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with VC by requiring reasonable control measures. As stated in the preamble to the proposed standard (40 Fr 59532, December 24, 1975), there is no known threshold level of effects for VC. Therefore, the only approach that would eliminate health risks associated with VC would ban its production and use. This approach was not selected. Rather, an approach was selected to minimize the health risks associated with VC by use of reasonable control measure.

On November 19, 1976, the Environmental Defense Fund (EDF) petitioned the United States Court of Appeals for the District of Columbia Circuit to review the standard. On March 24, 1977, the EDF and the EPA moved to dismiss the proceedings on the basis of a settlement agreement requiring the EPA to propose amendments which would require increased efficiency of existing control equipment, require more stringent control of new sources, and prohibit increases in emissions within the vicinity of an existing source due to new construction. The preamble to the proposed amendments was to state that the EPA's policy for regulating carcinogens under Section 112 of the Clean Air Act would include a general goal of eliminating emissions of carcinogens and that the EPA would initiate a review of the VC standard 3 years after the promulgation of the amendments.

On June 2, 1977, the amendments were proposed (42 FR 28154). Many comments pertaining to policy, technological feasibility, and procedural aspects of the proposed amendments were received. Review of these comments indicated that additional technical data and cost information were required before the proposed amendments, or revisions of the proposed amendments, could be promulgated.

Meanwhile, the EDF filed a petition with the EPA requesting the establishment of a comprehensive program for regulating airborne carcinogens under Section 112 of the Clean Air Act. The aspects of the EDF's petition concerning the development of standards under Section 112 were similar to those proposed in the June 2, 1977, amendments to the VC standard. Based on the similarity of the proposed amendments and the EDF's requested comprehensive program for regulating airborne carcinogens, the EPA believed that it should not take final action on the proposed VC amendments until after it had acted on the EDF's petition.

On October 10, 1979 (44 FR 58642), the EPA proposed "Policy and Procedures for Identifying, Assessing, and Regulating Airborne Substances Posing a Risk of Cancer." This proposal addressed several issues which were central to the proposed VC amendments. It also articulated the EPA's conclusion that Section 112 does not express an intent to eliminate totally all risks from emissions of airborne carcinogens. The EPA's selection of the level of control for a hazardous air pollutant emission standard would not be based on a policy that requires zero emissions of carcinogens. This policy is consistent with the basis for other recent actions under Section 112. For example, standards for benzene from coke ovens and leaks from equipment components in benzene service are not based on a zero emissions policy but rather on a reasonable level of control, which considers emissions and health risks.

The EPA believes it is not appropriate to leave the proposed amendments to the VC standard in effect or to promulgate amendments based on the proposed amendments. Therefore, the June 2, 1977, proposal is withdrawn. As described in the following section of this notice, the EPA began a review study to obtain additional technical data and cost information and to determie whether other amendments to the standard are needed. New amendments developed as a result of the review study are proposed in this notice.

Review of VC Standard

Early in 1980 the EPA began a review of the VC standard. The primary purpose of the review was to investigate the adequacy and appropriateness of the standard in light of policy decisions, health studies, control technology developments, and enforcement and compliance experience which have occurred since the standard was first promulgated. The review consisted of a screening study of: (1) Existing and new control technologies, (2) sources not regulated by the standard, and (3) enforcement and compliance experience since promulgation of the standard. Information and data evaluated during this study were obtained through literature searches, plant visits, and interviews with industrial representatives and EPA regional personnel involved in enforcement and surveillance of the VC-emitting industries. The information and data are presented in a document that may be obtained as described in the ADDRESSES section of this preamble. Decisions based on this review are summarized in the next two sections of this preamble.

As another aspect of the review of the VC standard, the EPA's Carcinogen Assessment Group reviewed new health studies that have become available since the standard was promulgated. This review included a study of the estimated carcinogenic strength of VC (the VC unit risk number) and focused on whether this number should be changed to reflect new informaton. Since the current standard was promulgated, new occupational studies have confirmed qualitatively that liver and brain cancer incidence are asociated with population exposure to atmospheric VC. However, none of these new studies have sufficient exposure information to warrant a refinement of the quantitative cancer risk estimate.

Findings and Conclusions of the Review Study

The findings and conclusions of the VC review study are presented in the following subsections. The first subsection discusses the need and basis for the current standard. The second subsection addresses the level of control required by the current standard. The third subsection identifies source categories not covered by the current standard and evaluates the appropriateness of regulating these sources.

(1) Need and Basis for Current Standard

The current VC standard was established based on judgments concerning the costs and benefits of the standard to society. The standard is not designed to eliminate VC exposure risk entirely. Rather, it strikes a balance between public health protection and the cost of that protection. Data (evaluated before the current standard was established) strongly indicate that VC causes or contributes to the development of angiosarcoma, other cancers, and various noncarcinogenic disorders in people with occupational exposure and in animals with experimental exposure to VC. Although no dose-response data are available at the concentrations of VC found in the ambient air, the EPA concluded when the standard was established that any atmospheric concentration of VC poses some public heath risk. To eliminate the risk of VC exposure entirely, a complete prohibition of all VC emissions would be necessary. This would require the closure of the entire industry and result in serious, adverse economic impacts. Furthermore, the EPA concluded at the time the current standard was established that a complete prohibition of all VC emissions would not be desirable or necessary. The EPA

volume of inert substances in the vent stream and, consequently, the cost for supplemental fuel required for incineration. Comments received on this proposed amendment focused primarily on the high expense and large energy requirements associated with the production of oxygen.

The review study identified no control technology for oxychlorination vents at EDC/VC plants that had not been considered during the development of the original standard. Additionally, the EPA reevaluated the cost of retrofit incinerator controls and reached the same conclusion drawn in the development of the original standard. As before, the high cost associated with incinerating oxychlorination vents at existing EDC/VC plants makes this level of control unreasonable. Thus, the current standard of 0.2 g/kg EDC is considered still to be the most reasonable level of control for existing oxychlorination vents. In addition, the review study concluded that significant new construction or modification of EDC/VC plants is not expected. At this time, only one new EDC/VC facility is reportedly planned. (BF Goodrich has plans to construct an EDC/VC facility in Convent, Louisiana.) Oxychlorination vents at new EDC/VC plants will be regulated by the proposed standards of performance for air oxidation processes (40 CFR Part 60 Subpart III) or by the BACT or LAER requirements of new source review regulations applicable in specific locations to a level comparable to that achievable through the use of incineration. Because the technologically achievable level of control is assured through the current requirements, the EPA concluded that investigation of additional control (i.e., incineration) was not required for oxychlorination vents.

Reactor Opening—0.02 g/kg PVC Product. The current VC standard restricts emissions during polymerization reactor openings. The standard was based on reactor purging and on a reduction in the frequency of reactor openings. An increased level of control was not proposed in the 1977 amendments. (The level of control provided by the current standard, 0.02 g/kg of PVC product, reduces VC emissions to about 1.36 Mg per year for a model PVC plant.) During the review of the standard, no technology was identified that would provide additional VC reductions beyond the level of the current standard. Therefore, the EPA is not investigating further the control of reactor openings.

Combined Sources After Resin Stripping. The sources of VC emissions covered under the current standard include blend tanks, dryers, centrifuges, storage silos, bagging operations, and any sources following the stripper. Control of these emissions is based on either stripping the PVC resin to a specified (based on resin type) residual VC level (i.e., 400 ppm for suspension, bulk, solution, and latex resins; and 2,000 ppm for dispersion resins) or controlling the emissions from all sources following the stripper with a control device. The 1977 proposed amendments would have required "new resins" to be stripped to lower levels (i.e., 100 ppm for suspension, bulk, solution, and latex resins; and 500 ppm for dispersion resins). When the amendments were proposed, the EPA believed that some resins could meet the proposed limits; whereas, for other resins the manufacturer would have been required to develop improved stripping technology or not to produce the resin.

Industry comments stated that most dispersion, copolymer, and bulk resins would suffer degradation if more stringent emission limits were imposed. Additionally, the commenters noted the inherent difficulties in defining a "new resin." Information submitted by commenters indicated that minor adjustments to resin compositions are made routinely, and completely new resins are rarely, if ever, made. As a result of these comments, the EPA concluded that it is impossible in many cases to distinguish between new and existing resins and still have any resins covered by the proposed amendments. Further, the proposed amendments did not address what levels of control could be achieved by improved stripping technology. For these reasons, the EPA chose to evaluate whether higher levels of control are achievable for all resins, or only for some special classes of resins.

The review study found that resin stripping technology has improved since the current standard was promulgated, and that some processors can achieve lower resin residual VC levels than those required in the original standard. In certain cases, some resins can meet the more stringent levels specified in the previously proposed amendments. However, other processors manufacturing resins of differing grades and characteristics can only marginally comply with the original standard. Because of the wide variation in resin grades and characteristics, it cannot be concluded that, even though a particular resin made by one company can meet a particular level, any other resin or similar resins produced by another company could also meet that level. Furthermore, in some cases these processors meeting the more stringent limits proposed previously are stripping these resins to this low level to offset emissions from those resins which are more difficult to strip. Without this ability to average the emissions and reductions among resins, these processors might not achieve the current standard. Exempting resin grades known to be difficult to strip is not feasible because these resins cannot readily be defined. For the foregoing reasons, the EPA has concluded that there is no demonstrated level of control which could significantly and consistently reduce residual VC levels in resins to levels below that required by the current standard. Therefore, the EPA is not investigating further the control of the combined sources after stripping.

Equipment Leaks. Because little was known about leak detection and elimination programs for control of equipment leaks from components in VC service, specific requirements for these programs were not included in the current standard. Instead, each plant was required to institute and implement a formalized leak detection and elimination program incorporating both a fixed-point monitor and a portable monitor. Plant-specific programs were subject to approval by the Administrator. Consequently, due to site-specific differences among plants, as well as variations in leak definitions and monitoring practices, differences in control of equipment leaks among the plants have resulted. Since the standard was promulgated, the EPA has obtained more information pertaining to the control of equipment leaks from components in VC service. With the information obtained form the development of other standards, an effective leak detection and repair program based on use of a portable monitor can now be specified for equipment covered by this program. The specific leak detection and repair requirements are discussed in the Administrative Revisions section of this preamble.

Relief Valve Discharge Standard. Sources of VC emissions covered by this standard include discharges from relief valves on pressure vessels, transfer lines, and other equipment in EDC/VC and PVC plants. The standard is based on emission control by a combination of equipment and process modifications, and operational procedures, found in plants during development of the standard. An exact combination of modifications and operational procedures was not specified. Instead, a performance standard (i.e., an emission

transfer lines, and other equipment in EDC/VC and PVC plants. The control techniques considered as the basis of the standard involve a combination of equipment modifications, process modifications, and operational procedures. An exact combination of modifications and operational procedures was not specified in the current standard; rather, a performance standard (i.e., an emission standard) was established because different combinations of the modifications and procedures were expected to be equally effective in controlling relief valve discharges.

Based on 6 years of enforcement and compliance experience, the EPA has concluded that the relief discharge standard has resulted in: (1) Significant reductions in the frequency and quantity of VC discharges from relief valves, (2) significant use of agency resources to evaluate individual discharges for preventability, and (3) uncertainty on the part of producers regarding whether they comply with the standard. Additionally, the EPA learned some of VC and PVC believe that this part of the current standard applies only to discharges through safety relief valves and that discharges through other pressure relief devices, such as rupture disks or manual or automatic vent valves, are not covered. This interpretation is not compatible with the intent behind the current standard. To provide more efficient enforcement by decreasing the burden of individual preventability assessments on the EPA, and to provide a better understanding to plant operators of the goal of the standard, the EPA is proposing to reformat the standard for relief valve discharges and to define the emission points covered by this standard to include appropriately all pressure relief devices. As discussed more completely in the following sections, the EPA is proposing to change the format of the numerical limits in the standard to reflect the number of discharges that occur from those plants complying with the format of the current standard.

The EPA found in the review study that efforts by all EDC/VC and PVC producers to comply with the standard are reflected in their preformance (in terms of size and frequency of discharges) since the standard went into effect. In general, a reduction in the reported frequency and size of relief valve discharges by PVC producers has occurred since 1978. A further decrease in relief valve discharges by the PVC industry occurred between 1980 and 1981. Performance by the EDC/VC industry exhibited a less marked trend of decreased discharges over the compliance period. Following an initial drop in relief valve discharges after the standard went into effect, the frequency and quantity of relief valve discharges by EDC/VC plants have decreased slightly or remained relatively constant.

General Basis for Numerical Limits. In selecting the proposed numerical limits, EPA first evaluated in detail the recent performance (1981 to 1983) of five PVC plants and one EDC/VC plant. These plants were chosen based on discussions with EPA Regional Office personnel and industry and were intended to represent plants with good relief valve discharge records. In general, the EPA's evaluation of these plants indicates that each has adopted the combination of equipment, operational procedures and attitude toward prevention of relief discharges intended by the current standard, and that their resulting performance is consistent with compliance with the current standard. The EPA's evaluation found that a few discharges may continue to occur from some plants that comply with the standard. This observation is consistent with the expectation held by the EPA when the standard was written.

In order to revise the standard in terms of numerical limits representing compliance with the current format of the standard, this evaluation separated PVC and EDC/VC plants. For plants, relief valve discharge performance data were further separated by source (reactor vs. nonreactor) and by resin type The EPA then reviewed the performance of 25 additional PVC plants and 12 additional EDC/VC plants. The EPA reviewed this large set of plants to ensure that the level of performance demonstrated by the evaluated plants could be achieved by all PVC and EDC/VC plants.

The numerical limits presented in the Findings section of this preamble are based on an evaluation of the number of discharges representing the demonstrated performance level associated with compliance with the provisions of the existing standard.

Format for Numerical Limits. The EPA visited the five PVC plants evaluated in detail. As expected, the EPA found differences in the combinations of hardware and operational procedures associated with control of relief valve discharges of each of the plants. Furthermore, no exact relationship was found between the effectiveness of specific hardware items and operational procedures and prevention of discharges. In the EPA's judgment, the various combinations of hardware and operational procedures implemented by each of the plants along with the attitudes adopted toward preventing relief valve discharges represent the types of control measures that the standard intended. In particular, the EPA concluded that the low frequency of discharges by the visited plants was indicative of their degree of effort to prevent relief valve discharges. Consistent with the goal of this proposed revision, the EPA decided that an alternative numerical emission limit based on performance resulting under the current standard could be revised in a format that would be easier to understand by enforcement and industry personnel.

The EPA investigated two basic ways of expressing relief valve discharge performance for PVC plants. One format is based on mass emissions, for example, the pounds of VC discharged per million pounds of PVC produced (lb VC/MM lb PVC). Based on a review of methods used by industry to determine the amount of VC discharged from relief valves, the EPA was unable to identify a sufficiently accurate method for measuring discharge quantities from relief valves. At present, producers are required only to estimate discharge quantities for reporting purposes. Demonstration of compliance with a lb VC/MM lb PVC limit would require producers to measure the amount of VC discharged during an incident. Because a suitable measurement method was not identified, the EPA decided not to redefine relief valve discharge performance by PVC plants in a lb VC/MM lb PVC format.

Another format is based on the frequency (i.e., number per unit time) of discharge from occurrences. No method for measuring the amount of VC discharged from relief valves is needed because only the occurrence of a release is required for this format. The occurrence of a discharge can be determined by monitoring process parameters as well as inspecting relief valve performance reports. Thus, of the two basis ways of expressing relief valve performance that were considered, the EPA selected a format based on the frequency of discharges.

Based on this decision, the EPA then considered how the format would be applied to PVC and EDC/VC plants. At PVC plants, the frequency of discharges from polymerization reactors and associated process equipment may be related to the fact that a batch process is used to produce most types of PVC. For batch PVC production processes, the opportunity for discharges is related to the number of times a new

discharge frequencies indicated that plants with the lowest polymerization batch frequencies typically experience about one discharge in a 12-month period. The EPA concluded that for most plants a 12-month reporting period (rolling every 6-months) was both suitable and appropriate for determining compliance with the proposed numerical limits. For plants producing only a small amount of a particular resin (i.e., low number of polymerization batches), an apparent violation of the standard may result from a single discharge occurrence during a 12-month compliance period as described below.

For a PVC plant producing a single resin type to meet the numerical limit for reactor discharges (i.e., 0.035 discharges/100 batches), it must experience and average of no more than one discharge per 2,858 polymerization batches over the preceding 12-month period. An average reactor discharge frequency exceeding one discharge per 2,858 batches would be a violation of the standard. However, if the plant made less than 2,858 polymerization batches over the 12-month compliance period, a single discharge occurrence would be an apparent violation of the standard (i.e., the discharge frequency per 100 batches would exceed 0.035). Because insufficient batches were made, the reported discharge frequency per 100 batches would not correctly reflect the performance by that plant in comparison to other plants complying with the standard. In rectifying the undue compliance burden posed on plants with small numbers of batches by the discharge/100 batch format and the selected 12-month compliance period, the EPA is proposing to add additional provisions affecting the number of batches used to calculate the discharge frequency. For PVC plants producing less than 2,858 batches of a particular resin, the minimum number of 2,858 batches will be used when determining compliance with the numerical limits.

PVC plants producing more than one resin type must demonstrate compliance separately for reactor discharges occurring from different resin production processes. Only the relief valve discharges and polymerization batches specific to each resin type are considered for determining compliance. However, for determining compliance with the standard for nonreactor discharges, the total number of polymerization batches (regardless of resin type) are counted.

To determine the number of polymerization batches produced for purposes of assessing compliance, the following guidelines apply. A "polymerization batch" consists of each sequence of charging VC and other materials to the reactor, heating reactor, contents, polymerization of reactor contents, and removal (i.e., blowdown) of reactor contents. Any batch that is aborted following charging of VC to the reactor is nonetheless counted as a polymerization batch in assessing compliance. For PVC plants producing bulk resin, a single "polymerization batch" includes both prepolymerization and postpolymerization reactor operations.

Discharge frequency can be recorded in two ways. Discharge frequency can be recorded on the basis of discharge events (involving discharges from one or more relief valves) or on individual relief valve discharges. In most cases, plants currently report discharges individually when they occur from relief valves on separate equipment. However, certain equipment such as polymerization reactors that are equipped with multiple relief valves may experience discharges simultaneously from more than one relief valve. Most plants currently report such multiple discharges from a single piece of equipment as a single discharge. Thus, the performance levels serving as the basis for the numerical limits represent individual discharges and not multiple discharge events except when they occur from a single piece of equipment. For determining compliance with the numerical limits, discharge frequency is to be recorded on the basis of individual discharges except when simultaneous discharges occur from relief valves on the same piece of equipment.

A relief valve discharge in considered to be any venting through a pressure relief device to prevent or relieve an overpressure condition from equipment in VC service that results in emissions of VC directly or indirectly to the atmosphere. In determining whether or not a relief valve discharge results in emissions to the atmosphere, the controlling factor is the ultimate disposition of the gases. Venting to a manifold or header system that ultimately discharges to the atomsphere constitutes a relief valve discharge. If the manifold or header discharges gases through a control device meeting the 10 ppmv VC emission limit, the venting does not constitute a relief valve discharge.

For purposes of reporting compliance status with the limits, plants will be required to calculate their discharge per batch frequencies with sufficient precision to demonstrate that performance is either equal to, below of in excess of the limits. Based on operating history, relief valve discharge performance by certain plants is expected to be much better than the respective limits. For example, some new suspension resin PVC plants produce about 5,000 batches during a 12-month compliance period. One and two discharges at one of these plants during a compliance period would result in a discharge performance of 0.02 and 0.05 discharges per 100 batches, respectively. The second discharge during the compliance period would be a violation of the proposed 0.035 discharges per 100 batches limit despite the fact that the first discharge would result in performance well below the limit. These types of plants were considered in selecting the proposed limits and reporting procedures for relief valve discharges. The result that plants of this type must perform well below the limits in the standard in order to be in compliance is consistent with the proposed limits, which were selected to represent an upper boundary on the number of allowable discharges intended by the standard. The EPA expects that plants using the best technology and procedures should be able to perform better than the proposed limits.

Reporting Requirements. The current standard for relief valve discharges requires producers to report discharges within 10 days of the incident. The EPA is proposing to eliminate the 10 day reporting requirements and to require reporting of all discharges on a quarterly basis. Although compliance is to be determined on a semiannual basis, quarterly reporting of discharges is appropriate because violations of the standard may occur well before the end of the 6-month period. Quarterly reporting notifies enforcement personnel of potential violations and violations that have already occurred prior to the end of the compliance period so that corrective actions can take place sooner following the end of the compliance period. Information to be included in the semiannual report for individual relief valve discharges is to be reduced to include only the date, time, source, cause and estimated amount of each discharge occurrence. The semiannual report will also inlcude information on compliance status.

In addition, plants will now be required to maintain relief valve discharge records for 3 years, because of the potentially significant increase in the time period between a discharge occurrence and reporting of the discharge.

Effective Date of Revision. The current standard as written will remain

detection and repair requirements on effective existing plans.

Leak Detection and Repair Requirements. The EPA established leak detection and repair requirements (40 CFR Part 61 Subpart V) for certain equipment in volatile hazardous air pollutant (VHAP) service on June 6, 1984. These requirements were established in conjunction with the final standard for benzene equipment leaks. The requirements of Subpart V generally apply to pumps, compressors, pressure relief devices, sampling connection systems, open-ended valves or lines, valves, flanges and other connectors, and product accumulator vessels. These requirements reflect the level of control that the EPA considers reasonable for equipment covered by developing standards for VHAP. The EPA is therefore proposing to add VC to the list of substances covered by Subpart V.

Subpart V would substantively affect only valves and flanges in VC service within this industry. All other equipment in VC service are already required by the VC standard to comply with equipment and work practice standards consistent with those in Subpart V. For example, pumps and compressors meeting the dual mechanical seal requirements of the current VC standard will be in compliance with the Subpart V requirements. In addition, the sampling connection systems requirements of Subpart V are essentially the same as the current standard. The use of rupture discs for controlling leaks from pressure relief devices, as required by the VC standard, is consistent with the "no detectable emissions" requirement included in Subpart V. Requirements for controlling leaks from pressure relief devices are described in more detail later in this section. Thus, Subpart V will affect primarily valves and flanges in VC service by requiring a specific monitoring schedule, leak definition and repair provisions.

Compliance with the provisions of Subpart V will be used to determine compliance with the portable monitor leak detection and elimination requirements in the current VC standard (40 CFR 61.65(b)(8)(ii)), and therefore, the current standard is being revised to reflect this change. However, process units within VC and PVC plants in which the percentage of leaking valves is equal to or less than 2.0 percent are considered by the EPA to be effectively controlling VC emissions from leaking valves. For these process units, the existing leak detection and elimination program will continue to be allowed while the percentage of leaking valves is 2.0 percent or less. Any process unit in which the percentage of leaking valves is found to exceed 2.0 percent will be required to comply with the provisions of Subpart V.

The Subpart V requirements for valves are based on a leak detection and repair program that requires (1) monthly monitoring for valves in gas/vapor and light liquid service, (2) an initial attempt at repairing these valves within 5 days after detection of a leak, (3) repair of leaking valves within 15 days after detection of the leak unless repair would require a process unit shutdown, and (4) repair of valves during the next process unit shutdown after repair is delayed until a process unit shutdown. Valves found not to leak for 2 successive months can be monitored quarterly until leaks are detected. Monitoring of equipment to detect leaks is conducted in accordance with Method 21 and a leak is defined as a measured organic concentration equal to or greater than 10,000 parts per million by volume (ppvm). For a complete description of the leak detection and repair requirements, see Subpart V (49 FR 23498, June 6, 1984).

In addition, Subpart V contains standards for other types of equipment (e.g., flanges, and open ended valves or lines). Standards for flanges include monitoring with a portable instrument under prescribed procedures within 5 days of observing evidence of a potential leak by visual, audible or other means. Open-ended valves or lines are required to be capped, blinded or fitted with a second valve. These provisions are not expected to significantly affect producers with these types of equipment in VC service. The equipment and procedures employed as normal practice by these producers or as a result of the current VC standard are expected generally to ensure compliance with Subpart V.

Pressure Relief Devices. The EPA proposed and promulgated the work practices, equipment, design and operational standards in the current standard before explicit legal authority existed in Section 112. These requirements are found in § 61.65(b). In August of 1977, Congress amended Section 112 to allow the use of these requirements. Section 112 of the Clean Air Act requires that an emission standard (i.e., a performance standard) be established for control of a hazardous air pollutant unless, in the judgment of the EPA, it is not feasible to prescribe or enforce such a standard. An emission standard allows for some flexibility in complying with the standard, since any control technique that achieves that standard may be applied. Section 112(e)(2) defines the following conditions under which it is not feasible to prescribe or enforce an emission standard: (1) If the pollutants cannot be emitted through a conveyance designed and constructed to emit or capture the pollutant; or (2) if the application of measurement methodology is not practicable due to technological or economic limitations. Section 112(e)(1) allows that if an emission standard is not feasible to prescribe or endorce, then the EPA may istead promulgate a design, equipment, work practice, or operational standard, or combination thereof.

The EPA has reviewed the design, equipment, work practice and operational requirements contained in the current VC standard. The only sources covered by the current standard with one of the requirements for which a performance standard (i.e., an emission standard) is feasible are pressure relief devices. As discussed below, the EPA is setting a "no detectable emissions" limit for these sources. For the other sources, the EPA is reinstating those requirements as set forth in the current standard.

The EPA selected the use of rupture disks as the basis for the current standard for pressure relief devices. When the integrity of ruptures disks is maintained, equipment leaks through the relief device are eliminated. Rupture disks normally maintain their integrity unless an overpressure occurs. After the occurrence of an overpressure, replacement of the rupture disk once again eliminates equipment leaks of VC through the pressure relief device.

For emission control techniques that eliminate equipment leaks, such as the use of rupture disks, a "no detectable emissions" limit is feasible. An instrument reading of less than 500 parts per million by volume (ppmv) above a background concentration based on Reference Method 21 can be used to indicate whether equipment leaks have been eliminated; that is, that the equipment has "no detectable emissions."

The "no detectable emission" limit would not apply to discharges through the pressure relief device during overpressure relief. (These releases are covered under §§ 61.64(a) and 61.65(a).) The standard would specify, however, that the relief device be returned to a state of "no detectable emissions" within 5 days after such a discharge. The standard would further require an annual test to verify the "no detectable emissions" status of the pressure relief devices and a test after each over

Other. In addition to the revisions described above, a review of the recordkeeping and reporting requirements of the current standard was performed to identify ways to ease recordkeeping and reporting burden on plants and to identify any additional recordkeeping and/or reporting needs. The EPA identified two areas where the reporting burden on plants could be reduced. The current reporting requirements for residual VC monomer specifications and reactor opening measurements require that results of all compliance tests be reported in semiannual reports. The EPA is proposing to allow plants to report only test results that show exceedences of the respective standards. If no exceedences occur, plants will be required to indicate that fact in the semiannual report. This type of exception reporting is currently allowed for demonstration of compliance with the 10 ppmv standard for process vents. The second area is the requirement to report relief valve discharges within 10 days of their occurrence. The EPA is proposing to allow plants to report relief valve discharge occurrences on a quarterly basis rather than within 10 days of their occurrence. Furthermore, the reporting requirements for relief valve discharges have been streamlined by dropping the need to report actions taken and implemented preventive measures for each discharge. Information on the date, time, source, cause and estimated amount of individual relief valve discharge will be included with the semiannual reports along with information on compliance status.

Additional semiannual reporting requirements being added for PVC producers are the number of reactor openings and the design capacity number of polymerization batches for each resin type. This requirement will provide general information to facilitate review of industry-wide compliance status during past reporting periods.

Specific recordkeeping and reporting requirements are included as part of the revisions to the leak detection and repair requirements. The recordkeeping requirements include preparation of an initial log to record equipment component identification, physical tagging of equipment components which leak, and maintaining a record of equipment leaks and repair action. Included in the reporting requirements are the number of equipment leaks and the repair status of leaking components. Depending on the particular leak detection and repair program in place, these requirements may represent an increase or decrease in the overall recordkeeping and reporting currently practiced by individual plants.

The EPA concluded that the current recordkeeping requirements, as specified in 40 CFR 61.71, are still appropriate. However, the EPA is proposing to extend the current recordkeeping requirements for all reporting activities from 2 to 3 years.

The net impact of the revised recordkeeping and reporting requirements proposed by the EPA is estimated to be a decrease in a paperwork burden of about 2.8 person-years.

It should be noted that all Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Section 101(14) hazardous substances such as vinyl chloride are subject to reporting requirements under Section 103(a) of CERCLA. CERCLA requires that persons in charge of vessels or facilities from which hazardous substances have been released in quantities (RQs) immediately notify the National Response Center (NRC) of the release. The toll-free 24-hour telephone number of the NRC is 800-424-8802 and in Washington, D.C. metropolitan area it is (202) 426-2675. (See CERCLA Section 103 and 48 FR 23552, May 25, 1983.)

Vinyl chloride was assigned a statutory 1 pound reportable quantity under Section 101(14) until adjusted by regulation, and is presently undergoing assessment for both chronic toxicity and carcinogenicity. Its RQ will be adjusted pending the outcome of these reviews by the Office of Emergency and Remedial Response. Federally permitted releases under CERCLA (See CERCLA Section 101(1) and 48 FR 23552) are not subject to CERLA notification requirements or liabilities. However, releases of hazardous substances that are not subject to a permit or control regulation must be reported.

Regulatory Flexibility Analysis

The Regulatory Flexibility Act of 1980 requires that adverse effects of all Federal regulations upon small businesses be identified. According to the current guidelines of the Small Business Administration (SBA), a small business that produces or processes VC is one that has 500 employees or less. Currently, none of the existing producers or processors that are affected by the standard are estimated to be small by this definition. Since none of the companies meets the SBA definition of small business, no regulatory flexibility analysis is required. Even if an analysis were required, the proposed administrative revisions do not increase the cost of compliance with the standard.

Public Hearing

If requested, a public hearing will be held to discuss the proposed revisions to the VC standard in accordance with sections 112(b)(1)(B) and 307(d)(5) of the Clean Air Act. Persons wishing to make oral presentations on the proposed revisions should contact the EPA at the address given in the ADDRESSES section of this preamble. Oral presentations will be limited to 15 minutes each. Any member of the public may file a written statement before, during, or within 30 days after the hearing. Written statements should be addressed to the Central Docket Section address given in the ADDRESSES section of this preamble.

A verbatim transcript of the hearing and written statements will be available for public inspection and copying during normal working hours at the EPA's Central Docket Section in Washington, D.C. (see ADDRESSES section of this preamble).

Docket

The docket is an organized and complete file of all the information submitted to or otherwise considered by the EPA in the development of this proposed rulemaking. The principal purposes of the docket are: (1) To allow interested parties to identify and locate documents so that they can effectively participate in the rulemaking process, and (2) to serve as the record in case of judicial review (except for interagency review materials [§ 307(d)(7)(A)]).

Miscellaneous

In accordance with section 117 of the Act, publication of this proposal was preceded by consultation with appropriate advisory committees, independent experts, and Federal departments and agencies. The Administrator will welcome comments on all aspects of the proposed regulation, including health, and economic and technological issues.

The information collection requirements in this proposed rule have been submitted for approval to the Office of Management and Budget (OMB) under the Paperwork Reduction Act of 1980, 44 U.S.C. 3501 *et seq.* Comments on these requirements should be submitted to the Office of Information and Regulatory Affairs of OMB, marked "Attention: Desk Officer for EPA", as well as to the EPA docket described above. The final rule will respond to any OMB or public comments on the information collection requirements.

§ 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 each exhaust gas stream from each reactor is not to exceed 10 ppm (average for 3-hour period or as determined in accordance with § 61.67(g)(1)), except as provided in paragraph (a)(2) of this section and § 61.65(a).

* * * * *

(b) *Stripper.* The concentration of vinyl chloride in each exhaust gas stream from each stripper is not to exceed 10 ppm (average for 3-hour period or as determined in accordance with § 61.67(g)(1)), 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 each exhaust gas stream 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 (average for 3-hour period or as determined in accordance with § 61.67(g)(1)), 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 each exhaust gas stream from each monomer recovery system is not to exceed 10 ppm (average for 3-hour period or as determined in accordance with § 61.67(g)(1)), 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.

* * * * *

4. By revising existing paragraphs § 61.64(a)(2) and by removing (a)(3) as follows:

§ 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:

* * * * *

(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 poly vinyl chloride product, except as provided in paragraphs (f)(1) and (f)(2) of this section, with the product determined on a dry solids basis. This requirement does not apply to prepolymerization reactors in the bulk process. This requirement does apply to postpolymerization reactors in the bulk process, where the product means the gross product of prepolymerization and postpolymerization.

* * * * *

5. By revising paragraph (e) introductory text and adding paragraph (e)(3) to § 61.64 as follows:

§ 61.64 Emission standard for polyvinyl chloride plants.

* * * * *

(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) is 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, except as provided in paragraph (f) of this section:

* * * * *

(3) The provisions of this paragraph apply at all times including when off-specification or other types of resins are made.

6. By adding paragraph (f) to § 61.64 as follows:

§ 61.64 Emission standard for polyvinyl chloride plants

* * * * *

(f) *Reactor used as stripper.* When a nonbulk resin reactor is used as a stripper this paragraph may be applied in lieu of § 61.64 (a)(2) and (e)(1):

(1) The weighted average emissions of vinyl chloride from reactor opening loss and all sources following the reactor used as a stripper from all grades of polyvinyl chloride resin stripped in the reactor on each calendar day may not exceed:

(i) 202 g/kg (0.00202 lb/lb) of polyvinyl chloride product for dispersion polyvinyl chloride resins, excluding latex resins, with the product determined on a dry solids basis.

(ii) 0.42 g/kg (0.00042 lb/lb) of polyvinyl chloride product for all other polyvinyl chloride resins, including latex resins, with the product determined on a dry solids basis.

7. By revising paragraph (a) to § 61.65 as follows:

§ 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 discharges.* (1) Polyvinyl chloride plants (suspension, dispersion, latex, and bulk processes).

(i) *Reactor.* The number of discharges to the atmosphere from relief valves on polyvinyl chloride reactors in vinyl chloride service is not to exceed the following limits except as provided in paragraph (a)(1)(iii) of this section. For all reactors producing suspension resins within a PVC plant, the number of relief valve discharges is not to exceed 0.035 discharges per 100 polymerization batches nor 4 discharges per year. For all reactors producing dispersion and latex resins within a PVC plant, the number of relief valve discharges is not to exceed 0.035 discharges per 100 polymerization batches. For all reactors including prepolymerization and postpolymerization reactors, producing bulk resins within a PVC plant the number of relief valve discharges is not to exceed 0.035 discharges per 100 polymerization batches.

(ii) The number of discharges to the atmosphere from relief valves on equipment (excluding polyvinyl chloride reactors) in vinyl chloride service is not to exceed 0.025 discharges per 100 polymerization batches nor 3 discharges per year except as provided in paragarph (a)(1)(iii) of this section.

(iii) The limits specified in pafagraphs (a)(1)(i) and (a)(1)(ii) of this section may be exceeded when only one relief valve discharge to the atmosphere occurs during the 12-month period preceding the close of the 6-month reporting period.

(2) Polyvinyl chloride plants (solution and other continuous PVC production processes). The number of discharges to the atmosphere from relief valves on all equipment in vinyl chloride service is not to exceed 1 discharge per year.

(3) *Ethylene dichloride and vinyl chloride plants.* The number of discharges to the atmosphere from relief valves on equipment in vinyl chloride service is not to exceed 4 discharges per year.

(4) Each relief valve discharge that contributes to a relief valve discharge frequency in excess of any limit prescribed in paragarphs (a)(1), (a)(2) and (a)(3) of this paragraph constitutes

9. By revising paragraph (b)(4) to § 61.65 as follows:

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

* * * * * *

(b) *Fugitive emission sources.*

* * * * * *

(4) *Leaks from relief valves.* Vinyl chloride emissions due to leaks from each relief valve on equipment in vinyl chloride service shall comply with § 61.242-4 of Subpart V of this part.

* * * * *

10. By revising paragraph (b)(7) of § 61.65 as follows:

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

* * * * * *

(b) *Fugitive emission sources.*

* * * * * *

(7) *Samples.* Unused portions of samples containing at least 10 percent by weight vinyl chloride are to be returned to the process or destroyed in a control device from which the concentration of vinyl chloride in the exhaust gas does not exceed 10 ppm. Sampling techniques are to be such that sample containers in vinyl chloride are purged into a closed process system.

11. By revising paragraphs (b)(8) introductory text, (b)(8)(ii), and (b)(8)(v) to § 61.65 as follows:

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

* * * * * *

(b) *Fugitive emission sources.*

* * * * * *

(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 lead detection and repair program consistent with the provisions of Subpart V of this part. The program is to be implemented within 90 days of the effective date of these regulations, unless a waiver of compliance is granted under § 61.11. Approval of a program will be granted by the Administrator provided he finds:

(i) * * *

(ii) It includes a reliable and accurate portable hydrocarbon detector to be used consistent with the provisions of Subpart V of this part. An owner or operator is exempt from § 61.242-1(d), §§ 61.242-7 (a), (b) and (c), § 61.246 and § 61.247 of Subpart V of this part for any process unit in which the percentage of leaking valves is demonstrated to be equal to or less than 2.0 percent, as determined in accordance with the following:

(A) A performance test as specified in paragraph (b)(8)(ii)(C) of this section shall be conducted initially within 90 days of the effective date of these regulations, annully and at times requested by the Administrator.

(B) For each performance test, a minimum of 200 or 90 percent of the total valves in VOC service (as defined in § 60.481 of Subpart VV of Part 60) within the process unit shall be randomly selected and monitored within 1 week by the methods specified in § 61.245(d) of Subpart V of this part. If an instrument reading of 10,000 ppm or greater is measured, a leak is detected. The leak percentage shall be determined by dividing the number of valves in VOC service for which leaks are detected by the number of tested valves in VOC service.

(C) If a leak is detected, it shall be repaired in accordance with § 61.242-7 (d) and (e) of Subpart V of this part.

(D) The results of the performance test shall be submitted in writing to the Administrator in the first semiannual report following the performance test as part of the reporting requirements of § 61.70.

(E) Any process unit in which the percentage of leaking valves is found to be greater than 2.0 percent must comply with all provisions of Subpart V of this part within 90 days.

* * * * *

(v) It contains a plan of action to be taken when a leak is detected consistent with Subpart V of this part.

12. By revising § 61.66 as follows:

§ 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.

13. By revising paragraph (f) of § 61.67 as follows:

§ 61.67 Emission tests.

* * * * * *

(f) The owner or operator shall retain at the plant and make available, upon request, for inspection by the Administrator, for a minimum of 3 years, records of emission test results and other data needed to determine emissions.

14. By revising paragraphs (g)(3) introductory text, (g)(3)(i), and (g)(3)(iii) of § 61.67 as follows:

§ 61.67 Emission tests.

* * * * * *

(g) * * *

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

(i) The number of strippers (or reactors using as 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) * * *

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

* * * * * *

15. By revising paragraph (g)(5) introductory text and adding paragraph (g)(6) to § 61.67 as follows:

§ 61.67 Emission tests.

* * * * * *

(g) * * *

(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 specified by the Administrator for each individual plant at the time of the determination based on the plant's operation.

* * * * *

(6) For a reactor that is used as a stripper, the emissions of vinyl chloride from reactor opening loss and all sources following the reactor used as a stripper for which an emission limit is prescribed in § 61.64(f) are 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.

(i) For each batch stripped in the reactor, the following measurements are to be made:

(A) The concentration (ppm) of vinyl chloride in resin after stripping, measured according to paragraph (g)(3) of this section;

(B) The reactor vacuum (mm Hg) at end of strip from plant instrument; and

(C) The reactor temperature (°C) at end of strip from plant instrument.

§ 61.70 Reporting.

(a)(1) The owner or operator of any source to which this subpart applies shall submit to the Administrator on September 15 and March 15 of each year a report in writing containing the information required in paragraphs (c), (d) and (e) of this section and on December 15 and June 15 of each year a report in writing containing the information required in paragraph (e) of this section, except as provided in paragraph (a)(2).

(2) In the case of an existing source that submits semiannual reports on an approved fixed schedule other than September 15 and March 15, the approved semiannual reporting schedule shall be used to report the information required in paragraphs (c), (d) and (e) of this section. In addition, the information required in paragraph (e) of this section will be reported exactly 3 months following the semiannual reporting dates.

(3) The first report is to be submitted following the first full 3 month reporting period after the initial report is submitted.

19. By revising paragraph (c)(1) of § 61.70 as follows:

§ 61.70 Reporting.

* * * * *

(c) * * *

(1) The owner or operator shall include in the report a record of the vinyl chloride content of emissions for each 3-hour period during which average emissions are in excess of the emission limits in § 61.62 (a) or (b), § 61.63(a), or § 61.64 (a)(1), (b), (c), or (d), or during which average emissions are in excess of the emission limits specified 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)(i)(ii), (b)(2), (b)(5), (b)(6)(ii), or (b)(9)(ii). If emissions in excess of the emission limits are not detected, the report shall contain a statement that no excess emissions have been detected. The emissions are to be determined in accordance with § 61.68(e).

20. By revising paragraph (c)(2) introductory text, removing paragraphs (c)(2)(iv), revising paragraph (c)(2)(iii) and revising (c)(2)(v) and (c)(2)(vi) introductory text to § 61.70 as follows:

§ 61.70 Reporting.

* * * * *

(c) * * *

(2) In polyvinyl chloride plants for which a stripping operation is used to attain the emission level prescribed in § 61.64(e), the owner or operator shall include in the report a record of the vinyl chloride content in the polyvinyl chloride resin.

(i) * * *

(ii) * * *

(iii) The vinyl chloride content in each sample is to be determined by Test Method 107 as prescribed in § 61.67(g)(3).

(iv) [Reserved]

(v) The report to the Administrator by the owner or operator is to include a record of any 24-hour average resin vinyl chloride concentration, as determined in this paragraph, in excess of the limits prescribed in § 61.64(e). The vinyl chloride content found in each sample required by paragraphs (c)(2)(i) and (c)(2)(ii) of this section shall be averaged separately for each type of resin, over each calendar day and weighted according to the quantity of each grade of resin processed by the stripper(s) that calendar day, according to the following equation:

$$A_{T_i}=\frac{\sum_{j=1}^{n} P_{G_j} M_{G_j}}{Q_{T_i}}=\frac{P_{G_1} M_{G_1}+P_{G_2} M_{G_2}+\cdots+P_{G_n} M_{G_n}}{Q_{T_i}} \quad (1)$$

where:

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

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

T_i = Type of resin: $i=1,2 \ldots m$ 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_j resin, in ppm.

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

G_j = Grade of resin: e.g., G_1, G_2, and G_3.

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

If no 24-hour average resin vinyl chloride concentrations in excess of the limits prescribed in § 61.64(e) are measured, the report shall state that no excess resin vinyl chloride concentrations were measured.

(vi) The owner or operator shall retain at the source and make available for inspection by the Administrator for a minimum of 3 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) * * *

(B) * * *

* * * * * * *

21. By revising paragraph (c)(3) of § 61.70 as follows:

§ 61.70 Reporting.

* * * * *

(C) * * *

(3) The owner or operator shall include in the report a record of any emissions from each reactor opening in excess of the emission limits prescribed in § 61.64(e)(2). Emissions are to be determined in accordance with § 61.67(g)(5), except that emissions for each reactor are to be determined. If emissions in excess of the emission limits are not detected, the report shall include a statement that excess emissions have not been detected.

* * * * *

22. By adding paragraph (c)(4) to § 61.70 as follows:

§ 61.70 Reporting

* * * * *

(c) * * *

(4) In polyvinyl chloride plants for which stripping in the reactor is used to attain the emission level prescribed in § 61.64(f), the owner or operator shall include in the report a record of the vinyl chloride emissions from reactor opening loss and all sources following the reactor used as a stripper.

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

(ii) The vinyl chloride content in each sample is to be determined by Test Method 107 as prescribed in § 61.67(g)(3).

(iii) The combined emission from reactor opening loss and all sources following the reactor used as a stripper are to be determined for each batch stripped in a reactor according to the procedure prescribed in § 61.67(g)(8).

(iv) The report to the Administrator by the owner or operator is to include a record of any 24-hour average combined reactor opening loss and emissions from all sources following the reactor used as a stripper as determined in this paragraph, in excess of the limits prescribed in § 61.64(f). The combined reactor opening loss and emissions from

initially and remain unchanged unless significant changes to the design capacity occur.

24. By revising paragraph (a) introductory text of § 61.71 as follows:

§ 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 3 years:

* * * * *

25. By adding the words "vinyl chloride" to the definition of the term "volatile hazardous air pollutants" in § 61.241 of Subpart V as follows:

§ 61.241 Definitions.

* * * * *

"Volatile hazardous air pollutant" or "VHAP" means a substance regulated under this part for which a standard for equipment leaks of the substance has been proposed and promulgated. Benzene is a VHAP. Vinyl chloride is a VHAP.

(Sec. 112 Clean Air Act of 1976)

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Current Developments

Litigation

D.C. CIRCUIT REJECTS VINYL CHLORIDE RULE, BUT ACCEPTS USE OF COST IN AIR ACT STANDARDS

In setting standards for hazardous emissions from industrial sources, the Environmental Protection Agency must base its review primarily on health concerns, but the agency can also consider cost and technological feasibility in setting emission limits, an 11-judge panel of the U.S. Court of Appeals for the District of Columbia Circuit ruled July 28.

However, the agency's use of cost and feasibility constraints in withdrawing a 1977 proposed standard for vinyl chloride emissions was improper under the Clean Air Act, according to the D.C. Circuit. The agency improperly substituted technological limitations for health concerns as the primary consideration in withdrawing the proposal, the appeals court said (*NRDC v. EPA*, CADC, No. 85-1150).

The en banc panel vacated a November 1986 holding by a three-judge panel of the court that allowed EPA to withdraw vinyl chloride standards to consider whether they imposed "unreasonable" regulatory costs (CADC, 25 ERC 1105; Current Developments, Nov. 14, 1986, p. 1169).

EPA originally issued the standard in 1976, requiring emission reductions of 95 percent, but the agency opted to propose stricter standards in 1977 in response to litigation over the rules. In 1985, EPA withdrew the proposal, citing concern that no control technology was demonstrated that could reduce emissions below the 1976 standards. The Natural Resources Defense Council challenged the action.

Judge Robert H. Bork determined in 1986 that the Air Act requires EPA to provide "an ample margin of safety to protect public health," but the agency can use its "discretion and judgment to bear on scientific uncertainty" in preparing emission limits.

EPA Must Ascertain 'Safe' Level

But Bork wrote on behalf of the panel in the July 28 ruling that EPA failed to make a preliminary determination as to what constituted a "safe" level of vinyl chloride emissions. Congress' requirement that the standard provide for an "ample margin of safety" meant the agency had to make an initial finding of what is "safe," according to Bork.

Cost and technological feasibility factors do not enter into the safety determination, Bork said. Once a safe level is assured, EPA may use cost and technological considerations in determining what is an "ample margin" to provide in the standard, Bork said.

On a review of Congress' intent in Section 112 of the Air Act, Bork said the legislative history of the hazardous air pollutant provision is "ambiguous" as to whether cost and technological feasibility can be considered.

The D.C. Circuit and U.S. Supreme Court have ruled on the issue of cost and technological feasibility considerations, Bork said, but the cases dealt with provisions other than Section 112. In other sections, Congress indicated, through statutory language or legislative history, that cost and feasibility review was precluded, although no such indication appears with Section 112, Bork said.

On the other hand, the 1977 amendments to the Air Act on hazardous air pollutants did not represent Congress' "ratification" of EPA's approach to the vinyl chloride standards in 1976, which included consideration of costs and technological feasibility, Bork said. He continued that "we cannot be certain that Congress was aware of the content of the vinyl chloride regulations."

Because there is no "clear congressional intent to preclude" cost and feasibility limitations, EPA can consider such factors, Bork concluded.

NRDC Raises Scientific Uncertainty

NRDC argued that the agency should prohibit emissions where EPA cannot develop a safe threshold level for exposure to emissions, but the D.C. Circuit rejected the argument. Congress indicated in using the language "ample margin of safety" that EPA had "great latitude in meeting its responsibility" under the Air Act, according to Bork.

Emphasizing the likelihood of scientific uncertainty about the dangers posed by hazardous air pollutants, Bork indicated that Congress provided EPA with discretion in dealing with the uncertainty involved with each emission standard.

If EPA were required to impose a zero-level of emissions in cases where safe threshold limits were questionable, it would force the court to conclude that "Congress mandated massive economic and social dislocations by shutting down entire industries," which would be an unreasonable conclusion, Bork said.

The agency is not sure how the ruling will affect further rulemakings under the Air Act or other statutes, according to Earl Salo, an EPA assistant general counsel who worked on the case. EPA may end up looking at whether other standards incorporated consideration of "safe" levels before technological and cost concerns were applied, Salo told BNA July 29.

Air Pollution

BILL WOULD REPEAL EPA SANCTION POWERS, BUT SPECIFY CONTROLS IN NON-ATTAINMENT AREAS

A bill introduced July 28 by Rep. Henry A. Waxman (D-Calif) would replace construction bans for cities that cannot attain the federal air quality standards for ozone and carbon monoxide by Dec. 31 with mandated control measures.

In an approach similar to that taken in S 1351 in the Senate, Waxman's bill would place cities into three classes, based on the extent to which they exceed air pollution standards, and require different control strategies for each class. Cities with moderate attainment problems would be exempted from Clean Air Act sanctions the bill would not repeal.

Under the measure, no sanctions would apply for simple failure to meet ambient air quality standards. Instead, sanctions would be imposed on areas that fail to adopt the control measures mandated for their non-attainment classes. Failure to meet air quality standards, however, would cause a state to be moved into the next class.

around the point of exposure to a hazardous substance and alter the size of an exposed population "until you get whatever level you think you want to clean up to," the staff member charged.

We have a clearly developed position on our side that the ACL process is illegal under RCRA and "we take it on [under superfund] in that context, too," he said.

Continuing Fight Foreseen

The law states that ACLs may not be used instead of applicable laws or standards "if the process assumes a point of human exposure beyond the boundary of a facility, as defined at the conclusion of the remedial investigation and feasibility, except" in three specific instances.

However, the staff member acknowledged that the issue will be a "continuing fight" because the language does not unambiguously eliminate the use of ACLs where a maximum contaminant level for a pollutant has been established.

"It's our position that it is inappropriate where an MCL exists; it's the interpretation we're pressing for and it's now apparent EPA is going to take a different interpretation," he said.

Quarles: 'Cadillac Cleanups'

John Quarles, an attorney with Morgan, Lewis & Bockius, which represents many potentially responsible parties at superfund sites, told BNA Nov. 10 that strict adherence to Drinking Water Act standards will be prohibitively expensive or unachievable in many instances, and result in what he called "Cadillac cleanups."

"My interpretation of the statutory language is that it would permit ACLs at superfund sites if the required criteria demonstrating the absence of risk could be met," Quarles, a former EPA Deputy Administrator, said.

In an Oct. 17 memorandum to clients, Quarles said that in discussions with Thomas, the Administrator made it clear to him "that he regards that authorization to set ACLs, and particularly the explicit congressional debate on this subject before the ACL authority was written into the statute, as having great significance." (See related item in this issue.)

Quarles said the RCRA cleanup program has been logjammed by disagreement over the applicability of ACLs and that the issue has the potential to snarl the superfund program as well.

Litigation

APPEALS COURT UPHOLDS EPA WITHDRAWAL OF PROPOSED VINYL CHLORIDE EMISSIONS RULE

Withdrawal by the Environmental Protection Agency of proposed national hazardous emission standards strictly limiting vinyl chloride under Section 112 of the Clean Air Act was upheld Nov. 4 by a federal appeals court.

The U.S. Court of Appeals for the District of Columbia, in a suit brought by the Natural Resources Defense Council Inc., ruled that Section 112 authorizes EPA to consider feasibility factors in withdrawing proposed standards that would have strictly limited vinyl chloride emissions, with a goal of zero emissions (*NRDC v. EPA*, No. 85-1150).

EPA issued vinyl chloride standards in 1976, requiring emission reductions of 95 percent. The Environmental Defense Fund challenged the adequacy of the standards, and EPA settled the litigation by proposing stricter standards in June 1977. However, EPA withdrew the proposed standards in January 1985, claiming they would not be feasible to implement.

Following the agency's withdrawal decision, NRDC petitioned the appeals court to reinstate the proposed standards, charging that the agency's decision would return vinyl chloride regulation to the 1976 standards, which NRDC claimed were inadequate to protect public health.

In upholding EPA's withdrawal action, the appeals court concluded that agency decisions in setting emission standards under Section 112 need not be restricted to considerations of public health.

Court Cites 'Unreasonable' Costs

The appeals court observed that the agency, in withdrawing the 1977 proposal, said the standards would have imposed "unreasonable" regulatory costs and that no control technology has been demonstrated for reducing emissions below that required by the 1976 standards.

Judge Robert H. Bork, joined by Judge Harry T. Edwards, dealt with Section 112's language requiring EPA to set emission standards for hazardous air pollutants that will provide "an ample margin of safety to protect public health." According to Judge Bork, the language implied that EPA can bring "discretion and judgment to bear on scientific uncertainty" in deciding on vinyl chloride standards.

Judge Bork said that limiting the agency's consideration to health-based factors alone could not have been the intent of the Act, because "deciding how much uncertainty to allow from a strictly health-based perspective would always lead to the same answer—none."

A review of the history of the 1970 Air Act amendments proved to be "ambiguous" in terms of factors to consider in setting standards for hazardous air pollutants, Judge Bork said.

Dangers Said Uncertain in Trace Amounts

If evidence "positively demonstrated" that a given substance endangered public health in trace amounts, EPA might be able to prohibit any emissions of that substance, according to the circuit judge. However, an area of uncertainty exists concerning health effects of vinyl chloride at trace levels, Judge Bork commented.

EPA is allowed to use its discretion to "protect against dangers [the agency] cannot know" by setting standards as strict as possible, "given both available technology and the requirement that the cost of reduction not be grossly disproportionate to the level achieved," according to Judge Bork.

In that range of uncertainty, he added, EPA's considerations of feasibility in setting standards "seem natural, perhaps inevitable, choices." By emphasizing available technology, the agency ensured maximum regulation "without the economic and social displacement that would accompany the closing of an industry or any substantial part of an industry."

Dissent Emphasizes Public Health Concerns

Judge J. Skelly Wright dissented, claiming the "clear decision" by Congress was that Section 112 emission standards "should reflect public health considerations alone." The agency's discretion under Section 112 must account for an "ample margin of safety," without any reference to "feasibility considerations, either technological or economic," Judge Wright maintained.

Without "solid statistics for harm," he said, "the costs of regulation will always dominate" an agency's decision on the extent of regulation necessary.

The elimination of "entire industries" is not likely under a stricter standard, Judge Wright said, commenting that the

majority's fear of industry disruption was "greatly exaggerated."

Because many air pollutants are carcinogens, Judge Wright said, they can pose a danger at any concentration, and Congress was aware that these substances would require "the strictest regulation without regard to cost, even if the extent of that danger might be unclear at the third decimal point."

EPA 'Pleased' with Ruling

Earl Salo, EPA acting assistant general counsel, told BNA Nov. 5 he was "very pleased" with the federal appeals court decision. "We are not especially surprised," he said, "since we have been interpreting the statute this way for a long time. What is unusual here is that it took 15 years before we got a case right on point."

Salo said the 1976 standards, which are the ones in effect following the appeals court ruling, approximate the best technologically achievable reductions of vinyl chloride.

Litigation

COURT UPHOLDS EPA EMISSION STANDARDS, REJECTS AGENCY TIMING FOR IMPOSING LIMITS

Federal limits on nitrogen oxide and particulate emissions from heavy-duty motor vehicles were upheld by a federal appeals court Nov. 7, but the court ruled that the Environmental Protection Agency failed to follow requirements under the Clean Air Act concerning the time that the emission standards would take effect.

EPA improperly required engine manufacturers to comply with a nitrogen oxide standard issued in 1985 by the 1988 model year, according to the U.S. Court of Appeals for the District of Columbia Circuit. The Air Act requires a four-year lead time between when a standard is issued and when it takes effect, the court determined (*NRDC v. Thomas*, No. 85-1294).

Although EPA was "gratified" that the court upheld the majority of the agency's standard-setting actions, there was some disappointment with the D.C. Circuit's reading of requirements for lead times under the Air Act, according to Nancy A. Ketcham-Colwill, an attorney in EPA's Office of General Counsel.

Parties Challenging Emission Standards

The D.C. Circuit rejected challenges to the nitrogen oxide and particulate standards raised by the Natural Resources Defense Council Inc., which was joined by six environmental groups and four individuals. In addition, the Engine Manufacturers Association, joined by five engine manufacturers and a trade association, challenged the strictness and timing of the standards.

EPA issued emission standards for heavy-duty trucks in March 1985, requiring a reduction of nitrogen oxide emissions to 6 grams per brake horsepower-hour (g/BHP-hr) and particulate emissions to 0.6 g/BHP-hr by the 1988 model year (Current Developments, March 15, 1985, p. 1910).

The agency was under a court order to issue the standards, due to an NRDC suit against EPA for failing to prepare standards in time for the 1985 model year (*NRDC v. Ruckelshaus*, 21 ERC 1953; Sept. 15, 1984, p. 792).

Inadequate Lead Time Provided

Even though the nitrogen oxide standard was supposed to be in effect by the 1985 model year, EPA cannot use its delay in issuing a standard as a reason to circumvent the four-year lead time mandated in the Act, the appeals court determined. Therefore, the standard cannot go into effect until the 1990 model year, the court ruled.

In addition, the agency incorrectly imposed nitrogen oxide standards for light duty trucks that are also regulated as heavy-duty vehicles, according to the D.C. Circuit. The agency regulates light-duty trucks that weigh between 6,000 and 8,500 pounds as heavy-duty vehicles, the court noted.

EPA understood the statutory requirements for a four-year lead time for imposing emission limits, but the agency had hoped the court would recognize that EPA wanted to minimize delay in carrying out the 1985 standards, Ketcham-Colwill told BNA Nov. 12.

Balancing Said Required in Setting Standards

The appeals court rejected the environmental group's challenge to the technological adequacy of the standard for nitrogen oxide emissions, holding that EPA did not have to set a standard based on the achievements of the leader in technology for the motor vehicle industry.

Congress intended EPA's standard setting to be a balancing process, accounting for industrywide factors such as cost, noise, energy, and safety, according to the D.C. Circuit. Congress did not express, with "laser-like clarity," requirements for the use of one manufacturer's engine design as the baseline for setting emission standards, the appeals court observed.

Although there is reference to the use of technological leaders in the legislative history of the Air Act, EPA provided a reasonable approach in determining that the emission standards were to be set at a level "geared to what the more progressive manufacturers could achieve," the appeals court said. The agency must also consider the other factors, including cost, the D.C. Circuit noted.

Emission Averaging Upheld

EPA's willingness to let engine manufacturers average emission levels among engine types to meet standards was also challenged by the environmental groups. The agency should have required each engine type to meet an emission standard, and the averaging of emissions by a manufacturer could lead to minimal penalties for non-complying engine types, according to the groups.

The appeals court agreed with the agency's argument that averaging of emissions will provide more flexibility to manufacturers to allocate costs among different engine operations. At the same time, the court said, averaging will ensure that standards are met.

Non-compliance penalties will not be undermined by emission averaging, according to the D.C. Circuit, because a manufacturer can still be penalized if an entire fleet of engines fails to meet a standard.

California's Challenge Rejected

California challenged EPA's decision to base nitrogen oxide limits on the ability of diesel engine manufacturers to comply with the requirements. Although the appeals court agreed that it might have been more appropriate for EPA to set stricter standards based on gasoline vehicle compliance, the court said it could not review the state's objections.

The state failed to raise its complaints during the public comment period when the limits were proposed, and was precluded from raising the objections in court, according to the D.C. Circuit.

Engine Manufacturers' Challenges

The engine manufacturers complained that EPA based particulate emission standards on its prediction as to future

0013-9211/86/$0+.50

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 (GC), nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. *Applicability and Principle*

1.1 Applicability. This method applies to the measurement of 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 forms, such as sheet or cubes. This method is not acceptable where methods from Section 304(h) of the Clean Water Act, 33 U.S.C. 1251 et seq. (the Federal Water Pollution Control Amendments of 1972 as amended by the Clean Water Act of 1977) are required.

1.2 Principle. The basis for this method relates to the vapor equilibrium that is established at a constant known temperature in a closed system between RVCM, PVC resin, water, and air. The RVCM in a PVC resin will equilibrate rapidly in a closed vessel, provided that the temperature of the PVC resin is maintained above the glass transition temperature of that specific resin.

[1.2 amended by 52 FR 20398, June 1, 1987]

2. *Range and Sensitivity*

The lower limit of detection of vinyl chloride will vary according to the sampling and chromatographic system. The system should be capable of producing a measurement for a 50-ppm vinyl chloride standard that is at least 10 times the standard deviation of the system background noise level.

[2. revised by 52 FR 20398, June 1, 1987]

3. *Interferences*

The chromatograph columns and the corresponding operating parameters herein described normally provide an adequate resolution of vinyl chloride; however, resolution interferences may be encountered on some sources. Therefore, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis requirements, subject to the approval of the Administrator. Approval is automatic provided that the tester produces confirming data through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and has the data available for review by the Administrator.

4. *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 percent for a sample with a mean of 2.09 ppm, 4.16 percent for a sample with a mean of 1.66 ppm, and 8.29 percent for a sample with a mean of 62.66 ppm.

5. *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 gas must be vented prior to removal of the vial from the instrument turntable. Vials must be vented through a hypodermic needle connected to an activated charcoal tube to prevent release of vinyl chloride into the laboratory atmosphere. The charcoal must be replaced prior to vinyl chloride breakthrough.

6. *Apparatus*

6.1 Sampling. The following equipment is required:

6.1.1 Glass bottles. 60-ml (2-oz) capacity, with wax-lined screw-on tops, for PVC samples.

6.1.2 Glass Vials. Headspace vials, with Teflon-faced butyl rubber sealing discs, for water samples.

[6.1.2 revised by 52 FR 20398, June 1, 1987]

6.1.3 Adhesive Tape. To prevent loosening of bottle tops.

6.2 Sample Recovery. The following equipment is required:

[6.2 revised by 52 FR 20398, June 1, 1987]

6.2.1 Glass Vials. Headspace vials, with butyl rubber septa and aluminum caps. Silicone rubber is not acceptable.

6.2.2 Analytical Balance. Capable of determining sample weight within an accuracy of ± 1 percent.

6.2.3 Vial Sealer. To seal headspace vials.

6.2.4 Syringe. 100-µl capacity.

6.3 Analysis. The following equipment is required:

6.3.1 Headspace Sampler and Chromatograph. Capable of sampling and analyzing a constant amount of headspace gas from a sealed vial, while maintaining that vial at a temperature of 90°C± 0.5°C. The chromatograph shall be equipped with a flame ionization detector. Perkin-Elmer Corporation Models F-40, F-42, F-45, HS-6, and HS-100, and Hewlett-Packard Corporation Model 19395A have been found satisfactory. Chromatograph backflush capability may be required.

[6.3.1 revised by 52 FR 20398, June 1, 1987]

6.3.2 Chromatographic Columns. Stainless steel 1 m by 3.2 mm and 2 m by 3.2 mm, both containing 50/80-mesh Porapak Q. The analyst may use other columns provided that the precision and accuracy of the analysis of vinyl chloride standards are not impaired and he has available for review information confirming that there is adequate resolution of the vinyl chloride peak. (Adequate resolution is defined as an area overlap of not more than 10 percent of the vinyl chloride peak by an interferent peak. Calculation of area overlap is explained in Appendix C, Procedure 1: "Determination of Adequate Chromatographic Peak Resolution.") Two 1.83 m columns, each containing 1 percent Carbowax 1500 on Carbopak B, have been suggested for samples containing acetaldehyde.

6.3.3 Thermometer. 0 to 100°C, accurate to ± 0.1°C.

[6.3.3 amended by 52 FR 20398, June 1, 1987]

6.3.4 Integrator-Recorder. To record chromatograms.

[Former 6.3.4 and 6.3.5 removed, former 6.3.6 revised and redesignated as 6.3.4, and new 6.3.5 added by 52 FR 20398, June 1, 1987]

6.3.5 Barometer. Accurate to ± 1 mm Hg.

6.3.6 Regulators. For required gas cylinders.

[Former 6.3.7 and 6.3.8 removed and former 6.3.9 and 6.3.10 redesignated as 6.3.6 and 6.3.7, respectively by 52 FR 20398, June 1, 1987]

6.3.7 Headspace Vial Pre-Pressurizer. Nitrogen pressurized hypodermic needle inside protective shield. (Blueprint available from Test Support Section, Emission Measurement Branch, Office of Air Quality Planning and Standards, Environmental Protection Agency, Mail Drop 19, Research Triangle Park, N.C. 27711.)

7. *Reagents*

Use only reagents that are of chromatographic grade.

7.1 Analysis. The following items are required for analysis:

7.1.1 Hydrogen. Zero grade.

7.1.2 Nitrogen or Helium. Zero grade.

[7.1.2 revised by 52 FR 20398, June 1, 1987]

7.1.3 Air. Zero grade.

7.1.4 Water. Interference free.

[7.1.4 added by 52 FR 20398, June 1, 1987]

[Appendix B, Method 107]

7.2 Calibration. The following items are required for calibration:

7.2.1 Cylinder Standards (4). Gas mixture standards (50-, 500-, 2000- and 4000-ppm vinyl chloride in nitrogen cylinders). The tester may use cylinder standards to directly prepare a chromatograph calibration curve as described in Section 8.2. If the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of ±3 percent or better (see Section 7.2.1.1). (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than ±5 percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified vinyl chloride concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

7.2.1.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of vinyl chloride in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a 3-point calibration curve. It is recommended that the manufacturer maintain (1) a high-concentration calibration standard (between 4000 and 8000 ppm) to prepare his calibration curve by an appropriate dilution technique and (2) a low-concentration calibration standard (between 50 and 500 ppm) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration calibration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source of error and correct it, then repeat the 3-point calibration.

7.2.1.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared (with 99 mole percent vinyl chloride) in accordance with the procedure described in Section 7.1 of Method 106 or by (b) calibrating it against vinyl chloride cylinder Standard Reference Materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be within 5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

[7.2.1.2 amended by 52 FR 20398, June 1, 1987]

8. *Procedure*

8.1 Sampling.

8.1.1 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 and fill a 60-ml sample bottle under the tap, and immediately tighten a cap on the bottle. Wrap adhesive tape around the cap and bottle to prevent the cap 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. All samples should be kept refrigerated.

[8.1.1 amended by 52 FR 20398, June 1, 1987]

8.1.2 Water Sampling. 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, with the 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.

[8.1.2 amended by 52 FR 20398, June 1, 1987]

8.2 Sample Recovery. Samples must be run within 24 hours.

8.2.1 Resin Samples. The weight of the resin used must be between 0.1 and 4.5 grams. An exact weight must be obtained (±1 percent) for each sample. In the case of suspension resins, a volumetric cup can be prepared for holding the required amount of sample. When the cup is used, open the sample bottle, and add the cup volume of resin to the tared sample vial (tared, including septum and aluminum cap). Obtain the exact sample weight, add 100μl or about two equal drops of water, and immediately seal the vial. Report this value on the data sheet; it is required for calculation of RVCM. In the case of dispersion resins, the cup cannot be used. Weigh the sample in an aluminum dish, transfer the sample to the tared vial, and accurately weigh it in the vial. After prepressurization of the samples, condition them for a minimum of 1 hour in the 90° C bath. Do not exceed 5 hours.

Prepressurization is not required if the sample weight, as analyzed, does not exceed 0.2 gram. It is also not required if solution of the prepressurization equation yields an absolute prepressurization value that is within 30 percent of the atmospheric pressure.

NOTE: Some aluminum vial caps have a center section that must be removed prior to placing into sample tray. If the cap is not removed, the injection needle will be damaged.

[8.2.1 amended by 52 FR 20398, June 1, 1987]

8.2.2 Suspension Resin Slurry and Wet Cake Samples. Decant the water from a wet cake sample, and turn the sample bottle upside down onto a paper towel. Wait for the water to drain, place approximately 0.2 to 4.0 grams of the wet cake sample in a tared vial (tared, including septum and aluminum cap) and seal immediately. Then determine the sample weight (±1 percent). All samples, weighing over 0.2 gram, must be prepressurized prior to conditioning for 1 hour at 90°C, except as noted in Section 8.2.1. A sample of wet cake is used to determine total solids (TS). This is required for calculating the RVCM.

[8.2.2 amended by 52 FR 20398, June 1, 1987]

8.2.3 Dispersion Resin Slurry and Geon Latex Samples. The materials should not be filtered. Sample must be thoroughly mixed. Using a tared vial (tared, including septum and aluminum cap) add approximately eight drops (0.25 to 0.35 g) 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 (±1 percent). Condition the vial for 1 hour at 90 °C in the analyzer bath. Determine the TS on the slurry sample (Section 8.3.5).

[8.2.3 amended by 52 FR 20398, June 1, 1987]

8.2.4 Inprocess Wastewater Samples. Using a tared vial (tared, 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 (±1 percent). Condition the vial for 1 hour at 90°C in the analyzer bath.

[8.2.4 amended by 52 FR 20398, June 1, 1987]

8.3 Analysis.

8.3.1 Preparation of Equipment. Install the chromatographic column and condition overnight at 160° C. In the first operation, Porapak columns must be purged for 1 hour at 230° C.

Do not connect the exit end of the column to the detector while conditioning. Hydrogen and air to the detector must be turned off while the column is disconnected.

8.3.1.1 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 produce a flow rate of 30.0 cc/min. Accurately measure the flow rate at the exit end of the column using the soap film flowmeter and a stopwatch, with the oven and column at the analysis temperature. After the instrument program advances to the "B" (backflush) mode, adjust the nitrogen pressure regulator to exactly balance the nitrogen flow rate at the detector as was obtained in the "A" mode.

b. Vial Prepressurizer Nitrogen. After the nitrogen carrier is set, solve the following

equation and adjust the pressure on the vial prepressurizer accordingly.

$$P = \frac{T_1}{T_2}\left[P_1 - \frac{P_{w1} - P_{w2}}{7.50}\right] - 10 \text{ k Pa}$$

Where:

T_1 = Ambient temperature, °K.
T_2 = Conditioning bath temperature, °K.
P_1 = Gas chromatograph absolute dosing pressure (analysis mode), k Pa.
P_{w1} = Water vapor pressure @ 90° C (525.8 mm Hg).
P_{w2} = Water vapor pressure @ 22° C (19.8 mm Hg).
7.50 = mm Hg per k Pa.
10 k Pa = Factor to adjust the prepressurized pressure to slightly less than the dosing pressure.

Because of gauge errors, the apparatus may over-pressurize the vial. If the vial pressure is at or higher than the dosing pressure, an audible double injection will occur. If the vial pressure is too low, errors will occur on resin samples because of inadequate time for head-space gas equilibrium. This condition can be avoided by running several standard gas samples at various pressures around the calculated preasure, and then selecting the highest pressure that does not produce a double injection. All samples and standards must be pressurized for 60 seconds using the vial prepressurizer. The vial is then placed into the 90° C conditioning bath and tested for leakage by placing a drop of water on the septum at the needle hole. A clean, burr-free needle is mandatory.

c. 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/min. Check with bubble flowmeter.

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

8.3.1.2 Temperature Adjustments. Set temperatures as follows:

a. Oven (chromatograph column), 140° C.
b. Dosing Line, 150° C.
c. Injection Block, 170° C.
d. Sample Chamber, Water Temperature, 90° C ± 1.0° C.

8.3.1.3 Ignition of Flame Ionization Detector. Ignite the detector according to the manufacturer's instructions.

8.3.1.4 Amplifier Balance. Balance the amplifier according to the manufacturer's instructions.

8.3.2 Programming the Chromatograph. Program the chromatograph as follows:

a. I—Dosing or Injection Time. The normal setting is 2 seconds.
b. A—"Analysis Time." The normal setting is approximately 70 percent of the VCM retention time. When this timer terminates, the programmer initiates backflushing of the first column.
c. B—Backflushing Time. The normal setting is double the "analysis time."
d. W—Stabilization Time. The normal setting is 0.5 min to 1.0 min.
e. X—Number of Analyses Per Sample. The normal setting is one.

8.3.3 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 vials should be placed in the corresponding numbered positions in the turntable. Insert samples in the following order:

Position 1 and 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).

[8.3.3 amended by 52 FR 20398, June 1, 1987]

8.3.4 Start Chromatograph Program. When all samples, including standards, have been conditioned at 90° C for 1 hour, start the analysis program according to the manufacturer's instructions. These instructions must be carefully followed when starting and stopping a program to prevent damage to the dosing assembly.

8.3.5 Determination of 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. The TS are then calculated as the final sample weight divided by initial sample weight.

9. *Calibration*

Calibration is to be performed each 8-hour period the chromatograph is used. Alternatively, calibration with duplicate 50-, 500-, 2,000-, and 4,000-ppm standards (hereafter described as a four-point calibration) may be performed on a monthly basis, provided that a calibration confirmation test consisting of duplicate analyses of an appropriate standard is performed once per plant shift, or once per chromatograph carrousel operation (if the chromatograph operation is less frequent than once per shift). The criterion for acceptance of each calibration confirmation test is that both analyses of 500-ppm standards [2,000-ppm standards if dispersion resin (excluding latex resin) samples are being analyzed] must be within 5 percent of the most recent four-point calibration curve. If this criterion is not met, then a complete four-point calibration must be performed before sample analyses can proceed.

[9. revised by 52 FR 20398, June 1, 1987]

9.1 Preparation of Standards. Calibration standards are prepared as follows: Place 100μl or about two equal drops of distilled water in the sample vial, then fill the vial with the VCM/nitrogen standard, rapidly seat the septum, and seal with the aluminum cap. Use a ⅛-in. stainless steel line from the cylinder to the vial. Do not use rubber or Tygon tubing. The sample line from the cylinder must be purged (into a properly vented hood) for several minutes prior to filling the vials. After purging, reduce the flow rate to 500 to 1000 cc/min. Place end of tubing into vial (near bottom). Position a septum on top of the vial, pressing it against the ⅛-in. filling tube to minimize the size of the vent opening. This is necessary to minimize mixing air with the standard in the vial. Each vial is to be purged with standard for 90 seconds, during which time the filling tube is gradually slid to the top of the vial. After the 90 seconds, the tube is removed with the septum, simultaneously sealing the vial. Practice will be necessary to develop good technique. Rubber gloves should be worn during the above operations. The sealed vial must then be pressurized for 60 seconds using the vial prepressurizer. Test the vial for leakage by placing a drop of water on the septum at the needle hole. Prepressurization of standards is not required unless samples have been prepressurized.

[9.1 amended by 52 FR 20398, June 1, 1987]

9.2 Preparation of Chromatograph Calibration Curve.

Prepare two vials each of 50-, 500-, 2,000-, and 4,000-ppm standards. Run the calibration samples in exactly the same manner as regular samples. Plot A_v, the integrator area counts for each standard sample, versus C_v, the concentration of vinyl chloride in each standard sample. Draw a straight line through the points derived by the least squares method.

[9.2 amended by 52 FR 20398, June 1, 1987]

[Appendix B, Method 107]

10. *Calculations*

10.1 Response Factor. If the calibration curve described in Section 9.2 passes through zero, an average response factor, R_f, may be used to facilitate computation of vinyl chloride sample concentrations.

To compute R_f, first compute a response factor, R_s, for each sample as follows:

$$R_s = \frac{A_s}{C_s} \qquad \text{Eq. 107-1}$$

R_s = Response factor, area counts/ppm.
A_s = Chromatogram area counts of vinyl chloride for the sample, area counts.
C_s = Concentration of vinyl chloride in the standard sample, ppm.

V_s = Volume of vapor phase, cm^3.

$$= V_v - \frac{m(TS)}{1.36} - \frac{m(1-TS)}{0.9653}$$

Sum the individual response factors, and calculate R_f. If the calibration curve does not pass through zero, use the calibration curve to determine each sample concentration.

[10.1 revised by 52 FR 20398, June 1, 1987; corrected by 53 FR 36972, September 23, 1988]

10.2 Residual Vinyl Chloride Monomer Concentration, (C_{rvc}) or Vinyl Chloride Monomer Concentration. Calculate C_{rvc} in ppm or mg/kg as follows:

[10.2 revised by 52 FR 20398, June 1, 1987]

$$C_{rvc} = \frac{A_s P_a}{R_f T_1}\left[\frac{M_v V_g}{R m} + K_p (TS) T_2 + K_w (1 - TS) T_2\right] \qquad \text{Eq. 107-2}$$

Where:
A_s = Chromatogram area counts of vinyl chloride for the sample.
P_a = Ambient atmospheric pressure, mm Hg.
R_f = Response factor in area counts per ppm VCM.
T_1 = Ambient laboratory temperature, °K.
M_v = Molecular weight of VCM, 62.5 g/mole.
V_s = Volume of the vapor phase, cm^3.
R = Gas constant, (62360 cm^3) (mm Hg)/(mole)(°K).
m = Sample weight, g.
K_p = Henry's Law Constant for VCM in PVC @ 90° C, 6.52×10^{-6} g/g/mm Hg.
TS = Total solids expressed as a decimal fraction.
T_2 = Equilibrium temperature, °K.
K_w = Henry's Law Constant for VCM in water @ 90° C, 7×10^{-7} g/g/mm Hg.
V_v = Vial volume, cm^3.
1.36 = Density of PVC at 90°C, g/cm^3.
0.9653 = Density of water at 90°C, g/cm^3.

$$= V_v - \frac{m(TS)}{1.36} - \frac{m(1-TS)}{0.9653}$$

Results calculated using these equations represent concentration based on the total sample. To obtain results based on dry PVC content, divide by TS.

11. *Bibliography*

[11. head revised by 52 FR 20398, June 1, 1987]

1. B.F. Goodrich. Residual Vinyl Chloride Monomer Content of Polyvinyl Chloride Resins, Latex, Wet Cake, Slurry and Water Samples. B.F. Goodrich Chemical Group Standard Test Procedure No. 1005-E. B.F. Goodrich Technical Center, Avon Lake, Ohio. October 8, 1979.

2. Berens, A.R. The Diffusion 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. Journal of Applied Polymer Science. *19*:3169-3172. 1975.

5. Manafield, R.A. The Evaluation of Henry's Law Constant (Kp) and Water Enhancement in the Perkin-Elmer Multifract F-40 Gas Chromatograph. B.F. Goodrich, Avon Lake, Ohio. February 10, 1978.

METHOD 107A—DETERMINATION OF VINYL CHLORIDE CONTENT OF SOLVENTS, RESIN-SOLVENT SOLUTION, POLYVINYL CHLORIDE RESIN, RESIN SLURRY, WET RESIN, AND LATEX SAMPLES

Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph (GC) or by those who are unfamiliar with source sampling because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. *Applicability and Principle*

1.1 Applicability. This is an alternative method and applies to the measurement of the vinyl chloride content of solvents, resin solvent solutions, polyvinyl chloride (PVC) resin, wet cake slurries, latex, and fabricated resin samples. This method is not acceptable where methods from Section 304(h) of the Clean Water Act, 33 U.S.C. 1251 et seq., (the Federal Water Pollution Control Act Amendments of 1972 as amended by the Clean Water Act of 1977) are required.

1.2 Principle. The basis for this method lies in the direct injection of a liquid sample into a chromatograph and the subsequent evaporation of all volatile material into the carrier gas stream of the chromatograph, thus permitting analysis of all volatile material including vinyl chloride.

2. *Range and Sensitivity*

The lower limit of detection of vinyl chloride in dry PVC resin is 0.2 ppm. For resin solutions, latexes, and wet resin, this limit rises inversely as the nonvolatile (resin) content decreases.

With proper calibration, the upper limit may be extended as needed.

3. *Interferences*

The chromatograph columns and the corresponding operating parameters herein described normally provide an adequate resolution of vinyl chloride. In cases where resolution interferences are encountered, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis problem, subject to the approval of the Administrator. Approval is automatic, provided that the tester produces confirming data through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and has the data available for review by the Administrator.

4. *Precision and Reproducibility*

A standard sample of latex containing 181.8 ppm vinyl chloride analyzed 10 times by the alternative method showed a standard deviation of 7.5 percent and a mean error of 0.21 percent.

A sample of vinyl chloride copolymer resin solution was analyzed 10 times by the alternative method and showed a standard deviation of 5.6 percent at a level of 35 ppm.

5. *Safety*

Do not release vinyl chloride to the laboratory atmosphere during preparation of standards. Venting or purging with vinyl chloride monomer (VCM) air mixtures must be held to minimum. When purging is required, the vapor must be routed to outside air. Vinyl chloride, even at low-ppm levels, must never be vented inside the laboratory.

[Appendix B, Method 107A]

6. Apparatus

6.1 Sampling. The following equipment is required:

6.1.1 Glass Bottles. 16-oz wide mouth wide polyethylene-lined, screw-on tops.

6.1.2 Adhesive Tape. To prevent loosening of bottle tops.

6.2 Sample Recovery. The following equipment is required:

6.2.1 Glass Vials. 20-ml capacity with polycone screw caps.

6.2.2 Analytical Balance. Capable of weighing to ±0.01 gram.

6.2.3 Syringe. 50-microliter size, with removable needle.

6.2.4 Fritted Glass Sparger. Fine porosity.

6.2.5 Aluminum Weighing Dishes.

6.2.6 Sample Roller or Shaker. To help dissolve sample.

6.3 Analysis. The following equipment is required:

6.3.1 Gas Chromatograph. Hewlett Packard Model 5720.A or equivalent.

6.3.2 Chromatograph Column. Stainless steel, 6.1 m by 3.2 mm, packed with 20 percent Tergitol E-35 on Chromosorb W AW 60/80 mesh. The analyst may use other columns provided that the precision and accuracy of the analysis of vinyl chloride standards are not impaired and that he has available for review information confirming that there is adequate resolution of the vinyl chloride peak. (Adequate resolution is defined as an area overlap of not more than 10 percent of the vinyl chloride peak by an interfering peak. Calculation of area overlap is explained in Apendix C, Procedure 1: "Determination of Adequate Chromatographic Peak Resolution.")

6.3.3 Valco Instrument Six-Port Rotary Valve. For column back flush.

6.3.4 Septa. For chromatograph injection port.

6.3.5 Injection Port Liners. For chromatograph used.

6.3.6 Regulators. For required gas cylinders.

6.3.7 Soap Film Flowmeter. Hewlett Packard No. 0101-0113 or equivalent.

6.4 Calibration. The following equipment is required:

6.4.1 Analytical Balance. Capable of weighing to ±0.0001 g.

6.4.2 Erlenmeyer Flask With Glass Stopper. 125 ml.

6.4.3 Pipets. 0.1, 0.5, 1, 5, 10, and 50 ml.

6.4.4 Volumetric Flasks. 10 and 100 ml.

7. Reagents

Use only reagents that are of chromatograph grade.

7.1 Analysis. The following items are required:

7.1.1 Hydrogen Gas. Zero grade.

7.1.2 Nitrogen Gas. Zero grade.

7.1.3 Air. Zero grade.

7.1.4 Tetrahydrofuran (THF). Reagent grade.

Analyze the THF by injecting 10 microliters into the prepared gas chromatograph. Compare the THF chromatogram with that shown in Figure 107A-1. If the chromatogram is comparable to A, the THF should be sparged with pure nitrogen for approximately 2 hours using the fritted glass sparger to attempt to remove the interfering peak. Reanalyze the sparged THF to determine whether the THF is acceptable for use. If the scan is comparable to B, the THF should be acceptable for use in the analysis.

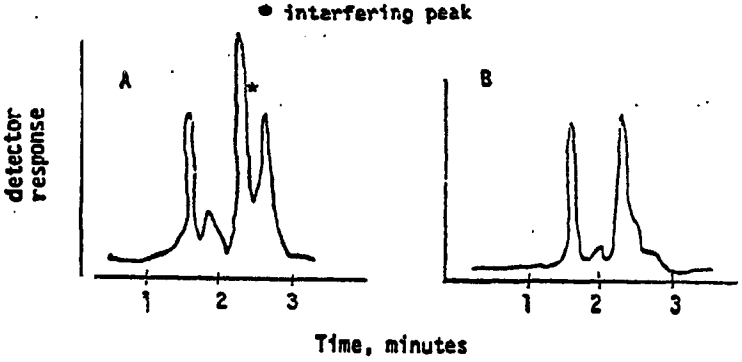

Figure 107A-1

7.1.5 N, N-Dimethylacetamide (DMAC). Spectrographic grade. For use in place of THF.

7.2 Calibration. The following item is required:

7.2.1 Vinyl Chloride 99.9 Percent. Ideal Gas Products lecture bottle, or equivalent. For preparation of standard solutions.

8. Procedure

8.1 Sampling. Allow the liquid or dried resin to flow from a tap on the tank, silo, or pipeline until the tap has been purged. Fill a wide-mouth pint bottle, and immediately tightly cap the bottle. Place an identifying label on each bottle and record the date, time, sample location, and material.

8.2 Sample Treatment. Sample must be run within 24 hours.

8.2.1 Resin Samples. Weigh 9.00 ± 0.01 g of THF or DMAC in a tared 20-ml vial. Add 1.00 ± 0.01 g of resin to the tared vial containing the THF or DMAC. Close the vial tightly with the screw cap, and shake or otherwise agitate the vial until complete solution of the resin is obtained. Shaking may require several minutes to several hours, depending on the nature of the resin.

8.2.2 Suspension Resin Slurry and Wet Resin Sample. Slurry must be filtered using a small Buchner funnel with vacuum to yield a wet resin sample. 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 resin sample is weighed into a tared 20-ml vial with THF or DMAC as described earlier for resin samples (8.2.1) and treated the same as the resin sample. A sample of the wet resin is used to determine total solids as required for calculating the residual VCM (Section 8.3.4).

8.2.3 Latex and Resin Solvent Solutions. Samples must be thoroughly mixed. Weigh 1.00 ± 0.01 g of the latex or resin-solvent solution into a 20-ml vial containing 9.00 ± 0.01 g of THF or DMAC as for the resin samples (8.2.1). Cap and shake until complete solution is obtained. Determine the total solids of the latex or resin solution sample (Section 8.3.4).

8.2.4 Solvents and Non-viscous Liquid Samples. No preparation of these samples is required. The neat samples are injected directly into the GC.

8.3 Analysis.

8.3.1 Preparation of GC. Install the chromatographic column, and condition overnight at 70° C. Do not connect the exit end of the column to the detector while conditioning.

[Appendix B, Method 107A]

8.3.1.1 Flow Rate Adjustments. Adjust the flow rate as follows:

a. Nitrogen Carrier Gas. Set regulator on cylinder to read 60 psig. Set column flow controller on the chromatograph using the soap film flowmeter to yield a flow rate of 40 cc/min.

b. Burner Air Supply. Set regulator on the cylinder at 40 psig. Set regulator on the chromatograph to supply air to the burner to yield a flow rate of 250 to 300 cc/min using the flowmeter.

c. Hydrogen. Set regulator on cylinder to read 60 psig. Set regulator on the chromatograph to supply 30 to 40 cc/min using the flowmeter. Optimize hydrogen flow to yield the most sensitive detector response without extinguishing the flame. Check flow with flowmeter and record this flow.

d. Nitrogen Back Flush Gas. Set regulator on the chromatograph using the soap film flowmeter to yield a flow rate of 40 cc/min.

8.3.1.2 Temperature Adjustments. Set temperature as follows:

a. Oven (chromatographic column) at 70° C.

b. Injection Port at 100° C.

c. Detector at 300° C.

8.3.1.3 Ignition of Flame Ionization Detector. Ignite the detector according to the manufacturer's instructions. Allow system to stabilize approximately 1 hour.

8.3.1.4 Recorder. Set pen at zero and start chart drive.

8.3.1.5 Attenuation. Set attenuation to yield desired peak height depending on sample VCM content.

8.3.2 Chromatographic Analyses.

a. Sample Injection. Remove needle from 50-microliter syringe. Open sample vial and draw 50-microliters of THF or DMAC sample recovery solution into the syringe. Recap sample vial. Attach needle to the syringe and while holding the syringe vertically (needle uppermost), eject 40 microliters into an absorbent tissue. Wipe needle with tissue. Now inject 10 microliters into chromatograph system. Repeat the injection until two consecutive values for the height of the vinyl chloride peak do not vary more than 5 percent. Use the average value for these two peak heights to compute the sample concentration.

b. Back Flush. After 4 minutes has elapsed after sample injection, actuate the back flush valve to purge the first 4 feet of the chromatographic column of solvent and other high boilers.

c. Sample Data. Record on the chromatograph strip chart the data from the sample label.

d. Elution Time. Vinyl chloride elutes at 2.8 minutes. Acetaldehyde elutes at 3.7 minutes. Analysis is considered complete when chart pen becomes stable. After 5 minutes, reset back flush valve and inject next sample.

8.3.3 Chromatograph Servicing.

a. Septum. Replace after five sample injections.

b. Sample Port Liner. Replace the sample port liner with a clean spare after five sample injections.

c. Chromatograph Shutdown. If the chromatograph has been shut down overnight, rerun one or more samples from the preceding day to test stability and precision prior to starting on the current day's work.

8.3.4 Determination of Total Solids (TS). For wet resin, resin solution, and PVC latex samples, determine the TS for each sample by accurately weighing approximately 3 to 5 grams of sample into a tared aluminum pan. The initial procedure is as follows:

a. Where water is the major volatile component: Tare the weighing dish, and add 3 to 5 grams of sample to the dish. Weigh to the nearest milligram.

b. Where volatile solvent is the major volatile component: Transfer a portion of the sample to a 20-ml screw cap vial and cap immediately. Weigh the vial to the nearest milligram. Uncap the vial and transfer a 3- to 5-gram portion of the sample to a tared aluminum weighing dish. Recap the vial and reweigh to the nearest milligram. The vial weight loss is the sample weight.

To continue, now place the weighing pan in a 130° C oven for 1 hour. Remove the dish and allow to cool to room temperature in a desiccator. Weigh the pan to the nearest 0.1 mg. Total solids is the weight of material in the aluminum pan after heating divided by the net weight of sample added to the pan originally times 100.

9. *Calibration of the Chromatograph*

9.1 Preparation of Standards. Prepare a 1 percent by weight (approximate) solution of vinly chloride in THF or DMAC by bubbling vinyl chloride gas from a cylinder into a tared 125-ml glass-stoppered flask containing THF or DMAC. The weight of vinyl chloride to be added should be calculated prior to this operation, i.e., 1 percent of the weight of THF or DMAC contained in the tared flask. This must be carried out in a laboratory hood. Adjust the vinyl chloride flow from the cylinder so that the vinyl chloride dissolves essentially completely in the THF or DMAC and is not blown to the atmosphere. Take particular care not to volatize any of the solution. Stopper the flask and swirl the solution to effect complete mixing. Weigh the stoppered flask to nearest 0.1 mg to determine the exact amount of vinyl chloride added.

Pipet 10 ml of the approximately 1 percent solution into a 100-ml glass-stoppered volumetric flask, and add THF or DMAC to fill to the mark. Cap the flask and invert 10 to 20 times. This solution contains approximately 1,000 ppm by weight of vinyl chloride (note the exact concentration).

Pipet 50-, 10-, 5-, 1-, 0.5-, and 0.1-ml aliquots of the approximately 1,000 ppm solution into 10 ml glass stoppered volumetric flasks. Dilute to the mark with THF or DMAC, cap the flasks and invert each 10 to 20 times. These solutions contain approximately 500, 100, 50, 10, 5, and 1 ppm vinyl chloride. Note the exact concentration of each one. These standards are to be kept under refrigeration in stoppered bottles, and must be renewed every 3 months.

9.2 Preparation of Chromatograph Calibration Curve.

Obtain the GC for each of the six final solutions prepared in Section 9.1 by using the procedure in Section 8.3.2. Prepare a chart plotting peak height obtained from the chromatogram of each solution versus the known concentration. Draw a straight line through the points derived by the least squares methods.

10. *Calculations*

10.1 Response Factor. From the calibration curve described in Section 9.2, select the value of C_s that corresponds to H_s for each sample. Compute the response factor, R_f, for each sample as follows:

$$R_f = \frac{C_s}{H_s} \qquad \text{Eq. 107A-1}$$

where:

R_f = Chromatograph response factor, ppm/mm.

C_s = Concentration of vinyl chloride in the standard sample, ppm.

H_s = Peak height of the standard sample, mm.

[10.1 corrected by 53 FR 36972, September 23, 1988]

10.2 Residual vinyl chloride monomer concentration (C_{rm}) or vinyl chloride monomer concentration in resin:

$$C_{rm} = 10H_sR_f \qquad \text{Eq. 107A-2}$$

Where:

C_{rm} = Concentration of residual vinyl chloride monomer, ppm.

H_s = Peak height of sample, mm.

R_f = Chromatograph response factor.

[10.2 corrected by 53 FR 36972, September 23, 1988]

10.3 Samples containing volatile material, i.e., resin solutions, wet resin, and latexes:

$$C_{rm} = \frac{H_sR_f(1{,}000)}{TS} \qquad \text{Eq. 107A-3}$$

where:

TS = Total solids in the sample, weight fraction.

[10.3 corrected by 53 FR 36972, September 23, 1988]

10.4 Samples of solvents and in process wastewater:

$$C_{RVC} = \frac{H_sR_f}{0.888} \qquad \text{Eq. 107A-4}$$

Where:

0.888 = Specific gravity of THF.

[10.4 corrected by 53 FR 36972, September 23, 1988]

11. *Bibliography*

1. Communication from R. N. Wheeler, Jr., Union Carbide Corporation. Part 61 National Emissions Standards for Hazardous Air Pollutants Appendix B, Method 107—Alternate Method, September 19, 1977.

METHOD 108—DETERMINATION OF PARTICULATE AND GASEOUS ARSENIC EMISSIONS

[Method 108 added by 51 FR 28025, August 4, 1986]

1. *Applicability and Principle*

1.1 Applicability. This method applies to the determination of inorganic arsenic (As)

[Appendix B, Method 108]