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ENVIRONMENTAL PROTECTION AGENCY

NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS

Standard For Vinyl Chloride

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Subpart F—National Emission Standard for Vinyl Chloride

[41 FR 46559, October 21, 1976]

§ 61.60 Applicability.

(a) This subpart applies to plants which produce:

(1) Ethylene dichloride by reaction of oxygen and hydrogen chloride with ethylene.

(2) Vinyl chloride by any process, and/or

(3) One or more polymers containing any fraction of polymerized vinyl chloride.

(b) This subpart does not apply to equipment used in research and development if the reactor used to polymerize the vinyl chloride processed in the equipment has a capacity of no more than 0.19 m³ (50 gal).

(c) Sections of this subpart other than §§ 61.61, 61.64 (a)(1), (b), (c), and (d); 61.67; 61.68; 61.69; 61.70; and 61.71 do not apply to equipment used in research and development if the reactor used to polymerize the vinyl chloride processed in the equipment has a capacity of greater than 0.19 m³ (50 gal) and no more than 4.07 m³ (1100 gal).

[42 FR 29005, June 7, 1977]

§ 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 a way 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 solid 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.

(t) "Standard temperature" means a temperature of 20° C (69° F).

(u) "Standard pressure" means a pressure of 760 mm of Hg (29.92 in. of Hg).

[42 FR 29005, June 7, 1977]

§ 61.62 Emission standard for ethylene dichloride plants.

[42 FR 29005, June 7, 1977]

(a) Ethylene dichloride purification: The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from any equipment used in ethylene dichloride purification is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b)(6)(i) before being opened.

(b) Oxychlorination reactor: Except as provided in § 61.65(a), emissions of vinyl chloride to the atmosphere from each oxychlorination reactor are not to exceed 0.2 g/kg (0.0002 lb/lb) of the 100 percent ethylene dichloride product from the oxychlorination process.

§ 61.63 Emission standard for vinyl chloride plants.

An owner or operator of a vinyl chloride plant shall comply with the requirements of this section and § 61.65.

(a) Vinyl chloride formation and purification: The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from any equipment used in vinyl chloride formation and/or purification is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b)(6)(i) before being opened.

§ 61.64 Emission standard for polyvinyl chloride plants.

An owner or operator of a polyvinyl chloride plant shall comply with the requirements of this section and § 61.65.

(a) Reactor: The following requirements apply to reactors:

(1) The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each reactor is not to exceed 10 ppm, except as provided in paragraph (a)(2) of this section and § 61.65(a).

(2) The reactor opening loss from each reactor is not to exceed 0.02 g vinyl chloride/Kg (0.00002 lb vinyl chloride/lb) of polyvinyl chloride product, with the product determined on a dry solids basis. This requirement applies to any vessel which is used as a reactor or as both a reactor and a stripper. In the bulk process, the product means the gross product of prepolymerization and postpolymerization.

(3) Manual vent valve discharge: Except for an emergency manual vent valve discharge, there is to be no discharge to the atmosphere from any manual vent valve on a polyvinyl chloride reactor in vinyl chloride service. An emergency manual vent valve discharge means a discharge to the atmosphere which could not have been avoided by taking measures to prevent the discharge. Within 10 days of any discharge to the atmosphere from any manual vent valve, the owner or operator of the source from which the discharge occurs shall submit to the Administrator a report in writing containing information on the source, nature

and cause of the discharge, the date and time of the discharge, the approximate total vinyl chloride loss during the discharge, the method used for determining the vinyl chloride loss, the action that was taken to prevent the discharge, and measures adopted to prevent future discharges.

(b) Stripper: The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each stripper is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b) (6) (i) before being opened.

(c) Mixing, weighing, and holding containers: The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each mixing, weighing, or holding container in vinyl chloride service which precedes the stripper (or the reactor if the plant has no stripper) in the plant process flow is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b) (6) (i) before being opened.

(d) Monomer recovery system. The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each monomer recovery system is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b) (6) (i) before being opened.

(e) Sources following the stripper(s): The following requirements apply to emissions of vinyl chloride to the atmosphere from the combination of all sources following the stripper(s) [or the reactor(s) if the plant has no stripper(s)] in the plant process flow including but not limited to, centrifuges, concentrators, blend tanks, filters, dryers, conveyor air discharges, baggers, storage containers, and inprocess wastewater:

(1) In polyvinyl chloride plants using stripping technology to control vinyl chloride emissions, the weighted average residual vinyl chloride concentration in all grades of polyvinyl chloride resin processed through the stripping operation on each calendar day, measured immediately after the stripping operation is completed, may not exceed:

(i) 2000 ppm for polyvinyl chloride dispersion resins, excluding latex resins;

(ii) 400 ppm for all other polyvinyl chloride resins, including latex resins, averaged separately for each type of resin; or

(2) In polyvinyl chloride plants controlling vinyl chloride emissions with technology other than stripping or in addition to stripping, emissions of vinyl chloride to the atmosphere may not exceed:

(i) 2 g/kg (0.002 lb/lb) product from the stripper(s) [or reactor(s) if the plant has no stripper(s)] for dispersion

polyvinyl chloride resins, excluding latex resins, with the product determined on a dry solids basis;

(ii) 0.4 g/kg (0.0004 lb/lb) product from the strippers [or reactor(s) if the plant has no stripper(s)] for all other polyvinyl chloride resins, including latex resins, with the product determined on a dry solids basis.

§ 61.65 Emission standard for ethylene dichloride, vinyl chloride and polyvinyl chloride plants.

An owner or operator of an ethylene dichloride, vinyl chloride, and/or polyvinyl chloride plant shall comply with the requirements of this section.

(a) Relief valve discharge: Except for an emergency relief discharge, there is to be no discharge to the atmosphere from any relief valve on any equipment in vinyl chloride service. An emergency relief discharge means a discharge which could not have been avoided by taking measures to prevent the discharge. Within 10 days of any relief valve discharge, the owner or operator of the source from which the relief valve discharge occurs shall submit to the Administrator a report in writing containing information on the source, nature and cause of the discharge, the date and time of the discharge, the approximate total vinyl chloride loss during the discharge, the method used for determining the vinyl chloride loss, the action that was taken to prevent the discharge, and measures adopted to prevent future discharges.

(b) Fugitive emission sources:

(1) Loading and unloading lines: Vinyl chloride emissions from loading and unloading lines in vinyl chloride service which are opened to the atmosphere after each loading or unloading operation are to be minimized as follows:

[42 FR 29005, June 7, 1977]

(i) After each loading or unloading operation and before opening a loading or unloading line to the atmosphere, the quantity of vinyl chloride in all parts of each loading or unloading line that are to be opened to the atmosphere is to be reduced so that the parts combined contain no greater than 0.0038 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 agi-

tated 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 chloride 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)(8)(vi) of this section. The calibration is to be done with either:

(A) A calibration gas mixture prepared from the gases specified in sections 5.2.1 and 5.2.2 of Test Method 106 and in accordance with section 7.1 of Test Method 106; or

(B) A calibration gas cylinder standard containing the appropriate concentration of vinyl chloride. The gas composition of the calibration gas cylinder standard is to have been certified by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration does not change greater than ± 5 percent from the certified value. The date of gas cylinder preparation, certified vinyl chloride concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the manufacturer to the buyer. If a gas chromatograph is used as the vinyl chloride monitoring system, these gas mixtures may be directly used to prepare a chromatograph calibration curve as described in section 7.3 of Test Method 106. The requirements in section 5.2.3.1 and 5.2.3.2 of Test Method 106 for certification of cylinder standards and for establishment and verification of calibration standards are to be followed.

[42 FR 29005, June 7, 1977]

(iv) The location and number of points to be monitored and the frequency of monitoring provided for in the program are acceptable when they are compared with the number of pieces of equipment in vinyl chloride service and the size and physical layout of the plant.

(v) It contains an acceptable plan of action to be taken when a leak is detected.

(vi) It contains a definition of leak which is acceptable when compared with the background concentrations of vinyl chloride in the areas of the plant to be monitored by the vinyl chloride monitoring system. Measurements of background concentrations of vinyl chloride in the areas of the plant to be monitored by the vinyl chloride monitoring system are to be included with the description of the program. The definition of leak for a given plant may vary among the different areas within the plant and is also to change over time as background concentrations in the plant are reduced.

(9) Inprocess wastewater: Vinyl chloride emissions to the atmosphere from inprocess wastewater are to be reduced as follows:

(i) The concentration of vinyl chloride in each inprocess wastewater stream containing greater than 10 ppm vinyl chloride measured immediately as it leaves a piece of equipment and before being mixed with any other inprocess wastewater stream is to be reduced to no more than 10 ppm by weight before being mixed with any other inprocess wastewater stream which contains less than 10 ppm vinyl chloride; before being exposed to the atmosphere, before being discharged to a wastewater treatment process; or before being discharged untreated as a wastewater. This paragraph does apply to water which is used to displace vinyl chloride from equipment before it is opened to the atmosphere in accordance with § 61.64(a)(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)(2) 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 ≥ 4.75 m³ 1,250 gal in volume for which an emission limit is prescribed in § 61.66(b)(6) (i) prior to opening the equipment and using Test Method 106, a portable hydrocarbon detector, or an equivalent or alternative method. The method of measurement is to meet the requirements in § 61.67(g)(8)(i)(A) or (g)(8)(i)(B).

[41 FR 53017, December 3, 1976]

§ 61.66 Equivalent equipment and procedures.

Upon written application from an owner or operator, the Administrator may

approve use of equipment or procedures which have been demonstrated to his satisfaction to be equivalent in terms of reducing vinyl chloride emissions to the atmosphere to those prescribed for compliance with a specific paragraph of this subpart. For an existing source, any request for using an equivalent method as the initial measure of control is to be submitted to the Administrator within 30 days of the effective date. For a new source, any request for using an equivalent method is to be submitted to the Administrator with the application for approval of construction or modification required by § 61.07.

§ 61.67 Emission tests.

(a) Unless a waiver of emission testing is obtained under § 61.13, the owner or operator of a source to which this subpart applies shall test emissions from the source.

(1) Within 90 days of the effective date in the case of an existing source or a new source which has an initial startup date preceding the effective date, or

(2) Within 90 days of startup in the case of a new source, initial startup of which occurs after the effective date.

(b) The owner or operator shall provide the Administrator at least 30 days prior notice of an emission test to afford the Administrator the opportunity to have an observer present during the test.

(c) Any emission test is to be conducted while the equipment being tested is operating at the maximum production rate at which the equipment will be operated and under other relevant conditions as may be specified by the Administrator based on representative performance of the source.

(d) [Reserved]

(e) When at all possible, each sample is to be analyzed within 24 hours, but in no case in excess of 72 hours of sample collection. Vinyl chloride emissions are to be determined within 30 days after the emission test. The owner or operator shall report the determinations to the Administrator by a registered letter dispatched before the close of the next business day following the determination.

[42 FR 29006, June 7, 1977]

(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 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)(3), (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) 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.

(iii) For gas streams containing more than 10 percent oxygen the concentration of vinyl chloride as determined by Test Method 106 is to be corrected to 10 percent oxygen (dry basis) for determination of emissions by using the following equation:

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

where:

C_b (corrected) = The concentration of vinyl chloride in the exhaust gases, corrected to 10-percent oxygen.

C_b = The concentration of vinyl chloride as measured by Test Method 106.

20.9 = Percent oxygen in the ambient air at standard conditions.

10.9 = Percent oxygen in the ambient air at standard conditions, minus the 10.0-percent oxygen to which the correction is being made.

Percent O_2 = Percent oxygen in the exhaust gas as measured by Reference Method 3 in Appendix A of Part 60 of this chapter.

(iv) For those emission sources where the emission limit is prescribed in terms of mass rather than concentration, mass emissions in kg/100 kg product are to be determined by using the following equation:

$$C_{bx} = \frac{[C_b (2.60) Q 10^{-9}] [100]}{Z}$$

where:

C_{bx} = kg vinyl chloride/100 kg product.

C_b = 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^{-9} = Conversion factor for ppm.

Z = Production rate (kg/hr).

[42 FR 29006, June 7, 1977]

(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:

$$C_{bx} = \frac{[C_b R 10^{-9}] [100]}{Z}$$

where:

C_{bx} = kg vinyl chloride/100 kg product.

C_b = 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^{-9} = Conversion factor for ppm.

Z = Production rate (kg/hr), determined in accordance with a method which has been submitted to 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.

(b) 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 emissions/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 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), and (b) (2), (b) (5), (b) (6) (ii), and (b) (9) (ii).

[41 FR 53017, December 3, 1976]

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

[41 FR 53017, December 3, 1976]

(1) A calibration gas mixture prepared from the gases specified in sections 5.2.1 and 5.2.2 of Test Method 106 and in accordance with section 7.1 of Test Method 106, or

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(2) A calibration gas cylinder standard containing the appropriate concentration of vinyl chloride. The gas composition of the calibration gas cylinder standard is to have been certified by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration does not change greater than ±5 percent from the certified value. The date of gas cylinder preparation, certified vinyl chloride concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the manufacturer to the buyer. If a gas chromatograph is used as the vinyl chloride monitoring system, these gas mixtures may be directly used to prepare a chromatograph calibration curve as described in section 7.3 of Test Method 106. The requirements in sections 5.2.3.1 and 5.2.3.2 of Test Method 106 for certification of cylinder standards and for establishment and verification of calibration standards are to be followed.

[42 FR 29006, June 7, 1977]

§ 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) The owner or operator of any source to which this subpart applies shall submit to the Administrator on September 15 and March 15 of each year a report in writing containing the information required by this section. The first semiannual report is to be submitted following the first full 6 month reporting period after the initial report is submitted.

[41 FR 53017, December 3, 1976]

(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 operation, and identified by resin type and grade and the date and time the batch is completed. The corresponding quantity of material processed in each stripper batch is to be recorded and identified by resin type and grade and the date and time the batch is completed.

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(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 each sample required by 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:

$$A_{T_i} = \frac{\sum_i P_{G_i} M_{G_i}}{Q_{T_i}} = \frac{P_{G_1} M_{G_1} + P_{G_2} M_{G_2} + \dots + P_{G_n} M_{G_n}}{Q_{T_i}}$$

where:

A = 24-hour average concentration of type T_i resin in ppm (dry weight basis).

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

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

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

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

G_i = Grade of resin; e.g., G_1, G_2 , and G_3 .

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

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(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.

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(3) A record of emissions measured in accordance with § 61.68.

[42 FR 29006, June 7, 1977]

(4) A daily operating record for each polyvinyl chloride reactor, including pressures and temperatures.

[42 FR 29006, June 7, 1977]

3. *Interferences.* Acetaldehyde, which can occur in some vinyl chloride sources, will interfere with the vinyl chloride peak from the Chromasorb 102 column. See sections 4.3.2 and 5.4. 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.

[42 FR 29005, June 7, 1977]

4. Apparatus.

4.1 Sampling (Figure 104-1).

4.1.1 Probe—Stainless steel, Pyrex glass, or Teflon tubing according to stack temperature, each equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample line—Teflon, 6.4 mm outside diameter, of sufficient length to connect probe to bag. A new unused piece is employed for each series of bag samples that constitutes an emission test.

4.1.3 Male (2) and female (2) stainless steel quick-connects, with ball checks (one pair without) located as shown in Figure 104-1.

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4.1.4 Tedlar bags, 100 liter capacity—To contain sample. Teflon bags are not acceptable. Aluminized Mylar bags may be used, provided that the samples are analyzed within 24 hours of collection.

4.1.5 Rigid leakproof containers for 4.1.4, with covering to protect contents from sunlight.

4.1.6 Needle valve—To adjust sample flow rate.

4.1.7 Pump—Leak-free. Minimum capacity 2 liters per minute.

4.1.8 Charcoal tube—To prevent admission of vinyl chloride to atmosphere in vicinity of sampler.

4.1.9 Flow meter—For observing sample flow rate; capable of measuring a flow range from 0.10 to 1.00 liter per minute.

4.1.10 Connecting tubing, Teflon, 6.4 mm outside diameter to assemble sample train (Figure 104-1).

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4.1.11 Pitot tube—Type S (or equivalent), attached to the probe so that the sampling flow rate can be regulated proportional to the stack gas velocity.

4.2 Sample recovery.

4.2.1 Tubing—Teflon, 6.4 mm outside diameter, to connect bag to gas chromatograph sample loop. A new unused piece is employed for each series of bag samples that constitutes an emission test, and is to be discarded upon conclusion of analysis of those bags.

4.3 Analysis.

4.3.1 Gas chromatograph—With flame ionization detector, potentiometric strip chart recorder and 1.0 to 5.0 ml heated sampling loop in automatic sample valve.

4.3.2 Chromatographic column. Stainless steel, 2 m x 3.3 mm, containing 80/100 mesh Chromasorb 102. A secondary column of GE SP-95, 20 percent on 80/80 mesh AW Chromasorb F, stainless steel, 2 m x 3.3 mm or Porapak Q, 80/100 mesh, stainless steel, 1 m x 3.3 mm is required if acetaldehyde is present. If used, a secondary column is placed after the Chromasorb 102 column. The combined columns should then be operated at 120° C.

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4.3.3 Flow meters (2)—Rotameter type, 0 to 100 ml/min capacity, with flow control valves.

4.3.4 Gas regulators—For required gas cylinders.

4.3.5 Thermometer—Accurate to one degree centigrade, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer—Accurate to 5 mm Hg, to measure atmospheric pressure around gas chromatograph during sample analysis.

4.3.7 Pump—Leak-free. Minimum capacity 100 ml/min.

4.4 Calibration.

4.4.1 Tubing—Teflon, 6.4 mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar bags—Sixteen-inch square size, separate bag marked for each calibration concentration.

4.4.3 Syringe—0.5 ml, gas tight.

4.4.4 Syringe—50 ml, gas tight.

4.4.5 Flow meter—Rotameter type, 0 to 1000 ml/min range accurate to $\pm 1\%$, 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. Use one of the following options: either 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 Vinyl chloride, 99.9+ percent. Pure vinyl chloride gas certified by the manufacturer to contain a minimum of 99.9 percent vinyl chloride for use in the preparation of standard gas mixtures in Section 7.1. If the gas manufacturer maintains a bulk cylinder supply of 99.9+ percent vinyl chloride, the certification analysis may have been performed on this supply rather than on each gas cylinder prepared from this bulk supply. The date of gas cylinder preparation and the certified analysis must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer.

5.2.2 Nitrogen gas, Zero grade, for preparation of standard gas mixtures.

5.2.3 Cylinder standards (3). Gas mixture standards (80, 10, and 5 ppm vinyl chloride in nitrogen cylinders) for which the gas composition has been certified by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration does not change greater than ± 5 percent from the certified value. The date of gas cylinder preparation, certified vinyl chloride concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer. These gas mixture standards may be directly used to prepare a chromatograph calibration curve as described in section 7.2.

5.2.3.1 Cylinder standards certification. The concentration of vinyl chloride in nitrogen in each cylinder must have been certified by the manufacturer by a direct analysis of each cylinder using an analytical procedure that the manufacturer had calibrated on the day of cylinder analysis. The calibration of the analytical procedure shall, as a minimum, have utilized a three-point calibration curve. It is recommended that the manufacturer maintain two calibration standards and use these standards in the following way: (1) a high concentration standard (between 80 and 100 ppm) for preparation of a calibration curve by an appropriate dilution technique; (2) a low concentration standard (between 5 and 10 ppm) for verification of the dilution technique used.

5.2.3.2 Establishment and verification of calibration standards. The concentration of each calibration standard must have been established by the manufacturer using

METHOD 104—DETERMINATION OF VINYL CHLORIDE FROM STATIONARY SOURCES

[41 FR 46559, October 21, 1976]

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

[42 FR 29005, June 7, 1977]

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^{-4} mg and 4×10^{-4} mg.

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