

Chapter NR 449

CONTROL OF VINYL CHLORIDE EMISSIONS

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Note: Corrections made under s. 13.93 (2m) (b) 7., Stats., Register, January, 1997, No. 493.

NR 449.01 Applicability; purpose. (1) APPLICABILITY. This chapter applies to plants which produce ethylene dichloride by reaction of oxygen and hydrogen chloride with ethylene, vinyl chloride by any process, one or more polymers containing any fraction of polymerized vinyl chloride and any combination of these products and to all owners and operators of these plants.

(2) PURPOSE. This chapter is adopted under ss. 285.11, 285.13, 285.17 and 285.27, Stats., to establish emission limitations and sampling and testing procedures for vinyl chloride air contaminant sources and to create additional monitoring, reporting and recordkeeping requirements for owners or operators of a vinyl chloride air contaminant source in order to protect air quality.

Note: This chapter is based on the federal regulations contained in 40 CFR part 61, Subpart F.

History: Renum. from NR 154.19 (6) (a) and am., cr. (2), Register, September 1986, No. 369, eff. 10-1-86; am. (1), Register, May, 1992, No. 437, eff. 6-1-92.

NR 449.02 Definitions. The definitions contained in chs. NR 400 and 445 apply to the terms used in this chapter. In addition, the following definitions apply to the terms used in this chapter:

(1) "Bulk resin" means a resin which is produced by a polymerization process in which no water is used.

(2) "Dispersion resin" means a resin manufactured in such a way as to form fluid dispersions when dispersed in a plasticizer or a plasticizer and diluent mixture.

(3) "Ethylene dichloride plant" includes any plant which produces ethylene dichloride by reaction of oxygen and hydrogen chloride with ethylene.

(4) "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.

(5) "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.

(6) "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.

(7) "In vinyl chloride service" means a piece of equipment that contains or contacts either a liquid that is at least 10% by weight vinyl chloride or a gas that is at least 10% by volume vinyl chloride.

(8) "Latex resin" means a resin which is produced by a polymerization process which initiates from free radical catalyst sites and is sold undried.

(9) "Polyvinyl chloride plant" includes any plant where vinyl chloride alone or in combination with other materials is polymerized.

(10) "Reactor" means a vat or vessel, which may be jacketed to permit temperature control, designed to contain chemical reactions.

(10m) "Run" means the net period of time during which an emission sample is collected.

(11) "Slip gauge" means a gauge which has a probe that moves through the gas to 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.

(11m) "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.

(12) "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 or vacuum, or both. 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.

(13) "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.

(14) "Vinyl chloride plant" includes any plant which produces vinyl chloride by any process.

(15) "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.

(16) "Vinyl chloride reactor" includes any vessel in which vinyl chloride is partially or totally polymerized into polyvinyl chloride.

(17) "Vinyl chloride reactor opening loss" means the emission of vinyl chloride occurring when a reactor is vented to the atmosphere for any purpose other than an emergency relief discharge as defined in ss. NR 449.06 (1) (c) and 449.07 (1).

(18) "Wastewater treatment process" includes any process which modifies characteristics such as biological or chemical oxygen demand, total suspended solids, or pH, usually for the purpose of meeting effluent guidelines and standards, but does not include any process the purpose of which is to remove vinyl chloride from water to meet requirements of this chapter.

History: Renum. from NR 154.01, cr. (intro.) and (10), Register, September, 1986, No. 369, eff. 10-1-86; (10m), (11m), and (18), renum from NR 400.02 (82), (92) and (101), Register, May, 1992, No. 437, eff. 6-1-92; am. (intro.), Register, December, 1995, No. 480, eff. 1-1-96.

NR 449.03 Exemptions. (1) EXEMPTION. This chapter 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 cubic meters (50 gallons).

(2) **PARTIAL EXEMPTION.** Sections of this chapter other than ss. NR 449.06 (1) (a), (2), (3), (4), 449.09 to 449.13 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 cubic meters (50 gallons) and no more than 4.07 cubic meters (1100 gallons).

History: Renum. from NR 154.19 (6) (b) and (c) and am. Register, September, 1986, No. 369, eff. 10-1-86.

NR 449.04 Emission standards for ethylene dichloride plants. (1) **ETHYLENE DICHLORIDE PURIFICATION.** The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from any equipment used in ethylene dichloride purification may not exceed 10 parts per million, except as provided in s. NR 449.07 (1). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in s. NR 449.07 (2) (f)1. before being opened.

(2) **OXYCHLORINATION REACTOR.** Except as provided in s. NR 449.07 (1), emissions of vinyl chloride to the atmosphere from each oxychlorination reactor may not exceed 0.20 gram/kilogram (0.00020 pound/pound) of the 100% ethylene dichloride product from the oxychlorination process.

History: Renum. from NR 154.19 (6) (d) and am. Register, September, 1986, No. 369, eff. 10-1-86; am. (2), Register, May, 1992, No. 437, eff. 6-1-92.

NR 449.05 Emission standard for vinyl chloride plants. An owner or operator of a vinyl chloride plant shall comply with the requirements of this section and s. NR 449.07.

(1) **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 or purification, or both, may not exceed 10 parts per million, except as provided in s. NR 449.07 (1). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in s. NR 449.07 (2) (f)1. before being opened.

History: Renum. from NR 154.19 (6) (e) and am. Register, September, 1986, No. 369, eff. 10-1-86.

NR 449.06 Emission standards for polyvinyl chloride plants. An owner or operator of a polyvinyl chloride plant shall comply with the requirements of this section and s. NR 449.07.

(1) **REQUIREMENTS FOR VINYL CHLORIDE REACTORS.** (a) The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each vinyl chloride reactor may not exceed 10 parts per million, except as provided in par. (b) and s. NR 449.07 (1).

(b) The vinyl chloride reactor opening loss from each vinyl chloride reactor may not exceed 0.020 gram vinyl chloride/kilogram (0.00020 pound vinyl chloride/pound) of polyvinyl chloride product, with the product determined on a dry solids basis. This requirement applies to any vessel which is used as a vinyl chloride reactor or as both a vinyl chloride reactor and a stripper. In the bulk process, the product means the gross product of prepolymerization and postpolymerization.

(c) Except for an emergency manual vent valve discharge, there may 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 department a report in writing containing information on the source, nature and cause of the discharge, the method used for determining the vinyl chloride loss, the action

that was taken to abate the discharge, and measures adopted to prevent future discharges.

(2) **REQUIREMENT FOR STRIPPERS.** The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each stripper may not exceed 10 parts per million, except as provided in s. NR 449.07 (1). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in s. NR 449.07 (2) (f) 1. before being opened.

(3) **REQUIREMENT FOR 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 may not exceed 10 parts per million, except as provided in s. NR 449.07 (1). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in s. NR 449.07 (2) (f)1. before being opened.

(4) **REQUIREMENT FOR MONOMER RECOVERY SYSTEMS.** The concentration of vinyl chloride in any exhaust gases discharged to the atmosphere from each monomer recovery system may not exceed 10 parts per million, except as provided in s. NR 449.07 (1). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in s. NR 449.07 (2) (f)1. before being opened.

(5) **REQUIREMENTS FOR SOURCES FOLLOWING STRIPPERS.** The following requirements apply to emissions of vinyl chloride to the atmosphere from the combination of all sources following strippers, or vinyl chloride reactors if the plant has no strippers, 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:

(a) 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:

1. 2000 parts per million for polyvinyl chloride dispersion resins, excluding latex resins.

2. 400 ppm for all other polyvinyl chloride resins, including latex resins, averaged separately for each type of resin.

(b) 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:

1. 2.0 grams/kilogram (0.0020 pound/pound) product from the strippers (or vinyl chloride reactors if the plant has no strippers) for dispersion polyvinyl chloride resins, excluding latex resins, with the product determined on a dry solids basis.

2. 0.40 gram/kilogram (0.00040 pound/pound) product from the strippers, or vinyl chloride reactors if the plant has no strippers, for all other polyvinyl chloride resins, including latex resins, with the product determined on a dry solids basis.

History: Renum. from NR 154.19 (6) (f) and am. Register, September, 1986, No. 369, eff. 10-1-86; am. (1) (b), (5) (b) 1. and 2., Register, May, 1992, No. 437, eff. 6-1-92.

NR 449.07 Emission standards for ethylene dichloride, vinyl chloride and polyvinyl chloride plants. An owner or operator of an ethylene dichloride, vinyl chloride, or polyvinyl chloride plant shall comply with the requirements of this section.

(1) **RELIEF VALVE DISCHARGE.** Except for an emergency relief discharge, there may 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 department 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.

(2) FUGITIVE EMISSION SOURCES. (a) Vinyl chloride emissions from loading and unloading lines in vinyl chloride service which are opened to the atmosphere after each loading and unloading operation shall be minimized as follows:

1. After each loading and 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 shall be reduced so that the parts combined contain no greater than 0.0038 cubic meter (0.13 cubic feet) of vinyl chloride, at standard temperature and pressure.

2. Any vinyl chloride removed from a loading or unloading line in accordance with subd. 1. shall be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases may not exceed 10 parts per million, or equivalent as provided in s. NR 449.08.

(b) During loading or unloading operations, the vinyl chloride emissions from each slip gauge in vinyl chloride service shall 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 may not exceed 10 parts per million, or equivalent as provided in s. NR 449.08.

(c) 1. Rotating pumps. Vinyl chloride emissions from seals on all rotating pumps in vinyl chloride service shall be minimized by installing sealless pumps, pumps with double mechanical seals, or equivalent as provided in s. NR 449.08. If double mechanical seals are used, vinyl chloride emissions from the seals shall be minimized by maintaining the pressure between the 2 seals so that any leak that occurs is into the pump, by ducting any vinyl chloride between the 2 seals through a control system from which the concentration of vinyl chloride in the exhaust gases may not exceed 10 parts per million, or equivalent as provided in s. NR 449.08.

2. Reciprocating pumps. Vinyl chloride emissions from seals on all reciprocating pumps in vinyl chloride service shall be minimized by installing double outboard seals, or equivalent as provided in s. NR 449.08. If double outboard seals are used, vinyl chloride emissions from the seals shall be minimized by maintaining the pressure between the 2 seals so that any leak that occurs is into the pump, by ducting any vinyl chloride between the 2 seals through a control system from which the concentration of vinyl chloride in the exhaust gases may not exceed 10 parts per million, or equivalent as provided in s. NR 449.08.

3. Rotating compressors. Vinyl chloride emissions from seals on all rotating compressors in vinyl chloride service shall be minimized by installing compressors with double mechanical seals, or equivalent as provided in s. NR 449.08. If double mechanical seals are used, vinyl chloride emissions from the seals shall be minimized by maintaining the pressure between the 2 seals so that any leak that occurs is into the compressor, by ducting any vinyl chloride between the 2 seals through a control system from which the concentration of vinyl chloride in the exhaust gases may not exceed 10 parts per million, or equivalent as provided in s. NR 449.08.

4. Reciprocating compressors. Vinyl chloride emissions from seals on all reciprocating compressors in vinyl chloride service shall be minimized by installing double outboard seals, or equivalent as provided in s. NR 449.08. If double outboard seals are used, vinyl chloride emissions from the seals shall be minimized by maintaining the pressure between the 2 seals so that any leak that occurs is into the compressor, by ducting any vinyl chloride between the 2 seals through a control system from which the

concentration of vinyl chloride in the exhaust gases may not exceed 10 parts per million, or equivalent as provided in s. NR 449.08.

5. Agitators. Vinyl chloride emissions from seals on all agitators in vinyl chloride service shall be minimized by installing agitators with double mechanical seals, or equivalent as provided in s. NR 449.08. If double mechanical seals are used, vinyl chloride emissions from the seals shall be minimized by maintaining the pressure between the 2 seals so that any leak that occurs is into the agitated vessels, by ducting any vinyl chloride between the 2 seals through a control system from which the concentration of vinyl chloride in the exhaust gases may not exceed 10 parts per million, or equivalent as provided in s. NR 449.08.

(d) Vinyl chloride emissions due to leakage from each relief valve on equipment in vinyl chloride service shall 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 s. NR 449.08.

(e) Except as provided in s. NR 449.06 (1) (c), all gases which are manually vented from equipment in vinyl chloride service shall be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases may not exceed 10 parts per million, or equivalent as provided in s. NR 449.08.

(f) 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) shall be minimized as follows:

1. Before opening any equipment for any reason, the quantity of vinyl chloride shall be reduced so that the equipment contains no more than 2.0% by volume vinyl chloride or 0.0950 cubic meter (25 gallons) of vinyl chloride, whichever is larger, at standard temperature and pressure.

2. Any vinyl chloride removed from the equipment in accordance with subd. 1. shall be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases may not exceed 10 parts per million, or equivalent as provided in s. NR 449.08.

(g) Unused portions of samples containing at least 10% by weight vinyl chloride shall be returned to the process, and sampling techniques shall be such that sample containers in vinyl chloride service are purged into a closed process system.

(h) Vinyl chloride emissions due to leaks from equipment in vinyl chloride service shall be minimized by instituting and implementing a formal leak detection and elimination program. The owner or operator of a source on which construction or modification commenced after February 1, 1984 shall submit a description of the program to the department for approval. The program shall be submitted within 45 days after startup unless a waiver is granted by the department. If a waiver of compliance is granted, the program is to be submitted on a date scheduled by the department. Approval of a program shall be granted by the department provided it finds:

1. 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.

2. 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 parts per million and is of such design and size that it can be used to measure emissions from localized points.

3. 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 shall be conducted with a concentration of vinyl chloride equal to the concentration defined as a leak according to subd. 6. The calibration shall be done with either one of the following:

a. A calibration gas mixture prepared from the gases specified in section 5.2.1 and 5.2.2 and in accordance with section 7.1 of Method 106 of 40 CFR part 61, Appendix B, incorporated by reference in s. NR 484.04.

b. A calibration gas cylinder standard containing the appropriate concentration of vinyl chloride. The gas composition of the calibration gas cylinder standard shall 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 plus or minus 5% 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 Method 106 of 40 CFR part 61, Appendix B, incorporated by reference in s. NR 484.04. The requirements in sections 5.2.3.1 and 5.2.3.2 of Method 106 for certification of cylinder standards and for establishment and verification of calibration standards shall be followed.

4. 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.

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

6. 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. Measurement of background concentrations of vinyl chloride in the areas of the plant to be monitored by the vinyl chloride monitoring system shall 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.

(i) Vinyl chloride emissions to the atmosphere from inprocess wastewater shall be reduced as specified in this paragraph.

1. The concentration of vinyl chloride in each inprocess wastewater stream containing greater than 10 parts per million vinyl chloride measured immediately as it leaves a piece of equipment and before being mixed with any other inprocess wastewater stream shall be reduced to no more than 10 parts per million by weight before being mixed with any other inprocess wastewater stream which contains less than 10 parts per million 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 s. NR 449.06 (1) (b) or par. (f), 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 s. NR 449.06 (1) (b) or par. (f).

2. Any vinyl chloride removed from the inprocess wastewater in accordance with subd. 1. shall be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases may not exceed 10 parts per million, or equivalent as provided in s. NR 449.08

(3) STANDARD OPERATING PROCEDURE. The requirements in sub. (2) (a), (b) and (c) to (h) shall be incorporated into a standard operating procedure and made available upon request for inspection by a department representative. The standard operating procedure shall include provisions for measuring the vinyl chloride in equipment 4.75 cubic meters (1,250 gallons) in volume for which an emission limit is prescribed in sub. (2) (f) 1. prior to opening the equipment and using Method 106 of 40 CFR part 61, Appendix B, incorporated by reference in s. NR 484.04, a portable hydrocarbon detector, or an equivalent or alternative method. The method of measurement shall meet the requirements s. NR 449.09 (6) (e) 1. a. or b.

History: Renum. from NR 154.19 (6) (g) and am. Register, September, 1986, No. 369, eff. 10-1-86; am. (2) (f) 1., Register, May, 1992, No. 437, eff. 6-1-92; am. (2) (h) 3. and (3), Register, December, 1995, No. 480, eff. 1-1-96; am. (2) (h) 3. (Intro.) and a., Register, November, 1999, No. 527, eff. 12-1-99.

NR 449.08 Equivalent equipment and procedures.

Upon written application from an owner or operator, the department may approve use of equipment or procedures which have been demonstrated to the department's satisfaction to be equivalent in terms of reducing vinyl chloride emissions to the atmosphere to those prescribed for compliance with a specific section of this chapter. Any request for using an equivalent method shall be submitted to the department with the application for a permit to construct or modify and operate the vinyl chloride source.

History: Renum. from NR 154.19 (6) (h) and am. Register, September, 1986, No. 369, eff. 10-1-86.

NR 449.09 Emission tests. (1) Unless a waiver of emission testing is obtained from the department, each owner or operator of a source to which this section applies on which construction or modification commenced after February 1, 1984 shall test emissions from the source within 90 days of startup.

(2) The department shall be notified at least 30 days prior to a stack or performance test to afford the department the opportunity to have a representative present to witness the testing procedures.

(3) Any emission test shall 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 department based on the representative performance of the source.

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

(5) The owner or operator shall retain at the plant and make available, upon request, for inspection by a department representative, for a minimum of 2 years, records of emission test results and other data needed to determine emissions.

(6) Unless otherwise specified, the owner or operator shall use Methods of 40 CFR part 61, Appendix B, incorporated by reference in s. NR 484.04, for each test as required by pars. (a) to (e) unless an equivalent method or an alternative method has been approved by the department. If the department finds reasonable grounds to dispute the results obtained by an equivalent or alternative method, the department 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 department may notify the owner or operator that approval of the method previously considered to be equivalent or alternative is withdrawn.

(7) Unless otherwise specified, the owner or operator shall use Methods of 40 CFR part 61, Appendix B, incorporated by reference in s. NR 484.04, for each test as required by pars. (a) to (e) unless an equivalent method or an alternative method has been approved by the department. If the department finds reasonable grounds to dispute the results obtained by an equivalent or alternative method, the department 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 department may notify the owner or operator that approval of the method previously considered to be equivalent or alternative is withdrawn.

(a) Method 106 of 40 CFR part 61, Appendix B, incorporated by reference in s. NR 484.04, shall be used to determine the vinyl chloride emissions from any source for which an emission limit is prescribed in ss. NR 449.04 (1) or (2), 449.05 (1), 449.06 (1) (a), (2), (3) or (4), or from any control system to which reactor emis-

sions are required to be ducted in s. NR 449.06 (1) (b) or to which fugitive emissions are required to be ducted in s. NR 449.07 (2) (a) 2., (b), (c), (f) 2. or (i) 2.

1. For each run, one sample shall be collected. The sampling site shall be at least 2 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 shall be determined from the following equation:

$$\text{equivalent diameter} = 2 (\text{length})(\text{width}) / \text{length} + \text{width}$$

The sampling point in the duct shall be at the centroid of the cross section. The sample shall be extracted at a rate proportional to the gas velocity at the sampling point. The sample shall be taken over a minimum of one hour, and shall contain a minimum volume of 50 liters corrected to standard conditions.

2. Each emission test shall consist of 3 runs. For the purpose of determining emissions, the average of results of all runs shall apply. The average shall be computed on a time weighted basis.

3. For gas streams containing more than 10% oxygen the concentration of vinyl chloride as determined by Method 106 shall be corrected to 10% 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:

$C_{b(\text{corrected})}$ is the concentration of vinyl chloride in the exhaust gases, corrected to 10% oxygen

C_b is the concentration of vinyl chloride as measured by Method 106

20.9 is the percent oxygen in the ambient air at standard conditions

10.9 is the percent oxygen in the ambient air at standard conditions minus the 10% oxygen to which the correction is being made

percent O_2 is the percent oxygen in the exhaust gas as measured by Method 3 of 40 CFR part 60, Appendix A, incorporated by reference in s. NR 484.04

4. For those emission sources where the emission limit is prescribed in terms of mass rather than concentration, mass emissions in kilograms per 100 kilograms product shall be determined by using the following equation:

$$C_{BX} = [C_b(2.60) Q (10^{-6})] [100]/Z$$

where:

C_{BX} is the kg vinyl chloride/100 kg product

C_b is the concentration of vinyl chloride as measured by Method 106

2.60 equals the density of vinyl chloride at one atmosphere and 20°C in kg/m^3

Q is the volumetric flow rate in m^3/hr as determined by Method 2 of 40 CFR part 60, Appendix A, incorporated by reference in s. NR 484.04

10^{-6} is the conversion factor for parts per million

Z is the production rate (kilograms/hour)

(b) Method 107 of 40 CFR part 61, Appendix B, incorporated by reference in s. NR 484.04, shall be used to determine the concentration of vinyl chloride in each inprocess wastewater stream for which an emission limit is prescribed in s. NR 449.07 (2) (i) 1.

(c) Where a stripping operation is used to attain the emission limit in s. NR 449.06 (5), emissions shall be determined using Method 107 of 40 CFR part 61, Appendix B, incorporated by reference in s. NR 484.04, as follows:

1. The number of strippers and samples and the types and grades of resin to be sampled shall be determined by the department for each individual plant at the time of the test based on the plant's operation.

2. Each sample shall be taken immediately following the stripping operation.

3. The corresponding quantity of material processed by each stripper shall be determined on a dry solids basis and by a method submitted to and approved by the department.

4. At the prior request of the department, the owner or operator shall provide duplicates of the samples required in subd. 1.

(d) Where control technology other than or in addition to a stripping operation is used to attain the emission limit in s. NR 449.06 (5), emissions shall be determined as follows:

1. Method 106 of 40 CFR part 61, Appendix B, incorporated by reference in s. NR 484.04, shall be used to determine atmospheric emissions from all of the process equipment simultaneously. The requirements of par. (a) shall be met.

2. Method 107 of 40 CFR part 61, Appendix B, incorporated by reference in s. NR 484.04, shall be used to determine the concentration of vinyl chloride in each inprocess wastewater stream subject to the emission limit prescribed in s. NR 449.06 (5). The mass of vinyl chloride in kilograms per 100 kilograms product in each inprocess wastewater stream shall be determined by using the following equation:

$$C_{BX} = [C_d R (10^{-6})] [100]/Z$$

where:

C_{BX} is the kg vinyl chloride/100 kg product

C_d is the concentration of vinyl chloride as measured by Method 107 of 40 CFR part 61, Appendix B

R is the water flow rate in l/hr determined in accordance with a method which has been submitted to and approved by the department

10^{-6} is the conversion factor for parts per million

Z is the production rate (kg/hr), determined in accordance with a method which has been submitted and approved by the department

(e) The vinyl chloride reactor opening loss for which an emission limit is prescribed in s. NR 449.06 (1) (b) shall be determined. The number of reactors for which the determination shall be made shall be specified by the department for each individual plant at the time of the determination based on the plant's operation. For a vinyl chloride reactor that is also used as a stripper, the determination may be made immediately following the stripping operation.

1. Except as provided in subd. 2., the vinyl chloride reactor opening loss shall be determined using the following equation:

$$C = W(2.60)(10^{-6})(C_b)/YZ$$

where:

C is the kg vinyl chloride emissions/kg product

W is the capacity of the vinyl chloride reactor in m^3

2.60 is the density of vinyl chloride at one atmosphere and 20°C in kg/m^3

10^{-6} is the conversion factor for ppm

C_b is ppm by volume vinyl chloride as determined by Method 106 of 40 CFR part 61, Appendix B, incorporated by reference in s. NR 484.04, or by a portable hydrocarbon detector which measures hydrocarbons with a sensitivity of at least 10 ppm

Y is the number of batches since the vinyl chloride reactor was last opened to the atmosphere

Z is the average kg of polyvinyl chloride produced per batch in the batches since the vinyl chloride reactor was last opened to the atmosphere

a. If Method 106 is used to determine the concentration of vinyl chloride (C_b), the sample shall be withdrawn at a constant rate with a probe of sufficient length to reach the vessel bottom from the manhole. Samples shall 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 (C_b), a probe of sufficient length to reach the vessel bottom from the service access hole shall be used to make the measurements. One measurement shall be made within 6 inches of the vessel bottom, one near the vessel center and one near the vessel top. Measurements shall be made at each location until the reading is stabilized. All hydrocarbons measured shall be assumed to be vinyl chloride.

c. The production rate of polyvinyl chloride (Z) shall be determined by a method submitted to and approved by the department.

2. A calculation based on the number of evacuations, the vacuum involved, and the volume of gas in the reactor is hereby approved by the department as an alternative method for determining reactor opening loss for past polymerization reactors in the manufacture of bulk resins.

History: Renum. from NR 154.19 (6) (i) and am. Register, September, 1986, No. 369, eff. 10-1-86; correction in (6) (e) 1. b., made under s. 13.93 (2m) (b) 5., Stats., Register, May, 1992, No. 437; am. (6) (intro.) (a) (intro.) 3., 4., (b), (c) (intro.) (d) 1. and 2., (e) 1. (intro.), Register, December, 1995, No. 480, eff. 1-1-96.

NR 449.10 Emission monitoring. (1) A vinyl chloride monitoring system shall be used to monitor on a continuous basis the emissions from the sources for which emission limits are prescribed in ss. NR 449.04 (1) and (2), 449.05 (1) and 449.06 (1) (a), (2) to (4), and for any control system to which vinyl chloride reactor emissions are required to be ducted in s. NR 449.06 (1) (b) or to which fugitive emissions are required to be ducted in s. NR 449.07 (2) (a) 2., (b), (e), (f) 2. and (i) 2.

(2) The vinyl chloride monitoring system used to meet the requirement in sub. (1) shall 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 s. NR 449.07 (2) (h) 2. may be used to meet the requirements of this section.

(3) A daily span check shall be conducted for each vinyl chloride monitoring system used. For all of the emission sources listed in sub. (1), except the one for which an emission limit is prescribed in s. NR 449.04 (2), the daily span check shall be conducted with a concentration of vinyl chloride equal to 10 parts per million. For the emissions source for which an emission limit is prescribed in s. NR 449.04 (2), the daily span check shall 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 s. NR 449.09. The calibration shall be done with:

(a) A calibration gas mixture prepared from the gases specified in sections 5.2.1 and 5.2.2 and in accordance with section 7.1 of Method 106 of 40 CFR part 61, Appendix B, incorporated by reference in s. NR 484.04, or

(b) A calibration gas cylinder standard containing the appropriate concentration of vinyl chloride. The gas composition of the calibration gas cylinder standard shall 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 plus or minus 5% from the certified value. The date of gas cylinder preparation, certified vinyl chloride con-

centration 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 Method 106 of 40 CFR part 61, Appendix B, incorporated by reference in s. NR 484.04. The requirements in sections 5.2.3.1 and 5.2.3.2 of Method 106 for certification of cylinder standards and for establishment and verification of calibration standards shall be followed.

History: Renum. from NR 154.19 (6) (j) and am. Register, September, 1986, No. 369, eff. 10-1-86; am. (3) (a) and (b), Register, December, 1995, No. 480, eff. 1-1-96.

NR 449.11 Initial report. (1) The owner or operator of any source to which this chapter applies and on which construction or modification is commenced after February 1, 1984 shall notify the department in writing that the equipment and procedural specifications in s. NR 449.07 (2) (a) to (h) are being implemented.

(2) The statement shall be submitted to the department within 90 days of the initial startup date. The statement shall contain the information specified in this subsection.

(a) A list of the equipment installed for compliance,

(b) A description of the physical and functional characteristics of each piece of equipment,

(c) 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 s. NR 449.07 (2) (a) 1. and (f) 1., and

(d) A statement that each piece of equipment is installed and that each piece of equipment and each procedure is being used.

History: Renum. from NR 154.19 (6) (k) and am. Register, September, 1986, No. 369, eff. 10-1-86.

NR 449.12 Semiannual report. (1) The owner or operator of any source subject to this chapter shall submit to the department on September 15 and March 15 of each year a report in writing containing the information required by this section.

(2) The first semiannual report shall be submitted within 180 days of the initial startup date of a source on which construction or modification commenced after February 1, 1984.

(3) Unless otherwise specified, the owner or operator shall use the Methods of 40 CFR part 61, Appendix B, incorporated by reference in s. NR 484.04, to conduct emission tests as required by pars. (b) and (c), unless an equivalent or an alternative method has been approved by the department. If the department finds reasonable grounds to dispute the results obtained by an equivalent or alternative method, the department 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 department may notify the owner or operator that approval of the method previously considered to be equivalent or alternative is withdrawn.

(a) 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 s. NR 449.04 (1) or (2), 449.05 (1) or 449.06 (1) (a), (2), (3) or (4), or for any control system to which reactor emissions are required to be ducted in s. NR 449.06 (1) (b) or to which fugitive emissions are required to be ducted in s. NR 449.07 (2) (a) 2., (b), (e), (f) 2. or (i) 2. The emissions shall be measured in accordance with s. NR 449.10.

(b) In polyvinyl chloride plants for which a stripping operation is used to attain the emission level prescribed in s. NR 449.06 (5), the owner or operator shall include in the report a record of the vinyl chloride content in the polyvinyl chloride resin. Method 107 of 40 CFR part 61, Appendix B, incorporated by reference in s. NR 484.04, shall be used to determine vinyl chloride content in accordance with this paragraph.

1. If batch stripping is used, one representative sample of polyvinyl chloride resin shall 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 shall be recorded and identified by resin type and grade and the date and time the batch is completed.

2. If continuous stripping is used, one representative sample of polyvinyl chloride resin shall be taken for each grade of resin processed, whichever is more frequent. The sample shall 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 8-hour period shall be recorded and identified by resin type and grade and the date and time it represents.

3. The quantity of material processed by the stripper shall be determined on a dry solids basis and by a method submitted to and approved by the department.

4. At the prior request of the department, the owner or operator shall provide duplicates of the samples required in subds. 1. and 2.

5. The report to the department by the owner or operator shall include the vinyl chloride content found in each sample required by subds. 1. and 2., 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 or strippers that calendar day, according to the following equation:

$$A_{T_i} = \frac{\sum_{i=1}^n P_{G_i} M_{G_i}}{Q_{T_i}} = \frac{P_{G_1} M_{G_1} + P_{G_2} M_{G_2} + \dots + P_{G_n} M_{G_n}}{Q_{T_i}}$$

where:

A_{T_i} is the 24-hour average concentration of type T_i resin in ppm (dry weight basis)

Q_{T_i} is the total production of type T_i resin over the 24-hour period in kilograms

T_i is the type of resin

M_{G_i} is the concentration of vinyl chloride in one sample of grade G_i resin in parts per million

P_{G_i} is the production of grade G_i resin represented by the sample in kilograms

G_i is the grade of resin (e.g., G_1 , G_2 and G_3)

n is the total number of grades of resin produced during the 24-hour period

6. Records of all data needed to furnish the information required by subd. 5. shall be retained at the source and made available for inspection by a department representative for a minimum of 3 years. The records shall contain:

a. The vinyl chloride content found in all the samples required in subds. 1. and 2., 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 or strippers identified by the resin type and grade and the time and date it represents.

(c) 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 s. NR 449.06 (1) (b). Emissions shall be determined in accordance with s. NR 449.09 (6) (e), 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.

History: Renum. from NR 154.19 (6) (l) and am. Register, September, 1986, No. 369, eff. 10-1-86; am. (3) (intro.) (a), (b) (intro.) and 5., Register, December, 1995, No. 480, eff. 1-1-96; am. (3) (b) 6. intro., Register, January, 1997, No. 493, eff. 2-1-97.

NR 449.13 Recordkeeping. The owner or operator of any source subject to this chapter shall retain the information specified in this section at the source and make it available for inspection by a department representative for a minimum of 2 years.

(1) A record of the leaks detected by the vinyl chloride monitoring system, as required by s. NR 449.07 (2) (h), including the concentrations of vinyl chloride measured, analyzed, and recorded by the vinyl chloride detector, the location of each measurement and the date and approximate time of each measurement.

(2) A record of the leaks detected during routine monitoring with the portable hydrocarbon detector and the action taken to repair the leaks, as required by s. NR 449.07 (2) (h).

(3) A record of emissions measured in accordance with s. NR 449.10.

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

History: Renum. from NR 154.19 (6) (m) and am. Register, September, 1986, No. 369, eff. 10-1-86.

