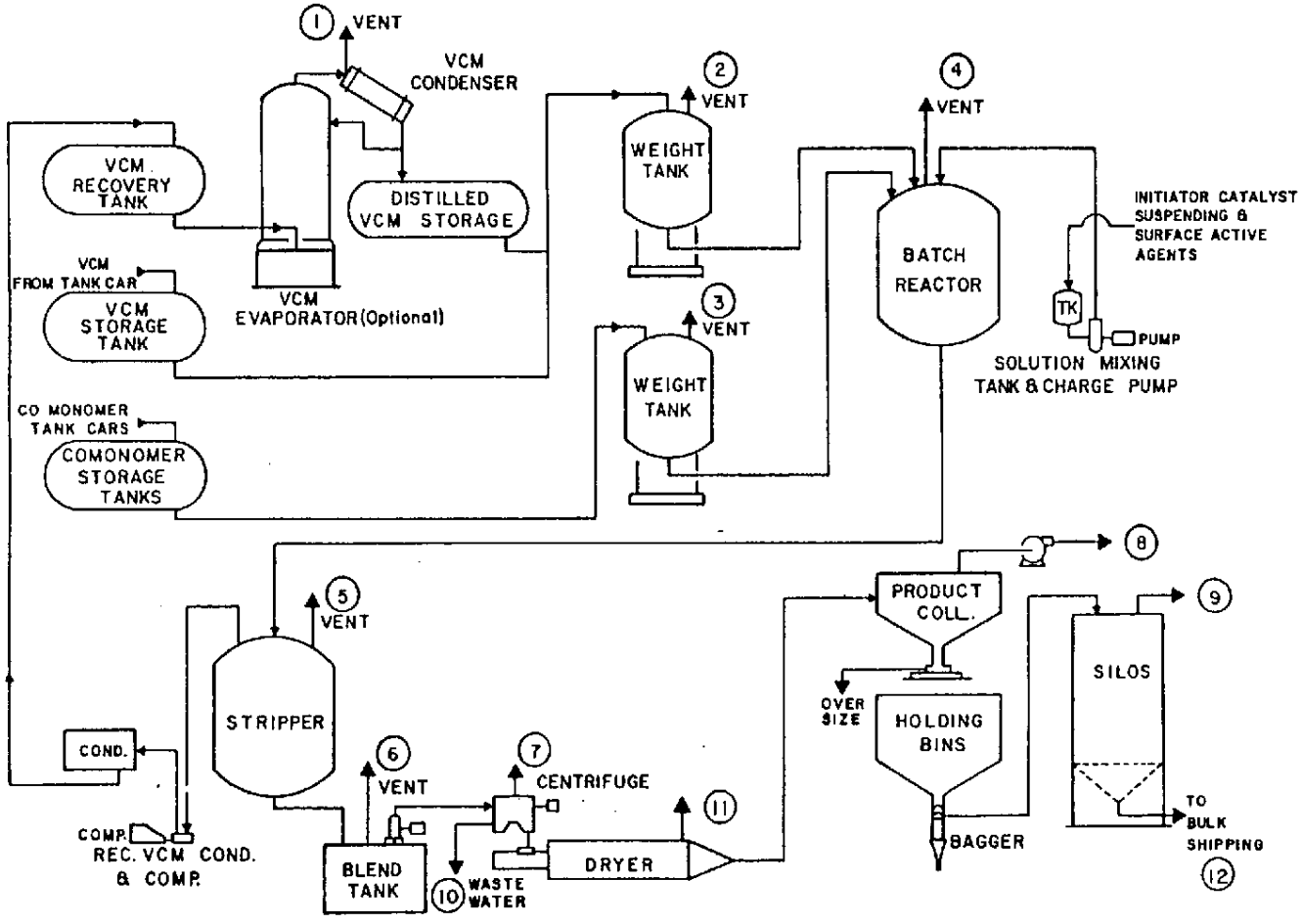

Figure 3.4. Polyvinyl chloride process flow diagram using suspension polymerization.

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 8.0 atmospheres.

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 other volatilized chemicals drive off are transferred to the recovery system. In some plants the vinyl chloride is processed through a 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 potential 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.

The reactor emissions, Key (4), may arise when a run-away condition develops and due to residual vinyl chloride vapor that may be present when the reactor manhole is opened for cleaning.

Table 3.5: The potential 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

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 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 stablizes 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].

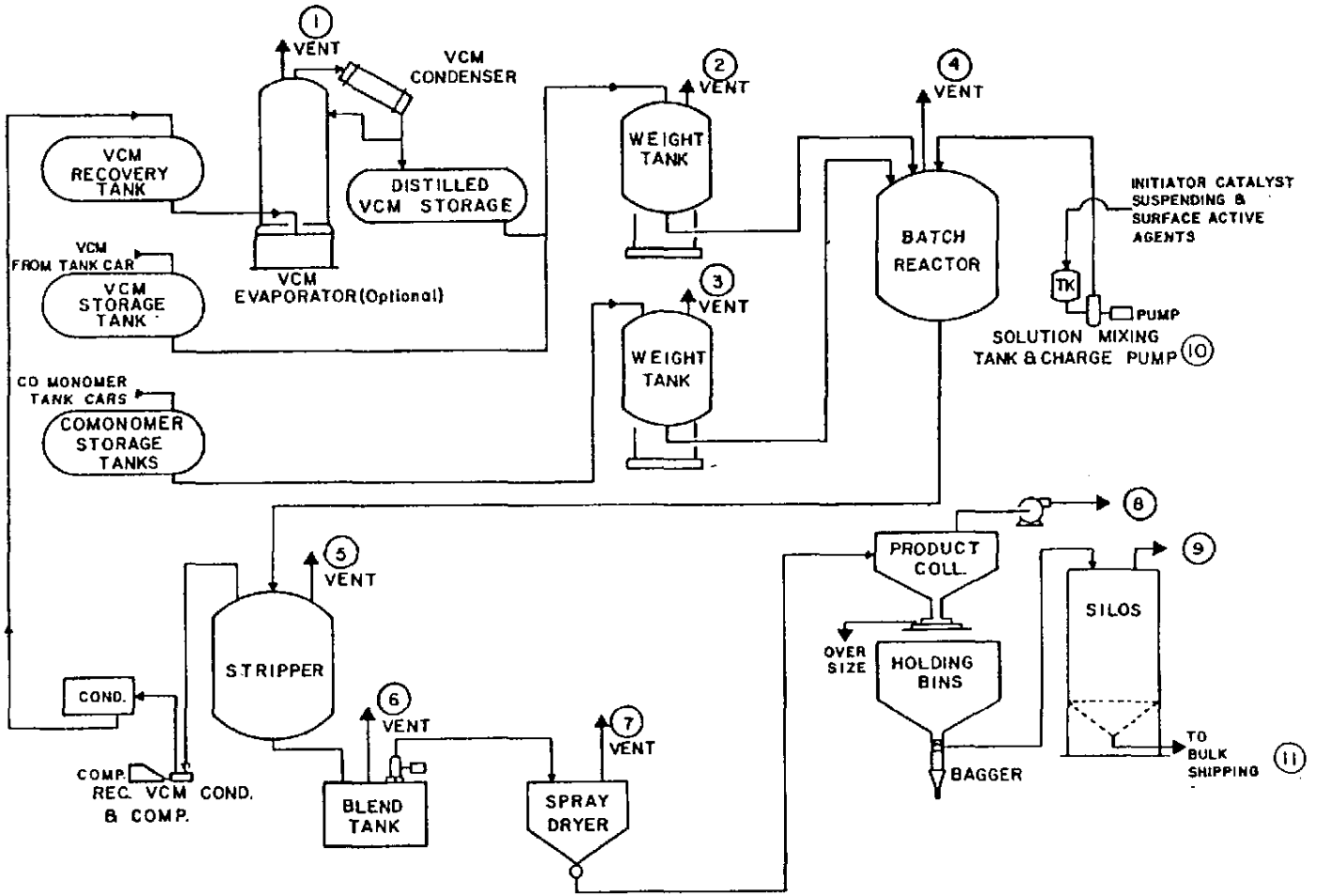

Figure 3.5. Polyvinyl chloride process flow diagram using emulsion (i.e., dispersion) polymerization.

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

Table 3.6: The potential emission points identified by the 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

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 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

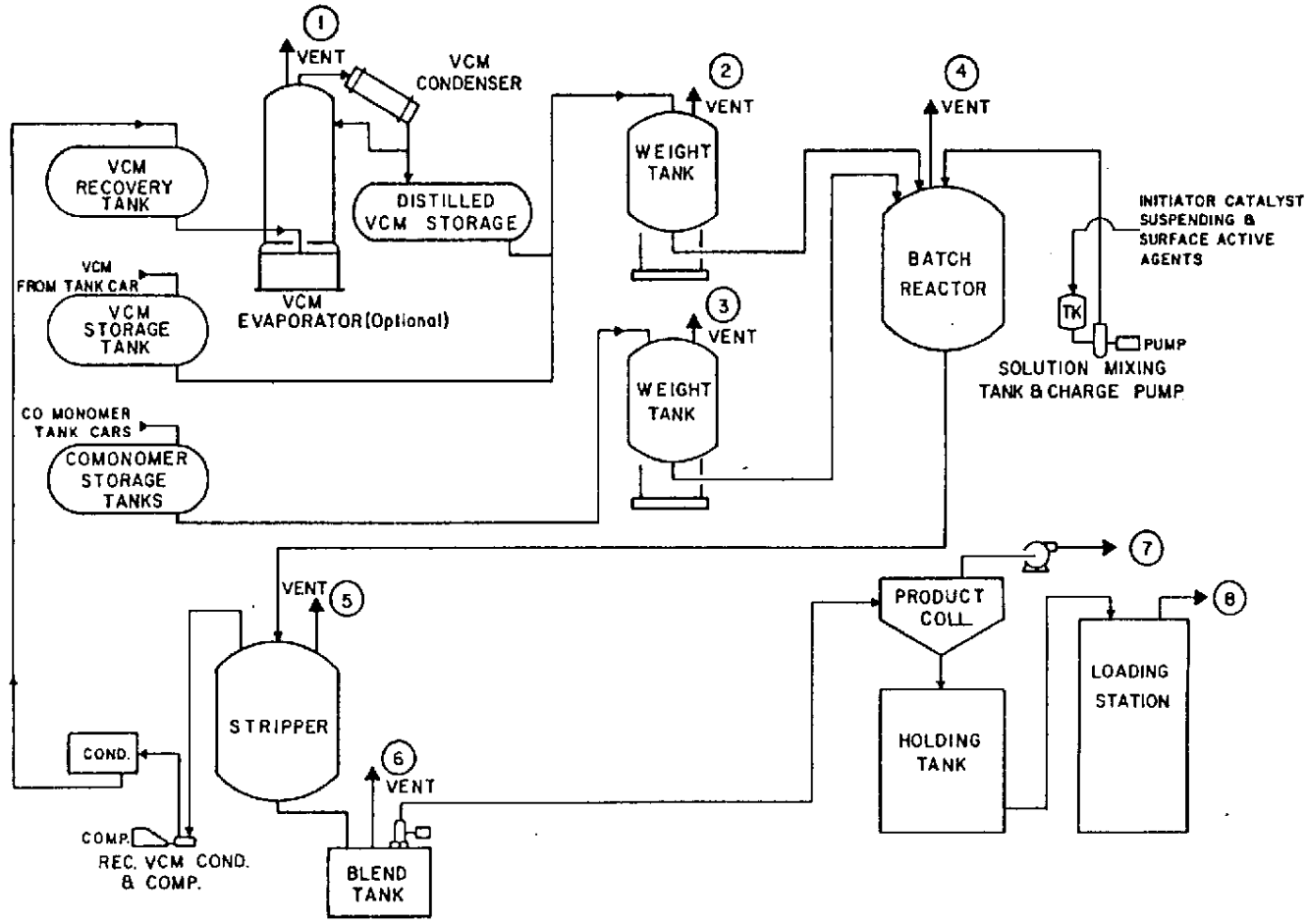

Figure 3.6. Polyvinyl chloride latex process flow diagram using emulsion (i.e., dispersion) polymerization.

Table 3.7: The potential 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

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 wastewater 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 potential 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 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].

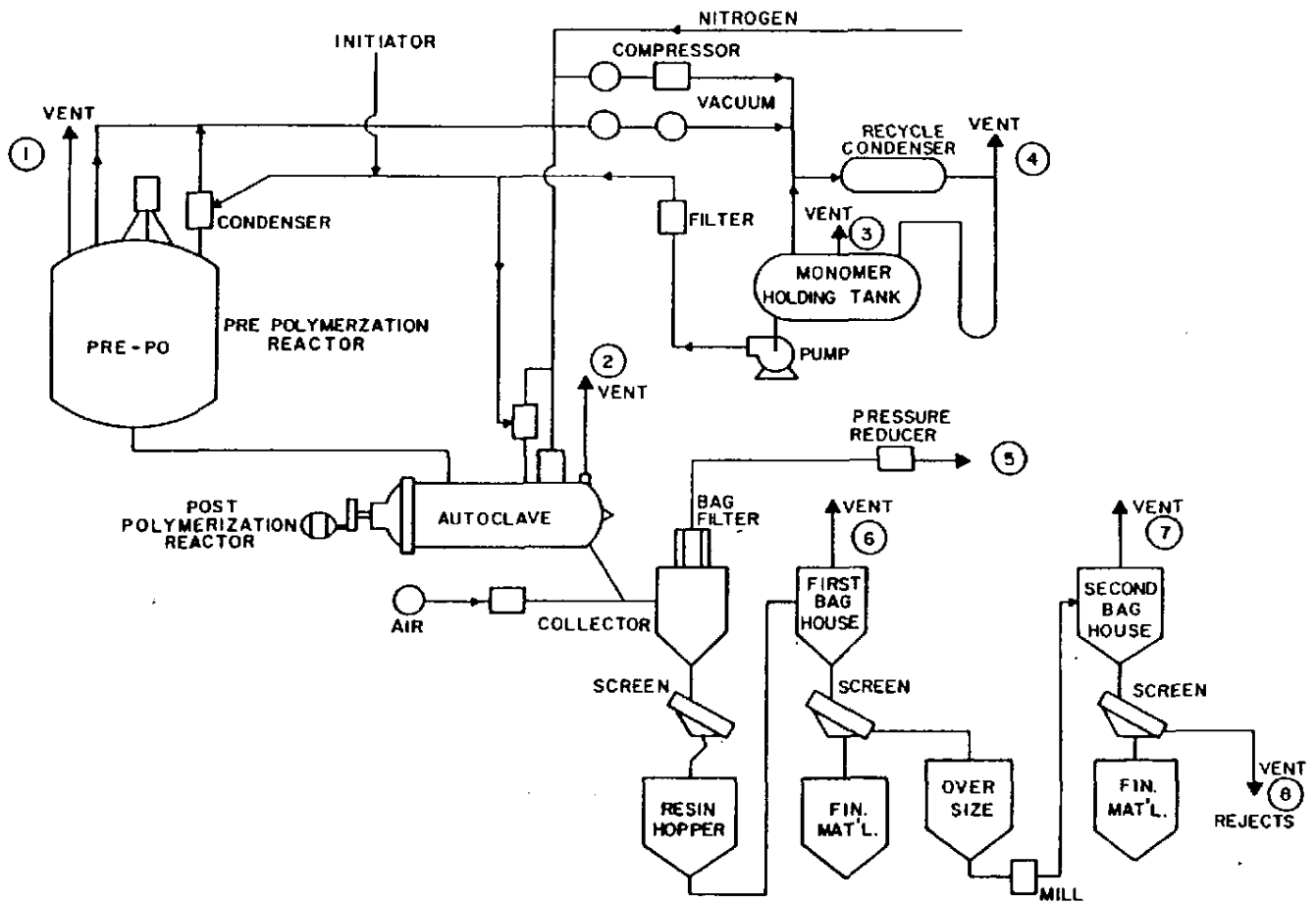

Figure 3.7. Polyvinyl chloride process flow diagram using bulk polymerization.

Table 3.8: The potential 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	Intermittent
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

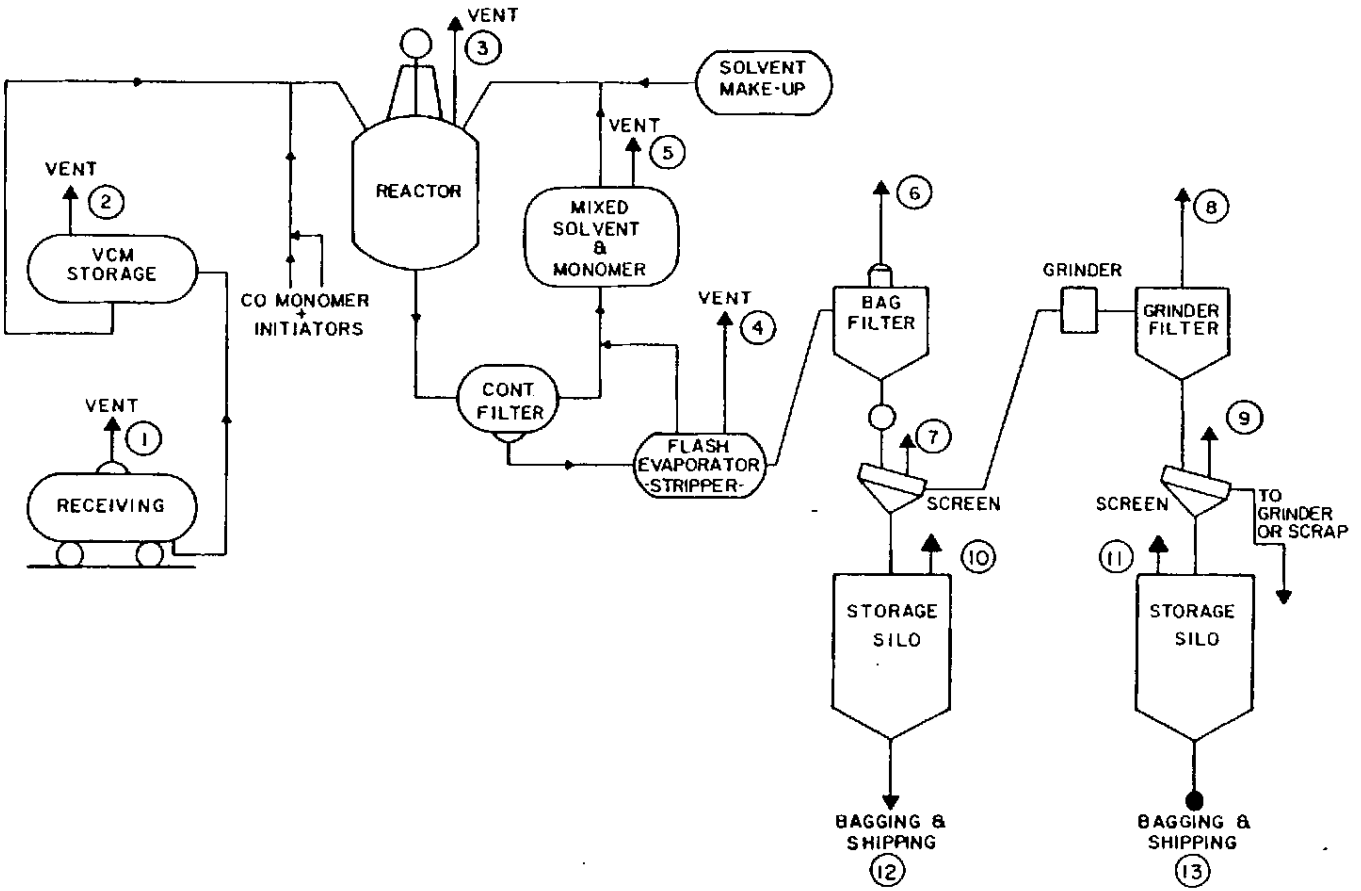

Figure 3.8. Early polyvinyl chloride process flow diagram using solvent polymerization.

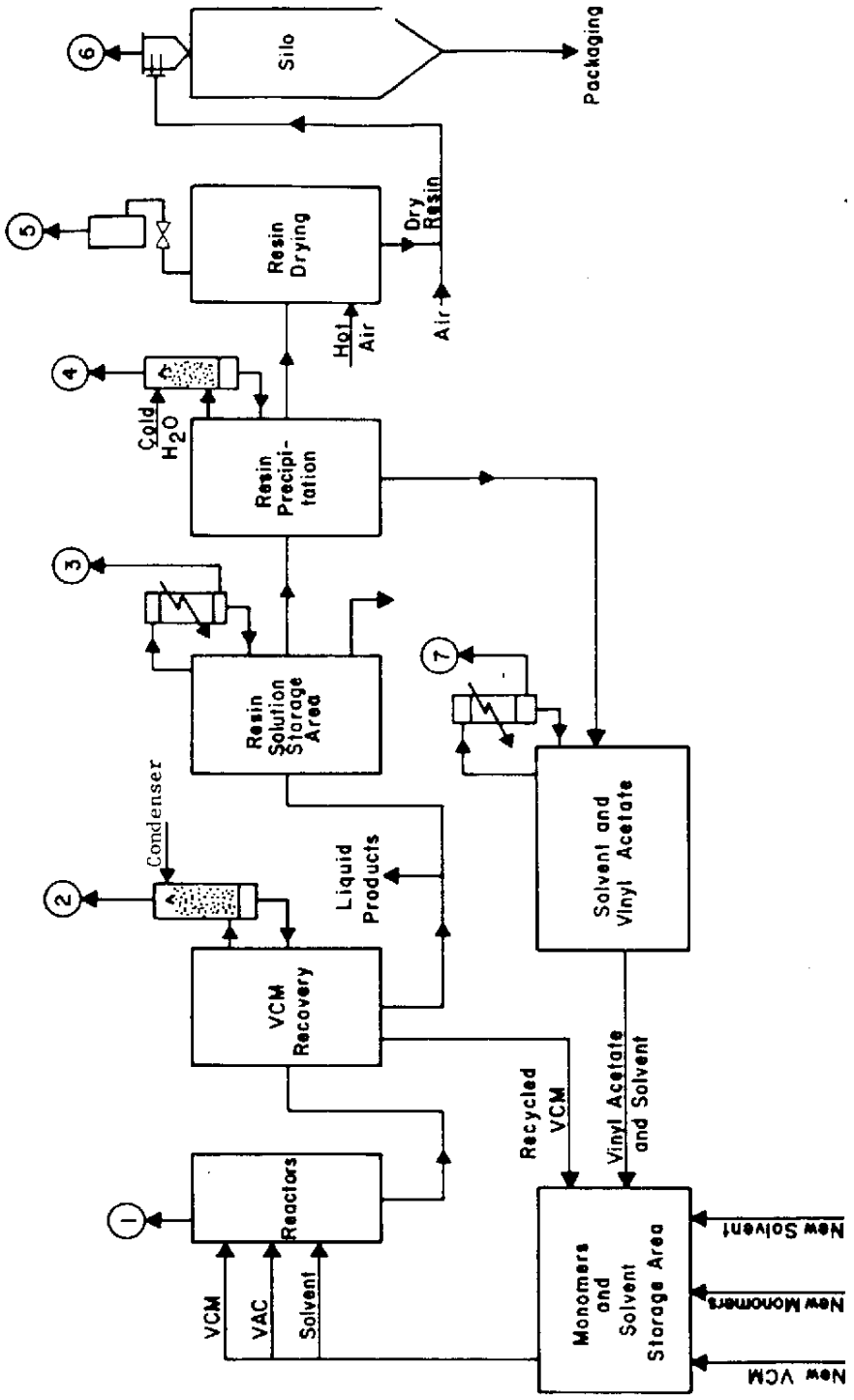

Figure 3.9. More recent polyvinyl chloride process flow diagram using solvent polymerization.

Table 3.9: The potential 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: The potential 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 Condenser	2,3,4	Continuous
Resin Drying	5	Continuous
Silo	6	Continuous
Solvent and Vinyl Acetate Condenser	7	Continuous
Fugitive	Entire Plant	Intermittent/ Continuous

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.

HC

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 [4].

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 equipment. In Figure 3.10 the EDC refining equipment is shown to be part of the EDC oxychlorination plant. The crude oroduced 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.

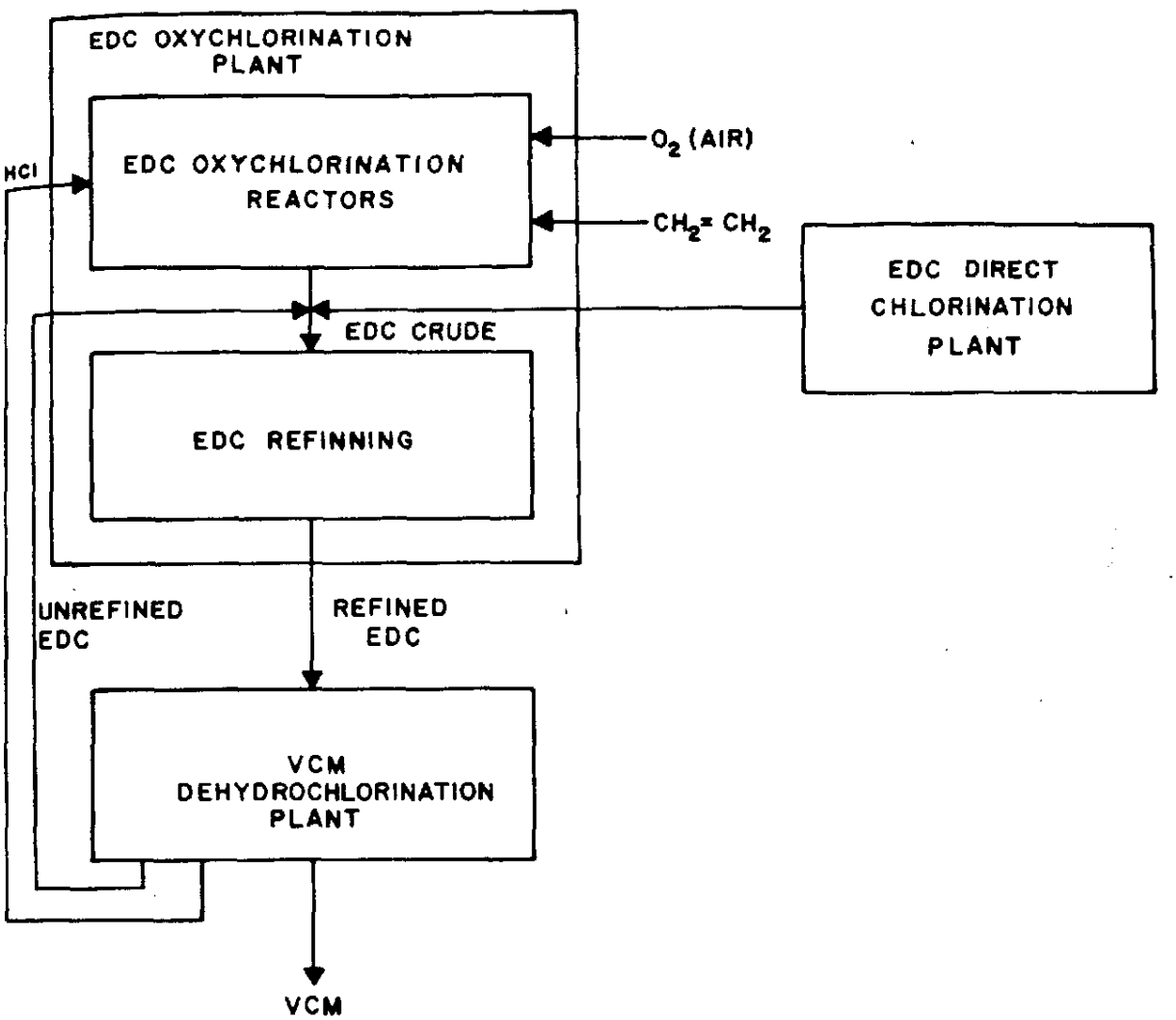

Figure 3.10. Block diagram of a balanced oxychlorination-dehydrochlorination process.

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 ins ections 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 equipment used was constructed according to unique specifications. The operation of the equipment 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 3.39 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 3.39	Incinerators

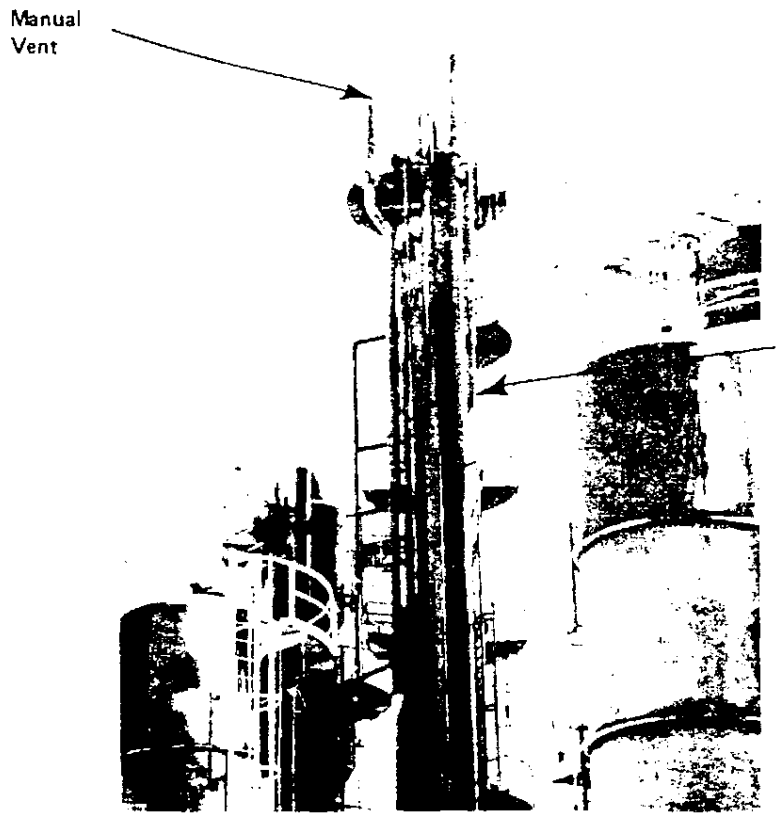

Figure 3.11 Large capacity EDC reactor using the oxychlorination process is located in the tall vessel. The oxychlorination manual vent is the open ended pipe, rising above the top of the reactor on the left side.

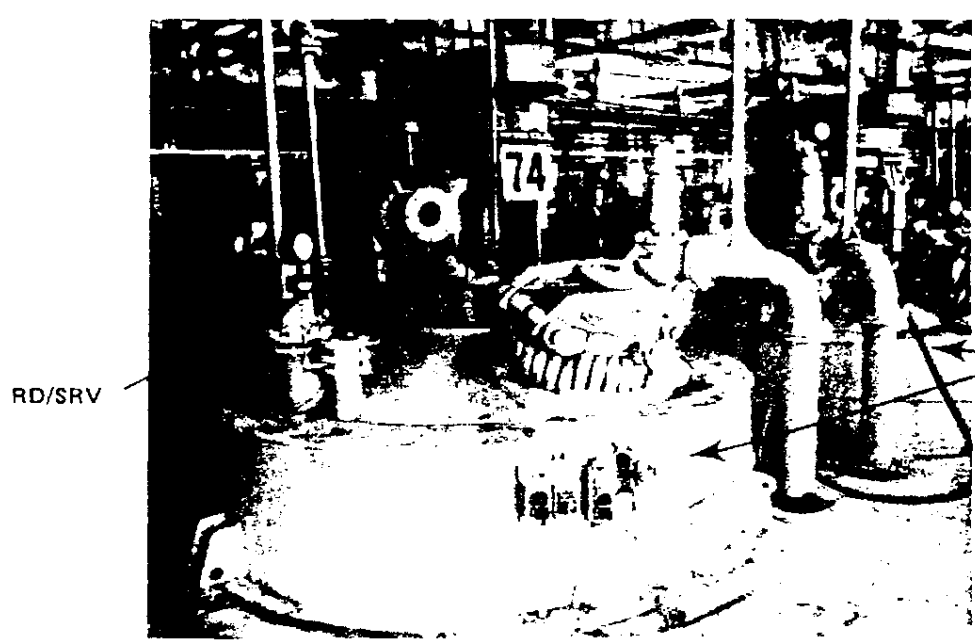

Figure 3.12 The tops of medium capacity, side-by-side PVC reactors using the emulsion process may be seen. Individual RD/SRV and manual vents may also be seen mounted on top of each reactor.

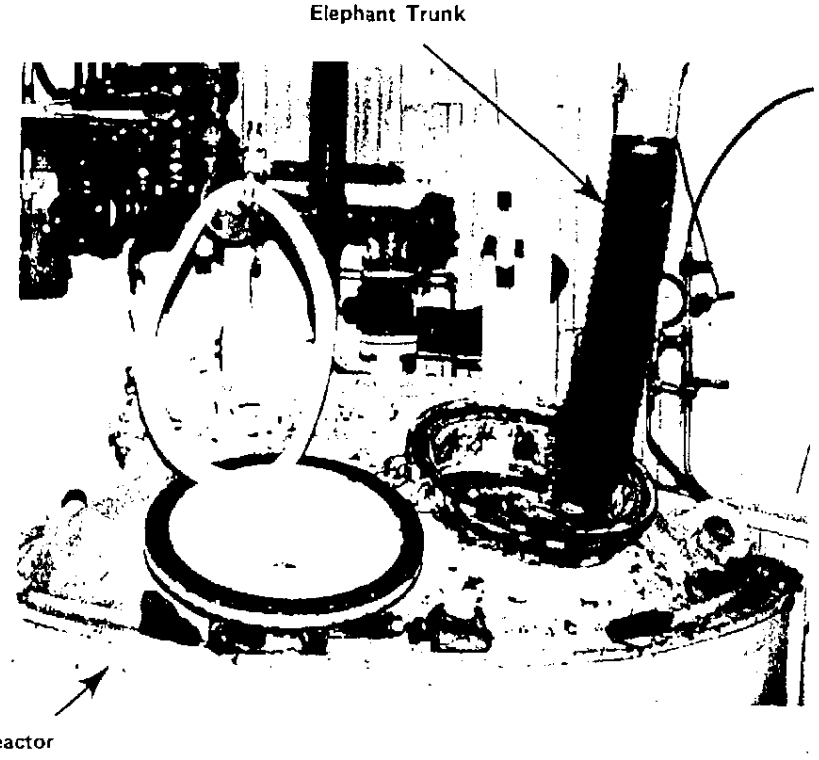

Figure 3.13 Small size PVC reactor with cover removed to clean reactor in preparation for next polymerization run. Prior to removing cover the PVC and water solution were removed and transferred to stripper. "Elephant trunk" is placed through the opening to vent vinyl chloride gas through "trunk" to 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.

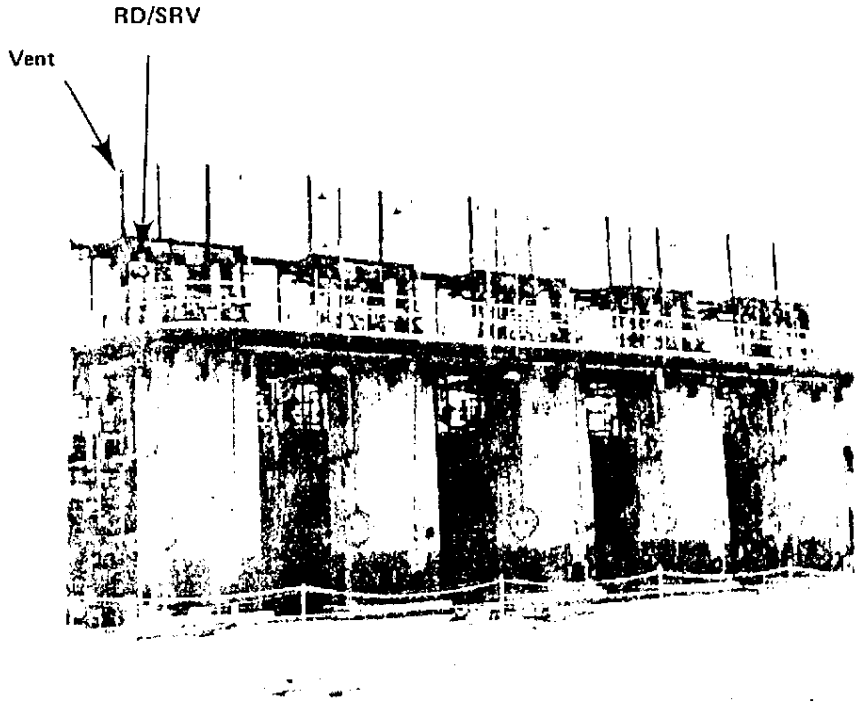

Figure 3.14 Medium capacity side-by-side PVC reactors using solvent process. Individual RD/SRV and manual vents connected to vinyl chloride recovery system may also be seen. Lower portion of reactors comprise the heating elements to raise the contents to the temperature required for polymerization.

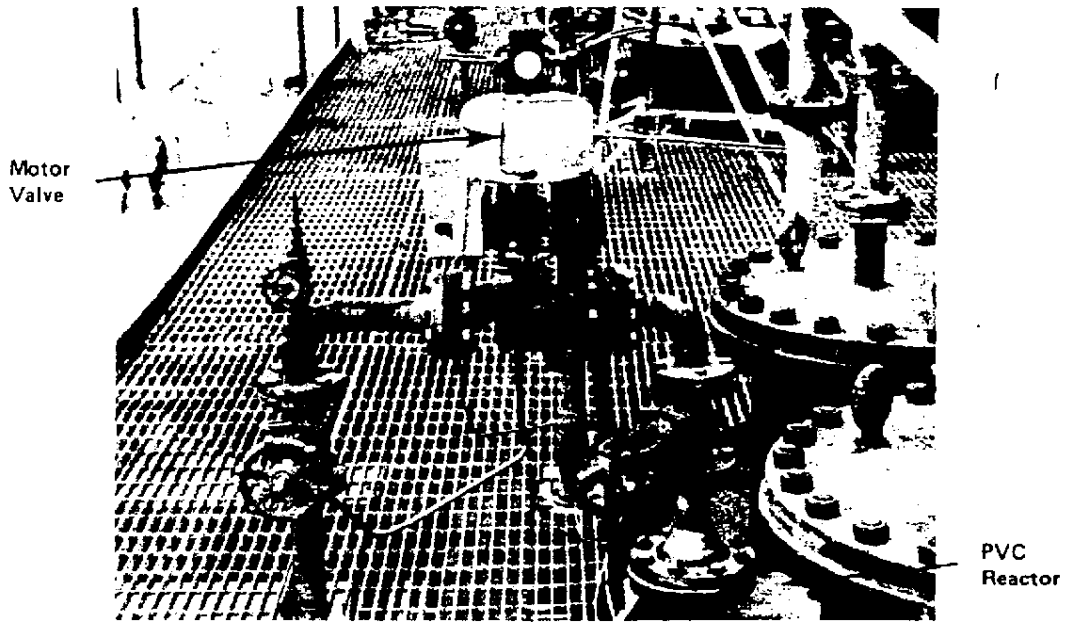

Figure 3.15 The top of medium capacity, side-by-side PVC reactors using solvent process. Foreground shows a motor valve for emergency venting through to the VC monomer recovery system.

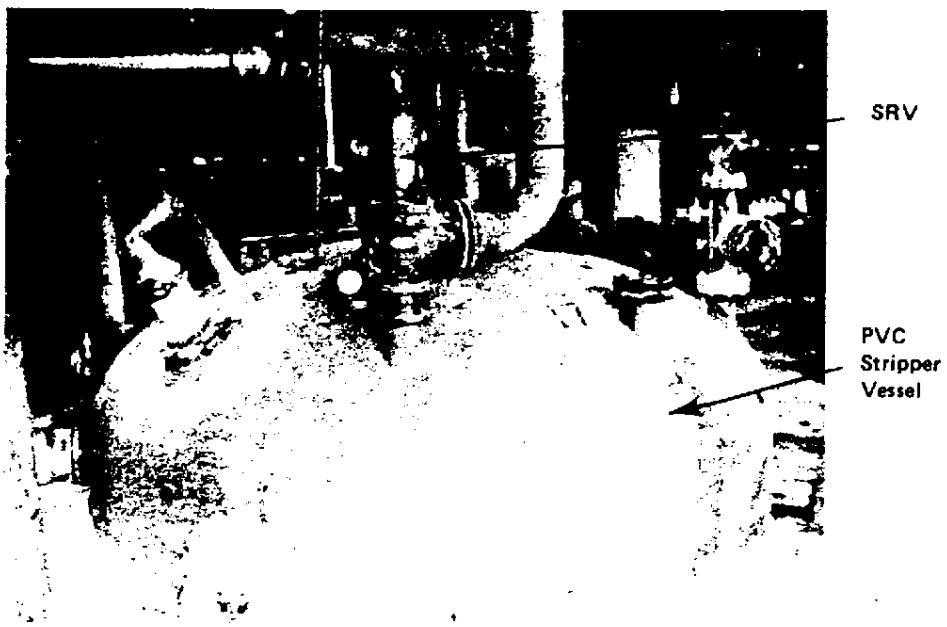

Figure 3.16 The top of a small capacity PVC stripper vessel used in the suspension, emulsion and latex processes, showing an SRV.

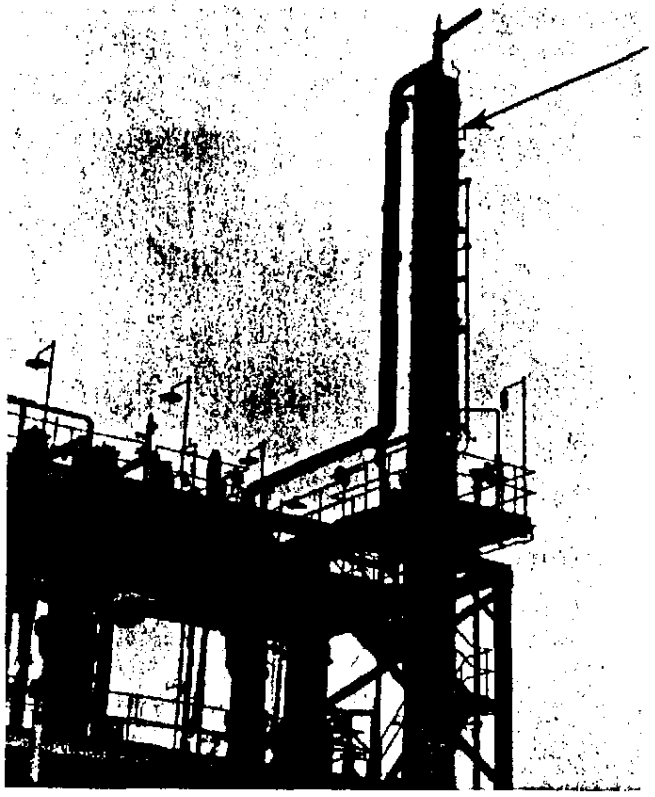

Figure 3.17 A stripper column is shown that removes VC from a PVC-varnish solution resulting from the solvent polymerization process.

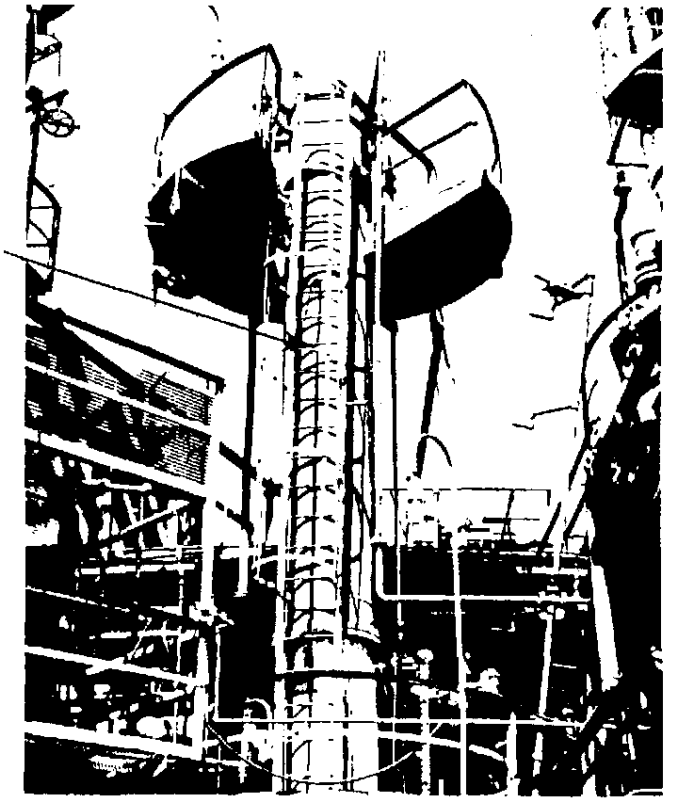

Figure 3.18 A typical wastewater stripper column is shown that may be found in EDC, VC and PVC plants.

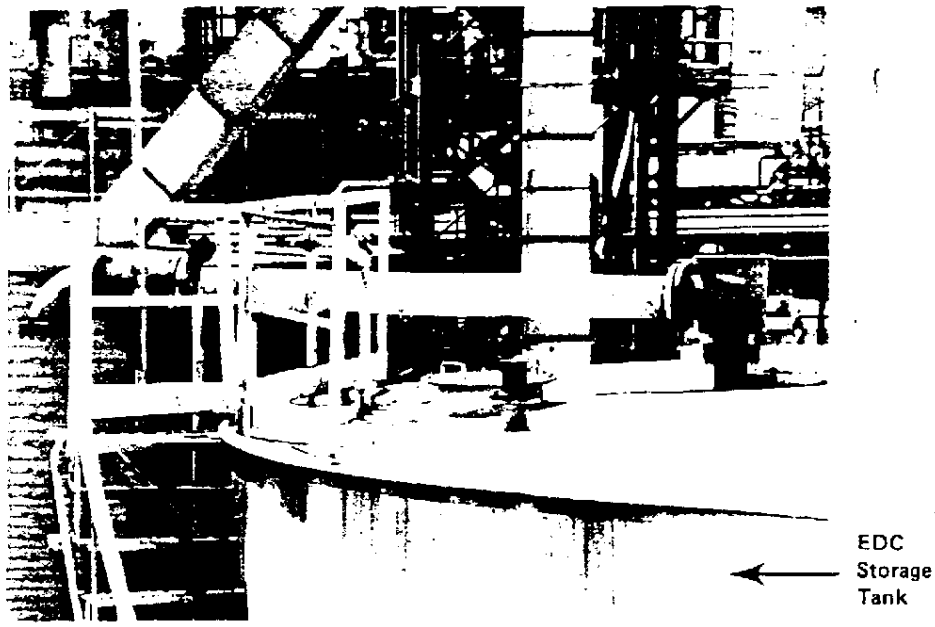

Figure 3.19 The top of an EDC storage tank is shown with its vent.

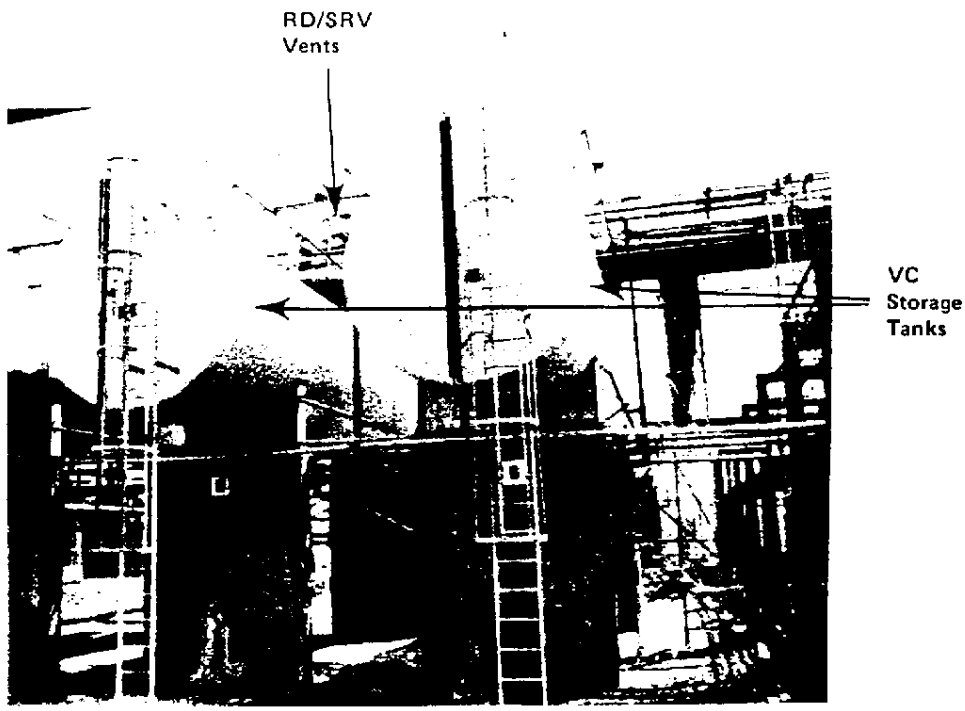

Figure 3.20 Cylindrical, side-by-side, above ground VC storage tanks are shown. RD/SRV vents may be seen on pipe rack above tanks.

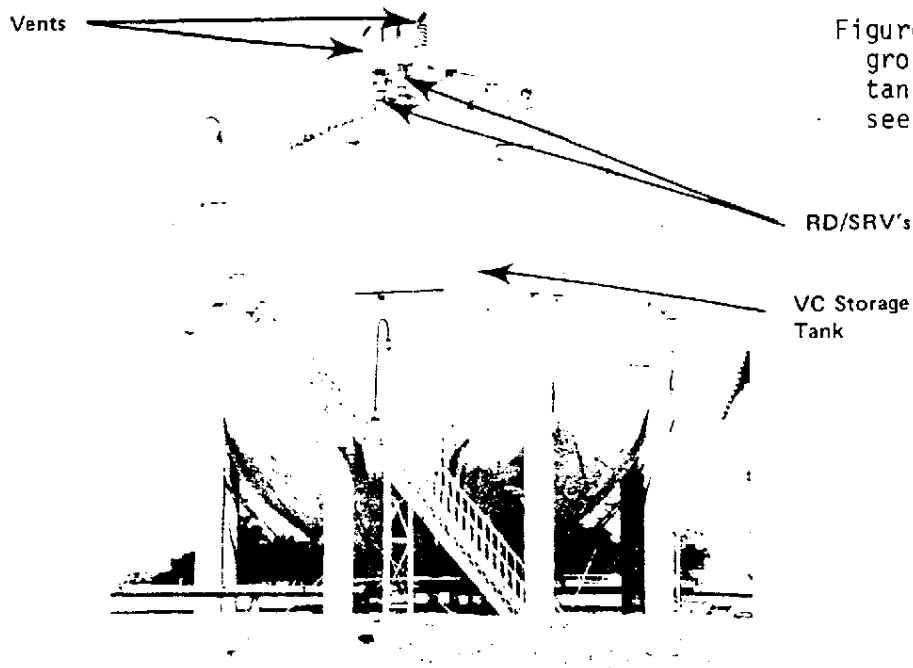

Figure 3.21 Spherical, above ground vinyl chloride storage tanks. RD/SRV vents may be seen perched on top of sphere

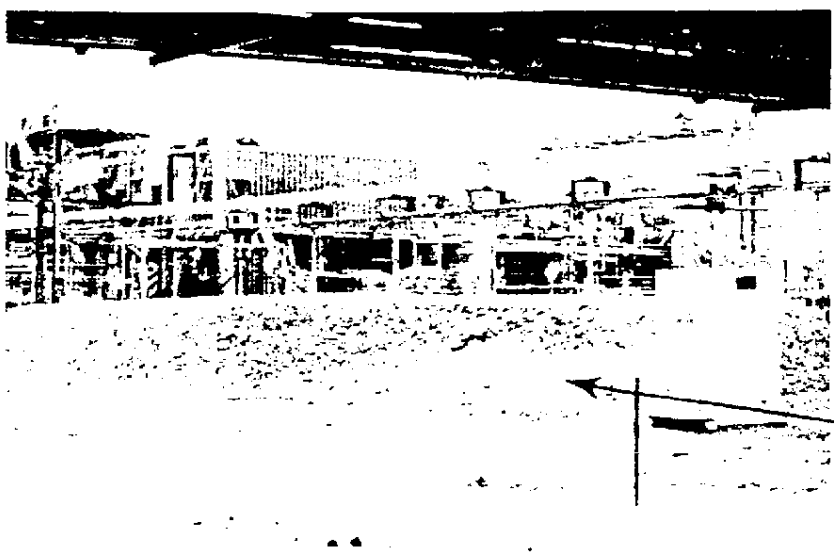

Figure 3.22 Underground VC monomer storage tank area is shown.

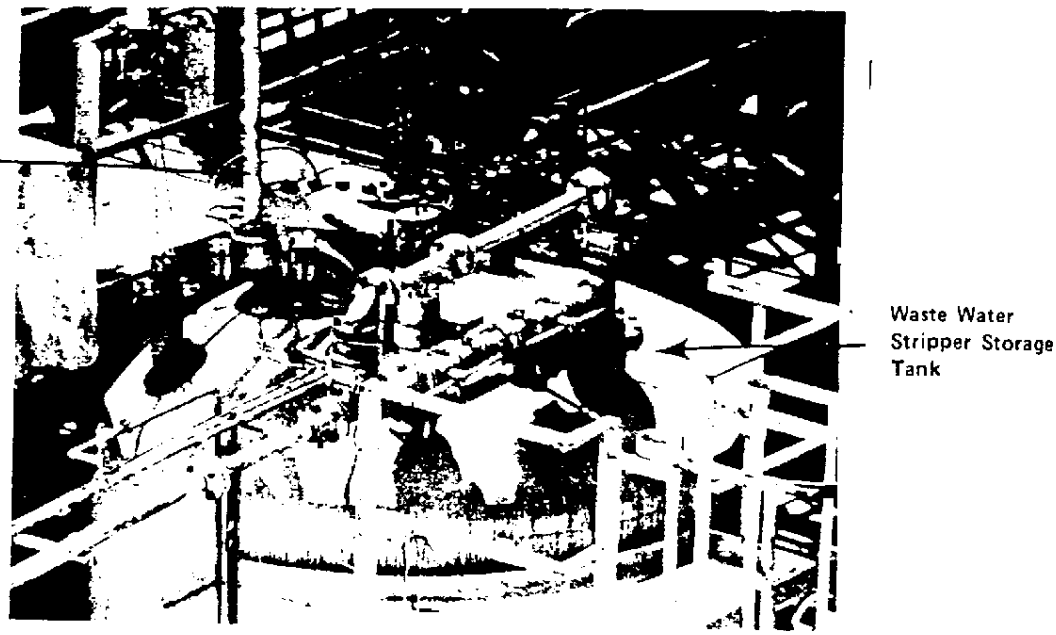

Figure 3.23 Wash water stripper storage tank with its vent mounted at the top of the tank in an EDC-VC plant.

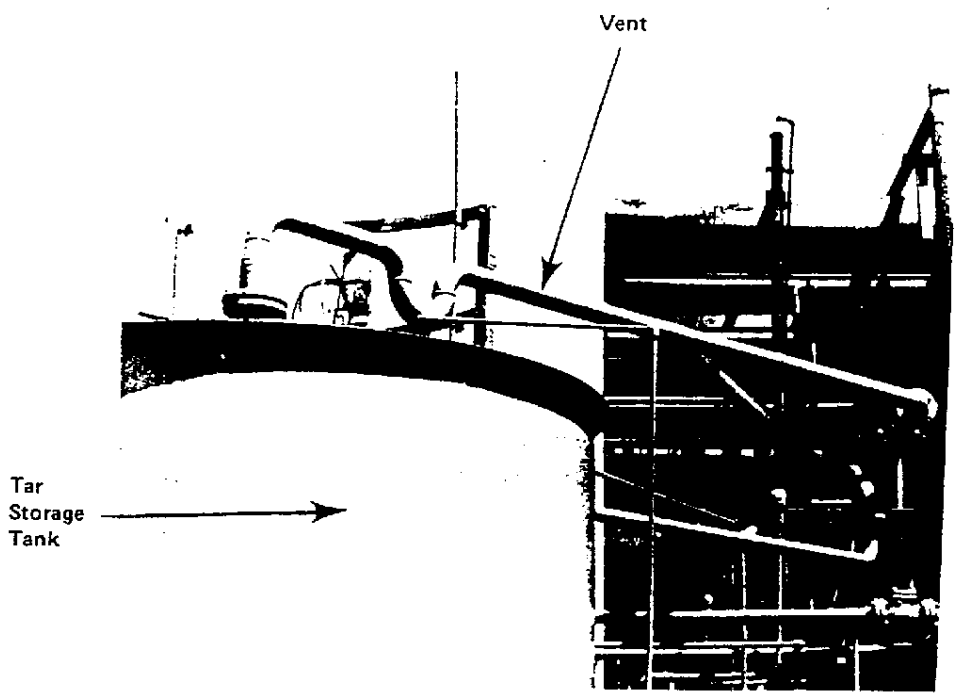

Figure 3.24 Upper portion of tar storage tank shown with vent.

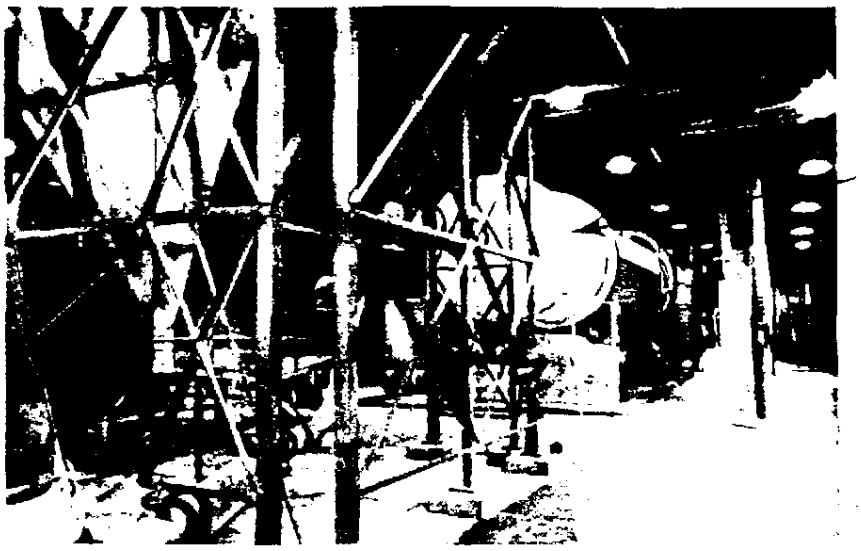

Figure 3.25 PVC suspension resin rotary dryer and dust collector. Drying is accomplished by the application of heat and rotary action.

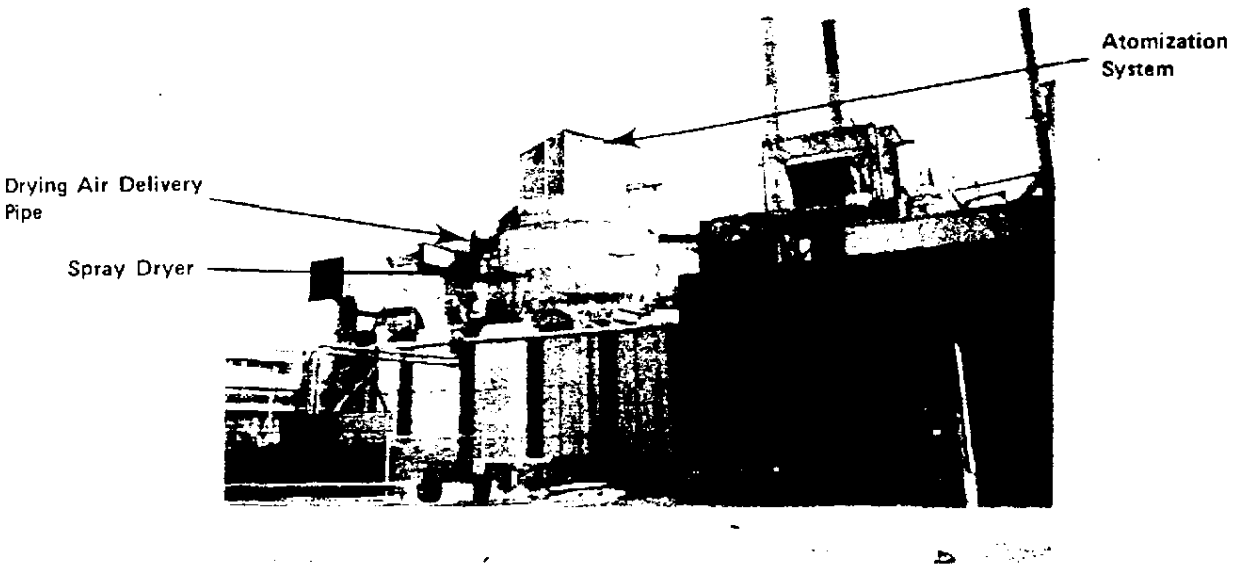

Figure 3.26 PVC dispersion resin spray drying takes place in the cylindrical building. Large diameter feed pipe, seen at the left of the dryer, carries drying air to the top of the dryer. Housing for the atomization system is perched at top of dryer.

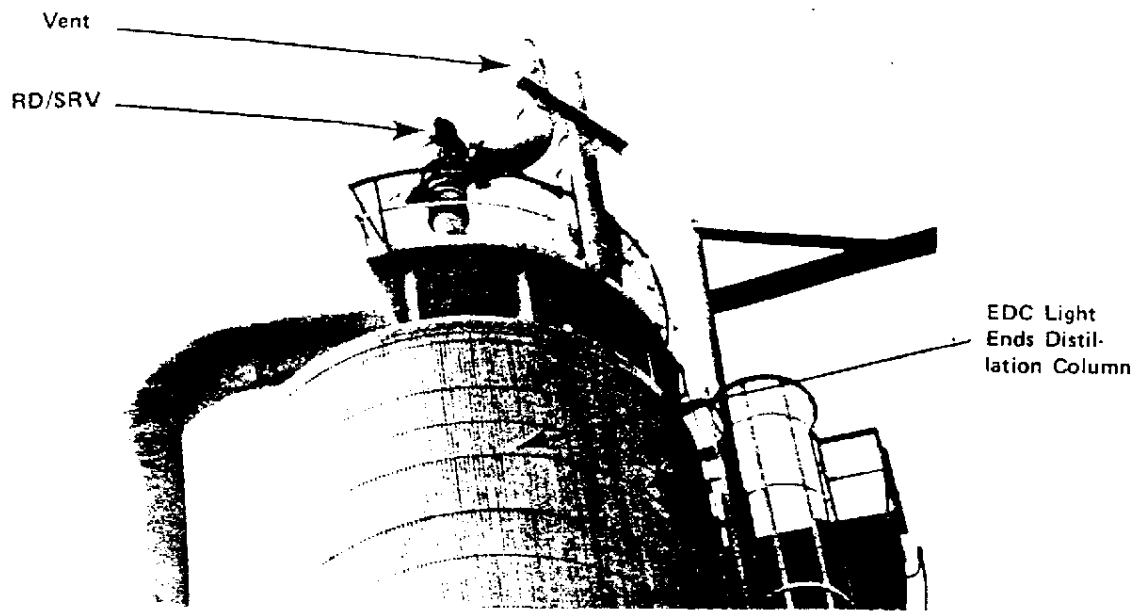

Figure 3.27 An EDC light ends distillation column is shown with its RD/SRV vent.

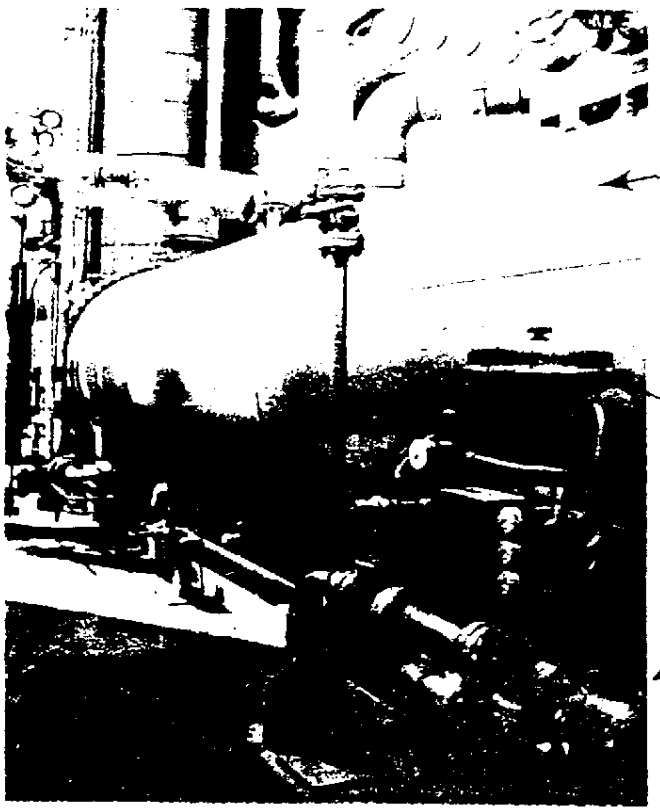

Figure 3.28 VCM column condenser and condenser vent motor valve.

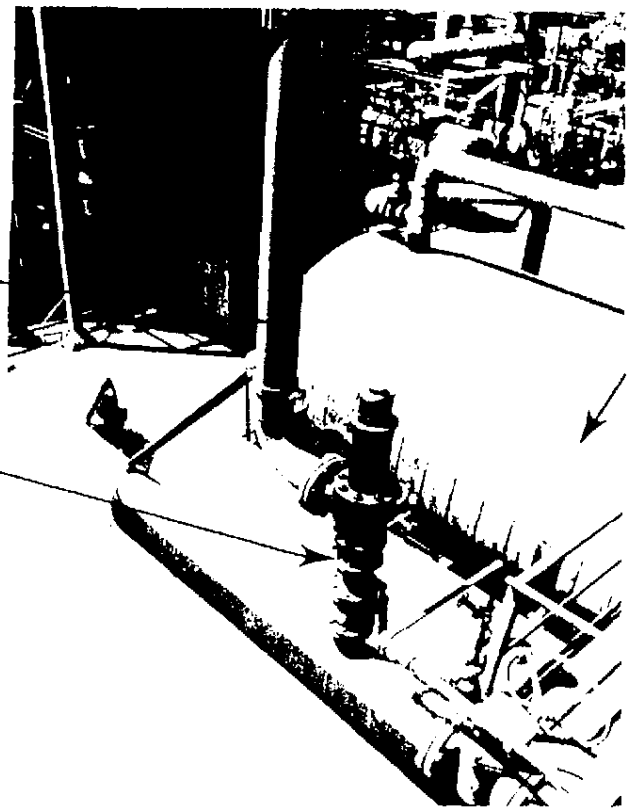

Figure 3.29 The top of an EDC light ends column reflex accumulator showing the RD/SRV vent.

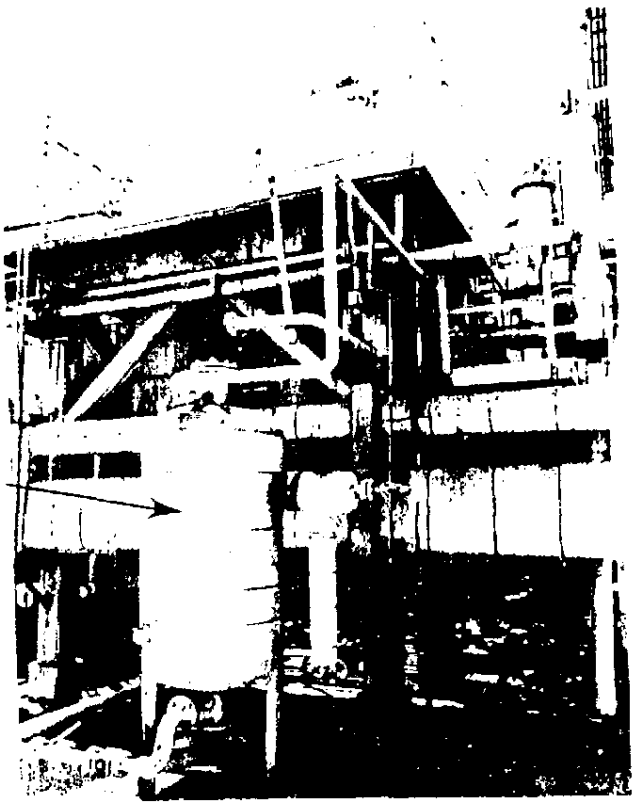

Figure 3.30 In the foreground the light ends dryer regeneration liquid knockout vessel is shown in balanced EDC-VC plant.

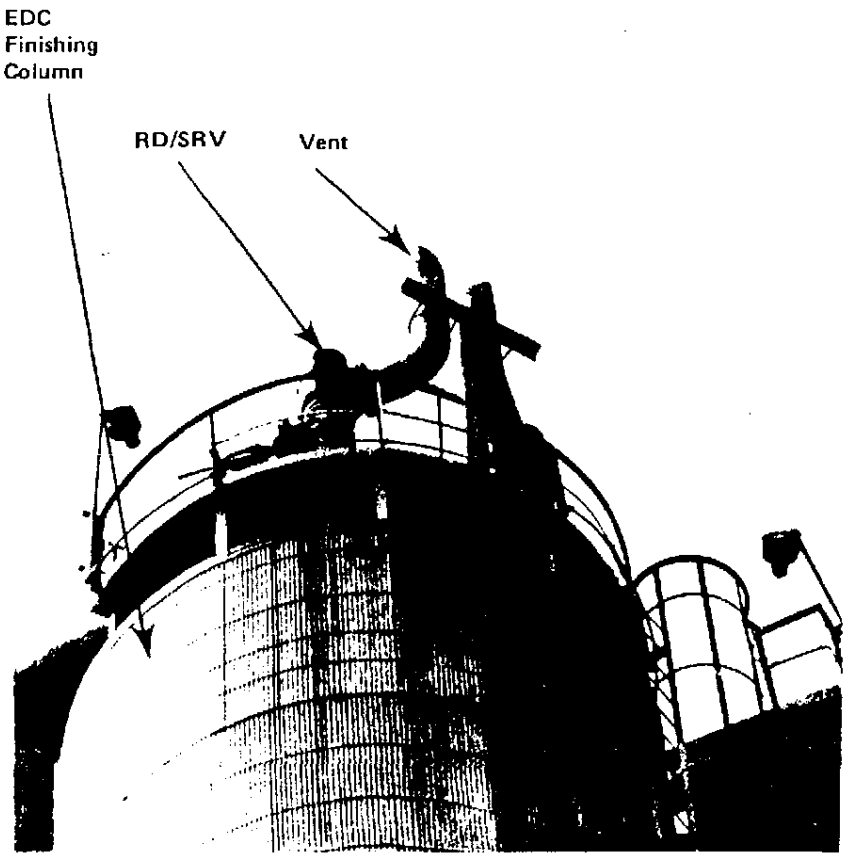

Figure 3.31 An EDC finishing column with the RD/SRV and its vent mounted on the top. (In some installations the finishing column performs the function of the light ends distillation column while in others it encompasses the functions of both the light and heavy ends columns.)

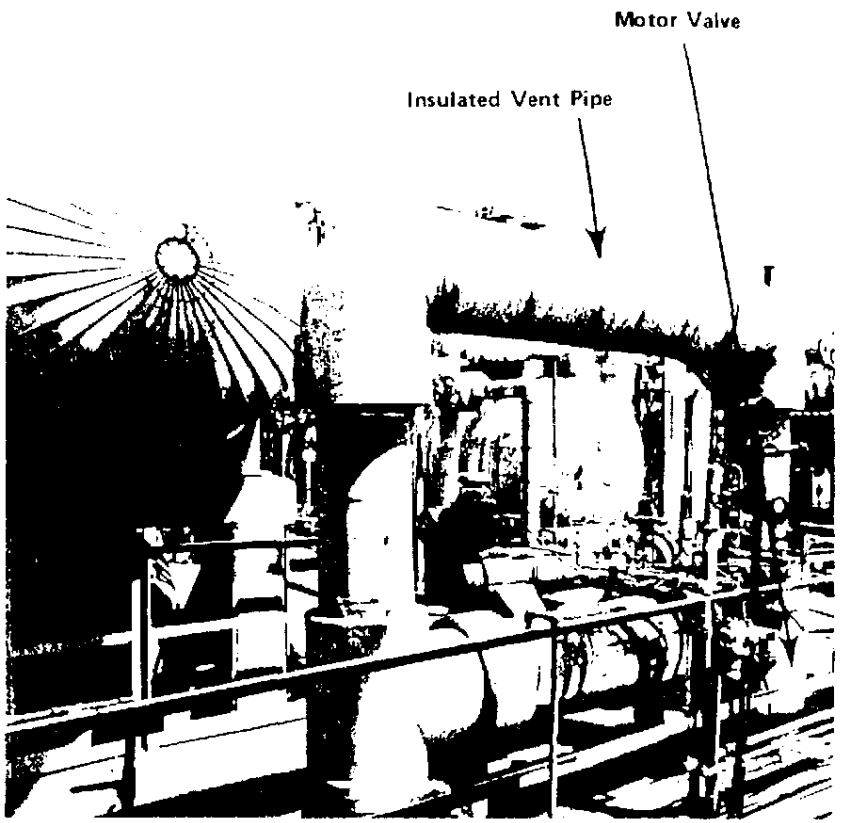

Figure 3.32 Foreground shows the insulated vent piping and motor valve from the reactor refrigerator condenser vessel in a balanced EDC oxychlorination plant.

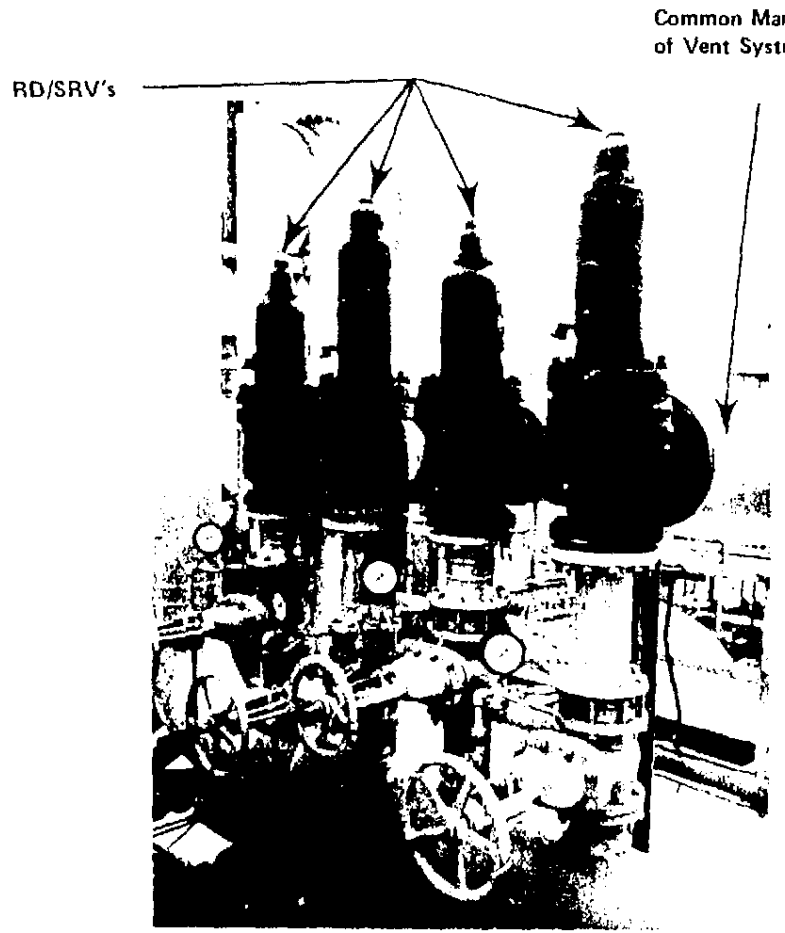

Figure 3.33 Typical RD/SRV assembly with the vents from each connected to a manifold of the vent system.

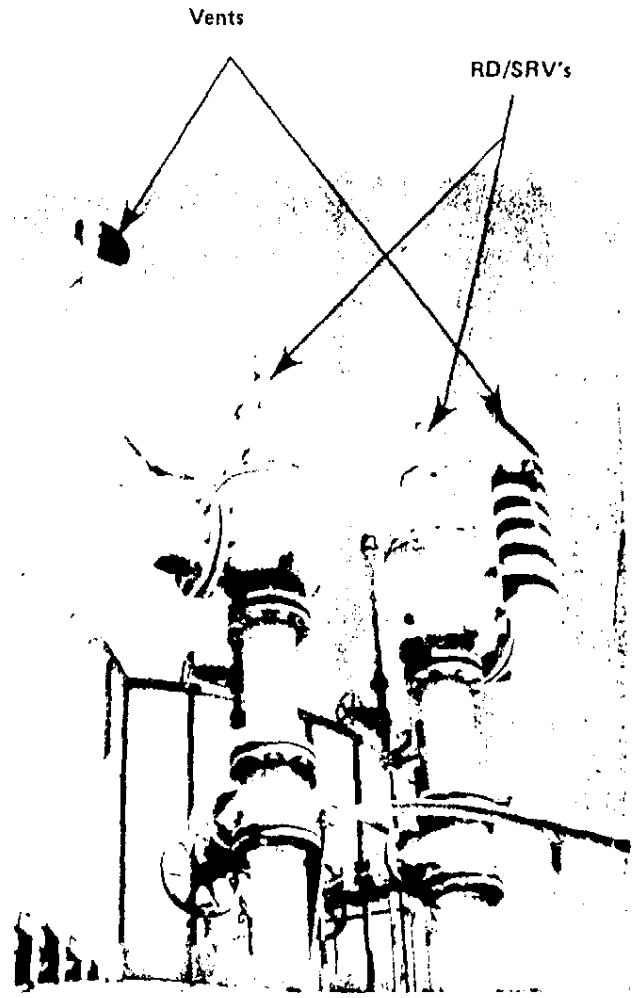

Figure 3.34 Dual RD/SRV vents mounted at top of spherical vinyl chloride storage tank.

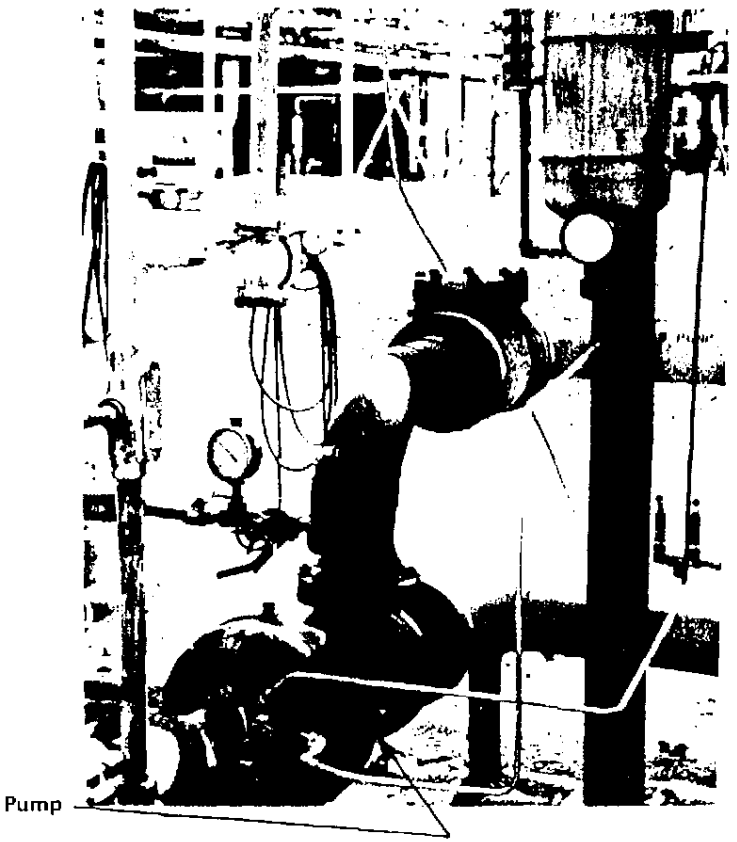

Figure 3.35 Typical pump and double mechanical seal.

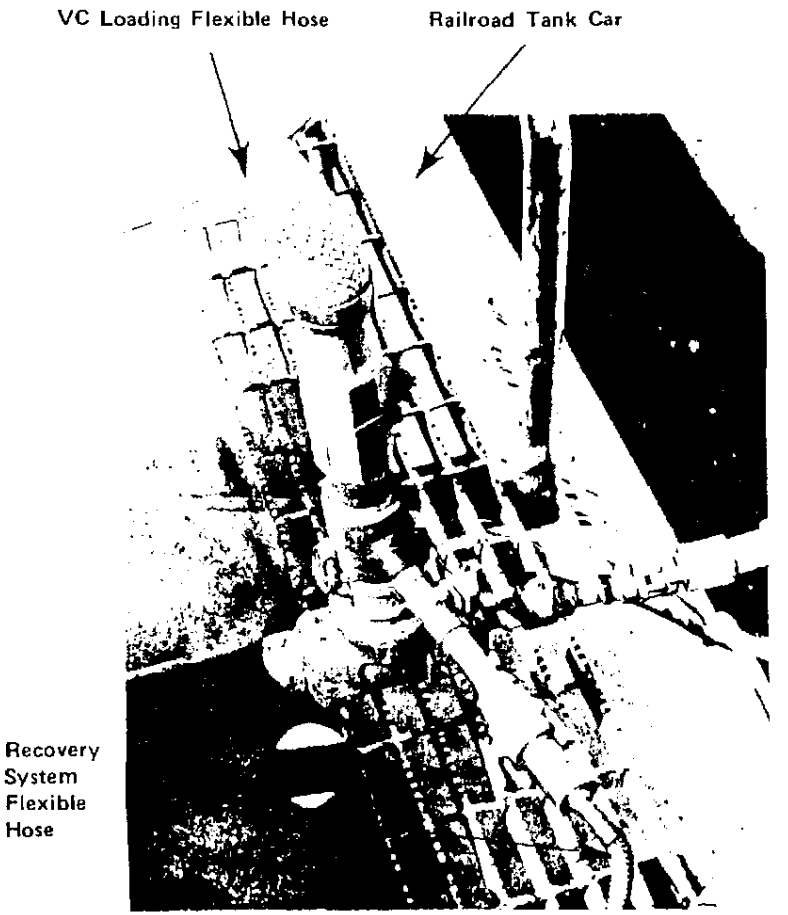

Figure 3.36 Top connections on railroad tank car shown with flexible hose attached for VC loading. Smaller diameter flexible hose in the foreground is connected to recovery system.

diameter flexible hose in the foreground is connected to recovery system.

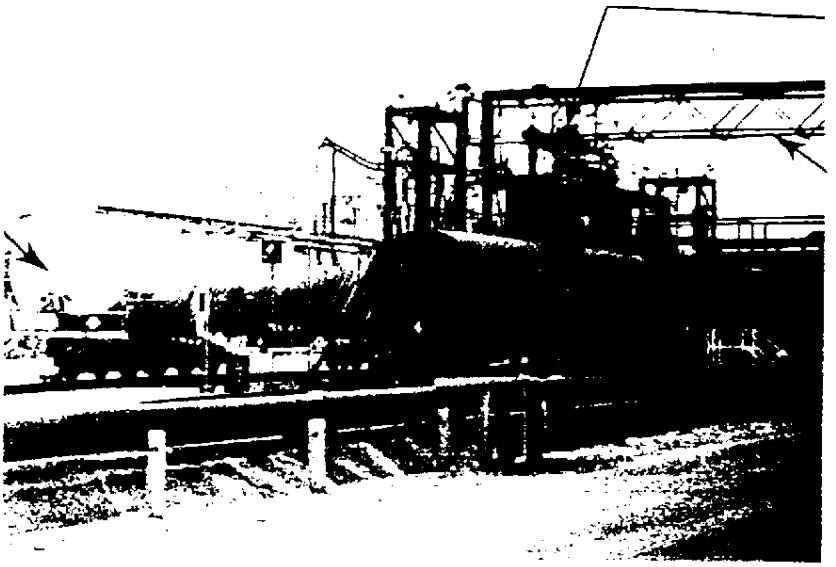

Figure 3.37 Railroad tank car loading platform shown with pipe rack support for flexible hose VC feed and recovery system in VC plant.

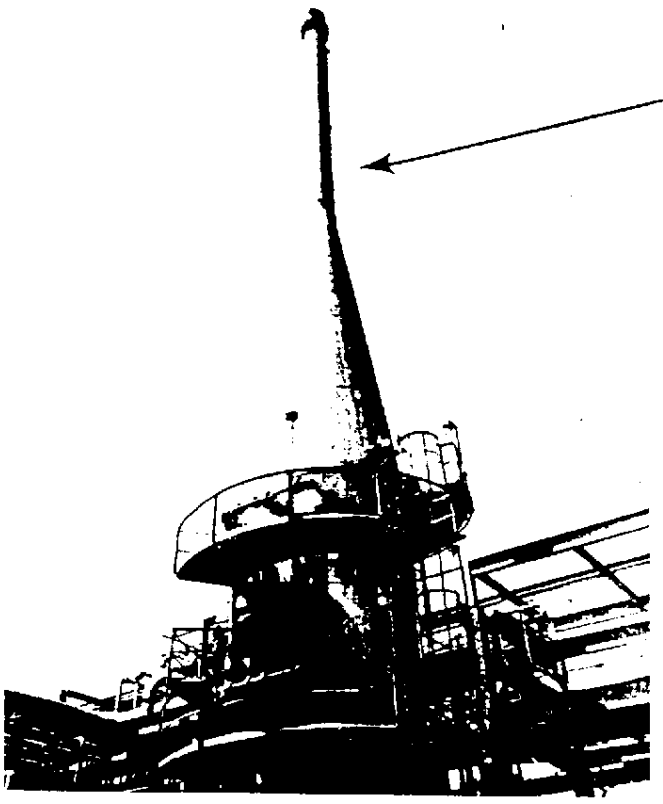

Figure 3.38 Oxychlorination vent scrubber stack.

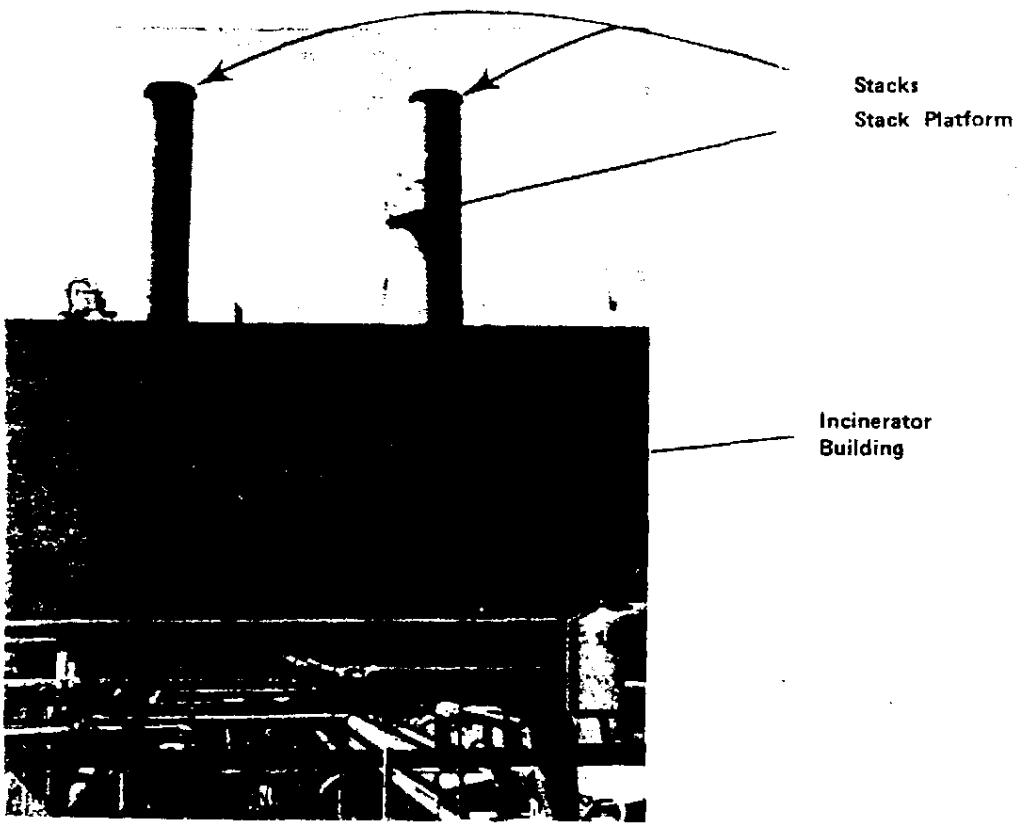

Figure 3.39 Incinerator and stacks of a PVC plant showing the platform (center stack) on which stack samples are taken to determine VC emission concentration.

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 equipment with respect to the specific process(es) or function(s) it serves. 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 challanges, 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.

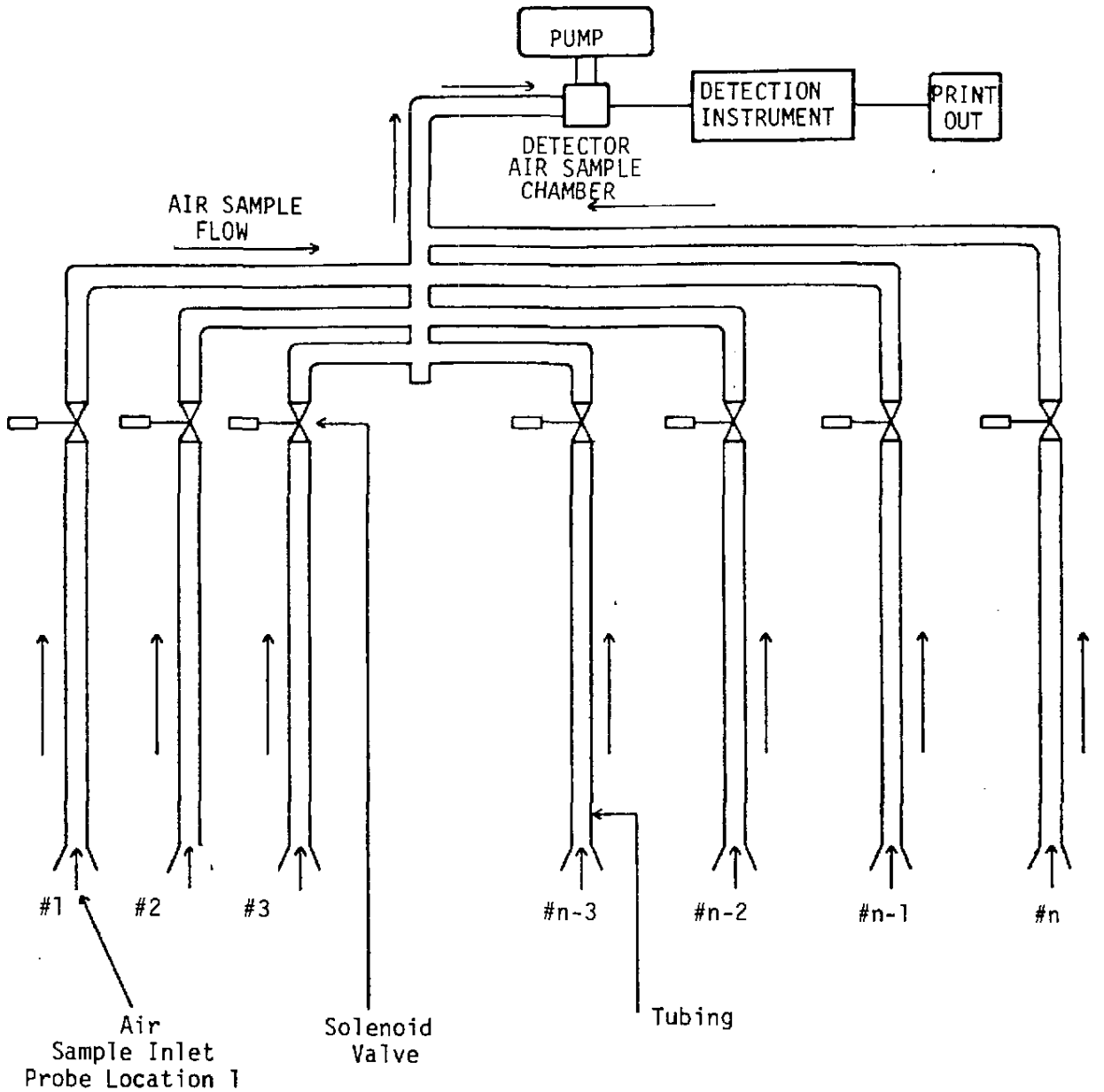

Figure 4.1: Schematic diagram of continuous monitoring system for vinyl chloride emissions.

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 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.

5.0 INSPECTOR SAFETY

Prior to inspecting an EDC-VC, VC, or PVC plant, an inspector should check the plant's records to determine whether any leaks have occurred in the past several days and whether any leaks are currently being experienced.

Before entering a plant the inspector should check to assure he has the proper safety equipment, including safety shoes, safety glasses, hard hat, and a respirator specified for use with vinyl chloride. Any safety regulations and plant emergency responses should be noted by the inspector.

6.0 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. Questions which may be answered prior to the actual inspection (or verified after the inspection) are identified on the forms by an asterisk. Suggested sources for this data, from records on file at EPA Regional Offices, include plant Standard Operating Procedures, the Leak Detection Program and Initial, Semi-annual and other required reports. High potential

leak sources and any violations can be identified from previous inspection reports. If this data is recorded on the forms prior to the inspection, it should be confirmed during the inspection and any inconsistencies noted. Similar notations should be made on the forms when data collected during the inspection is later compared with data from Regional Office records.

6.1 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.

6.2 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.

6.3 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 potential emission points.

6.4 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.

6.5 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)

Inspection Date_____
Inspector's Name_____
Firm's Name_____
Firm's Address_____

NESHAPS INSPECTION FOR VINYL CHLORIDE EMISSIONS COMPLIANCE

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

* Data may be available from records on file at EPA Regional Offices.

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)_____.

* Data may be available from records on file at EPA Regional Offices.

* Data may be available from records on file at EPA Regional Offices.

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

c) What is the average elasped 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. List any SRV's which do not use RD's or vent to recovery system or to gas hold tank.

Location in Plant	Comments

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 double outboard seal, and does not duct emissions through a control system, or maintain proper pressurization between seals or equivalent.

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 test.

Equipment/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 there additional emissions which were not properly and accurately reported in the appropriate Semi-annual Report?

☐ Yes ☐ No

4. If the response to No. 3 is Yes, 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.

* Data may be available from records on file at EPA Regional Offices.

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* List information of emergency discharges to the atmosphere.

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

9. 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

10. 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

e(s).

11. 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			

12. 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

13* Review analytical records of vinyl chloride concentration in reactor vapor space to determine "reactor opening loss" of reactor (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

14* 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

15. 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 equipment 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: _____

SAL 000049963

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 µℓ? ☐ 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 0.1% carbowax on carbopak A (or Carbopak B) Perkin-Elmer No. 105-0133 or equivalent:_____

7. Thermometer

a) Range 0 to 100°C, with accuracy ± 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

$$\overline{X} = \frac{1}{n} \sum_{i=1}^{n} X_i \qquad \text{(A-1)}$$

where

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

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

n = Number of absolute measurements,

$\overline{X}$ = Mean value.