COMPLIANCE MANUAL

COMPLIANCE WITH VCM EMISSION STANDARD

ABERDEEN PVC PLANT

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I. INTRODUCTION

The Aberdeen Plant manufactures polyvinyl chloride (PVC) resin via batch suspension polymerization. Vinyl chloride, a colorless vapor at ambient conditions, has been identified as the cause of serious health problems. The EPA has promulgated specific emission limitations regarding the chemical.

As a user of vinyl chloride, the Aberdeen Plant is subject to compliance with the EPA's emission standard. Since identification of the associated health problems with vinyl chloride, the plant has expended substantial funds (in excess of $10 MM) to control emission sources and develop emission containment technology.

The facilities for containment of vinyl chloride emissions are essentially complete. Proper operation of the facilities will allow the Aberdeen Plant to contain emissions to the extent required by the EPA's regulation.

This document is written to describe the emission containment facilities and techniques employed by the plant. Information on facilities and methods of compliance are described as well as specific operating procedures that are used.

The Compliance Manual is organized into various sections. Section II contains the Emission Standard as it appeared in the Federal Register on October 21, 1976. Section III describes the general containment philosophy and approach used at Aberdeen. Section IV relates to the specific types of approaches used to achieve or demonstrate compliance. Sections V, VI, and VII contain specifics of compliance with each part of the EPA regulation. These sections are used to segregate 1) facilities which in themselves result in compliance 2) facilities for which calculational methods are needed to show compliance 3) facilities for which emission testing or sampling is needed to prove compliance.

For those facilities which require testing, the testing methods and procedures are described in Section VIII.

Recordkeeping requirements are described in Section IX.

The standard further requires a "Leak Detection and Elimination Plan". Aberdeen developed such a plan and it has been in force since mid-1977. The plan is included in Section X.

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ABERDEEN PVC PLANT

II. NATIONAL EMISSION STANDARD FOR HAZARDOUS AIR POLLUTANTS STANDARD FOR VINYL CHLORIDE

Attached is the subject document as it appeared in the Federal Register on October 21, 1976.

federal register

THURSDAY, OCTOBER 21, 1976

PART II:

ENVIRONMENTAL PROTECTION AGENCY

■

NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS

Standard For Vinyl Chloride

CHAPTER I—ENVIRONMENTAL PROTECTION AGENCY

SUBCHAPTER C—AIR PROGRAMS

[FRL 618-1]

PART 61—NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS

Standard for Vinyl Chloride

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

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

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

Summary of the Standard

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

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

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

Health and Environmental Impacts

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

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

Changes in the standard since proposal do not affect the level of control required. Thus, the environmental impact of the promulgated standard is, with one exception, the same as that described in Chapter 6 of Volume I of the *Standard Support and Environmental Impact Statement*. According to data submitted by the Society of Plastics Industry, Inc. (SPI), the impact on water consumption in the draft environmental impact statement was overstated. In estimating the impact on water consumption, EPA based its estimates on worst case conditions. That is, EPA assumed that those control systems with the greatest water usage would be employed and that there would be no recycling of water. There is no regulation which would require water recycling. According to SPI, the control system utilizing the most water will not be used generally by the industry and economic factors will cause plants to recycle much of the water. Therefore, according to SPI the impact of the standard on water consumption will be negligible.

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

The potential secondary environmental impacts of the standard are either insignificant or will be minimized without additional action, except for one adverse impact. Hydrogen chloride is already emitted by process equipment at ethylene dichloride-vinyl chloride plants and by other petrochemical plants in the complexes where ethylene dichloride-vinyl chloride plants are typically located. An incinerator used to attain the standard at an ethylene dichloride-vinyl chloride plant could increase hydrogen chloride emissions by several fold. Typically, however, due to the corrosion problems which would otherwise occur both on plant property and in the community, plants use scrubbers to control already existing hydrogen chloride emissions. Hydrogen chloride emissions resulting from control of vinyl chloride emissions are expected to be controlled for the same reason. If even a moderately efficient scrubber (98 percent control) were used to control the hydrogen chloride emissions resulting from incineration of vinyl chloride emissions, the increase in hydrogen chloride emissions from a typical ethylene dichloride-vinyl chloride plant due to the standard would be reduced to 35 percent. However, EPA plans to further evaluate the need to control hydrogen chloride emissions, since diffusion model results indicate that under "worst-case" meteorological conditions, the hydrogen chloride emissions from the process equipment and the incinerator combined would cause maximum ambient concentrations of hydrogen chloride in the vicinity of ethylene dichloride-vinyl chloride plants to be in the same range or somewhat higher than existing foreign standards and National Academy of Sciences (NAS) guidelines for public exposure.

Economic Impact

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

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

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

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

It is estimated that the price of polyvinyl chloride resins will rise by approximately 7.3 percent in order to maintain precontrol profitability and also to recover the total annualized control costs necessitated by the standard at ethylene dichloride-vinyl chloride plants and polyvinyl chloride plants. This increase is estimated to translate into a maximum consumer price increase in goods fabricated from polyvinyl chloride resins of approximately 3.5 percent. Recovery of effluent annualized costs plus maintenance of precontrol profitability is estimated to add approximately 2 percent to polyvinyl chloride resin prices and result in an additional maximum consumer price increase of 1 percent.

Public Participation

During the public comment period, 50 comment letters on the proposed standard were received. There were 24 from industry; 3 from environmental groups; 15 from Federal, State, and local agencies; and 8 from individual citizens. As required by section 112(b)(1)(B) of the Act, a public hearing was held on the proposed standard on February 3, 1976, in Washington, D.C. Presentations were made by the Environmental Defense Fund, the Society of the Plastics Industry, Inc., Dow Chemical Company, Diamond Shamrock Corporation, and Air Products and Chemicals, Inc. Copies of the comment letters received, the public hearing record, and a summary of the comments with EPA's responses are available for public inspection and copying at the EPA Public Information Reference Unit, Room 2922 (EPA Library), 401 M Street, SW., Washington, D.C. In addition, copies of the comment summary and Agency responses may be obtained upon written request from the Public Information Center (PM-215), Environmental Protection Agency, 401 M Street, SW., Washington, D.C. 20460 (specify *Standard Support and Environmental Impact Statement, Emission Standard for Vinyl Chloride, Volume II*).

Significant Comments and Changes to the Proposed Regulation

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

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

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

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

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

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

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

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

(3) *Selection of source categories.* In the preamble to the proposed standard EPA recognized that some small research and development facilities may exist where the emissions of vinyl chloride are insignificant and covering these facilities under the standard would be unnecessary and inappropriate. However, EPA did not have sufficient information available to clearly define which facilities should be excluded from the standard, and encouraged interested parties to submit such information during the comment period. Based on the information submitted, EPA decided to exempt polyvinyl chloride reactors and associated equipment from applicability of all parts of the standard if the reactors are used in research and development and have a capacity of no more than 0.19 m³ (50 gal). Reactors in this size range can generally be found in a laboratory, whereas the larger reactors are typically pilot scale facilities. Emissions from laboratory scale equipment are relatively small, and application of the controls required by the standard would be expensive and impractical. EPA also decided to exempt research and development facilities containing reactors greater than 0.19 m³ (50 gal) and no more than 4.07 m³ (1100 gal) in capacity from all parts of the standard except the 10 ppm limit for reactors, strippers, monomer recovery systems, and mixing, weighing and holding containers. EPA decided not to require these facilities to meet other parts of the standard because of the technical problems involved in doing so. For example, the standard for reactor opening is based in part on reducing the frequency of opening the reactor. Research and development reactors have to be opened after every batch for thorough cleaning. Also, stripping technology is developed individually for each resin in research and development equipment. Therefore, attainment of the stripping limitations in the research and development equipment would not always be possible. The 4.07 m³ (1100 gal) figure was selected as an upper cut-off point because there are no commercial reactors smaller than this.

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

The contents of a reactor can be manually vented to a gasholder or other holding vessel. However, in some cases, such as during severe weather conditions, several reactors may be out of control at one time. There would be insufficient holding capacity under these conditions to manually vent the contents of all the reactors to a gasholder. Therefore, when all other measures to prevent relief valve discharges have been exhausted, manual venting will be permitted as a last resort before the relief valve opens. The same notification procedures are required for manual venting to the atmosphere as are required for relief discharges.

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

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

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

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

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

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

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

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

Section 61.66 of the proposed standard provided for the use of equivalent methods of control which have been approved by EPA. The promulgated standard requires that the plant owner or operator submit a request for determination of equivalency within 30 days of the promulgation date if the alternative control method is intended as the initial means of control. The purpose of this is to provide time for EPA to evaluate the method before the plant has to be in compliance (for existing sources, 90 days after the promulgation date). EPA also suggests that this request for determination of equivalency be accompanied by a request for waiver of compliance pursuant to section 112(c)(1)(B)(ii) of the Act. The request for a waiver for compliance should provide for the case where EPA determines that a method is not equivalent and the plant needs to purchase other equipment. In no case will the waiver of compliance be extended beyond two years from the date of promulgation.

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

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

The requirements for stripping polyvinyl chloride resins to specified levels have been revised in §§ 61.64(e), 61.67(g)(3)(ii), and 61.70(c)(2)(i) so that measurement of the vinyl chloride levels in the resins is to be made immediately after stripping is completed rather than as the resin is being transferred out of the stripper. This allows a plant to carry out operations in a stripper after stripping has been completed but before it is transferred out of the stripper. This is consistent with the original intent of the standard.

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

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

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

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

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

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

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

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

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

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

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

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

The proposed standard required that a semiannual report be submitted every 180 days. The promulgated standard specifies dates for the submittal of the reports. It also specifies that the first semiannual report does not have to be submitted until at least six months after the initial report is submitted.

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

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

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

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

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

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

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

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

AUTHORITY: Section 112 of the Clean Air Act as added by sec. 4(a) of Pub. L. 91-604, 84 Stat. 1685 (42 U.S.C. 1857c-7; Section 114 of the Clean Air Act, as added by sec. 4(a) of Pub. L. 91-604, 84 Stat. 1687, and amended by Pub. L. 93-319, sec. 6(a)(4), 88 Stat. 259 (42 U.S.C. 1857c-9); Section 301(a) of the Clean Air Act, as amended by sec. 15(c)(2) of Pub. L. 91-604, 84 Stat. 1713 (42 U.S.C. 1857g(a)).

Dated: October 12, 1976.

JOHN QUARLES,
Acting Administrator.

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

Subpart F—National Emission Standard for Vinyl Chloride

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

AUTHORITY: Section 112 of the Clean Air Act as added by sec. 4(a) of Pub. L. 91-604, 84 Stat. 1685 (42 U.S.C. 1857c-7); section 114 of the Clean Air Act, as added by sec. 4(a) of Pub. L. 91-604, 84 Stat. 1687, and amended by Pub. L. 93-319, sec. 6(a)(4), 88 Stat. 259 (42 U.S.C. 1857c-9); section 301(a) of the Clean Air Act, as amended by sec. 15(c)(2) of Pub. L. 91-604, 84 Stat. 1713 (42 U.S.C. 1857g(a)).

Subpart F—National Emission Standard for Vinyl Chloride

§ 61.60 Applicability.

(a) This subpart applies to plants which produce:

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

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

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

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

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

§ 61.61 Definitions.

Terms used in this subpart are defined in the Act, in subpart A of this part, or in this section as follows:

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

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

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

(d) "Slip gauge" means a gauge which has a probe that moves through the gas/liquid interface in a storage or transfer vessel and indicates the level of vinyl chloride in the vessel by the physical state of the material the gauge discharges.

(e) "Type of resin" means the broad classification of resin referring to the basic manufacturing process for producing that resin, including, but not limited to, the suspension, dispersion, latex, bulk, and solution processes.

(f) "Grade of resin" means the subdivision of resin classification which describes it as a unique resin, i.e., the most exact description of a resin with no further subdivision.

(g) "Dispersion resin" means a resin manufactured in such away as to form fluid dispersions when dispersed in a plasticizer or plasticizer/diluent mixtures.

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

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

(j) "Inprocess wastewater" means any water which, during manufacturing or processing, comes into direct contact with vinyl chloride or polyvinyl chloride or results from the production or use of any raw material, intermediate product, finished product, by-product, or waste product containing vinyl chloride or polyvinyl chloride but which has not been discharged to a wastewater treatment process or discharged untreated as wastewater.

(k) "Wastewater treatment process" includes any process which modifies

characteristics such as BOD, COD, TSS, and pH, usually for the purpose of meeting effluent guidelines and standards; it does not include any process the purpose of which is to remove vinyl chloride from water to meet requirements of this subpart.

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

(m) "Standard operating procedure" means a formal written procedure officially adopted by the plant owner or operator and available on a routine basis to those persons responsible for carrying out the procedure.

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

(o) "Ethylene dichloride purification" includes any part of the process of ethylene dichloride production which follows ethylene dichloride formation and in which finished ethylene dichloride is produced.

(p) "Vinyl chloride purification" includes any part of the process of vinyl chloride production which follows vinyl chloride formation and in which finished vinyl chloride is produced.

(q) "Reactor" includes any vessel in which vinyl chloride is partially or totally polymerized into polyvinyl chloride.

(r) "Reactor opening loss" means the emissions of vinyl chloride occurring when a reactor is vented to the atmosphere for any purpose other than an emergency relief discharge as defined in § 61.65(a).

(s) "Stripper" includes any vessel in which residual vinyl chloride is removed from polyvinyl chloride resin, except bulk resin, in the slurry form by the use of heat and/or vacuum. In the case of bulk resin, stripper includes any vessel which is used to remove residual vinyl chloride from polyvinyl chloride resin immediately following the polymerization step in the plant process flow.

§ 61.62 Emission standard for ethylene dichloride plants.

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

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

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

§ 61.63 Emission standard for vinyl chloride plants.

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

(a) Vinyl chloride formation and purification: The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from any equipment used in vinyl chloride formation and/or purification is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b)(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 which are opened to the atmosphere after each loading or unloading operation are to be minimized as follows:

(i) After each loading or unloading operation and before opening a loading or unloading line to the atmosphere, the quantity of vinyl chloride in all parts of each loading or unloading line that are to be opened to the atmosphere is to be reduced so that the parts combined contain no greater than 0.0038 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 agitated vessel; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(4) Leakage from relief valves: Vinyl chloride emissions due to leakage from each relief valve on equipment in vinyl chloride service are to be minimized by installing a rupture disk between the equipment and the relief valve, by connecting the relief valve discharge to a process line or recovery system, or equivalent as provided in § 61.66.

(5) Manual venting of gases: Except as provided in § 61.64(a)(3), all gases which are manually vented from equipment in vinyl chloride service are to be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(6) Opening of equipment: Vinyl chloride emissions from opening of equipment (including loading or unloading lines that are not opened to the atmosphere after each loading or unloading operation) are to be minimized as follows:

(i) Before opening any equipment for any reason, the quantity of vinyl 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 5.2.3 of Test Method 106, or

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

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

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

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

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

(i) The concentration of vinyl chloride in each inprocess wastewater stream containing greater than 10 ppm vinyl chloride measured immediately as it leaves a piece of equipment and before being mixed with any other inprocess wastewater stream is to be reduced to no more than 10 ppm by weight before being mixed with any other inprocess wastewater stream which contains less than 10 ppm vinyl chloride; before being exposed to the atmosphere, before being discharged to a wastewater treatment process; or before being discharged untreated as a wastewater. The paragraph does apply to water which is used to displace vinyl chloride from equipment before it is opened to the atmosphere in accordance with § 61.64(a)(2) or paragraph (b)(6) of this section, but does not apply to water which is used to wash out equipment after the equipment has already been opened to the atmosphere in accordance with § 61.64(a)(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 (1250 gal) in volume for which an emission limit is prescribed in § 61.65(b)(6)(i) prior to opening the equipment and using Test Method 106, a portable hydrocarbon detector, or an equivalent or alternative method. The method of measurement is to meet the requirements in § 61.67(g)(5)(i)(A) or (g)(5)(i)(B).

§ 61.66 Equivalent equipment and procedures.

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

§ 61.67 Emission tests.

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

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

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

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

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

(d) Each emission test is to consist of three runs. For the purpose of determining emissions, the average of results of all runs is to apply. The average is to be computed on a time weighted basis.

(e) All samples are to be analyzed within 24 hours, and vinyl chloride emissions are to be determined within 30 days after the emission test. The owner or operator shall report the determinations to the Administrator by a registered letter dispatched before the close of the next business day following the determination.

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

(g) Unless otherwise specified, the owner or operator shall use test Test Methods in Appendix B to this part for each test as required by paragraphs (g)(1), (g)(2), (g)(3), (g)(4), and (g)(5) of this section, unless an equivalent method or an alternative method has been approved by the Administrator. If the Administrator finds reasonable grounds to dispute the results obtained by an equivalent or alternative method, he may require the use of a reference method. If the results of the reference and equivalent or alternative methods do not agree, the results obtained by the reference method prevail, and the Administrator may notify the owner or operator that approval of the method previously considered to be equivalent or alternative is withdrawn.

(i) Test Method 106 is to be used to determine the vinyl chloride emissions from any source for which an emission limit is prescribed in §§ 61.62(a) or (b), § 61.63(a), or §§ 61.64(a)(1), (b), (c), or (d), or from any control system to which reactor emissions are required to be ducted in § 61.64(a)(2) or to which fugitive emissions are required to be ducted in §§ 61.65(b)(1)(ii), (b)(2), (b)(5), (b)(6)(ii), or (b)(9)(ii).

(ii) 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.

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

$$C_{A(\text{corrected})} = C_A \frac{10.9}{20.9 - \text{percent } O_2}$$

where:

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

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

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

10.9 = Percent oxygen in the ambient air at standard conditions, minus the 10 percent oxygen to which the correction is being made.

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

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

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

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

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^{-6} = Conversion factor for ppm.
Z = Production rate (kg/hr).

(2) Test Method 107 is to be used to determine the concentration of vinyl chloride in each inprocess wastewater stream for which an emission limit is prescribed in § 61.65(b)(9)(i).

(3) Where a stripping operation is used to attain the emission limit in § 61.64(e), emissions are to be determined using Test Method 107 as follows:

(i) The number of strippers and samples and the types and grades of resin to be sampled are to be determined by the Administrator for each individual plant at the time of the test based on the plant's operation.

(ii) Each sample is to be taken immediately following the stripping operation.

(iii) The corresponding quantity of material processed by each stripper is to be determined on a dry solids basis and by a method submitted to and approved by the Administrator.

(iv) At the prior request of the Administrator, the owner or operator shall provide duplicates of the samples required in paragraph (g)(3)(i) of this section.

(4) Where control technology other than or in addition to a stripping operation is used to attain the emission limit § 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:

$$C_{BX} = \frac{[C_d\ R\ 10^{-6}]\ [100]}{Z}$$

where:

C_{BX} = kg vinyl chloride/100 kg product.
C_d = the concentration of vinyl chloride as measured by Test Method 107.
R = water flow rate in t/hr, determined in accordance with a method which has been submitted to and approved by the Administrator.
10^{-6} = Conversion factor for ppm.
Z = Production rate (kg/hr), determined in accordance with a method which has been submitted and approved by the Administrator.

(5) The reactor opening loss for which an emission limit is prescribed in § 61.64(a)(2) is to be determined. The number of reactors for which the determination is to be made is to be specified by the Administrator for each individual plant at the time of the determination based on the plant's operation. For a reactor that is also used as a stripper, the determination may be made immediately following the stripping operation.

(i) Except as provided in paragraph (g)(5)(ii) of this section, the reactor opening loss is to be determined using the following equation:

$$C = \frac{W\ (2.60)\ (10^{-6})\ (Cb)}{YZ}$$

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^{-6} = Conversion factor for ppm.
Cb = ppm by volume vinyl chloride as determined by Test Method 106 or a portable hydrocarbon detector which measures hydrocarbons with a sensitivity of at least 10 ppm.
Y = Number of batches since the reactor was last opened to the atmosphere.
Z = Average kg of polyvinyl chloride produced per batch in the number of batches since the reactor was last opened to the atmosphere.

(A) If Method 106 is used to determine the concentration of vinyl chloride (Cb), the sample is to be withdrawn at a constant rate with a probe of sufficient length to reach the vessel bottom from the manhole. Samples are to be taken for 5 minutes within 6 inches of the vessel bottom, 5 minutes near the vessel center, and 5 minutes near the vessel top.

(B) If a portable hydrocarbon detector is used to determine the concentration of vinyl chloride (Cb), a probe of sufficient length to reach the vessel bottom from the manhole is to be used to make the measurements. One measurement will be made within 6 inches of the vessel bottom, one near the vessel center and one near the vessel top. Measurements are to be made at each location until the reading is stabilized. All hydrocarbons measured are to be assumed to be vinyl chloride.

(C) The production rate of polyvinyl chloride (Z) is to be determined by a method submitted to and approved by the Administrator.

(ii) A calculation based on the number of evacuations, the vacuum involved, and the volume of gas in the reactor is hereby approved by the Administrator as an alternative method for determining reactor opening loss for postpolymerization reactors in the manufacture of bulk resins.

§ 61.68 Emisison monitoring.

(a) A vinyle chloride monitoring system is to be used to monitor on a continuous basis the emissions from the sources for which emission limits are prescribed in § 61.62(a) and (b), § 61.63(a), and § 61.64(a)(1); (b), (c), and (d), and for any control system to which reactor emission are required to be ducted in § 61.65(b)(1)(ii), and (b)(2), (b)(5), (b)(6)(ii), and (b)(9)(ii).

(b) The vinyl chloride monitoring system(s) used to meet the requirement in paragraph (a) of this section is to be a device which obtains air sampels from one or more points on a continuous sequential basis and analyzes the samples with gas chromotography or, if the owner or operator assumes that all hydrocarbons measured are vinyl chloride, with infrared spectrophotometry, flame ion detection, or an equivalent or alternative method. The vinyl chloride monitoring system used to meet the requirements in § 61.65(b)(8)(i) may be used to meet the requirements of this section.

(c) A daily span check is to be conducted for each vinyle 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 determined to be equivalent to the emission limit for that source based on the emission test required by § 67.67. The calibration is to be done with either:

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

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

§ 61.69 Initial report.

(a) An owner or operator of any source to which this subpart applies shall submit a statement in writing notifying the Administrator that the equipment and procedural specifications in §§ 61.65(b)(1), (b)(2), (b)(3), (b)(4), (b)(5), (b)(6), (b)(7), and (b)(8) are being implemented.

(b)(1) In the case of an existing source or a new source which has an initial startup date preceding the effective date, the statement is to be submitted within 90 days of the effective date, unless a waiver of compliance is granted under § 61.11, along with the information required under § 61.10. If a waiver of compliance is granted, the statement is to be submitted on a date scheduled by the Administrator.

(2) In the case of a new source which did not have an initial startup date preceding the effective date, the statement is to be submitted within 90 days of the initial startup date.

(c) The statement is to contain the following information:

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

(2) A description of the physical and functional characteristics of each piece of equipment.

(3) A description of the methods which have been incorporated into the standard operating procedures for measuring or calculating the emissions for which emission limits are prescribed in §§ 61.65(b)(1)(i) and (b)(6)(i),

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

§ 61.70 Semiannual report.

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

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.

(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 emisison level prescribed in § 61.64(e), the owner or operator shall include in the report a record of the vinyl chloride content in the polyvinyl chloride resin. Test Method 107 is to be used to determine vinyl chloride content as follows:

(i) If batch stripping is used, one representative sample of polyvinyl chloride resin is to be taken from each batch of each grade of resin immediately following the completion of the stripping, and grade and the date and time the batch is completed. The corresponding quantity of material processed in each stripper batch is to be recorded and identified by resin type and grade and the date and time the batch is completed.

(ii) If continuous stripping is used, one representative sample of polyvinyl chloride resin is to be taken for each grade of resin processed or at intervals of 8 hours for each grade of resin which is being processed, whichever is more frequent. The sample is to be taken as the resin flows out of the stripper and identified by resin type and grade and the date and time the sample was taken. The corresponding quantity of material processed by each stripper over the time period represented by the sample during the eight hour period, is to be recorded and identified by resin type and grade and the date and time it represents.

(iii) The quantity of material processed by the stripper is to be determined on a dry solids basis and by a method submitted to and approved by the Administrator.

(iv) At the prior request of the Administrator, the owner or operator shall provide duplicates of the samples required in paragraphs (c)(2)(i) and (c)(2)(ii) of this section.

(v) The report to the Administrator by the owner or operator is to include the vinyl chloride content found in all the samples required in paragraphs (c)(2)(i) and (c)(2)(ii) of this section, averaged separately for each type of resin, over each calendar day and weighted according to the quantity of each grade of resin processed by the stripper(s) that calendar day, according to the following equation:

$$A_{T_j} = \frac{\sum_{i=1}^{n} P_{a_i} M_{a_i}}{Q_{T_j}} = \frac{P_{a_1} M_{a_1} + P_{a_2} M_{a_2} + \ldots + P_{a_n} M_{a_n}}{Q_{T_j}}$$

A = 24-hour average concentration of type T_j resin in ppm.
Q = Total production of type T_j resin over the 24-hour period, in kg.
T_j = Type of resin; $j = 1, 2, \ldots m$ where m is total number of resin types produced during the 24-hour period.
M = Concentration of vinyl chloride in one sample of grade G_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_n.
n = Total number of grades of resin produced during the 24-hour period.

(vi) The owner or operator shall retain at the source and make available for inspection by the Administrator for a minimum of 2 years records of all data needed to furnish the information required by paragraph (c)(2)(v) of this section: The records are to contain the following information:

(A) The vinyl chloride content found in all the samples required in paragraphs (c)(2)(i) and (c)(2)(ii) of this section, identified by the resin type and grade and the time and date of the sample, and

(B) The corresponding quantity of polyvinyl chloride resin processed by the stripper(s), identified by the resin type and grade and the time and date it represents.

(3) The owner or operator shall include in the report a record of the emissions from each reactor opening for which an emission limit is prescribed in § 61.64(a)(2). Emissions are to be determined in accordance with § 61.67(g)(5), except that emissions for each reactor are to be determined. For a reactor that is also used as a stripper, the determination may be made immediately following the stripping operation.

§ 61.71 Recordkeeping.

(a) The owner or operator of any source to which this subpart applies shall retain the following information at the source and make it available for inspection by the Administrator for a minimum of two years:

(1) A record of the leaks detected by the vinyl chloride monitoring system, as required by § 61.65(b)(8), including the concentrations of vinyl chloride as measured, analyzed, and recorded by the vinyl chloride detector, the location of each measurement and the date and approximate time of each measurement.

(2) A record of the leaks detected during routine monitoring with the portable hydrocarbon detector and the action taken to repair the leaks, as required by § 61.65(b)(8), including a brief statement explaining the location and cause of each leak detected with the portable hydrocarbon detector, the date and time of the leak and any action taken to eliminate that leak measured in accordance with § 61.68.

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

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

METHOD 106—DETERMINATION OF VINYL CHLORIDE FROM STATIONARY SOURCES

INTRODUCTION

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling, as there are many details that are beyond the scope of this presentation. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. Principle and Applicability.

1.1 An integrated bag sample of stack gas containing vinyl chloride (chloroethylene) is subjected to chromatographic analysis, using a flame ionization detector.

1.2 The method is applicable to the measurement of vinyl chloride in stack gases from ethylene dichloride, vinyl chloride and polyvinyl chloride manufacturing processes, except where the vinyl chloride is contained in particulate matter.

2. Range and Sensitivity.

The lower limit of detection will vary according to the chromatograph used. Values reported include 1×10^{-7} mg and 4×10^{-7} mg.

3. Interferences.

Acetaldehyde, which can occur in some vinyl chloride sources, will interfere with the vinyl chloride peak from the Chromosorb 102 column. See sections 4.3.2 and 6.4. If resolution of the vinyl chloride peak is still not satisfactory for a particular sample, then chromatograph parameters can be further altered with prior approval of the Administrator. If alteration of the chromatograph parameters fails to resolve the vinyl chloride peak, then supplemental confirmation of the vinyl chloride peak through an absolute analytical technique, such as mass spectroscopy, must be performed.

4. Apparatus.

4.1 Sampling (Figure 1).

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

to remove particulate matter.

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

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

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

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

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

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

4.2 Sample recovery.

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

4.3 Analysis.

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

4.3.2 Chromatographic column—Stainless steel, 2.0 × 3.2 mm, containing 80/100 mesh Chromosorb 102. A secondary colum of GE SF-96, 20% on 60/80 mesh AW Chromosorb P, stainless steel, 2.0 m × 3.2 mm, will be required if acetaldehyde is present. If used, the SF-96 column is placed after the Chromosorb 102 column. The combined columns should then be operated at 110°C.

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

4.3.4 Gas regulators—For required gas cylinders.

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

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

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

4.4 Calibration.

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

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

4.4.3 Syringe—0.5 ml, gas tight.

4.4.4 Syringe—50μl, gas tight.

4.4.5 Flow meter—Rotameter type, 0 to 1000 ml/min range accurate to ±1%, to meter nitrogen in preparation of standard gas mixtures.

4.4.6 Stop watch—Of known accuracy, to time gas flow in preparation of standard gas mixtures.

5. Reagents. It is necessary that all reagents be of chromatographic grade.

5.1 Analysis.

5.1.1 Helium gas or nitrogen gas—Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen gas—Zero grade.

5.1.3 Oxygen gas, or Air, as required by the detector—Zero grade.

5.2 Calibration.

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

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

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

6. Procedure.

6.1 Sampling. Assemble the sample train as in Figure 106-1. Perform a bag leak check according to Section 7.4. Observe that all connections between the bag and the probe are tight. Place the end of the probe at the centroid of the stack and start the pump with the needle valve adjusted to yield a flow of 0.5 lpm. After a period of time sufficient to purge the line several times has elapsed, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate proportional to the stack velocity. Direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

6.2 Sample storage. Sample bags must be kept out of direct sunlight. When at all possible, analysis is to be performed within 24 hours of sample collection.

6.3 Sample recovery. With a piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to withdraw gas from the bag through the sample loop. Plumb the equipment so the sample gas passes from the sample valve to the leak-free pump, and then to a charcoal tube, followed by a 0–100 ml/min rotameter with flow control valve.

6.4 Analysis. Set the column temperature to 100° C the detector temperature to 150° C, and the sample loop temperature to 70° C. When optimum hydrogen and oxygen flow rates have been determined verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 40 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for thirty seconds at the rate of 100 ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed and the attenuator setting. Record the laboratory pressure. From the chart, select the peak having the retention time corresponding to vinyl chloride, as determined in Section 7.2. Measure the peak area, A_m, by use of H_m, and a disc integrator or a planimeter. Measure the peak height, H_m. Record A_m and the retention time. Repeat the injection at least two times or until two consecutive vinyl chloride peaks do not vary in area more than 5%. The average value for these two areas will be used to compute the bag concentration.

Compare the ratio of H_m to A_m for the vinyl chloride sample with the same ratio for the standard peak which is closest in height. As a guideline, if these ratios differ by more than 10%, the vinyl chloride peak may not be pure (possibly acetaldehyde is present) and the secondary column should be employed (see Section 4.3.2).

6.5 Measure the ambient temperature and barometric pressure near the bag. (Assume the relative humidity to be 100 percent.) From a water saturation vapor pressure table, determine the record and water vapor content of the bag.

7. Calibration and Standards.

7.1 Preparation of vinyl chloride standard gas mixtures. Evacuate a sixteen-inch square Tedlar bag that has passed a leak check (described in Section 7.4) and meter in 5.0 liters of nitrogen. While the bag is filling, use the 0.5 ml syringe to inject 250μl of 99.9 + % vinyl chloride through the wall of the bag. Upon withdrawing the syringe needle, immediately cover the resulting hole with a piece of adhesive tape. This gives a concentration of 50 ppm of vinyl chloride. In a like manner use the other syringe to prepare dilutions having 10 and 5 ppm vinyl chloride concentrations. Place each bag on a smooth surface and alternately depress opposite sides of the bag 50 times to further mix the gases.

7.2 Determination of vinyl chloride retention time. This section can be performed simultaneously with Section 7.3. Establish chromatograph conditions identical with those in Section 6.3, above. Set attenuator to 1 × 1 position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed and the attenuator setting. Record peaks and detector responses that occur in the absence of vinyl chloride. Maintain conditions. With the equipment plumbing arranged identically to Section 6.3, flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the vinyl chloride calibration mixtures and activate the sample valve. Record the injection time. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This quantity, divided by the chart speed, is defined as the retention time. Record.

7.3 Preparation of chromatograph calibration curve. Make a gas chromatographic measurement of each standard gas mixture (described in Section 7.1) using conditions identical with those listed in Section 6.3 above. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with each standard gas mixture and activate the sample valve. Record C_s, the concentrations of vinyl chloride injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate A_s, the peak area multi-

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

... to attenuator setting. Repeat until two injection areas are within 5%, then plot those points vs C_s. When the other concentrations have been plotted, draw a smooth curve through the points. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

7.4 Bag leak checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks as follows. To leak check, connect a water manometer and pressurize the bag to 5–10 cm H_2O (2–4 in H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. Also check the rigid container for leaks in this manner.

(NOTE: An alternative leak check method is to pressurize the bag to 5–10 cm H_2O or 2–4 in. H_2O and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in-line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

8. Calculations.

8.1 Determine the sample peak area as follows:

$$A_s = A_m A_f$$

Equation 106–1

Where:

A_s = The sample peak area.
A_m = The measured peak area.
A_f = The attenuation factor.

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

$$C_b = \frac{C_s P_r T_i}{P_i T_r (1 - B_{ws})}$$

Equation 106–2

Where:

B_{ws} = The water vapor content of the bag sample, as analyzed.
C_b = The concentration of vinyl chloride in the bag sample in ppm.
C_s = The concentration of vinyl chloride indicated by the gas chromatograph, in ppm.
P_r = The reference pressure, the laboratory pressure recorded during calibration, mm Hg.
T_i = The sample loop temperature on the absolute scale at the time of analysis, °K.
P_i = The laboratory pressure at time of analysis, mm Hg.
T_r = The reference temperature, the sample loop temperature recorded during calibration, °K.

9. References.

1. Brown, D. W., Loy, E. W. and Stephenson, M. H. "Vinyl Chloride Monitoring Near the B. F. Goodrich Chemical Company in Louisville, Kentucky." Region IV, U.S. Environmental Protection Agency, Surveillance and Analysis Division, Athens, Georgia, June 24, 1974.

2. "Evaluation of A Collection and Analytical Procedure for Vinyl Chloride in Air," by G. D. Clayton and Associates, December 13, 1974. EPA Contract No. 68-02-1408, Task Order No. 2, EPA Report oN. 75-VCL-1.

3. "Standardization of Stationary Source Emission Method for Vinyl Chloride," by Midwest Research Institute, 1976. EPA Contract No. 68-02-1098, Task Order No. 7.

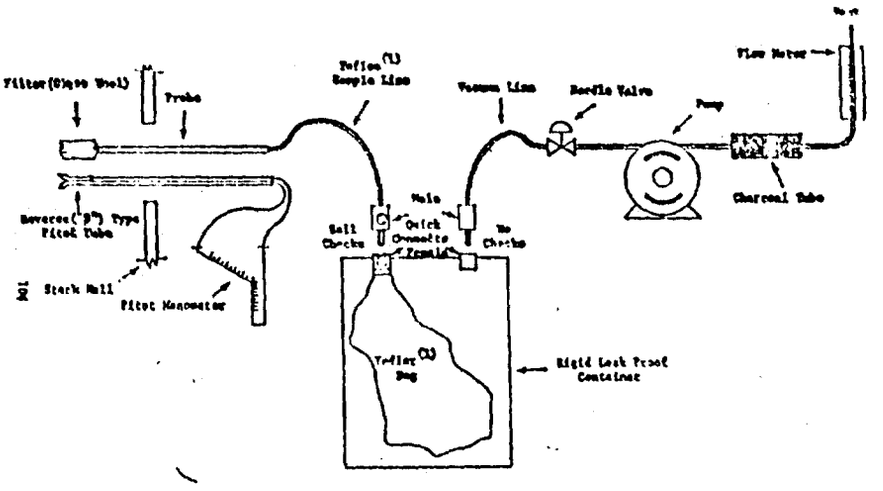

Figure 106-1. Integrated bag sampling train.

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

METHOD 107—DETERMINATION OF VINYL CHLORIDE CONTENT OF INPROCESS WASTEWATER SAMPLES, AND VINYL CHLORIDE CONTENT OF POLYVINYL CHLORIDE RESIN, SLURRY, WET CAKE, AND LATEX SAMPLES

INTRODUCTION

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with sampling, as there are many details that are beyond the scope of this presentation. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. Principle and Applicability.

1.1 The basis for this method relates to the vapor equilibrium which is established between RVCM, PVC, resin, water, and air in a closed system. It has been demonstrated that the RVCM in a PVC resin will equilibrate in a closed vessel quite rapidly, provided that the temperature of the PVC resin is maintained above the glass transition temperature of that specific resin.

1.2 This procedure is suitable for determining the vinyl chloride monomer (VCM) content of inprocess wastewater samples, and the residual vinyl chloride monomer (RVCM) content of polyvinyl chloride (PVC) resins, wet cake, slurry, and latex samples. It cannot be used for polymer in fused form, such as sheet or cubes. If a resolution of the vinyl chloride peak is not satisfactory for a particular sample, then chromatograph parameters may be altered with prior approval of the Administrator. If there is reason to believe that some other hydrocarbon with an identical retention time is present in the sample, then supplemental confirmation of the vinyl chloride peak through an absolute analytical technique, such as mass spectroscopy, should be performed.

2. Range and Sensitivity.

The lower limit of detection of vinyl chloride will vary according to the chromatograph used. Values reported include 1×10^{-4} mg and 4×10^{-4} mg. With proper calibration, the upper limit may be extended as needed.

3. Precision and Reproducibility.

An interlaboratory comparison between seven laboratories of three resin samples, each split into three parts, yielded a standard deviation of 2.63% for a sample with a mean of 2.09 ppm, 4.16% for a sample with a mean of 1.66 ppm, and 5.29% for a sample with a mean of 62.66 ppm.

4. Safety.

Do not release vinyl chloride to the laboratory atmosphere during preparation of standards. Venting or purging with VCM/air mixtures must be held to a minimum. When they are required, the vapor must be routed to outside air. Vinyl chloride, even at low ppm levels, must never be vented inside the laboratory. After vials have been analyzed, the pressure within the vial must be vented prior to removal from the instrument turntable. Vials must be vented into an activated charcoal tube using a hypodermic needle to prevent release of vinyl chloride into the laboratory atmosphere. The charcoal must be replaced prior to vinyl chloride breakthrough.

5. Apparatus.

5.1 Sampling.

5.1.1 Bottles—60 ml (2 oz), with waxed lined screw on tops, for PVC samples.

5.1.2 Vials—50 ml Hypo-vials,[1] sealed with Teflon faced Tuf-Bond discs for water samples.

5.1.3 Electrical tape—or equivalent, to prevent loosening of bottle tops.

5.2 Sample recovery.

5.2.1 Vials—With seals and caps, Perkin-Elmer Corporation No. 105-0118, or equivalent.

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

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

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

0106 or equivalent.

5.3 Analysis.

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

5.3.2 Chromatographic column—Stainless steel, 2 m×3.2 mm, containing 0.4% Carbowax 1500 on Carbopak A, Perkin-Elmer Corporation No. 105-0133, or equivalent. Carbopak C can be used in place of Carbopak

5.3.3 Thermometer—0 to 100° C, accurate to ±0.1° C, Perkin-Elmer No. 105-0109 or equivalent.

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

5.3.5 Septa—Sandwich type, for automatic dosing, 13 mm, Perkin-Elmer No. 105-1008, or equivalent.

5.3.6 Integrator - recorder — Hewlett - Packard Model 3380A, or equivalent.

5.3.7 Filter drier assembly (3)—Perkin-Elmer No. 2230117, or equivalent.

5.3.8 Soap film flowmeter—Hewlett Packard No. 0101-0113, or equivalent.

5.4 Calibration.

5.4.1 Regulators—for required gas cylinders.

6. Reagents.

6.1 Analysis.

6.1.1 Hydrogen gas—zero grade.

6.1.2 Nitrogen gas—zero grade.

6.1.3 Air—zero grade.

6.2 Calibration.

6.2.1 Standard cylinders (4)—one each of 50, 500, 2000, and 4000 ppm vinyl chloride in nitrogen, with certified analysis.

7. Procedure.

7.1 Sampling.

7.1.1 PVC sampling—Allow the resin or slurry to flow from a tap on the tank or silo until the tap line has been well purged. Extend a 60 ml sample bottle under the tap, fill, and immediately tightly cap the bottle. Wrap electrical tape around the cap and bottle to prevent the top from loosening. Place an identifying label on each bottle, and record the date, time, and sample location both on the bottles and in a log book.

7.1.2 Water sampling—Prior to use, the 9 ml vials (without the discs) must be capped with aluminum foil and muffled at 400°C for at least one hour to destroy or remove any organic matter that could interfere with analysis. At the sampling location fill the vials bubble-free, to overflowing so that a convex meniscus forms at the top. The excess water is displaced as the sealing disc is carefully placed, Teflon side down, on the opening of the vial. Place the aluminum seal over the disc and the neck of the vial and crimp into place. Affix an identifying label on the bottle, and record the date, time, and sample location both on the vials and in a log book. All samples must be kept refrigerated until analyzed.

7.2 Sample recovery. Samples must be run within 24 hours.

7.2.1 Resin samples—The weight of the resin used must be between 0.1 and 4.5 grams. An exact weight must be obtained (±0.001 gram) for each sample. In the case of suspension resins a volumetric cup can be prepared which will hold the required amount of sample. The sample bottle is opened, and the cup volume of resin is added to the tared sample vial (including septum and aluminum cap). The vial is immediately sealed and the exact sample weight is then obtained. Report this value on the data sheet as it is required for calculation of RVCM. In the case of relatively dry resin samples (water content <0.3 weight %), 100 µl of distilled water must be injected into the vial, after sealing and weighing, using a 100 µl syringe. In the case of dispersion resins, the cup cannot be used. The sample is instead weighed approximately in an aluminum dish, transferred to the tared vial and weighed accurately in the vial. The sample is then placed in the Perkin-Elmer head space analyzer (or equivalent) and conditioned for one hour at 90°C.

NOTE: Some aluminum vial caps have a center section which must be removed prior to placing into sample tray. If not removed, serious damage to the injection needle will occur.

7.2.2 Suspension resin slurry and wet cake samples—Slurry must be filtered using a small Buchner funnel with vacuum to yield wet cake. The filtering process must be continued only as long as a steady stream of water is exiting from the funnel. Excessive filtration time could result in some loss of VCM. The wet cake sample (0.10 to 4.5 grams) is added to a tared vial (including septum and aluminum cap) and immediately sealed. Sample weight is then determined to 3 decimal places. The sample is then placed in the Perkin-Elmer head space analyzer (or equivalent) and conditioned for one hour at 90°C. A sample of wet cake is used to determine TS (total solids). This is required for calculating the RVCM.

7.2.3 Dispersion resin slurry samples.—This material should not be filtered. Sample must be thoroughly mixed. Using a tared vial (including septum and aluminum cap) add approximately 8 drops (0.25 to 0.35 grams) of slurry or latex using a medicine dropper. This should be done immediately after mixing. Seal the vial as soon as possible. Determine sample weight accurate to 0.001 grams. Total sample weight must not exceed 0.50 grams. Condition the vial for one hour at 90°C in the analyzer. Determine the TS on the slurry sample (Section 7.3.5).

7.2.4 Inprocess wastewater samples—Using a tared vial (including septum and aluminum cap) quickly add approximately 1 cc of water using a medicine dropper. Seal the vial as soon as possible. Determine sample weight accurate to 0.001 gram. Condition the vial for two hours at 90°C in the analyzer.

7.3 Analysis.

7.3.1 Preparation of gas chromatograph—Install the chromatographic column and condition overnight at 150°C. Do not connect the exit end of the column to the detector while conditioning.

7.3.1.1 Flow rate adjustments—Adjust flow rates as follows:

a. Nitrogen carrier gas—Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to 1.3 kg/cm². Normal flows at this pressure should be 25 to 40 cc/minute. Check with bubble flow meter.

b. Burner air supply—Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to supply air to burner at a rate between 250 and 300 cc/minute. Check with bubble flowmeter.

3. Hydrogen supply—Set regulator on cylinder to read 30 psig. Set regulator on chromatograph to supply approximately 35±5 cc/minute. Optimize hydrogen flow to yield the most sensitive detector response without extinguishing the flame. Check flow with bubble meter and record this flow

7.3.1.2 Temperature adjustments—Set temperatures as follows:

a. Oven (chromatographic column), 50° C.

b. Dosing line, 140° C.

c. Injection block, 140° C.

d. Sample chamber, water temperature, 90° C±1.0° C.

7.3.1.3 Ignition of flame ionization detector—Ignite the detector according to the manufacturer's instructions.

7.3.1.4 Amplifier balance—Balance the amplifier according to the manufacturer's instructions.

7.3.2 Programming the chromatograph—Program the chromatograph as follows:

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

b. A—Analysis time—The normal setting is 6 minutes. Certain types of samples contain high boiling materials which can cause interference with the vinyl chloride peak on subsequent analyses. In these cases the analysis time must be adjusted to eliminate the interference. An automated backflush system can also be used to solve this problem.

c. B—Flushing—The normal setting is 0.2 minutes.

d. W—Stabilization time—The nomal setting is 0.2 minutes.

e. X—Number of analyses per sample—The normal setting is 1.

7.3.3 Preparation of sample turntable—Before placing any sample into turntable, be certain that the center section of the aluminum cap has been removed. The numbered sample bottles should be placed in the corresponding numbered positions in the turntable. Insert samples in the following order:

Positions 1 & 2—Old 2000 ppm standards for conditioning. These are necessary only after the analyzer has not been used for 24 hours or longer.

Position 3—50 ppm standard, freshly prepared.

Position 4—500 ppm standard, freshly prepared.

Position 5—2000 ppm standard, freshly prepared.

Position 6—4000 ppm standard, freshly prepared.

Position 7—Sample No. 7 (This is the first sample of the day, but is given as 7 to be consistent with the turntable and the integrator printout.)

After all samples have been positioned, insert the second set of 50, 500, 2000, and 4000 ppm standards. Samples, including standards must be conditioned in the bath of 90° C for 1 hour (not to exceed 5 hours).

7.3.4 Start chromatograph program—When all samples, including standards, have been conditioned at 90° C for 1 hour, start the analysis program according to the manufacturers' instructions. These instructions must be carefully followed when starting and stopping program to prevent damage to the dosing assembly.

7.3.5 Determination of total solids (TS).

For wet cake, slurry, resin solution, and PVC latex samples, determine TS for each sample by accurately weighing approximately 3 to 4 grams of sample in an aluminum pan before and after placing in a draft oven (105 to 110° C). Samples must be dried to constant weight. After first weighing return the pan to the oven for a short period of time and then reweigh to verify complete dryness. TS is then calculated as the final sample weight divided by initial sample weight.

8. Calibration.

Calibration is to be performed each eight-hour period when the instrument is used. Each day, prior to running samples, the column should be conditioned by running two of the previous days 2000 ppm standards.

8.1 Preparation of Standards.

Calibration standards are prepared by filling the vials with the vinyl chloride/nitrogen standards, rapidly seating the septum and sealing with the aluminum cap. Use a stainless steel line from the cylinder to the vial. Do not use rubber or tygon tubing. The sample line from the cylinder must be

[illegible] for several minutes prior to filling vials. After purging, reduce the flow rate to approximately 500–1000 cc/min. Place end of tubing into vial (near bottom) and after one minute slowly remove tubing. Place septum in vial as soon as possible to minimize mixing air with sample. After the standard vials are sealed, inject 100 μl of distilled water.

8.2 Preparation of chromatograph calibration curve.

Prepare two 50 ppm, two 500 ppm, two 2000 ppm, and two 4000 ppm standard samples. Run the calibration samples in exactly the same manner as regular samples. Plot A_s, the integrator area counts for each standard sample vs C_s, the concentration of vinyl chloride in each standard sample. Draw a line of best fit through the points.

9. Calculations.

9.1 Response factor.

From the calibration curve described in Section 8.2, above, select the value of C_s that corresponds to A_s for each sample. Compute the response factor, R_f, for each sample, as follows:

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

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

Calculate C_{vc} as follows:

$$C_{vc} = \frac{A_s P_a}{R_f T_1}\left(\frac{M_v V_v}{m_s R} + K T_1\right)$$

Equation 107-2

where:

C_{vc} = Concentration of vinyl chloride in the sample, in ppm.
P_a = Laboratory atmosphere pressure, mm Hg.
T_1 = Room temperature, °K.
M_v = Molecular weight of VCM (62.5).
V_v = Volume of vapor phase (vial volume less sample volume).
m_s = Weight of sample, grams.
R = Gas constant (62,360).
K = Henry's Law constant for VCM in PVC at 90°C, $K = 6.52 \times 10^{-4} = K_p$ for VCM in 1 cc (approximate) wastewater sample at 90°C, $K = 5.0 \times 10^{-4} = K_w$.
T_2 = Equilibration temperature, °K.

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

1. $T_1 = 22°$ C (295° K).
2. $T_2 = 90°$ C (363° K).
3. $P_a = 750$ mm. Hg.
4. $V_v = V_s - \frac{m_s}{1.4} = 23.5 - \frac{m_s}{1.4}$

where

V_s = Vial volume, cc (23.5).

5. Sample contains less than 0.5% water.

$$C_{vc} = \frac{A_s}{R_f}\left(4.197 \times 10^{-1} + \frac{5.988 \times 10^{-1}}{m_s}\right)$$

Equation 107-3

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

$$C_{vc} = \frac{A_s P_a}{R_f T_1} \times \left[\frac{M_v V_v}{R m_s} + K_p (TS)\, T_1 + K_w (1 - TS)\, T_1\right]$$

Equation 107-4

where:

T_1 = Total solids.

Note: K_w must be determined.

Results calculated using Equation 107-4 represent concentration based on the total sample. To obtain results based on dry PVC content, divide by TS.

For a 1 cc (approximate) wastewater sample, Equation 107-4 can be simplified to the following:

$$C_{vc} = \frac{A_s}{R_f}\left[\frac{5.988 \times 10^{-1}}{m_s} + (2.066 \times 10^{-3})\right]$$

Equation 107-5

10. References.

1. Residual Vinyl Chloride Monomer Content of Polyvinyl Chloride Resins and Wet Cake Samples, B. F. Goodrich Chemical Co. Standard Test Procedure No. 1005-T. B. F. Goodrich Technical Center, Avon Lake, Ohio. January 30, 1975.

2. Berens, A. R., "The Solubility of Vinyl Chloride in Polyvinyl Chloride," ACS-Division of Polymer Chemistry, Polymer Preprints *15* (2): 197, 1974.

3. Berens, A. R., "The Diffusion of Vinyl Chloride in Polyvinyl Chloride," ACS-Division of Polymer Chemistry, Polymer Preprints *15* (2): 203, 1974.

4. Berens, A. R., L. B. Crider, C. J. Tomanek and J. M. Whitney, Analysis for Vinyl Chloride in PVC Powders by Head-Space Gas Chromatography," to be published.

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III. GENERAL FACILITIES FOR COMPLIANCE

The vinyl chloride emission standard, as included in Section II, has a number of specific requirements. The general approach to achieving compliance has been:

1. Containment at the source. Typical of such items would be rupture disks, sample recirculation and double mechanical seals.

2. Collection and combination of all process vents and exhaust gases with final treatment via incineration. This was required by the need to reduce vapor exhaust streams to less than 10 ppm.

3. Collection of in-process wastewater with subsequent vacuum-steam stripping. This was required to achieve the in-process wastewater 10 ppm limitation.

4. Resin slurry steam stripping to a vacuum pump-compressor system to achieve the 400 ppm limitation.

5. Definition of specific operating conditions to achieve compliance on reactor opening loss and equipment opening. Steam purging to a vacuum system is used.

Attached Figure I describes the various specific areas used by the plant to achieve compliance. The lines with arrows indicate the direction of vinyl chloride containing vapor or liquid streams.

IV. SPECIFIC METHODS OF COMPLIANCE

The emission standard required substantial process modifications and development of various operating techniques.

To simplify the discussion of specific modifications and procedures which will be employed to achieve and maintain compliance we have divided the specific process requirements into three types. Sections V, VI and VII contain specifics of each of these types.

Type I -

The standard included requirements for specific physical modifications. The installation of these modifications results in compliance. Such items would include containment of exhaust vents, installation of rupture disks, installation of double mechanical seals, definition of operating procedures, collection of process wastewater, sample recirculation, prevention of relief valve discharges and an in force leak detection and elimination plan. Other than definition of these items, their appropriate installation and periodic inspection to assure proper operation, no other comliance efforts are involved.

Type II -

This type of requirement allows the specification of a specific operating technique with a proof via calculation as a route to indicating compliance. Essentially this involves purging or evacuation calculations to show that the operating method used is satisfactory to assure compliance is being achieved. This type is applicable to:

1) Reactor Opening Loss - Where the operating method used can be shown to purge the reactor vapor space.

2) Unloading Line Discharges During Disconnect - Where the line volume and the final line pressure is used to calculate the loss per disconnect. Thus a specific pressure or less results in achieving compliance.

3) Equipment Opening - Where the vessel volume, the steam purge quantity and time, and the final vessel pressure can be used to show a purging technique at which compliance is achieved.

Type II compliance utilizes theoretical evacuation and purging equations with an appropriate, conservative, efficiency factor to indicate a compliance condition.

IV. SPECIFIC METHODS OF COMPLIANCE (Cont.)

Type III -

This type of requirement demands periodic sampling to show maintenance of compliance. Sampling, analysis and data recording are outlined within the emission standard.

This type includes:

1) Analysis of final vent exhausts to the atmosphere. This must be less than 10 ppm.

2) Analysis of reactor slurry residuals VCM content which must be less than 400 ppm.

3) Analysis of inprocess wastewater which must be less than 10 ppm.

Attached is a Table which describes the type category into which each of the various standard requirements fall.

TABLE 2

SPECIFIC METHODS OF COMPLIANCE

ABERDEEN PVC PLANT

§ ITEM	GENERAL AREA	TYPE I	TYPE II	TYPE III	DOES NOT APPLY
61.64 (a) (1)	Reactor Exhaust to Atmosphere	X			
61.64 (a) (2)	Reactor Opening Loss		X		
61.64 (a) (3)	Manual Vent Valve Discharge	X			
61.64 (b)	Stripper Exhaust To Atmosphere				X
61.64 (c)	Mixing, Weighing, Holding Container Exhausts			X	
61.64 (d)	Monomer Recovery System Exhuasts	X			
61.64 (e) (1) (i)	Dispersion Resin Stripping				X
61.64 (e) (1) (ii)	Suspension Resin Stripping			X	
61.64 (e) (2)	Resin Concentrations When Not Stripping				X
61.65 (a)	Relief Valve Discharge	X			
61.65 (b) (1) (i)	Unloading Line Discharges During Disconnect		X		
61.65 (b) (1) (ii)	Unloading Line Emissions During Evacuation	X			
61.65 (b) (2)	Railcar Slip Gauge Emissions	X			
61.65 (b) (3) (i)	Rotating Pump Seals	X			
61.65 (b) (3) (ii)	Reciprocating Pump Seals	X			
61.65 (b) (3) (iii)	Rotating Compressor Seals	X			
61.65 (b) (3) (iv)	Reciprocating Compressor Seals	X			
61.65 (b) (3) (v)	Agitator Seals	X			
61.65 (b) (4)	Relief Valve Rupture Disks	X			
61.65 (b) (5)	Manual Vent Exhausts	X			
61.65 (b) (6) (i)	Equipment Opening		X		
61.65 (b) (6) (ii)	Equipment Opening Exhaust Gases	X			
61.65 (b) (7)	Sample Recirculation	X			
61.65 (b) (8)	Leak Detection and Elimination	X			
61.65 (b) (9) (i)	Inprocess Wastewater Stripping			X	
61.65 (b) (9) (ii)	Exhausts From Inprocess W.W. Stripping	X			
61.65 (c)	Operating Procedures	X			

V. METHODS OF COMPLIANCE - TYPE I

As previously indicated, Type I systems are physical modifications and/or plant practices which, in themselves, result in achieving compliance. As shown on Table 2 these items are:

1. Collection of reactor, recovery, unloading line, equipment opening, manual vent and wastewater stripping exhaust gases.

2. Installation of pump and compressor and agitator double mechanical seals.

3. Installation of rupture disks under relief valves.

4. Prevention of any but emergency relief valve discharges.

5. Sample recirculation requirements.

6. An in force leak detection and elimination program.

7. Associated operating procedures for each area.

On the following pages each specific area of the compliance is described. The emission sources, method of compliance and compliance procedure is defined.

V. METHODS OF COMPLIANCE - TYPE I

Item: § 61.64 (a) (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).

Problem: The reaction process in Aberdeen utilizes condenser cooling for maintaining reactor temperature control, for resin residual reduction during steam stripping and for reactor vapor space purging for opening loss compliance. The catalyst used generates inert gases such as CO_2. These inerts must be purged from the condenser or they will blanket the tubes and prevent effective cooling for control.

Emission Sources : The emission sources are the eight PVC reactors.

Method of Compliance: Previously these inert gases, with associated vinyl chloride, were vented to the atmosphere directly above the respective reactors. Procedures have now been instituted so the inert gases are vented into the recovery system. This procedure precludes emissions from the reactors and thus results in achieving compliance.

Compliance Procedure : Upon determining a need to vent the condenser of a reactor:

(1) Place mode selector into the "Emergency" position.
(2) Open the reactor condenser valve.
(3) Open the reactor recovery valve.
(4) Observe the recovery system pressure indicator.
(5) When pressure indication exceeds 20 to 30 psig, close the reactor recovery valve and reactor condenser valve.
(6) Return the reactor to the "Polymerization" mode.

V. METHOD OF COMPLIANCE - TYPE I

Item: § 61.64 (a) (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.

Problem: The Aberdeen Plant formerly operated 60, small (2200 gallon), PVC reactors. These small reactors periodically required manual venting to maintain control.

Emission Sources : The sources were the sixty small PVC reactors.

Method Of Compliance: The plant has shut down all of these reactors. They all have been physically removed from the plant. The plant now operates only large reactors. These polymerization reactors employ improved cooling technology which does not require any manual venting.

Compliance Procedure : No manual vent valve emissions occur as no manual venting is required.

V. METHODS OF COMPLIANCE - TYPE I

Item: § 61.64 (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.

Problem: Periodically, inert gases containing vinyl chloride accumulate in the recovery systems. This increases the system pressure and prevents acceptable recovery rates.

Emission Sources : The Plant operates three recovery systems:

(1) Module No. 1 Recovery System
(2) Module No. 2 Recovery System
(3) Emission Recovery System

Method Of Compliance: Vent equalization lines have been installed for each recovery monomer receivers. Thus the pressure buildup can be controlled by venting from these receivers to the vent gas incinerator.

Compliance Procedure : The equalization lines are installed and all valves remain open. No specific procedure is involved.

V. METHODS OF COMPLIANCE - TYPE I

Item: § 61.65 (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.

Problem: As required to meet operating safety codes (ASME & others) equipment in vinyl chloride service are all equipped with appropriate relief valves. Attached Table 3 lists the equipment at Aberdeen in vinyl chloride service with safety relief valves.

Emission Sources : See attached Table 3 for a listing of equipment in vinyl chloride service with safety relief valves.

Method Of Compliance: The relief valves will discharge only in case of an emergency.

Compliance Procedure : None.

TABLE 3

EQUIPMENT IN VINYL CHLORIDE SERVICE WITH SAFETY RELIEF VALVES

ABERDEEN PVC PLANT

Conoco Vess. No.	Description	No. of Relief Valves
43-001	VCM Sphere	2
89-201	East Storage Bullet	2
89-202	West Storage Bullet	2
89-305	Tank Farm K. O. Drum	1
45-731	D-300 Reactor	2
45-732	D-400 Reactor	2
45-734	D-500 Reactor	2
45-735	D-600 Reactor	2
45-011	Middle RVCM Receiver	1
45-012	South RVCM Receiver	1
45-013	Charge Receiver	1
45-027	North K. O. Scrubber	1
45-028	South K. O. Scrubber	1
45-017	North Seal Water Separator	1
45-018	South Seal Water Separator	1
55-008	North RVCM Condenser	1
55-009	South RVCM Condenser	1
45-005	RVCM Collect Tank	1
64-691	RVCM Filter	1
64-008	North Charge Filter	1
64-009	South Charge Filter	1
45-741	D-741 Reactor	2
45-742	D-742 Reactor	2
45-743	D-743 Reactor	2
45-744	D-744 Reactor	2
45-317	East RVCM Receiver	1
89-520	West RVCM Receiver	1
45-745	Charge Receiver	1
45-761	North K. O. Scrubber	1
45-760	South K. O. Scrubber	1
45-763	North Seal Water Separator	1
45-762	South Seal Water Separator	1
45-764	RVCM Collect Tank	1
55-338	East RVCM Condenser	1
55-337	West RVCM Condenser	1
45-026	T-701 Inlet Tank	1
45-308	T-702 Vac, Pump Disch. Tank	1
45-342	T-703 Comp. Discharge Tank	1

V. METHODS OF COMPLIANCE - TYPE I

Item: § 61.65 (b) (1) (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

Problem: To meet the requirement of § 61.65 (b) (1) (i) the line connections from the railcars must be evacuated. The vapors evacuated are required to be contained.

Emission Sources: These would be each of the three lines at each of the unloading spots if containment facilities were not in place.

Method of Compliance: During the evacuation procedure on the unloading lines the vapors are pulled by the emission recovery system. As this system ultimately discharges to the recovered monomer receivers in Module No. 1, any emission would occur at that point. As indicated, this source is directed to the incinerator which reduces the VCM content to less than 10 ppm.

Compliance Procedure: When the unloading of railcars is complete:

1. Turn off and isolate the unloading compressors.
2. Close the valves on the railcars.
3. Close the valves on the unloading lines.
4. Via the local switch, open the actuated valves into the recovery header to the emission recovery system.
5. Observe the line pressure.
6. When line pressure is reduced to the required amount, close the evacuation valves and proceed to disconnect the lines.

V. METHODS OF COMPLIANCE - TYPE I

Item: § 61.65 (b) (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 discharge 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.

Problem: Previously slip gauges were used to determine the liquid level in VCM railcars.

Emission Sources : Vinyl chloride railcars as received by the plant.

Method Of Compliance: All slip gauges have been replaced with totally enclosed, float type, level indicators. These devices are used only during loading of VCM cars, a procedure not applicable at the Aberdeen plant. During unloading, the appearance of vapor in the unloading line sight glass indicates the railcar is empty of liquid vinyl chloride. All three liquid vinyl chloride lines have been equipped with sight glasses to detect the change from liquid to vapor.

Compliance Procedure : As slip gauges are not used in Aberdeen, no specific procedure is involved.

V. METHODS OF COMPLIANCE - TYPE I

Item: § 61.65 (b) (3) (i)

Rotating Pumps: Vinyl chloride emissions from seals on all rotating pumps in vinyl chloride service are to be minimized by installing sealless pumps, pumps with double mechanical seals, or equivalent as provided in § 61.66. If double mechanical seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the pump; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

Problem: The plant has fifteen pumps in vinyl chloride service. All of these pumps are centrifugal, rotating, pumps. Previously, these pumps were equipped with single mechanical seals.

Emission Sources: Attached is a list of rotating pumps in vinyl chloride service (see Table 4).

Method of Compliance: Eleven of the process pumps in vinyl chloride service are located in the Module No. 1 or Module No. 2 reactor areas. These pumps have each been equipped with double mechanical seals. The sealing fluid is high pressure water. This high pressure water insures that any leak of the seal results in water entering the process rather than an emission of vinyl chloride.

The remaining four pumps are located in the vinyl chloride unloading area. These pumps are also equipped with double mechanical seals. The sealing fluid is an oil which is contained in a small reservoir above the pump. Circulation is via Thermosyphon action. The reservoir is vented to a recovery system such that a seal failure does not result in an emission of vinyl chloride.

Compliance Procedure: The seals in question do not require a specific operating procedure. To insure against seal leakage periodic inspections are desirable. The plant has developed an inspection check list which is attached. Inspections with the completion of the check list are done once per week by process engineering personnel.

TABLE 4

CHECKLIST - ROTATING PUMPS IN VINYL CHLORIDE SERVICE

ABERDEEN PVC PLANT

Conoco No.	Description	Seal Fluid	Seal Fluid Press.	Seal Fluid Flow	Seal Fluid Level	Any Leakage
72-217	East Bullet Pump					
72-218	West Bullet Pump					
72-126	North Sphere Pump					
72-270	South Sphere Pump					
72-044	East Charge Pump					
72-045	West Charge Pump					
72-869	RVCM Pump					
72-001	East Col. Tk. Pump					
72-002	West Col. Tk. Pump					
72-876	East Charge Pump					
72-875	West Charge Pump					
72-878	East RVCM Pump					
72-877	West RVCM Pump					
72-884	East Col. Tk. Pump					
72-883	West Col. Tk. Pump					

V. METHODS OF COMPLIANCE -TYPE I

Item: § 61.65 (b) (3) (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.

Problem: The plant does not use reciprocating pumps in vinyl chloride service.

Emission Sources: None

Method of Compliance: None required.

Compliance Procedure: None required.

V. METHODS OF COMPLIANCE - TYPE I

Item: § 61.65 (b) (3) (iii)

Rotating Compressors: 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.

Problem: The plant has thirteen centrifugal, rotating compressors in vinyl chloride service. Previously, these compressors were equipped with single mechanical seals.

Emission Sources: Attached is a list of rotating compressors in vinyl chloride service (see Table 5).

Method of Compliance: All of the rotating compressors in vinyl chloride service are now equipped with double mechanical seals. The sealing fluid is high pressure water. This high pressure water insures that any leak of the seal results in water entering the process rather than an emission of vinyl chloride.

Compliance Procedure: The seals in question do not require a specific operating procedure. To insure against seal leakage, periodic inspections are conducted. A check list for this inspection has been developed and is attached. Inspections are done once per week by process engineering personnel.

TABLE 5

CHECKLIST - ROTATING COMPRESSORS IN VINYL CHLORIDE SERVICE

ABERDEEN PVC PLANT

Conoco No.	Description	Seal Fluid	Seal Fluid Press.	Seal Fluid Flow	Seal Fluid Level	Any Leakage
72-711	East Compressor					
72-712	West Compressor					
72-792	North Compressor					
72-709	East Vac. Pump					
72-710	West Vac. Pump					
72-752	East E.R. Compressor					
72-753	West E.R. Compressor					
72-751	E.R. Vac. Pump					
72-904	Middle Compressor					
72-903	South Compressor					
72-712	North Compressor					
72-902	North Vac. Pump					
72-901	South Vac. Pump					

V. METHODS OF COMPLIANCE - TYPE I

Item: § 61.65 (b) (3) (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.

Problem: The plant utilizes reciprocating compressors for unloading vinyl chloride railcars. These are piston type compressor machines.

Emission Sources: The unloading area contains four reciprocating compressors.

Method of Compliance: The piston type compressors contain packing type seals. The space between the seals essentially vents into the crankcase head. Some of the compressors contain two sets of packing seals while some contain three packing type seals. In any case, leakage through the first, or process side seal, is vented into the crankcase head. The crankcase head is vented into the emission recovery system, thus any leakage through the seals is vented through a control system. As the exhaust gases from the emission recovery system are routed to the recovered monomer receivers in Module No. 1 and these receivers are vented to the incinerator, the regulation requirements are met.

Compliance Procedure: No specific compliance procedure is involved. Periodic operation checks will be made weekly by process engineering personnel.

COMPLIANCE MANUAL

ABERDEEN PVC PLANT

V. METHODS OF COMPLIANCE - TYPE I

Item: § 61.65 (b) (3) (v)

Agitator: Vinyl chloride emissions from seals on all agitators in vinyl chloride service are to be minimized by installing agitators with double mechanical seals, or equivalent as provided in § 61.66. If double mechanical seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the agitated vessel, by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

Problem: Previously, the plant operated as many as 60 small (2200 gallon) PVC polymerization reactors. These reactors were equipped with single mechanical seals on the agitators.

The plant also had larger reactors equipped with double mechanical seals.

Emission Sources: The sources were the 60 small reactors with the single mechanical seals and the large reactors with the double mechanical seals.

Method of Compliance: The plant has shut down all sixty of the small polymerization reactors. These have been removed from the plant and scrapped.

The plant now operates only eight large (18-20,000 gallon) reactors. Each agitator on these reactors is equipped with a double mechanical seal. High pressure sealing fluid is used to insure any leak is into the process rather than emitted to the atmosphere.

Compliance Procedure: The double mechanical seals in question do not require a specific operating procedure. To insure against leakage, periodic inspection is necessary. This inspection is done by operating personnel on each batch on each reactor. An additional inspection is done by engineering personnel once per week. The attached check list is used for the engineering inspection.

TABLE 6

CHECKLIST - AGITATORS IN VINYL CHLORIDE SERVICE

ABERDEEN PVC PLANT

Conoco No.	Description	Seal Fluid	Seal Fluid Press.	Seal Fluid Flow	Seal Fluid Level	Any Leakage?
51-031	D-300 Agitator					
51-032	D-400 Agitator					
51-185	D-500 Agitator					
51-186	D-600 Agitator					
51-101	D-741 Agitator					
51-102	D-742 Agitator					
51-103	D-743 Agitator					
51-104	D-744 Agitator					

V. METHODS OF COMPLIANCE - TYPE I

Item: § 61.65 (b) (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 relief valve discharge to a process line or recovery system, or equivalent as provided in § 61.66.

Problem: Per ASME and other code requirements, pressure vessels in vinyl chloride service are equipped with relief valves.

Emission Sources: The emission sources are the pressure vessels in vinyl chloride service. Attached is Table 7 which lists the vessels subject to this part of the regulation.

Method of Compliance: The vessels listed are equipped with rupture disks located between the equipment of the relief valves. On some equipment, specifically the VCM filters, the discharge of the relief valve is routed back into a pressure vessel.

Compliance Procedure: The rupture disks do not require a specific operating procedure. To insure against malfunctions, periodic inspections are made of all rupture disks in vinyl chloride service. A check list for this inspection has been developed and is attached. The inspections are conducted weekly by process engineering personnel.

TABLE 7

VCM SERVICE SV/RD VESSEL CHECKLIST

ABERDEEN PVC PLANT

Date _____
Inspector _____

Vessel No.			Vessel Design Press.	Vessel Design Temp.	Is Bl. Val. Lock. Open?	R.D. Press. Ga. Read.	R.D. Design Press.	R.D. Design Temp.	Action
I. Area 1 - VCM Unloading Area									
93-001	VCM Sphere No. 1		100	125					
	VCM Sphere No. 2		100	125					
89-201	East Bullet No.1		200	650					
	East Bullet No.2		200	650					
89-202	West Bullet No.1		200	650					
	West Bullet No.2		200	650					
45-305	Tank Farm K.O. Drum		150	366					
II. Area 2 - Module No. 1. PVC Reactors									
45-731	D-300R	RD1	200	200			N.A.		
	D-300R	RD2	200	200			N.A.		
	D-300R	SV	200	200			N.A.		
	D-300C	SV	200	200			N.A.		
45-732	D-400R	RD	200	200			N.A.		
	D-400R	SV	200	200			N.A.		
	D-400C	SV	200	200			N.A.		
45-734	D-500R	RD	200	200			N.A.		
	D-500R	SV	200	200			N.A.		
	D-500C	SV	200	200			N.A.		
45-735	D-600R	RD	200	200			N.A.		
	D-600R	SV	200	200			N.A.		
	D-600C	SV	200	200			N.A.		
III. Area 3 - Module No. 2 PVC Reactors									
45-741	D-701R	RD	200	200			N.A.		
	D-701R	SV	200	200			N.A.		
	D-701C	SV	200	200			N.A.		
45-742	D-702R	RD	200	200			N.A.		
	D-702R	SV	200	200			N.A.		
	D-702C	SV	200	200			N.A.		
45-743	D-703R	RD	200	200			N.A.		
	D-703R	SV	200	200			N.A.		
	D-703C	SV	200	200			N.A.		
45-744	D-704R	RD	200	200			N.A.		
	D-704R	SV	200	200			N.A.		
	D-704C	SV	200	200			N.A.		

TABLE 7 (Contd.)

VCM SERVICE SV/RD VESSEL CHECKLIST

ABERDEEN PVC PLANT

Date _____
Inspector _____

Vessel No.		Vessel Design Press.	Vessel Design Temp.	Is Bl. Val. Lock Open?	R.D. Press. Ga. Read.	R.D. Design Press.	R.D. Design Temp.	Actio
IV. Area 3 - Module No. 1 Charge & Recovery								
45-010	North RVCM Receiv.	150	150					
45-011	Midd. RVCM Receiv.	150	150					
45-012	South RVCM Receiv.	150	150					
45-013	Fresh VCM Receiv.	150	150					
45-027	North K.O. Scrubb.	150	150					
45-028	South K.O. Scrubb.	150	150					
45-017	North Seal Sep.	150	300					
45-018	South Seal Sep.	150	300					
45-005	RVCM Coll. Tank	150	400					
64-691	RVCM Filter	300	650					
64-008	North Chg. Filter	300	150					
64-009	South Chg. Filter	300	150					
45-026	E.R. Inlet Tank	150	350					
45-308	E.R. Inter. Tank	150	140					
45-342	E.R. Outlet Tank	150	140					
55-008	N. RVCM Cond.	150	400					
55-009	S. RVCM Cond.	150	400					
V. Area - Module No. 2 Charge & Recovery								
45-317	East RVCM Receiv.	150	150					
89-520	West RVCM Receiv.	150	150					
45-745	Fresh VCM Receiv.	150	150					
45-761	North K.O. Scrubb.	150	300					
45-760	South K.O. Scrubb.	150	300					
45-763	North Seal Sep.	150	300					
45-762	South Seal Sep.	150	300					
45-764	RVCM Coll. Tank	150	160					
55-338	E. RVCM Cond.	150	400					
55-337	W. RVCM Cond.	150	400					

N.I.S. - Not in service at time of inspection

V. METHODS OF COMPLIANCE - TYPE I

Item: § 61.65 (b) (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.

Problem: Equipment in vinyl chloride service is listed in Table 3.

Emission Sources: If manual venting were to occur, then the emissions sources would be equipment listed in Table 3.

Method of Compliance: Manual venting is prohibited by our operating procedures until equipment has been evacuated or purged as described for compliance in § 61.65 (b) (6) (i).

Compliance Procedure: Vessels are not manually vented until procedures relative to § 61.65 (b) (6) (i). Normal operating procedures do not involve manual venting. Refer to compliance procedures for § 61.65 (b) (6) (i) for details of equipment opening procedures.

V. METHODS OF COMPLIANCE - TYPE I

Item: § 61.65 (b) (6) (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.

Problem: Section § 61.65 (b) (6) (i) calls for reducing the vinyl chloride in equipment in vinyl chloride service to no more than 2.0 percent by volume vinyl chloride.

Emission Souces: Table 3 contains a list of equipment in vinyl chloride service. If emissions were to occur in violation of this part of the regulation, they would occur from equipment listed on Table 3.

Methods of Compliance: Prior to opening any equipment in vinyl chloride service specific evacuation and purging procedures are employed. The procedure results in compliance with § 61.65 (b) (6) (i).

During the procedures, all exhaust gases are routed through one of the three monomer recovery systems. No discharges occur from the vessels themselves.

Any emissions, should they occur, would ultimately be from the recovered monomer receiver in Module No. 1. As emissions from this source are incinerated, this procedure results in compliance with this section of the regulation.

Compliance Procedure: Specific procedures to meet this requirement involve first pulling a vacuum on the designated equipment and then purging for a finite period with steam while the prescribed recovery system continues to pull a vacuum. Specifics of the purging techniques are described under § 61.65 (b) (6) (i) in Section VI.

V. METHODS OF COMPLIANCE - TYPE I

Item: § 61.65 (b) (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.

Problem: The plant does not routinely sample any vinyl chloride streams. We rely upon analyses given to us by our VCM suppliers.

Very infrequent sampling of recovered monomer is possible. A specific evacuation method for the sampling bomb is available for this purpose.

Emission Sources: Not applicable.

Method of Compliance: A connection is available at the inlet to the emission recovery system. Following analysis the sample bomb (container) with the unused portion of the sample is attached to the connection and a vacuum is pulled. This results in recirculating the unused portion of the sample and achieving compliance with the regulation.

Compliance Procedure: For recirculation of ususued portion of sample:

1. Attach container to the connection just south of T-701 in the emission recovery system.
2. Open valves and pull a vacuum and container.
3. Shut valves and disconnect container.

For sampling:

1. Attach container to sampling connection at point.
2. Open valves and fill container. This may take several minutes.
3. Do not purge through container to the atmosphere as this is prohibited.
4. Close valves, disconnect sample container and take it immediately to the laboratory for analysis.

V. METHODS OF COMPLIANCE - TYPE I

Item: § 61.65 (b) (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.

Problem: A leak detection and elimination program must be formalized, approved by the EPA, and implemented to meet the requirement of this section.

Emission Sources: The potential emission sources are the equipment and piping in vinyl chloride service. The applicable plant areas are:

1. Railcar Unloading Area
2. Module No. 1 Reactor Area
3. Module No. 2 Reactor Area
4. Vent Gas Incinerator Area

Methods of Compliance: A formalized "Leak Detection Program" was submitted to the EPA on May 9, 1977. The EPA subsequently reviewed and approved the plan as accceptable. The plan has been in operation since August, 1977.

Compliance Procedure: Refer to Section X which contains the Leak Detection and Elimination program approved by the EPA and in force in the plant.

V. METHODS OF COMPLIANCE - TYPE I

Item: § 61.65 (b) (9) (ii)

Any vinyl chloride removed from the in-process 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.

Problem: Paragraph (b) (9) (i) calls for the stripping of in-process wastewater to 10 ppm. The exhaust gases which accrue from the stripping operation must be contained.

Emission Sources: If no controls were installed, the emissions would be from the wastewater stripping units.

Method of Compliance: The exhaust gases from the in-process wastewater stripping process are ducted into one of three recovery systems. These systems exhaust to the RVCM receivers, any emissions from which are ultimately incinerated.

Compliance Procedure: The in-process wastewater strippers are connected to the recovery systems. The specific procedure employed to strip in-process wastewater is described in Section VII.

V. METHODS OF COMPLIANCE - TYPE I

Item: §§ 61.65 (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 greater than 1250 gallons in volume for which an emission limit is prescribed in § 61.65 (b) (6) (i) prior to opening the equipment and using Test Method 106, a portable hydrocarbon detector or an equivalent or alternative method. The method of measurement is to meet the requirements in § 61.67 (g) (5) (i) (A) or (g) (5) (i) (B).

Problem: Operating procedures need to be defined for:

1) Unloading line disconnect
2) Slip gauges
3) Manual venting of gases
4) Opening of equipment
5) Sample recirculation
6) Leak detection and elimination

Emission Sources: The emission sources would be the vinyl chloride containing equipment involved in these operations.

Method of Compliance: Standard operating procedures are defined. These are indicated in each specific section.

Compliance Procedure: See the procedures described under each particular paragraph.

VI. METHODS OF COMPLIANCE - TYPE II

Type II systems involve the utilization of particular operating procedures which can be shown to achieve compliance. The proof of being in compliance involves the use of the operating procedure and a calculational method which shows the procedure reaches the desired condition. This type of compliance is applicable to three requirements within the standard.

1) Reactor Opening Loss

2) Unloading Line Discharges During Disconnect

3) Equipment Opening

On the following pages is the description of the emission problems, a definition of the operating procedure and an associated calculation showing that the operating proceudre, when used, will result in compliance.

VI. METHODS OF COMPLIANCE - TYPE II

Item: § 61.64 (a) (2)
The reactor opening loss from each reactor is not to exceed 0.02 g. vinyl chloride/Kg (.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.

Problem: Following reactor recovery, the solution is transferred to PVC blend tanks prior to drying. The reactor is rinsed with water. During this rinse, air enters the reactor as it does during dump equalization.

The air which contains some VCM is subsequently removed via steam jet evacuation prior to the next batch being charged. The exhaust from the steam jet constitutes the "reactor opening loss" as it does contain some vinyl chloride.

Emission Sources: The emission sources are the eight PVC reactors in Module No. 1 and Module No. 2. The actual point of emission is the exhaust from the steam jet evacuation discharge.

Method of Compliance: Compliance on this area is an adjunct to reactor steam stripping procedures in use. The plant utilizes reactors for resin slurry stripping thus avoiding emissions from multiple vessels.

Additionally, our reactors are equipped with direct mounted, reflux condensers. This allows refluxing of a considerable volume of vapor through the reactor vapor space.

Steam rates into the reactor and reflux rates at the end of recovery are specifically controlled to insure maximum purge through the vapor space. This purge volume can be calculated to show that the reactor opening condition prescribed by the EPA is being achieved.

Attached is a description of conditions which occur at the end of the recovery process. Purging calculations are also included which on a very conservative basis indicate sufficient purging occurs to meet the reactor opening condition.

As steam vapor is used as the purge media, a serious sample problem exists. As of now we have been totally unable to sample an atmosphere of essentially 100% steam at a slight negative pressure. The method proposed by the EPA is not adaptable to this condition. We are continuing to work with

Method of Compliance: (Cont.) vendors to obtain a device capable of analyzing the atmosphere within the reactor. Upon obtaining a suitable device when one is developed, we are confident we will be able to demonstrate compliance by analytical as well as calculational methods.

Compliance Procedure: The Federal Government requires us to reduce the VCM content of reactor slurry to a 400 ppm level before transfer of the slurry from the reactor to the blend tanks. In addition, we must also meet a requirement for reduction of VCM in the vapor space above the slurry in each reactor.

To meet the requirements of the government we steam strip each reactor batch prior to transfer to the blend tanks. It is most important that we properly and uniformly strip each batch so we can meet the government's requirements.

The following steam stripping procedure is to be used on every batch processed. Any variations in the procedure or any associated problems in the operation of the recovery system should be brought to the attention of the shift supervisor.

Recovery Procedure: (To be precisely followed for all products)

1. Kill reaction at conditions described on product formula sheet.
2. Start compressors and begin recovery.
3. Set temperature set point to 200°F and start steam into the reactor.
4. Wait until vacuum pumps come on.
5. Reset temperature set point to 230°F.
6. When reactor temperature reaches 215°F, turn emergency cooling water on the condenser.
7. Leave both steam and cooling water on during the next 10 minutes and continue recovering.
8. Evacuate dump valve during last five minutes of recovery.
9. Shut off steam, emergency cooling water and recovery system.
10. Dump reactor.
11. Sample slurry 5 to 10 minutes after start of dump.
12. During recovery the back pressure controller is to be set at 6".

REACTOR OPENING LOSS COMPLIANCE

ABERDEEN PVC PLANT

1. The reactor is used as a stripper in our process. Operating procedures result in achieving both the 400 ppm slurry level and reactor opening loss requirements.

2. During the stripping process, the reactor slurry is heated to 200°F and brought to a boiling condition at this temperature. The boiling is induced by the vacuum pump-compressor system. The reactor slurry temperature is subsequently raised to 215°F. During this period, boiling and thus purging of the vapor space continues to occur. While boiling at this point results in purging the vapor space with steam, this factor is not used in the reactor opening loss compliance calculation.

3. When boiling at 215°F is developed, specific operating procedures are used to maximize purging for 10 minutes. These conditions are:

    1. Full reflux cooling on the condenser.
    2. Maximum steam rate into the reactor.

    Steam rates are measured and typically are 17,000 to 23,000 pounds per hour. The base purge calculation rate used is 15,000 pounds per hour which is the lowest steam purge rate ever observed.

4. This base purge rate results in a vapor displacement volume of 67,000 cubic feet per batch. This is the calculated steam vapor emitted from the slurry surface at the operating conditions used.

5. The amount of liquid material in the reactor occupies 70% of total volume. A conservative assumption used in our calculation is that the purge vapor displacement applies to the entire reactor volume rather than the 30% which is the actual vapor space volume.

6. At the initiation of the purging condition at 215°F, the VCM content of the vapor space is probably about 5% or less. Again, for the calculation, a conservative assumption is made that the VCM content is 100%.

7. To determine the total volume of gas flow required to reduce the vapor from 100% to the less than 2500 ppm required, the "Classical Mixing Equation" is used. This equation is:

$$C = C_o e^{-Q/V\ t}$$

    where:

    C = Final vapor concentration (.002500 for 2500 ppm)
    C_o= Initial vapor concentration (1.0 for 100%)
    Q = Flow rate, cubic feet hour
    V = Volume to be purged (2523 cubic feet for Module No. 1 reactors and 2975 cubic feet for Module No. 2 reactors)
    t = Period of time for purging (10 minutes)

8. Resolution of the classical mixing equation yields:

Required Purge Volume In Module No. 1 = 15115 cu. ft.
Required Purge Volume In Module No. 2 = 17823 cu. ft.

9. Even with the various conservative assumptions made in 2, 3, 5, and 6, the actual purge volume is 4.43 or 3.76 greater than required.

10. Specific values related to this calculation are attached.

REACTOR OPENING LOSS CALCULATION DATA

ABERDEEN PVC PLANT

		MODULE NO. 1	MODULE NO. 2
1.	Average VCM Charge Amount, Lbs.	49,500	60,000
2.	Average Batch Conversion, %	80	80
3.	Average PVC Product Per Batch, Lbs.	39,600	48,000
4.	Allowable Emission, Lb./Lb. PVC	.00002	.00002
5.	Allowable Emission, Lb./Batch	0.792	0.960
6.	Allowable Emission, Lb. Mole/Batch	.012672	.015360
7.	Total Reactor Volume, Cu. Ft.	2,523	2,975
8.	Pressure, PSIG	0	0
9.	Temperature, °F	215	215
10.	Reactor Volume, Moles At T & P	5.12835	6.04710
11.	Mole Fraction Allowable Emission	.002471	.002540
12.	Purging Rate, Lb. Steam/Hr.	15,000	15,000
13.	Purging Time, Min.	10	10
14.	Purge Amount, Lbs.	2,500	2,500
15.	Steam Specific Volume, Cu. Ft./Lb.	26.8	26.8
16.	Vapor Purge Volume, Cu. Ft./Batch	67,000	67,000
17.	Req. V. P. Volume Via Classical Mixing Equipment	15,115	17,823
18.	Multiple Of Actual/Required	4.43	3.76

VI. METHODS OF COMPLIANCE - TYPE II

Item: § 61.65 (b) (1) (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 0.13 cu. ft. of vinyl chloride, at standard temperature and pressure.

Problem: The Aberdeen plant unloads vinyl chloride railcars. Unloading is via reciprocating compressors which pressure vapor into the car and thus, liquid out of the railcar. When the liquid is completely unloaded, the reciprocating compressors are reversed. Vapors are pulled off the compressors. To achieve compliance the vapor must be sufficiently removed so that the volume exposed to the atmosphere upon disconnect is within compliance.

Emission Sources: The emission sources are the unloading lines connected at the railcars.

Method of Compliance: The unloading lines are connected to a vacuum system. Upon completion of unloading the railcar valves are shut, the compressors are stopped. The lines are then pulled down via the emission recovery system to a specific vacuum such that compliance is achieved.

Compliance Procedure:

1. When railcar is unloaded, reverse the compressors and pull the cars to a 10 psig pressure.
2. Close valves on railcar.
3. Shutoff and isolate the compressors.
4. Return to railcar and actuated the valves for pull down to the emission recovery system.
5. Wait until pressure is reduced to less than 6.0 inches of vacuum.
6. Close block valve on unloading line. DTH 000115358
7. Shut actuated valve to emission recovery system.
8. Line may now be disconnected.

RAILCAR UNLOADING LINE COMPLIANCE

ABERDEEN PVC PLANT

1. The volume of the unloading hose was determined to be 1.2 gallons or 0.16 cu. ft.

2. To achieve compliance the pressure in the line must be reduced so the 0.16 cu. ft. contains less than 0.13 cu. ft. of vinyl chloride at standard conditions.

3. The required evacuation pressure is

$$P_F = \frac{0.13}{0.16} \times 760$$

$$= 617 \text{ MM Hg}$$
$$= 24.3 \text{ In Hg}$$

4. This is equivalent to a 5.6 in. Hg vacuum.

5. Compliance is achieved if the vacuum in the line is 5.6 in.Hg or more.

DTH 000115359

VI. METHODS OF COMPLIANCE - TYPE II

Item: § 61.65 (b) (6) (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 25 gallons of vinyl chloride, whichever is larger at standard temperature and pressure.

Problem: Periodically equipment must be opened for inspection, repairs or various other maintenance functions. The standard requires purging and/or evacuation to reduce the vinyl chloride content before opening.

Emission Sources: The potential emission sources would be the vessels in vinyl chloride service that could exceed the emission limitation. Attached Table 8 indicates these vessels.

Method of Compliance: Each of the vessels indicated on Table 8 has been equipped with a steam purge line. The line is designed with an orifice which allows purging with steam at a rate of 35 SCFM. These vessels are also tied into the recovery systems.

Upon a maintenance requirement the vessel is first evacuated to a vacuum with the recovery system. Steam is then injected into the vessel at a rate of 35 SCFM. The steam purges these vessels to the recovery system. After a prescribed amount of time the vinyl chloride content is reduced to the appropriate level.

Table 8 indicates the volume of each of the vessels and the required purging time to achieve compliance. Attached also is the calculational method used to determine the purging time needed to achieve compliance.

Compliance Procedure:

1. Isolate the vessel involved from the process by closing the appropriate valves.
2. Line up the vessel to a recovery system.
3. Start recovery system and pull vessel to a vacuum pressure.
4. Open steam line into vessel. Inject steam while continuing to pull with the recovery system.
5. Continue recovering and injecting steam until time required has elapsed.
6. If desired, continue purging for additional time to insure the complete removal of vapors.

Compliance Procedure: (Cont.)

7. Vessel may now be opened.
   a) Shut off steam.
   b) Close line to recovery system.
   c) Equalize pressure to atmosphere.
   d) Open vessel.

8. When opening the tank farm storage vessels or any of the VCM receivers use a portable hydrocarbon detector to measure VCM content upon opening.

TABLE 8
EQUIPMENT OPENING COMPLIANCE
ABERDEEN PVC PLANT

Conoco No.	Description	Volume, Gallons	Required Purging Time	Recommended Purging Time
43-001	VCM Sphere	700,000	2 days 16 hrs.	5 days
89-201	East Storage Bullet	60,000	5 hrs. 25 min.	12 hrs.
89-202	West Storage Bullet	60,000	5 hrs. 25 min.	12 hrs.
89-305	Tank Farm K.O. Drum	456	3 min.	10 min.
45-011	Middle RVCM Receiver	7,390	40 min.	60 min.
45-012	South RVCM Receiver	7,390	40 min.	60 min.
45-013	Charge Receiver	7,390	40 min.	60 min.
45-027	North K.O. Scrubber	590	3 min.	10 min.
45-028	South K.O. Scrubber	590	3 min.	10 min.
45-017	North Seal Water Separator	128	1 min.	10 min.
45-018	South Seal Water Separator	128	1 min.	10 min.
55-008	North RVCM Condenser	124	1 min.	10 min.
55-009	South RVCM Condenser	124	1 min.	10 min.
45-005	RVCM Collect Tank	560	3 min.	10 min.
64-691	RVCM Filter	25	1 min.	10 min.
64-008	North Charge Filter	40	1 min.	10 min.
64-009	South Charge Filter	40	1 min.	10 min.
45-317	East RVCM Receiver	7,390	40 min.	60 min.
89-520	West RVCM Receiver	7,390	40 min.	60 min.
45-745	Charge Receiver	8,000	43 min.	60 min.
45-761	North K.O. Scrubber	700	4 min.	10 min.
45-760	South K.O. Scrubber	700	4 min.	10 min.
45-763	North Seal Water Separator	200	2 min.	10 min.
45-762	South Seal Water Separator	200	2 min.	10 min.
45-764	RVCM Collect Tank	560	3 min.	10 min.
55-338	East RVCM Condenser	124	1 min.	10 min.
55-337	West RVCM Condenser	124	1 min.	10 min.
	RVCM Filter	25	1 min.	10 min.
	North Charge Filter	40	1 min.	10 min.
	South Charge Filter	40	1 min.	10 min.
45-026	T-701 Inlet Tank	566	3 min.	10 min.
45-308	T-702 Vac. Pump Disch. Tank	456	3 min.	10 min.
45-342	T-703 Comp. Discharge Tank	456	3 min.	10 min.

EQUIPMENT OPENING COMPLIANCE

ABERDEEN PVC PLANT

1. The required purging time was determined from the vessel volume, purge flow rate and the initial and final vinyl chloride concentrations.

2. The mixing equation is:

$$C = C_o\, e^{-Q/V\, t}$$

Where:

C = Final vapor concentration (.02 for 2%)
C_o = Initial vapor concentration (1.0 for 100%)
Q = Flow rate, cubic feet hour (2100 SCFH)
V = Volume to be purged
t = Period of time required for purging

3. Consider the RVCM receivers which have a volume of 7390 gallons of 988 cubic feet.

4. Plugging in the values to the mixing equation:

$$.02 = 1.0\, e^{-Q/988\, t}$$

$$-\ln .02 = Q/988\, t$$

$$3.91 = Q/988\, t$$

$$t = \frac{3.91 \times 988}{2100} \times \frac{5\ \text{psig}}{14.7\ \text{psig}} = 0.62 \text{ hours}$$

$$t \cong 40 \text{ minutes}$$

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VII. METHODS OF COMPLIANCE - TYPE III

As indicated previously, this type of compliance demands periodic sampling to show maintenance of compliance. Sampling, analysis and data recording requirements are outlined in the standard.

This type of compliance includes:

1) Analysis of final vent exhausts to the atmosphere. This must be less than 10 ppm.

2) Analysis of reactor slurry residuals VCM content which must be less than 400 ppm.

3) Analysis of inprocess wastewater which must be less than 10 ppm.

On the following pages in the description of the emission problems, is a definition of the operating procedure, sampling method and frequency which are applicable to compliance.

VII. METHODS OF COMPLIANCE - TYPE III

Item: § 61.64 (e)
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 stripping (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).

Problem: Any manual vents, inerts collection, etc. are collected and routed to the recovered VCM receivers in module No. 2. These exhausts are collected from:

Reactors
Manual Vent Valve Discharges
Monomer Recovery System Exhausts
Unloading Lines
Reciprocating Compressor Seals
Rotating Pump Seals
Manual Vent Exhausts
Equipment Opening Exhaust Gases
Sample Recirculation
Inprocess Wastewater Stripping

Eventually these exhausts pressure up the recovered VCM receivers and must be vented off. The concentration of the vent stream as it exits to the atmosphere must be less than 10 ppm to meet the standard requirements.

Emission Sources: The emission source would be the vent stream from the receiver if no further treatment were required. This vent is now directed to the incinerators. Thus the point of emission is now the vent exiting the incinerator.

Method-of Compliance: The receiver vent is first routed to a refrigeration system. The refrigeration system reduces the vinyl chloride content of the vent stream.

The stream then flows to the vent gas incinerator. This incinerator operates at 2200°F. The vinyl chloride is burned in the incinerator, a process which reduces its content to less than 10 ppm.

The vapor stream, following thermal treatment, is routed through a water scrubber to remove HCL and chlorine. It eventually discharges from the vent stack.

Compliance Procedure: The vent gas incinerator is kept in a ready mode at all times. Natural gas is used to keep the equipment ready to receive vinyl chloride. Upon a buildup in pressure in the recovered receivers the operator will:

1. Press "high fire" switch on the control panel.

2. This will slowly begin to vent vapor into the incinerator fire box.

3. The operator will continue to vent in this manner until the pressure drops off.

4. When ready the operator will press the "low fire" button on the control panel.

5. This will slowly decrease the vapor vent gas flow to the incinerator.

INCINERA CRUBBER DATA LOG Date _____

FIRST SHIFT			SECOND SHIFT			THIRD SHIFT		
11: A.M. Temp.		_____ _____	7:00 P.M. Temp.		_____ _____	3:00 A.M. Temp.		_____ _____
Vent Period 1	Start	_____	Vent Period 1	Start	_____	Vent Period 1	Start	_____
	End	_____		End	_____		End	_____
Vent Period 2	Start	_____	Vent Period 2	Start	_____	Vent Period 2	Start	_____
	End	_____		End	_____		End	_____
Vent Period 3	Start	_____	Vent Period 3	Start	_____	Vent Period 3	Start	_____
	End	_____		End	_____		End	_____
Any Alarms?			Any Alarms?			Any Alarms?		
Other Information:			Other Information:			Other Information:		
Operator: _____			Operator: _____			Operator: _____		

OUTSIDE OPERATING CHECK (First Shift)

Local Panel:
- TI-1 (Firebox = 2100-2500) _____
- TI-2 (Firebox = 2100-2500) _____
- TISH-3A (Refractory=2100-2500) _____
- TISH-3B (Refractory=2100-2500) _____
- Alarms? _____

Lower Level:
- TG-1 (Quench Outlet=90-150) _____
- TG-2 (Liquid Outlet=90-150) _____
- PI-1 (Scrub. Press.=1.5 to 7.0") _____
- Other _____

Upper Level:
- FI-1 (N.G. Flow=0-90) _____
- FI-2 (Stm. Flow= 0) _____
- FI-3 (Total H_2O=80-90) _____
- FI-4 (St Scrub. H_2O=50-60) _____

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Operator: _____

VII. METHODS OF COMPLIANCE - TYPE III

Item: § 61.64 (e) (1) (ii)
Sources following the stripper: The following requirements apply to emissions of vinyl chloride to the atmosphere from the combination of all sources following the stripper (or the reactors if the plant has no stripper) in the plant process flow including but not limited to, centrifuges, concentrators, blend tanks, filters, dryers, conveyor air discharges, baggers, storage containers, and improcess wastewater.

In polyvinyl chloride plants using stripping technology to control vinyl chloride emissions, the weighed residual average in all grades of polyvinyl chloride resin processed through the stripping operation on each calender day, measured immediately after the stripping operation is completed, may not exceed 400 ppm for polyvinyl chloride resin averaged separately for each type of resin.

Problem: The Aberdeen Plant produces only one type of resin, this is by the suspension process: The Aberdeen Plant utilizes stripping technology. The reactors are used as the stripping vessels. The standard requires stripping to a level of 400 ppm of less.

Emission Sources: The regulation states the concentration of vinyl chloride in resin as it exits the stripper must be less than 400 ppm.

Method of Compliance: Compliance is achieved through steam stripping in the reactor vessels following completion of reaction. The plant utilizes reactors for resin slurry stripping thus avoiding emissions from multiple vessels.

The reactors are equipped with direct mounted, reflux condensers. This allows refluxing of considerable material which substantially improves stripping efficiency.

Attached is the condidions used for the stripping recovery process.

Compliance Procedure: The Federal Government requires us to reduce the VCM content of reactor slurry to a 400 ppm level before transfer of the slurry from the reactor to the blend tanks. In addition, we must also meet a requirement for reduction of VCM in the vapor space above the slurry in each reactor.

To meet the requirements of the government we steam strip each reactor batch prior to transfer to the blend tanks. It is most important that we properly and uniformly strip each batch so we can meet the government's requirements.

Compliance Procedure: (Cont.) The following steam stripping procedure is to be used on every batch processed. Any variations in the procedure or any associated problems in the operation of the recovery system should be brought to the attention of the shift supervisor.

Recovery Procedure: (To be precisely followed for all products)

1. Kill reaction at conditions described on product formula sheet.
2. Start compressors and begin recovery.
3. Set temperature set point to 200°F and start steam into the reactor.
4. Wait until vacuum pumps come on.
5. Reset temperature set point to 230°F.
6. When reactor temperature reaches 215°F, turn emergency cooling water on the condenser.
7. Leave both steam and cooling water on during the next 10 minutes and continue recovering.
8. Evacuate dump valve during last five minutes of recovery.
9. Shut off steam, emergency cooling water and recovery system.
10. Dump reactor.
11. Sample slurry 5 to 10 minutes after start of dump.
12. During recovery the back pressure controller is to be set at 6".

VII. METHODS OF COMPLIANCE - TYPE III

Item: § 61.65 (b) (9) (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 untreated as a wastewater.

Problem: Water accumulates in the recovery system during the stripping and recovery process. This water collects in the:

K.O. Scrubbers (5)
Seal Water Separators (6)
RVCM Receivers (4)

Additionally water is used for vapor displacement on some equipment. This water is exposed to VCM vapor and, in untreated form, contains in excess of 10 ppm vinyl chloride.

Emission Sources: The process piping allows drainage to one of two process water stripping tanks. These vessels accumulate this water. Periodically the water is steam stripped at a vacuum to a recovery system. The wastewater is then pumped out of the stripper. The emission point is at the discharge of the pump, prior to entering the sewer system.

Method of Compliance: When a sufficient amount of water is collected, the water is steam stripped at a vacuum. The stripping operation reduces the vinyl chloride content to 10 ppm.

Compliance Procedure:

1. Line up tank to recovery system.
2. Start recovery system and pull down to a vacuum.
3. Begin to inject steam at maximum rate.
4. Inject steam at maximum rate to reach a water temperature of 200°F.
5. Continue to inject steam for 45 minutes. Allow temperature to rise to 230°F.
6. With steam injection and recovery continuing, pump out tank.
7. When tank is empty, shut off steam, recovery system and pump.
8. Utilize vapor steam injection on top of tank as a pump assist if needed.
9. Sampling is to be done at pump discharge as is necessary to monitor compliance.

VIII. TESTING METHODS FOR TYPE III

The Emission Standard requires, in some instances, sampling for compliance as well as for on going process emission monitoring. This sampling is specific for:

1. Exhaust emissions to the atmosphere which must be less than 10 ppm.
2. Slurry VCM residual level following stripping, which must be less than 400 ppm.
3. Inprocess wastewater discharge, which must be less than 10 ppm.

A. Sampling Information

1. Exhaust Emissions to the Atmosphere Which Must Be Less Than 10 PPM.

This sample will be obtained from the exhaust stack of the incinerators. Sampling for compliance will be by method 106. Sampling and analysis will be in precise accordance with method 106 as far as we can determine.

Following the emission test for compliance, the plant will conduct emission tests on a periodic basis to assure compliance is being maintained. For such testing we propose the following schedule:

a) Process sampling and analysis via a gas bag sample - 1 per week.

b) Process sampling and analysis via method 106 - 1 per quarter.

2. Slurry VCM Residual Level Following Stripping Which Must Be Less Than 400 PPM.

Following the stripping operation, the reactor product slurry is pumped to the Dryer area. Sampling of this stream will be at the discharge of the transfer pump to the blend tank area.

For compliance testing, three samples of each batch will be obtained. In accordance with the standard, the average value of the three samples will be used to determine compliance. Sampling equipment will be as described in the Federal Register.

The three samples will be taken after 5 minutes, 10 minutes, and 15 minutes after the start of the slurry transfer operation. This will insure the sampling is representative of the batch.

We suggest for compliance testing that a total of eight reactor batches be analyzed, one from each of the plant's reactor-strippers.

A. Sampling Information

2. (Cont.)

Following the testing for compliance verification the plant will conduct further testing on a periodic basis to insure compliance is being maintained. We suggest this be done on three reactor batches per week. Sampling on these three batches will be as discussed above.

3. Inprocess Wastewater Discharge, Which Must Be Less Than 10 PPM.

This sample will be obtained from the discharge of the process wastewater stripper following wastewater stripping. This sample is obtained prior to mixing with other wastewater and entrance into the wastewater treatment system.

For compliance testing we suggest obtaining three samples from each batch stripped, the three samples being obtained to insure a representative analysis. We further suggest a total of six stripping batches be analyzed.

Following the testing for compliance verification, the plant will conduct further testing on a periodic basis to insure compliance is being maintained. We suggest this be done on two stripped batches per week. Sampling will be as discussed above.

B. Analytical Information

1. Method 106

This analysis is applicable to emissions from the vent gas incinerator.

We have reviewed the method described in the Federal Register. To date our analyses have been via gas bag analysis. We are building a sampling device to meet the Federal Register's description. This device will be used for the initial emission testing and periodically thereafter for emission monitoring.

As far as we are able to determine our emission testing for compliance verification will meet all the requirements of method 106 as described in the Federal Register.

2. Method 107

This method is applicable for determining the vinyl chloride content of reactor slurry, and inprocess wastewater.

DETERMINATION OF VINYL CHLORIDE CONTENT OF IN-PROCESS WASTEWATER SAMPLES AND POLYVINYL CHLORIDE SLURRY

SCOPE

This method is designed to measure the residual vinyl chloride (RVCM) in PVC slurry samples and in waste water. It was taken from EPA Method 107.

METHOD OUTLINE

The slurry is filtered and a sample of the wet cake is sealed in a vial (for samples of water transfer 1 gm. to the vial). A separate sample of the wet cake is taken for a % solids measurement. The sample in the vial is heated to 90°C to drive the VCM into the headspace. A sample of the headspace is injected into a chromatograph. The vinyl peak is compared to a standard and the RVCM in ppm by weight is calculated.

APPARATUS

1. Perkin-Elmer F-42 automatic headspace gas chromatograph equipped with a FiD and back flush attachment.
2. Columns - precolumn 1/8" X 24" carbopac analytical 1/8" X 36" Phenylisocyanate/ durapac.
3. Recorder, 1 MV range.
4. Integrator or similar device to measure peak area (SP-4000 Data Processor is used).
5. Oven - Natural draft set at 100°C.
6. Vials and seals for F-42 (PE 105-0118).
7. Seal crimper for above vials.
8. Syringe, 100 µl gas-tight.
9. Thermometer accurate to 0.2° at 90°C.

REAGENTS

1. Vinyl chloride 99+%.
2. Standard Gas Cylinders, 50 ppm, 500 ppm, 5000 ppm. NBS certified gas blends of VCM in nitrogen.
3. Gases for F-42, zero grade air, nitrogen, hydrogen.
4. Nitrogen for VCl blends - 99+% purity.

B. Analytical Information

2. (Cont.)

The plant uses equipment essentially identical to the method described in the Federal Register. There are minor differences in the calculational procedure which have no effect on the calculated result.

Attached is a detailed description of the analysis and a Table 9 which specifically indicates the differences in calculation.

We propose to use this method both for verification of compliance and for ongoing process monitoring.

PROCEDURE

1. The Perkin-Elmer F-42 Chromatograph must be preset to operating conditions to resolve the VCM.

2. The circulating bath temperature should be at 90° ± 0.4°C.

3. Take the slurry sample and filter using vacuum and a buchner funnel for 15 seconds (until the water just quits coming off in a steady stream).

4. Take a preweighed vial and add a plug of the wet cake (about 1.5g). Cap vial and weight back to nearest mg. Put another plug of wet cake into a tared dish and reweigh.

5. Dry the sample in the dish at 100°C for 45 minutes and reweigh.

6. Record in a notebook the sample identification weight, and total solids content of wet cake.

7. Seal the vial containing the sample and put it into the F-42 tray - note its position in the notebook.

8. Prepare 3 standards by filling the vials with the VCM in nitrogen standards and rapidly seating the septum. The first standard is to be 50-60 ppm, the second is 500 ppm, and the third should match the highest reading expected. If gas blends are not available in the range required, then lab blends can be made from nitrogen and pure VCl as per Method 107.

9. The F-42 tray is loaded with the three standards first followed by the samples. The F-42 can be started after 1 hour of equilibration time.

10. For water samples transfer 1 gm. of sample to a pre-weighed vial. Reweigh the vial to nearest mg and seal. Treat as above.

11. Water samples are to be equilibrated for 2 hours rather than one hour. This can be done by being sure the water samples are the last samples in the tray.

CALCULATION

(TS) Solids Fraction = $\frac{\text{dry resin wt.}}{\text{wet resin wt.}}$

Convert the three standards to ppm based on resin using the following equation:

$$C_{RVCM} = A \frac{P}{T_1} \left[\frac{M}{R} \frac{V}{W} + K_p \, (TS) \, T_2 + K_w \, (1\text{-}TS) \, T_2 \right]$$

Where the following values are assumed:

C_{RVCM} = Concentration of VCM on an as is basis in resin or water.

CALCULATION (Cont.)

A = PPM, VCM in Vapor
P = Lab Pressure (760)
T_1 = Lab Temperature (295°K)
V = Volume of Vial (23.0cc)
R = Gas Constant (6.236×10^4)
W = Sample wt. (1.0 g)
TS = Solids Fraction (0.65)
Kp = Henry's Constant for Polymer (6.52×10^{-6})
Kw = Henry's Constant for Water (5.0×10^{-6})
T_2 = Water Bath Temperature (363°K)
M = Mole Weight of VCM (62.5)

SIMPLIFIED FOR CONSTANT FACTORS

$C_{RVCM} = A \times 0.065$ This factor is not altered unless lab temperature changes by more than ± 5°C or lab pressure does not vary more than ± 10mm.

The C_{RVCM} for each standard is calculated and entered in the data processor as the standard concentration. The data processor then does the following calculations using external standard method:

$$R_f = \frac{\text{Area Std.}}{C_{RVCM}}$$

$$\text{PPM, RVCM of (Resin \& Slurry)} = \frac{\text{Area Sample}}{R_f \times (SW \times TS)}$$

Where:

SW = the weight of the wet cake (gm) or water sample

(SW X TS) = Weight of dry resin (gm).

$$\text{PPM, RVCM of water sample} = \frac{\text{Area Sample}}{R_f \times SW}$$

NOTES:

1. The conditions for the F-42 with the specified columns are as follows:

(a)	Injector Temperature	150°C
(b)	Oven Temperature	80
(c)	Detector Temperature	150
(d)	Needle Temperature	150
(e)	Hydrogen Pressure	2.1 ATM
(f)	Air Pressure	2.6
(g)	Foreflush Pressure	1.9
(h)	Backflush Pressure	1.8

(Adjusted to give minimum baseline shift in backflush)

(i)	Dosing Time	3 sec.
(j)	Analysis Time	0.9 min.
(k)	Backflush Time	3.2 min.
(l)	Stabilization Time	2 min.
(m)	Detector Range	1

PREPARED BY: David Stone

APPROVED BY: Robert B. Martin

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TABLE 9

POINTS OF DIFFERENCES BETWEEN

EPA METHOD 107 AND RVCM ANALYSIS

AT ABERDEEN PLANT

EPA METHOD 107

Use 2 M X 3.2 MM column of 0.4% carbowax 1500 on carbopac C or equivalent.

Samples must be run within 24 hours.

Add 100 Nl water to bottle containing standard gas blends.

CALCULATION

Calculate each sample by the following equation:

$$C_{RVCM} = \frac{A\ P}{R\ T_1}\left[\frac{M\ V}{R\ W} + Kp\ (TS)\ T_2 + Kw\ (1-TS)\ T_2\right] / (TS)$$

C_{RVCM} = PPM, VCM in dry resin.

A = Area of VCM Peak

R = Response Factor = $\frac{\text{Area Std.}}{\text{PPM, VCM Vapor Std.}}$

P = Laboratory Pressure

T_1 = Laboratory Temperature

M = Mole Weight of VCM (62.5)

V = Volume of Vial Vapor Space

W = Sample Weight

R = Gas Constant (62,360)

Kp = Henry's Constant Polymer (6.52×10^{-6})

Kw = Henry's Constant Water (5.0×10^{-6})

T_2 = Water Bath Temperature (363°K)

TS = Total Solids

ABERDEEN

Initially used the specified column but found some interference peaks. Changed to a column previously found to resolve the VCM. It is a 1/8" X 36" column packed with durapac - Phenylisocyanate.

Samples are run daily except on weekends. Samples from 7:00 a.m. Friday to 7:00 a.m. Monday are all run on Monday.

Water was tried but no difference could be seen so for labor considerations, the practice was dropped.

CALCULATION

Method was simplified by considering everything constant except area of peak, response factor, sample wt., and total solids. Aberdeen constant values are listed below. The maximum possible error, as a result of these assumption, is ± 3.0% relative.

P = 760

T_1 = 22°C (295°K)

M = 62.5

V = 23.0

R = 62360

Kp = 6.52×10^{-6}

Kw = 5.0×10^{-6}

T_2 = 90°C (363°K)

The equation reduces to:

$$C_{RVCM} = \frac{A \times 0.065}{R \times W \times TS}$$

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The 0.065 constant is not changed unless lab temperature varies by more than ± 5°C and pressure remains within ± 10 mm.

IX. RECORDKEEPING REQUIREMENTS FOR COMPLIANCE

The plant will maintain emission records to insure maintenance of compliance and to enable emissions to be determined.

1. The operating records of each reactor batch including pressure and temperature charts. These will be used to:

   a) Insure operating conditions required for reactor opening loss are being employed.

   b) Insure operating conditions required for slurry stripping are being employed.

   c) Insure that no relief discharges are occurring from the reactors.

2. Emission monitoring results for slurry stripping on the three weekly test batches.

3. Emission monitoring results for inprocess wastewater stripping on the two weekly test batches.

4. Emission monitoring results for the vent gas incinerator exhaust gases.

5. Vent Gas Incinerator Daily operating log sheet.

6. a) Reactor Agitator Seal Check List
   b) Rotating Pump Seal Check List
   c) Rotating Compressor Seal Check List
   d) Vessel Rupture Disk Check List

7. Hydrocarbon Detection results from opening:

   a) VCM Sphere (1)
   b) VCM Bullets (2)
   c) Charge Receivers (2)
   d) RVCM Receivers (4)

   (These vessels exceed 1250 gallons)

8. Leak Detection data as described in Section X.

This information will be kept in an organized fashion and will be available for inspection by the Administrator for a minimum of two years.

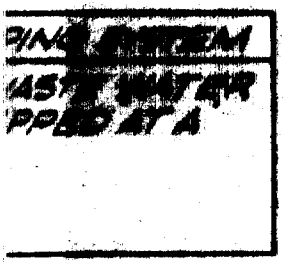
This data will be used for submittal of the semiannual report. We suggest the initial submittal be on March 15, 1979.

X. APPENDIX

Leak Detection and Elimination Plan

This plan was previously submitted to the EPA on May 9, 1977.

OVERSIZE



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ISU	DATE	DESCRIPTION	BY	CKD	A
1	9-1-78	ORIGINAL	CAC		

CONOCO CHEMICALS

ABERDEEN MISSISSIPP

FIGURE I

PVC PLANT

VINYL CHLORIDE EMISSION COMPLIANC

SCALE:

APPD:

DATE:

No.

DTH 000115382

DTH 000115383