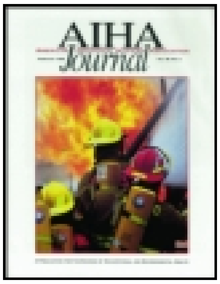

American Industrial Hygiene Association Journal
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/aiha20

Engineering control assessment of the plastics and resins industry… case study: manufacture of PVC by bulk polymerization

KENNETH S. SCHOULTZ [a] , JULIUS H. BOCHINSKI [b] & JAMES A. GIDEON [a b]

[a] Enviro Control, Inc., One Central Plaza, 11300 Rockville Pike, Rockville, Maryland 20852

[b] National Institute for Occupational Safety and Health (NIOSH), Robert A. Taft Laboratories, 4676 Columbia Parkway, Cincinnati, Ohio 45226

Published online: 04 Jun 2010.

As part of a control technology assessment of the plastics and resins industry, a bulk polymerization process manufacturing polyvinyl chloride is surveyed. Effective control techniques for reducing workplace concentrations of vinyl chloride include a computerized process design, an automatic air monitoring system for rapid leak detection, a novel local exhaust system, various equipment modifications to prevent leaks, and a PVC stripping operation. Personal and area sampling data are evaluated to determine the effectiveness of the overall control system. The control techniques can be applied to other processes where toxic materials are used.

Engineering control assessment of the plastics and resins industry . . . case study: manufacture of PVC by bulk polymerization

KENNETH S. SCHOULTZ, B.S., JULIUS H. BOCHINSKI, Ph.D. and JAMES A. GIDEON, M.S.
Enviro Control, Inc., One Central Plaza, 11300 Rockville Pike, Rockville, Maryland 20852; National Institute for Occupational Safety and Health (NIOSH), Robert A. Taft Laboratories, 4676 Columbia Parkway, Cincinnati, Ohio 45226

Introduction

A major portion of the research and development effort of the National Institute for Occupational Safety and Health (NIOSH) is directed toward the publication of criteria documents that present recommended standards for permissible employee exposures to potentially harmful chemical or physical agents in the workplace. The NIOSH documents provide the basis for regulatory standards of the Occupational Safety and Health Administration (OSHA) and are available to assist industrial health and safety programs.

In order to demonstrate how a given safe exposure in the workplace can be achieved, NIOSH is proposing a major, three-phase control technology program: (1) a series of industry-wide control technology assessments, designed to document and evaluate control technology options and outline research needs; (2) joint action by NIOSH and industry in research and development towards selected aims, primarily through industrial use of NIOSH demonstration grants; and (3) dissemination of the program results to aid industry in applying the control technology.

The plastics and synthetic resin industry, including the manufacture and compounding of thermoplastic and thermosetting resins and synthetic rubber (SIC codes 2821, 2823, 2824), was chosen for the first assessment. The contract was awarded to Enviro Control, Inc., (ECI) in July 1976, and the final report will be completed in November 1977.

ECI has completed in-plant studies of the control technology used in 16 polymerization and compounding processes, which provide a good representation of the type and extent of worker protection strategies in the industry as a whole. Particular attention has been given to the polyvinyl chloride (PVC) portion of the industry because of the extensive development and application of controls for vinyl chloride monomer (VCM) during the past several years. In general, the processes used to make different polymers are similar enough across the industry for intra-industry transfer of control technology to be practicable.

The following discussion presents the results of one case study of the manufacture of PVC by bulk polymerization.

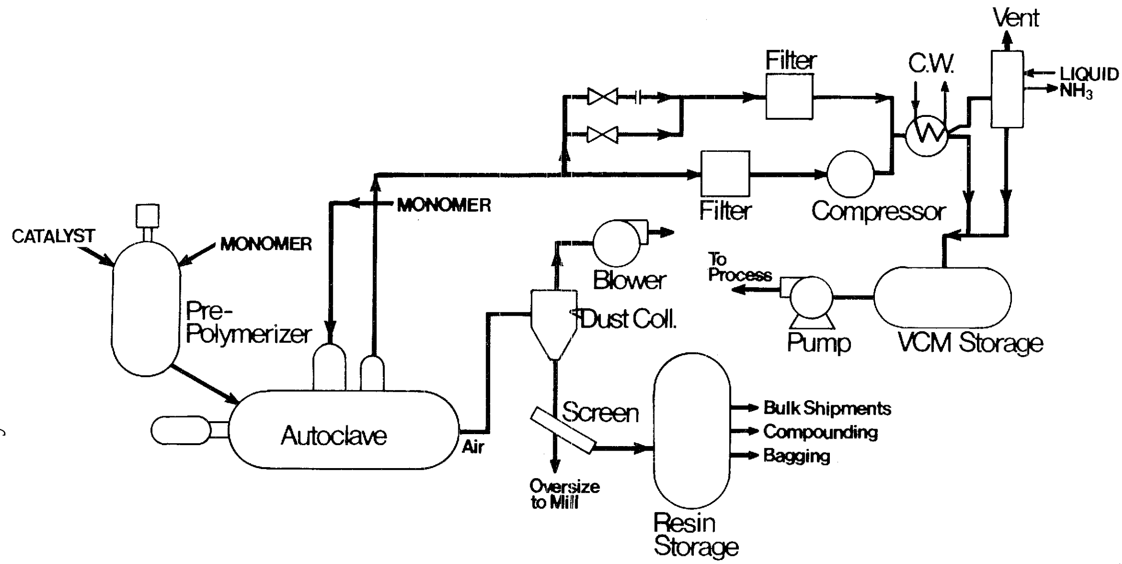

Figure 1 — Bulk polymerization process for polyvinyl chloride.

process summary

As shown in Figure 1, the major steps in this process are prepolymerization, polymerization, monomer recovery, and resin handling.

Prepolymerization involves the production of PVC nuclei from VCM in an agitated, vertical cylindrical tank. The procedure is to manually feed small quantities of additives into the tank through a spout, then pump in the VCM from the tank farm. A catalyst is used to initiate the reaction.

When the desired VCM conversion level is reached in the prepolymerizer (usually <10%), the batch is gravity-fed into a horizontal cylindrical autoclave, where the polymerization reaction goes to completion. Agitation is provided by a ribbon blender in the autoclave. The heat generated during the reaction is removed by a reflux condenser located vertically along the autoclave axis, and by the water-jacketed vessel surface.

At the completion of the reaction, unreacted VCM is vented to the condensers and compressors located in the monomer recovery area. Further monomer is recovered by stripping the resin of any unreacted VCM.

Most of the resin is transferred automatically to the product collector by connecting the air conveyance system directly to the autoclave. The remaining resin is removed manually, usually without anyone's having to enter the vessel. From the product collector, the resin is dropped into a hopper, then passed through several screens to standardize the PVC particle size. Oversize particles are diverted to a grinder and returned to the screens. The PVC product is pneumatically conveyed to storage or transferred to the compounding or bagging area.

toxic chemical agents and harmful physical stresses

vinyl chloride monomer

Federal regulations require that employee exposure to vinyl chloride shall not exceed an 8-hour time-weighted average of 1 ppm, or 5 ppm for any 15-minute period. Large quantities of this material are present in the prepolymerizers, autoclaves, and recovery system, and it is an extreme engineering challenge to control workplace emissions to such a low level. The plant described here was neither designed nor installed with this degree of control in mind, and a large amount of retrofitting with engineering controls was necessary. Therefore, most of the engineering controls evaluated during this case study are directed towards reducing workplace concentration of vinyl chloride.

polyvinyl chloride dust

Fully reacted polyvinyl chloride is considered a nuisance dust and has an 8-hour time-weighted average exposure limit of 15 mg/m^3 for total particulates. It may become airborne in the screening, grinding, and bagging operations.

noise

A potential for employee exposure to high noise levels exists in the polymerization, screening, and grinding areas.

control of vinyl chloride monomer

The VCM control system may be described under several headings:

1. Process design, modification, and maintenance
2. Leak detection and prevention
3. Local exhaust ventilation
4. General ventilation
5. Ongoing improvements

process design, modification, and maintenance

Inherent operating characteristics. The inherent operating characteristics of the bulk polymerization process permit a relatively high degree of employee exposure control. The process is totally enclosed until the polymerization autoclaves are opened for resin transfer. At this point, residual VCM levels are exceedingly low because of the effectiveness of the stripping operation.

The most important characteristic of the bulk process is that the VCM does not have to be suspended or emulsified in a liquid medium. This reduces the potential for employee exposure by (1) obviating the need for postpolymerization separation and drying operations, (2) eliminating the exposure associated with solvent recovery or monomer-contaminated wastewater disposal and treatment, and (3) allowing the use of low-temperature recovery condensers, which lessens the potential for leaks and decreases VCM concentration in the off-gas.

Computer control of process. The process cycle is almost totally computer controlled, thus reducing the possibility of significant VCM escape due to operator error or failure. When operator errors do occur, the reasons are analyzed to determine if additional prevention measures can be integrated into the computer

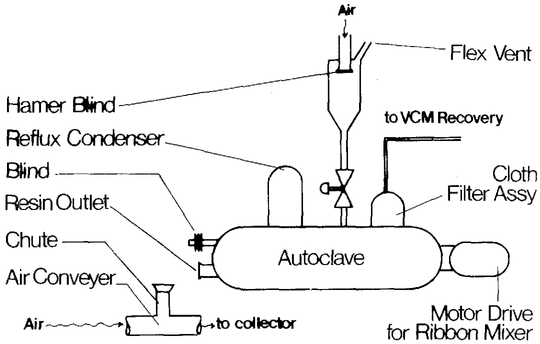

Figure 2 — Bulk process reactor.

control system. In addition, computer control reduces the number of on-site operators and their time spent in potential exposure areas. The operators spend a large portion of their time in safe exposure areas, such as screening and grinding sites, and nonexposure areas, such as the control room, which is under positive pressure.

Bulk process reaction system. The bulk process reaction system shown in Figure 2 was designed to totally enclose the reaction and stripping steps and to reduce maintenance requirements on the reactor and the VCM recovery equipment. The main features that result in reduced worker exposure are the following:

1. Stripping process: VCM stripping is undertaken in the autoclave following the polymerization cycle and is very important to the overall VCM control program. The general steps are as follows (refer to Figure 2):
   a. At the completion of the polymerization cycle, multi-stage recovery compressors draw two successive vacuums on the autoclave.
   b. During each evacuation, the autoclave is heated to facilitate VCM removal from the resin.
   c. Nitrogen is used to break the vacuum after the first evacuation to prevent the formation of explosive VCM/air mixtures.
   d. Air is used to break the vacuum after the second evacuation.
   e. The autoclave is opened for resin transfer after the air pressures inside and outside the autoclave are equalized.

2. Heat removal: In addition to the jacketed autoclave surface, a reflux vapor condenser is used to remove the heat generated during the polymerization reaction. Condensation of the VCM vapors on the condensers does not result in fouling of exchanger surfaces as would be the case if the exchanger were in direct contact with the liquid reacting mass. The need to enter the reactor vessel for maintenance purposes is therefore substantially reduced.

3. VCM vapor filtering: The VCM vapor removed after the completion of the polymerization step must be free of particulates to avoid damage to compressors and peripheral equipment in the VCM recovery area. The filter assembly is housed (refer to Figure 2) in a dome or manhead above the autoclave. The filter assembly consists of filter medium mounted on a 61 cm (24 in.)-diameter coarse screen basket. Potential exposure due to opening and cleaning the filter is reduced by scheduling the cleaning after the autoclave stripping operation. An air conveyance system for the finished resin permits emptying of the reactor under negative pressure, and the flow of air into the autoclave through the resin transfer manway prevents any residual monomer from escaping into the workplace.

VCM recovery operations. The VCM recovery operation was designed to minimize the use of compressors and to reduce the load on the compressors. The recovery area is shown in Figure 1. The recovery cycle begins with the VCM at pressures substantially above its condensation pressure. The VCM is passed directly to the condensers, until the system pressure drops to the VCM condensation pressure of 2.8 kg/cm^2 (40 psi). At this point, the values on the lines bypassing the compressor are closed, the valve on the line to the compressor is opened, and the remaining VCM is compressed above the condensation pressure and then condensed in the chilled condensor and returned to storage.

Dual blowout disc interlocks. Dual rupture discs (one under pressure and one spare) are employed on the prepolymerizers and autoclaves to minimize VCM loss to the atmosphere in the event of a rupture disc blowout. The handles of the valves preceding these two rupture discs are interlocked so as to automatically engage the spare rupture disc when the valve ahead of the ruptured disc is closed manually. This design feature counters human errors that could result in significant VCM emissions during an emergency.

Prepolymerization entry procedure. In order to minimize potential exposure when employees must enter the prepolymerizer, a vacuum of approximately 66 cm (26 in.) is pulled on the vessel, after which the vessel is returned to atmospheric pressure with nitrogen. Nitrogen is used to avoid potentially explosive gas mixtures. This sequence is repeated once, and the second vacuum break is with air. To increase the effectiveness of this pre-entry procedure, there are plans to provide additional heating capacity to this vessel to assist VCM removal.

Vent stack location. The vent stack outlet is located approximately 24.4 m (80 ft.) above the top of the process building. This stack height was chosen to prevent vented VCM from entering this or any other process building by putting the outlet above the eddies induced by the building. The vent stack is used to intermittently dispose of small quantities of VCM during normal operations and for venting VCM leaks until proper maintenance operations can be performed.

leak detection and prevention

Description of system. The process characteristics and modifications already described prevent extensive escape of VCM into the workplace; the major remaining emission source is leaks from valves, flanges, and compressor, pump, and agitator seals.

Rapid leak detection is an integral part of the VCM exposure reduction program. The detection system consists of two parts; each is essential to the program's effectiveness:

1. Process monitoring by gas chromatograph: Air samples are collected in sequence from a number of strategically located monitoring points. (The optimum locations are determined by extensive area

TABLE I
Seals for Compressors, Pumps, and Agitators

Application and Vendor	Seal Manufacturer	Seal Model No.
Recovery of VCM Pennsylvania Compressor	Pennsylvania Compressor	Vendor will supply details.
Pump for VCM Duriron Model Mark II	Crane	Type 9T QPICI (316)
Agitator on Prepolymerizer	Crane	Type 9B
Autoclave-Ribbon	Pechiney-Saint Gobain	Vendor will supply details.

sampling.) Each of the monitoring points is sampled every 6 minutes, and a continuous strip-chart recorder plots the VCM results in parts per million. Any individual reading from 1 ppm to 5 ppm activates a warning light in the control panel and in the process areas; a reading of greater than 5 ppm activates flashing red lights. The light system simultaneously indicates the need for respiratory protection and initiates the leak detection procedure. A computer alarm is activated upon detection of any VCM concentration in excess of 900 ppm. If this occurs an alarm is sounded and buildings are evacuated.

2. Portable hydrocarbon detector: When any warning light is activated, a designated employee goes to the strip-chart recorder and determines which monitoring point recorded a VCM level in excess of 1 ppm. He then takes a portable hydrocarbon detector and uses it to locate the leak. If the leak has not stopped or cannot be promptly repaired, one (or more) of the available flexible exhause hoses is opened and positioned to capture and exhaust the escaping VCM until maintenance personnel can correct the problem.

The circumstances of each leak are recorded and filed. A periodic evaluation of these records serves to pinpoint recurring problem areas.

Important equipment features. The following equipment features reduce leak occurrence and the potential for worker exposure:

1. Valves: Various types of valves have been evaluated for specific applications. In some instances, superior valves were found that reduced leaks and maintenance requirements. In general, most ball valves were phased out and replaced by butterfly valves.
2. Prepolymerizer: The agitator shafts have Pfaudler oil seals (refer to Table I) under nitrogen pressure greater than the maximum vessel pressure. It was reported that no replacements have been required for these seals in over 2 years, and leaks are infrequent.
3. Autoclave: The ribbon-mixer drive shaft seal (refer to Table I) is packed with grease under a pressure of approximately 14.0 kg/cm^2 (200 psi), which is greater than the maximum working pressure in the vessel. Preventive maintenance is required twice a week to make adjustments, which generally consist of manually adjusting the piston in the grease cartridge to maintain the required grease pressure. The packing usually lasts 1 year.
4. Compressor seals: The recovery compressor seals (refer to Table I) are pressurized with nitrogen at a pressure greater than the VCM pressure. Any leaks result in passage of nitrogen into the monomer recovery plumbing and build-up of noncondensable gases (N_2, etc.) in the recovery system. The computer system reacts to this situation by alerting the operators to check the compressor seal. However, compressor seal failure has been very rare.
5. Pumps: Pumps used for transporting VCM or process streams containing VCM are located outdoors. Teflon packing material is used in pump seals (refer to Table I) because of its resistance to VCM. Whenever possible, process streams are transported by gravity flow. This is an excellent example of alleviating a potential

source of exposure by eliminating the need for leak-prone equipment.

local exhaust ventilation

The usual purpose of local exhaust ventilation systems in industry is to remove emissions from permanent sources that cannot be controlled by process enclosure or other methods. As the PVC process is fully enclosed and without permanent emission sources, a novel local exhaust strategy is necessary — one flexible enough to deal effectively with leaks occurring in a variable and unpredictable manner.

The system that has been evolved is effective and is efficient from an energy-conservation standpoint. Thirty-four process points were selected on the basis of potential for leakage for installation of permanent exhaust hoods or flexible-hose entry sleeves. Because many of the process points are identical and repeated for each operating line, the total number of distinct types of exhaust takeoffs is reduced to 11, as follows:

1. Autoclave filter manheads — 11.32 m^3/min. (400 cfm)
2. Vacuum break valves—6.23 m^3/min. (220 cfm).
3. Autoclave drive end shaft seal — 11.32 m^3/min. (400 cfm)
4. Recovery manifold bleed valve — 5.66 m^3/min. (200 cfm)
5. Low-pressure VCM filters in the recovery area — 12.74 m^3/min. (450 cfm)
6. High-pressure VCM filters in the recovery area — 12.74 m^3/min. (450 cfm)
7. Prepolymerizer Yarway valves — 10.76 m^3/min. (380 cfm)
8. Additives entry funnel — 8.5 m^3/min. (300 cfm)
9. Autoclave shaft seal hood — 11.32 m^3/min. (400 cfm)
10. All blind flanges — 9.1 m^3/min. (300 cfm) to 11.32 m^3/min. (400 cfm)
11. Recovery compressor — 17.0 m^3/min. (600 cfm)

The indicated airflow rates are those used in design calculations for estimating required blower capacity. Actual flow rates are equal to or greater than design values.

The first seven of these exhaust points consist only of a duct connection sleeve into an enclosure surrounding the individual piece of equipment. The additives entry funnel exhaust (No. 8) consists simply of a flexible exhaust duct dropped into the funnel. The final three points consist of permanently affixed hoods that were designed to fit the geometry of the specific flange, autoclave, and compressor. Each of the hoods and enclosures can be exhausted by connecting it with 1 m (3 ft.) to 8 m (25 ft.) long individually accessible flexible exhaust ducts extending from a common main duct. An important secondary function of this system is the containment of leaks at process points other than those already listed. If there are no leaks in an area served by a given flexible duct, it is "deadheaded" or blocked off with metal plugs or branch dampers.

The distinctive feature of the system is that it is used solely as an adjunct to the leak detection and prevention program: i.e., the exhaust is provided to a given hood or enclosure sleeve only when a leak is detected.

The logic behind the system is simple and compelling. If the individual hoods or enclosures were exhausted constantly, leaks would be masked and the leak detection and prevention program would fail. This would be unacceptable because the overall VCM containment strategy hinges on engineering modifications that will prevent leaks rather than exhaust them. An additional objection to continual venting is the large expense of installing a system to clean exhausted air to meet the Environmental Protection Agency (EPA) requirements of no more than 10 ppm VCM in vented air.

general ventilation

The general ventilation system is shown in Figure 3. Under normal conditions the system provides approximately 19 air changes per hour during winter and 37 air changes per hour during summer or in emergency conditions. The emergency ventilation system is operated manually when the gas monitoring system detects 900 ppm or more of VCM.

The system is designed to induce a relatively consistent airflow pattern from the south to the north end of the building. The exhaust fans are located on two levels to correspond to the two

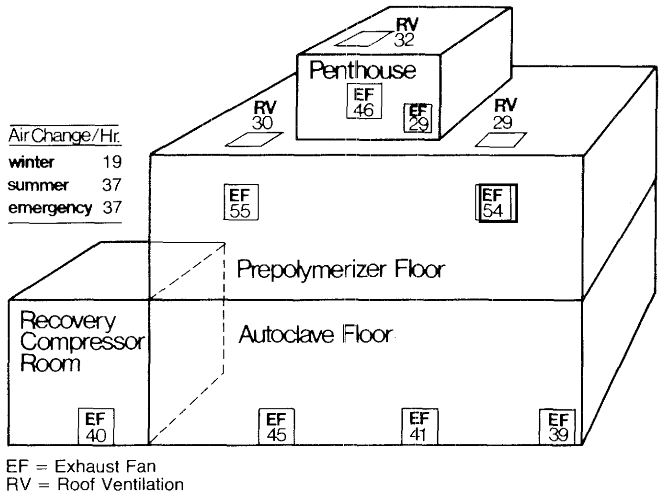

Figure 3 — General ventilation system.

process areas, separated by an open grate floor. This assists in reducing the amount of air flowing through the grating so that a leak in one process area will not cause high VCM levels in the other.

A solid floor was installed over the open grating between the penthouse and the main process building. This floor has eliminated VCM excursions in the penthouse by effectively segregating it from the process area where leaks may occur.

The benefits from the system are twofold. Of primary importance is the high air change rate, which dilutes any VCM leakage. Also the overall direction of flow is such that leaks in one area are unlikely to exert a large influence on other areas.

The VCM recovery room at the east end of the building was originally not partitioned off from the main process building. It was determined that VCM leaks in this area were affecting other areas of the main building. Because this area is infrequently entered by personnel, the connecting space was almost totally partitioned off with a block wall, causing a measured inward airflow of about 0.762 m/s (150 fpm) through open sections in the partition. Since this modification, no further excursions above threshold concentration have been induced by leaks from the recovery condenser or compressor.

ongoing improvements

Major modifications are now planned for reducing environmental emissions in compliance with the newly promulgated EPA regulations for vinyl chloride. These improvements are expected to have a beneficial effect also on worker exposure rates. Two major improvements have been planned:

1. The installation of a treatment system for reducing VCM concentrations in air exhausted to the atmosphere from the recovery system to 10 ppm by carbon adsorption or solvent absorption.
2. Better procedures before opening reaction vessels, to meet EPA's requirement of no more than .02 g VCM (in vapor space of reactor) per kg of resin product. Improvements may include an increase in the number of successive vacuums pulled on the vessel prior to opening.

vinyl chloride monomer monitoring — control system effectiveness

A full-scale VCM monitoring program was initiated in early 1974 and extensive data have been recorded. Area sampling data are provided by the gas chromatograph monitoring system. From 1974 to early 1976, all data points were recorded and summarized as weekly averages. To illustrate the effect of implemented control measures, monthly area sample averages are plotted in Figure 4. The reduction from 1974 to the first quarter of 1975, when most engineering controls had been installed, is striking.

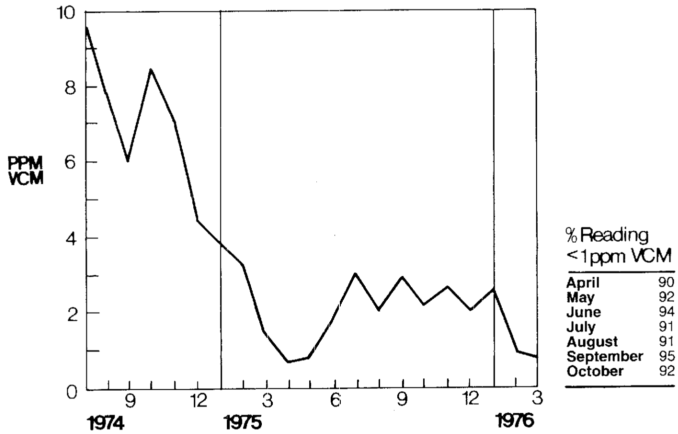

Figure 4 — Monthly gas chromatograph data averages.

Since March of 1976, area sampling data have been summarized in terms of percent readings under 1 ppm, as shown in Figure 4, where it will be seen that 90% or more of all VCM measurements are consistently below 1 ppm.

Each employee is also monitored every month with charcoal tube sampling devices, worn over a full shift and thus showing actual 8-hour time-weighted average exposure. Exposures of workers during 1974, 1975, and 1976 are summarized in Table II, where the reduction from 1974 to 1975, after installation of many controls, is very marked.

TABLE II
Average Distribution of VCM Results

Period	VCM, ppm <1	1-3	3-5	5-10	>10
1974	2%	34%	18%	22%	24%
1975	43%	37%	8%	9%	3%
1976	73%	17%	3%	5%	2%

It is unfortunate that there are no available data to reflect the relative effectiveness of each control technique. However, it is clear that no one control is independently sufficient to meet the 1 ppm VCM standard.

The program to reduce VCM exposure is not yet complete. Efforts are continuing to make better use of the currently installed controls, and where needs are pinpointed by the leak detection program additional controls are being implemented.

personal protective equipment for vinyl chloride monomer

The requirements for respiratory protection from VCM exposure have been integrated into the monitoring alarm-light system. Employees are required to use the full-face supplied-air line system when the amber light (reading of greater than 1 ppm) is activated. However, they may use a short air line and move from one air line connection to another. Respiratory protection is also required when workers are performing tasks that are known to cause exposures (e.g., changing flanges on VCM lines or entering process vessels). When the flashing red light (reading of greater than 5 ppm) appears, the full-face supplied-air line system again must be used, but a long air line is required and mobility is decreased. If the monitoring system picks up a reading of greater than 900 ppm, an alarm is sounded and the building is evacuated. In this situation, a self-contained air pack is required for reentry.

When employees enter an autoclave for cleaning, a Tyvek suit, a hood, and work gloves are required.

Work uniforms are provided daily and showers are recommended but not required.

control of other potential hazards

polyvinyl chloride dust

PVC resin may become airborne from leaks in the screening and grinding system. This is considered nuisance dust with a permissible time-weighted average exposure limit of 15 mg/m^3. Dust control is effected by maintaining the enclosed integrity of the screens and grinder, by ensuring good mechanical fits, and by keeping all enclosures under a slight negative pressure. The latter is accomplished by providing small ducts from the pneumatic transfer system to the hoppers, screens, and grinders. Horizontal surfaces are periodically cleaned of settled resin with industrial-grade vacuums. Operators rarely have to enter these areas, so isolation is considered a very effective control.

noise

Noise readings in the polymerization building average from 90 dBA to 92 dBA. The major sources of this noise are the agitator motors for the prepolymerizers and autoclaves, and one steam mixer that has not been modified as in Figure 5. Due to the fact that the operators' average exposure time in the area is less than 4 hours per day, hearing protection is not legally required. However, plant safety and health personnel feel that no extended exposure is tolerable and hence require hearing protection for employees who will be in the reaction area in excess of 1 hour at a stretch. Only two noise-abatement control modifications were noted. The mixing of cooling water with high-pressure steam in a pipe induced substantial line vibration and was causing very high noise levels. This situation was corrected by relocating the steam mixing jets on the inlet side of the pump (refer to Figure 5). Before-and-after sound-pressure levels were not available for comparison, but discussions with various operators indicated that this modification was very successful.

The resin transfer blowers (located outside) were exceptionally noisy. These blowers were totally enclosed in a block house. Noise levels in these areas were reduced to well below 90 dBA.

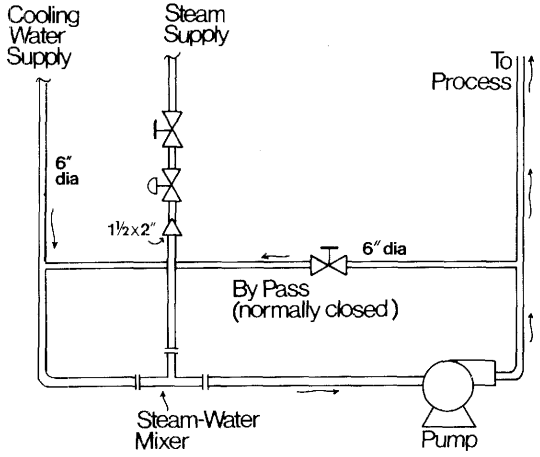

Figure 5 — Steam-water mixer.

conclusion

On the whole, the engineering challenge of controlling VCM in the workplace to 1 ppm has been met in the PVC bulk polymerization process. The VCM control system consists of a variety of engineering controls, each one of which must function in order to achieve the required conditions.

The emphasis is on process enclosure and good design to minimize the potential for VCM escape to the workplace due to equipment failure or operator error. Ventilation is used to supplement the process design and an ongoing program of improvements has been planned, to reduce both in-plant emissions and environmental pollution.

The principles implemented to control worker exposure in the bulk PVC process are generally applicable to a variety of other chemical operations and specifically applicable to other plastics manufacturing processes.

A final report of all 16 case studies, with recommendations for technology transfer and additional research and development, will be available in late 1977.

Accepted August 8, 1977