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Engineering Control Technology in Polyvinyl Chloride Polymerization Plants

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ENGINEERING CONTROL TECHNOLOGY IN POLYVINYL CHLORIDE POLYMERIZATION PLANTS

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The National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering has initiated a research program in control technology. The objective of this program is to facilitate the implementation of effective preventative measures in order to prevent occupational illness. The plastics and resins industry control technology assessment has recently been completed. The objectives of this study were to document and evaluate effective control technology for plastics and resins polymerization plants. Particular emphasis was given to PVC polymerization processes, since the relatively recent lowering in the personal exposure limit for vinyl chloride monomer (VCM) to an 8-hour 1 ppm time-weighted average has required the application of state-of-the-art controls. The present paper contains a summary of the control technology that was found to be effective in controlling VCM in processes manufacturing PVC by suspension, bulk, and dispersion polymerization.

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ABSTRACT

The National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering has initiated a research program in control technology. The objective of this program is to facilitate the implementation of effective preventative measures in order to prevent occupational illness. The plastics and resins industry control technology assessment has recently been completed. The objectives of this study were to document and evaluate effective control technology for plastics and resins polymerization plants. Particular emphasis was given to PVC polymerization processes, since the relatively recent lowering in the personal exposure limit for vinyl chloride monomer (VCM) to an 8-hour 1 ppm time-weighted average has required the application of state-of-the-art controls. The present paper contains a summary of the control technology that was found to be effective in controlling VCM in processes manufacturing PVC by suspension, bulk, and dispersion polymerization.

Controls necessary for VCM include process and equipment modification, isolation, local and general ventilation, work practices, personal protective equipment, workplace monitoring systems, employee/employer education, and ongoing effort by both workers and management. All of these components must function together as an integrated coordinated system in order to assure worker protection under normal operating conditions or under conditions of process upset or maintenance.

ACKNOWLEDGEMENT

The present paper is based primarily on the final report from a study entitled "Engineering Control Technology Assessment for the Plastics and Resins Industry," which was done by Enviro Control, Inc. (ECI), Rockville, Maryland under NIOSH contract 210-76-0122. The principal ECI investigators who prepared the report are Julius H. Bochinski and Kenneth Schoultz. This report will be published by NIOSH in June 1978. Much of the text in the present paper has been taken directly from case studies of this report dealing with PVC processes and with workplace monitoring systems. The author has completely reorganized the material, has rewritten some of it, and has added a significant amount of new material.

INTRODUCTION

The National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering, has begun a research program in the area of control technology. The objective of this program is to facilitate the implementation of effective preventative measures (particularly engineering controls) in order to minimize occupational illness. The first phase of the program involves a series of industry-wide control technology assessments. These control technology assessments are being conducted or planned for plastics and resins, foundries, textile finishing, non-ferrous smelters, dry cleaning, pesticides manufacturing and formulating, cotton processes, and coal conversion processes. The primary output of the studies is intended to be a document which will describe control techniques used by technically advanced companies in order to promote the application of these measures throughout the industry on a voluntary basis. The control technology assessment studies are structured so as to provide illustrative examples of effective controls rather than definitive cases of "best" controls. The studies are also designed to identify control problems which require further study (either by NIOSH or industry) in order to provide satisfactory solutions. Care is taken during the course of the studies to safeguard information which individual plants or companies regard as proprietary or "trade secret."

The implementation of effective preventative measures on a voluntary basis by industry will have several positive effects. First, the mutual industry/labor/government objective of preventing occupational illness will be promoted. Second, the engineers and hygienists who are responsible for implementing effective control measures will benefit from the collective experiences (both successes and failures) of industry and will thus be able to function more efficiently. Finally, the Occupational Safety and Health Administration (OSHA) will probably be able to operate less in a "crisis" mode of regulation as preventative engineering control measures are more widely used.

The control technology assessment of the plastics and resins polymerization industry is the first of the NIOSH control technology studies to be completed. The plastics and resins control technology assessments were done through a 16-month contract to Enviro Control, Inc., (ECI), Rockville, Maryland, (Contract 210-76-0122). The study was initiated in response to a series of observed occupational health problems in the polymerization industry which have resulted from exposure to monomers (such as vinyl chloride or acrylonitrile), or from unknown sources (as in SBR plants).

The ECI control technology assessments involved a series of process control technology case studies, in which control strategies and hardware were described and evaluated for major polymerization processes with a variety of polymers. The recent intense level of research, development and application of control technology for vinyl chloride monomer (VCM) and the fact that vinyl chloride is manufactured by representative polymerization processes dictated that a major portion of the study should be devoted to vinyl chloride polymerization. The study involved an evaluation of control systems for thirteen polymerization processes: six for PVC, two for phenolics, and one each for ABS-SAN, polystyrene, SBR, epoxy, and TDI. A final report from the study is being published.

The present paper is intended to integrate the control technology that is used for vinyl chloride polymerization plants into a single discussion. Much of the information contained in the present paper is taken directly from the final ECI report. The discussion is intended to illustrate a number of innovative applications of control technology by the chemical industry, but not to function as a definitive description of necessary and sufficient controls for polymerization plants. In order to be of maximum use to the industrial community, the discussion includes substantial detail concerning the hardware (e.g., manufacturers' names) that is used in particular cases. Mention of a manufacturer's name does not constitute endorsement by NIOSH. On the contrary, NIOSH recognizes that the performance of different types of hardware (such as equipment seals) can often vary widely even in similar applications within a plant. Selection of brands of hardware must be done on a plant-by-plant, case-by-case basis.

PROCESSES AND HAZARDS

PVC POLYMERIZATION PROCESSES

Three major types of polymerization processes are used to manufacture polyvinyl chloride (PVC) from vinyl chloride monomer (VCM). These processes are mass (or bulk) polymerization, suspension polymerization, and emulsion (often called dispersion) polymerization. Polymerization reactions in general are highly exothermic, and the dramatic viscosity increase and phase change which accompanies the polymerization reaction can complicate the control of process and product parameters (such as temperature and polymer chain length). A summary of the three PVC polymerization processes is given below.

Suspension Polymerization

Suspension polymerization is the primary process for the manufacture of PVC resin in terms of production volume. A typical suspension polymerization reaction involves the addition of VCM, water and various additives to a polymerization reactor, agitation to suspend the VCM into 0.1-1 cm droplets with a continuous water phase, heatup of the reaction mix to initiate the polymerization reaction, and the application of cooling water to the reactor jacket in order to remove the heat of polymerization as the reaction proceeds. At the end of the reaction the PVC-water slurry is transferred to a vessel in which the unreacted VCM is removed (stripped) and subsequently recovered. The slurry is then pumped to a centrifuge that separates the water from the PVC particles, and the PVC wet cake from the centrifuge is dried and sent to bulk resin storage. Two suspension polymerization processes were surveyed in the ECI study. Flow sheets for these processes are shown in Figures 1 and 2. The minor differences in these flow sheets illustrate typical differences that exist between plants which employ the same basic process.

Dispersion polymerization

Dispersion polymerization is similar to suspension, except that dispersion polymerization involves the use of high shear mixers or emulsifiers to break the VCM into submicron droplets (micelles) prior to the polymerization reaction. Although the particle size has a large effect on reaction kinetics, major process equipment for dispersion polymerization is similar to that for suspension polymerization. The same reactors are often used for both types of polymerization. Resin recovery and drying steps may be somewhat different due to the particle size of the recovered product.

The ECI study involved two dispersion polymerization processes. Flow sheets for these processes are shown in Figures 3 and 4. Again, minor plant-to-plant process variations occur as indicated in the flow sheets.

Bulk Polymerization

The bulk polymerization process for PVC (which involves the use of licensed Pechiney-St. Gobain technology) is substantially different from suspension and dispersion polymerization. The bulk polymerization process involves the direct production of granular PVC in a reaction autoclave without the use of a dilution solvent as a heat transfer medium. The first process step involves the introduction of VCM with various additives to an agitated prepolymerization vessel. Around 10% of the VCM is polymerized to form PVC in the prepolymerizer (resulting in the formation of many PVC nuclei), and this reacting mix is then introduced to a horizontal cylindrical autoclave containing VCM and various additives. The resulting process of additional polymerization on the nuclei which had been formed in the prepolymerizer is roughly similar (in principle, at least) to a crystallization process. Heat removal is achieved primarily by condensation of

VCM vapors on jacketed reactor surfaces. Since the reaction temperature is maintained below the fusion point of PVC, a granular product is the result. At the completion of the reaction, unreacted VCM is stripped from the granular product by applying heat and vacuum to the reaction autoclave. The product is then transferred to bulk resin storage. Figure 5 shows a typical bulk polymerization process. The ECI study involved an evaluation of the control technology for two separate bulk polymerization processes.

HAZARDS AND EXPOSURE SOURCES

The following brief review of hazards, routes of occupational exposure, and key sources of exposure for PVC polymerization plants is intended to serve as a background for the discussion of control technology which follows.

Hazards

Vinyl chloride monomer is the chief recognized health hazard in the industry. The 8-hour time weighted average (TWA) permissilbe exposure limit (PEL) for VCM is 1 ppm, with a 15-minute ceiling of 5 ppm. PVC dust (8-hour TWA of 15 mg/m^3 total dust), noise (8-hour TWA of 90 dBA), various solvents and a variety of minor additives (which generally do not have PEL standards) are other recognized hazards. In general, the technological sophistication necessary to maintain personal exposure to VCM below 1 ppm TWA is adequate to control the other recognized hazards in the industry (except perhaps noise). Therefore the remainder of the discussion on controls deals exclusively with VCM.

Routes of Exposure

Since vinyl chloride monomer is a gas at room temperature, the chief route of occupational exposure is through inhalation. Prior to 1974, significant dermal contact with VCM which occurred in manual reactor cleaning was associated with acroosteolysis (bone degeneration in the hands). However, current VCM standards result in the use of sophisticated control measures (such as automated reactor cleaning) against respiratory exposure, and these also greatly reduce dermal exposure to VCM.

Sources of Exposure

VCM is normally contained in enclosed process systems during PVC polymerization in order to avoid occupational exposure. In general, any situation which violates the integrity of these enclosed process systems presents the potential for occupational exposure to the monomer. Receipt and handling systems for bulk VCM are seldom subject to equipment failure because of the nature (one-phase low viscosity compressed vapor) of bulk VCM. Processing of PVC after monomer stripping is likewise not an important source of exposure to VCM. High product stability and relatively low affinity of the monomer for water allow effective VCM stripping at the end of the polymerization process, so that further separation, drying and handling of the bulk polymer can be done with no apparent exposure problem to VCM. The steps between handling bulk VCM and the stripping of VCM from the final product polymer (including reactor charging, polymerization, handling the VCM-laden slurry, stripping, and VCM recovery) are the ones which require the application of effective control technology in order to prevent occupational exposure to VCM. Some potential sources of occupational exposure to VCM in polymerization plants are given in Table 1.

PRINCIPLES OF CONTROL

Respiratory exposure to vinyl chloride which may originate at the "problem" areas outlined in Table 1 is minimized through the application of a number of well-known principles of control. These principles are summarized in Table 2. Controls applied at or near the point of origin of the hazard are generally more effective at minimizing occupational exposure than controls which are applied to the general workplace. Most occupational hazards (including VCM) require controls at the point of origin of the hazard, in the general workplace

Table 1. Potential sources of occupational exposure to VCM

Operation	Exposure Source
Reactor charging	- opening reactors for adding batch (solid) ingredients
Polymerization	- failure of gaskets around reactor manways
	- agitator seal failure
Post-polymerization slurry handling	- pump seal failure
	- maintenance required on plugged lines and filters
	- failure at flanged or other connections
	- material sampling for quality control
Post-polymerization maintenance on reactor	- cleaning PVC crust from reactor internal surfaces
VCM recovery system	- equipment (compressor) failure
	- failure of seals on compressors
Handling of contaminated process waste	- scrap PVC from reactor cleaning
	- process wastewater
Handling of contaminated exhaust air	- inadvertent recirculation of VCM laden exhaust air from ventilation systems

environment, and at the individual worker. These controls must function together as an integrated, coordinated system in order to provide worker protection under normal operating conditions as well as under conditions of process upset or maintenance. Process or workplace monitoring/warning systems, the education of both workers and management concerning occupational health, and surveillance of controls to ensure proper use and operating conditions are also important ingredients of a complete control system for VCM.

Table 2. Principles of control

Point of application of the control measure	Control measure
At or near the hazard source	Substitution of non-hazardous or less hazardous material
	Process modification
	Equipment modification
	Isolation of the source
	Local exhaust ventilation
	Work practices
To the general workplace environment	General dilution ventilation
	Local room air cleaning devices
	Work practices
At or near the worker	Work practices
	Isolation of workers
	Personal protective equipment
Adjuncts to the above controls	Process monitoring systems
	Workplace monitoring systems
	Education of workers and management
	Surveillence and maintenance of controls
	Effective process-people interaction and feedback

CONTROL TECHNIQUES FOR VCM

Control of VCM in PVC polymerization plants involves the application of the principles of control to exposure sources such as those summarized above. Reduction of 8-hour TWA worker exposures to 1 ppm has been a difficult engineering challenge, and has required the use of virtually every available control technique (except material substitution for VCM). In all cases, the synthesis of a number of control techniques to form a control system has been required in order to meet the 1 ppm VCM standard. The following discussion describes the retrofit controls which have been installed on existing (pre-1974) PVC plants in order to meet the 1 ppm 8-hour TWA standard for VCM.

PROCESS MODIFICATION

Process design and modification is an effective means of reducing occupational exposure to VCM, in both bulk polymerization and suspension/dispersion polymerization processes. The inherent operating characteristics of the bulk polymerization process (Figure 5) 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 an aqueous or solvent medium. This reduces the potential for employee exposure by:

- eliminating post-polymerization separation and drying:
- eliminating the exposure associated with solvent recovery or monomer-

contaminated waste water disposal and treatment; and,

- allowing the use of low-temperature recovery condensers, which lessens the potential for leaks and decreases VCM concentration in the off-gas.

Another characteristic of the bulk polymerization process is the method by which the heat of polymerization is removed from the reaction autoclave. 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 condenser 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.

Process modifications are also useful in reducing exposure sources in suspension/emulsion polymerization processes. The most effective process modification to date is the installation of stripping operations to remove and subsequently recover residual vinyl chloride from the PVC slurry in the stripping tank and from the vapor space in the reactor, as indicated in Figures 1 through 4.

In general, slurry stripping operations employ both vacuum and heat to remove the VCM from the slurry. Details of many stripping processes are considered proprietary. In a typical stripping process, once the PVC slurry has been dumped from the reactor into a stripping tank, the recovery compressors draw vacuum on both vessels. The compressors are arranged in a two-stage operation with an intermediate heat exchanger between the first and second stages. A heat exchanger following the second compressor condenses the vinyl chloride at about 80 psi pressure. The condensed vinyl chloride is pumped to an accumulator and transferred to master tanks for future use. The inert gas accumulated in the system must be vented to the atmosphere following the final condenser stage after the second compressor. A refrigerated heat exchanger is used to reduce trace levels of vinyl chloride in the off-gas to acceptable standards as specified by the Environmental Protection Agency (EPA). During each shift, the system must be purged of accumulated water (which varies in quantity from a pint to a few gallons per shift) to avoid damage to compressor heads. A number of variations on the above process (such as stream stripping, bubbling nitrogen through the slurry, thin film evaporators, etc.) may be used for stripping.

The stripping operation reduces exposure in two ways: (1) residual vinyl chloride in the PVC slurry is substantially reduced (the levels are believed to be sufficiently low to prevent further exposure downstream of the stripping operation relative to the 1 ppm TWA standard), and (2) vinyl chloride in the empty reactor vapor space is removed to the degree that the vessel may be opened following the polymerization cycle without causing a significant release of vinyl chloride into the workplace. In general, the efficacy of slurry stripping depends on both the vapor-liquid equilibrium of the monomer-slurry system and on the thermal stability of the product polymer.

Another effective control measure involves the use of (proprietary) additives or coatings to the polymerization reactors which reduce the crusting of polymer on the reactor walls and other heat exchange surfaces.

The entry and cleaning frequency in one suspension polymerization process has been reduced to once every 100 batches by the development of proprietary anti-buildup coatings.

A final example of effective process modification/design involves the use of gravity flow to achieve slurry transfer in place of pumps. The equipment failure associated with pump seals is thus completely avoided.

EQUIPMENT DESIGN AND MODIFICATION

Modification of process equipment to achieve more complete enclosure with fewer breakdowns is the most common means of retrofit control in PVC polymerization plants. Examples of equipment modification are given below. By definition, these modifications tend to be "hardware" oriented.

Air Lock for Addition of Solid Additives to a Dispersion Polymerization Reactor

A potential for VCM escape exists when minor batch ingredients are dumped into PVC polymerization reactors. This potential is reduced substantially by the use of a simple air lock entry system as depicted in Figure 6.

The top valve is opened and the ingredients are dumped through the feed spout into the air lock. Any dust or vapors generated are removed by a flexible exhaust duct positioned in the spout. The top valve is closed, the bottom valve is opened and the ingredients drop into the tank. The bottom valve is then closed. Any VCM trapped in the air lock between batches would be exhausted when the top valve is opened at the start of the next charging operation.

Use of Dual Interlocked Rupture Discs on Bulk Polymerization Autoclaves

Two sets of rupture discs are employed on typical bulk polymerization prepolymerizers and autoclaves (as shown in Figure 7) to minimize "down time" in the event safe pressures are exceeded.

Each set consists of two rupture discs in series with a by-pass line coming out of the space between the two discs and a small relief valve that can discharge to a point downstream if the upper disc blows. This disc arrangement was devised to compensate for problems caused by persistent pin hole corrosion in the lower rupture discs. Substitution of available materials of construction did not eliminate the pin hole corrosion of the discs. The leaks created a condition which could have allowed the reactor pressure to go well beyond the safe working pressure; i.e., a leak would gradually allow the pressure across the lower disc to equalize. The autoclave pressure could then rise to twice the blow out pressure of the disc. The 10 psi relief valve by-pass prevents this condition from occurring and thus eliminates the potential for a catastrophic exposure caused by vessel rupture.

The valves preceding the discs are interlocked to assure positive engagement of the new rupture disc when the valve ahead of the ruptured disc is closed.

Equipment for the Treatment and Disposal of Contaminated Process Waste Water

Dispersion and suspension polymerization processes have various process waste water streams containing small quantitites of vinyl chloride that must be discharged. In order to eliminate these as a source of vinyl chloride escape to the workplace and also to the environment, it is necessary to remove the vinyl chloride from these streams prior to discharge into the sump. In one case a blend tank was modified to receive the liquid streams from:

- Blow downs from both compressor separators
- Recovered vinyl chloride filter drains
- Knockout pot drains
- Water drain from pure vinyl chloride weigh tank, recovered vinyl chloride storage tank and master mix tanks
- Water drain from recovered vinyl chloride receivers
- Drains from all charge filters

The tank is equipped with a relief valve set at 150 psi and pressure control devices to maintain vacuum at all times. The vacuum is applied via the vapor line connection (refer to Figure 8) to the inlet of the recovery system and varies from a maximum of 22 inches Hg at no load to as low as 4 inches Hg at maximum vapor loads. Heat for the operation is supplied solely by the sensible heat in the inlet water, which enters at approximately 100° to 120° F. The vinyl chloride recovered in the containment system is transferred to the vinyl chloride recovery system.

Seals and Fittings

Each PVC plant which was surveyed has an ongoing program to identify process seals and fittings which will minimize leaks of VCM to the workplace. The following are examples of particular seals and fittings which are being used in PVC polymerization plants.

The seals and fittings used in one bulk polymerization plant are as follows:

Valves --

FWI eccentric plug valves have replaced all Pacific ball valves. Plant engineering and maintenance personnel believe that historical data indicate that FWI valves are the best for VCM service at this plant.

Automatic blind valves manufactured by the Hilton Valve Company have been installed on several prepolymerizer lines. If the field tests continue to be successful, the valves will replace all manual blind valves. Then employees will not have to manually change these valves and exposure will be substantially reduced. The present manual blind valves will be retained as a backup. A double block and bleed system with Hills McKenna butterfly valves also worked well. However, workers did not accept the system because they could not readily determine if the valve was open or closed.

Agitator Shaft Seals --

Both ends of the autoclave have packed seals with grease maintained at 300 to 400 psi. A patent is pending for a sensing system that determines when excessive grease is used and, therefore, when maintenance is required.

The prepolymerizer agitator has double mechanical seals pressurized with mineral oil. These seals last one to two years without requiring maintenance. However, the preventive maintenance programs dictate that they be changed at the first of each year.

Recovery Compressor --

This compressor was a large source of VCM escape (refer to Figure 9). When the compressor was down (and before automatic valve 3 was installed), VCM would be forced by pressure differential from the recovery system back into the second stage of the compressor. From here it would pass through the first stage, into the crankcase, and finally into the workplace. To alleviate this problem, (1) automatic inlet and exit block valves were installed and are closed as soon as the compressor stops (this prevents VCM from bleeding back into the compressor); (2) double mechanical seals are used where the VCM came out of the crankcase; and, (3) inflatable rubber donuts encased in spool pieces were installed on the shaft just before it enters the crankcase.

The mechanical seals are pressurized with nitrogen during operation to prevent leakage to the work area. If seal failure occurs on the seal in contact with the process stream, the nitrogen will leak into the process stream.

Pumps --

Pumps used for transporting VCM or process streams containing VCM are located outdoors. The pumps are equipped with double mechanical seals with pressurized water/glycol solutions between the seals.

Autoclave leaks --

Periodically, leaks develop in welds on the agitator shafts. Since the autoclave pressure is much greater than the water pressure in the shaft, VCM leaks into the water. Until the welds can be permanently repaired, maintenance personnel use epoxy as a patching material. A vented air eliminator is used to concentrate and remove the VCM from the water that is used to pressurize the seal. The VCM release is vented to a stack. Any VCM dissolved in the water in the seal would be released when the reactor jackets are heated at the onset of the reaction.

A second bulk polymerization plant employed seals and fittings as follows:

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 with butterfly valves.

Prepolymerizer --

The agitator shafts have Pfaudler oil seals under nitrogen pressure greater than the maximum vessel pressure. It was reported that no replacements have been required for these seals in over two years and leaks are infrequent.

Autoclave --

The ribbon-mixer drive shaft seal is packed with grease under a pressure of approximately 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 consistsof manually adjusting the piston in the grease cartridge to maintain the required grease pressure. The packing usually lasts one year.

Compressor Seals --

The recovery compressor seals are pressurized with nitrogen at a pressure greater than the VCM pressure. Any leaks in a seal result in nitrogen leaking into the monomer-recovery plumbing and a build-up of noncondensable gases (N_2, etc.) in the recove system. The computer system will react to this situation by alerting the operators to check the compressor seal. However, compressor seal failure has been very rare.

Pumps --

Pumps used for transporting VCM or process streams containing VCM are located outdoors. Teflon packing material is used in pump seals because of its resistance to VCM.

Seals and fittings used in a dispersion/suspension polymerization process are as follows:

Seals --

The double mechanical seals are also used with compressors, pumps and agitators in both dispersion and suspension polymerization processes. Seals that are used with process streams containing VCM are often pressurized with a solution of glycerine and water. The glycerine is compatible with the process stream and reduces the risk of the seals freezing in cold weather, in addition to functioning as a lubricant.

Vinyl Chloride Weigh Scales --

Periodic leaks have occurred from the weigh scale relief line flanges and the rupture disc holders. Both were changed from 120 psi flat face to 150 psi raised face connections to reduce leakage. The raised flange is a male/female arrangement providing a smaller and more secure gasket contact area and, hence, a better seal. In addition, the male mating surface consists of a continuous spiral groove that prevents the direct passage of vinyl chloride to the workplace in the event of a leak. The modifications have been very successful.

As indicated in the above discussion, there is no consensus on the single most effective brand of seals or fittings for the PVC polymerization industry. Each plant has identified particular types of seals and fittings that are effective under the particular process conditions in the plant. Particular manufacturers names are given only as examples of specific applications, and their mention in the present paper is not an endorsement of that particular brand of equipment.

PROCESS OR EQUIPMENT ISOLATION

Process or equipment isolation is achieved through a number of techniques. One technique is the use of computers for process control. With a few exceptions, each PVC process is computer controlled. This allows a reduction in employee exposure because (1) the number of operators required to run the process is decreased; (2) the operators spend a significant amount of time in an enclosed control room (where exposure is essentially zero) maintained at a pressure slightly higher than the outside; and (3) operators do not have extensive interaction with the process which eliminates errors and the concomitant exposures.

Thus, the number of exposed employees, the amount of time spent in a potentially hazardous area and the likelihood of a significant release of vinyl chloride are all reduced.

A second technique is the use of physical barriers or distance to isolate equipment which is particularly likely to develop leaks. Limiting employee access to certain areas during particularly hazardous operations may also be used. VCM pumps are often located outdoors. VCM compressors are often isolated in ventilated enclosures. Other potentially troublesome pieces of process equipment are similarly isolated.

LOCAL EXHAUST VENTILATION

The process/equipment modification and isolation procedures described above are augmented by local exhaust ventilation.

The usual purpose of local exhaust ventilation systems in industry is to remove emissions of toxic contaminants from permanent process sources that are not controlled by process enclosure or other methods. Since PVC polymerization processes are designed to be fully enclosed and without permanent emission sources, a novel local exhaust strategy is necessary - one flexible enough to deal effectively with multiple, periodic leaks occurring in a variable and unpredictable manner.

The local exhaust systems that have been evolved for PVC processes are both effective and efficient from an energy-conservation standpoint. In one typical case (for bulk polymerization), a total of 34 process points were selected for installation of permanent exhaust hoods or flexible-hose entry sleeves, on the basis of potential for leakage. 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 (.189 m /s [400 cfm*])

(2) Vacuum brake valves (.104 m^3/s [220 cfm])

(3) Autoclave drive end shaft seal (.189 m^3/s [400 cfm])

(4) Recovery manifold bleed valve (.094 m^3/s [200 cfm])

(5) Low-pressure VCM filters in the recovery area (.212 m^3/s [450 cfm])

(6) High-pressure VCM filters in the recovery area (.212 m^3/s [450 cfm])

(7) Prepolymerizer Yarway valves (.179 m^3/s [380 cfm])

(8) Additives entry funnel (.142 m^3/s [300 cfm])

(9) Autoclave shaft seal hood (.189 m^3/s [400 cfm])

(10) All blind flanges (.156 - .189 m^3/s [300 - 400 cfm])

(11) Recovery compressor (.283 m^3/s [600 cfm])

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 custom 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 individually accessible flexible exhaust ducts (3' - 25' long) extending from a common main duct. An important

*These are design air flow rates used in calculations for estimating the required blower capacity, i.e., on the basis of these flow rates and the number of branches open at a given time the total cfm capacity was calculated. Actual flow rates are equal to or greater than design values.

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 on a "need" basis, when a leak is detected at that point.

The logic behind the system is simple and compelling. If the individual hoods or enclosures were exhausted constantly, leaks would be masked and could not be isolated and corrected, and the leak detection and prevention program would be circumvented. 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 is the large expense of installing a system to clean exhausted air to meet the EPA requirements of no more than 10 ppm VCM in vented air. Such a system would be necessary if leaks were allowed to continue and control depended solely on local exhaust ventilation.

GENERAL DILUTION VENTILATION

General ventilation is not intended to be a primary means of control in PVC polymerization plants. Figure 10 shows a typical general ventilation scheme for these plants. Under normal conditions the system provides approximately 19 air changes per hour during winter and 37 air changes per hour during summer and/or 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 for a relatively consistent airflow from the south to the north end of the building. The exhaust fans are located on two levels to correspond to the two process areas, separated by an open grate floor. This reduces 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 into 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 provides dilution to reduce VCM concentrations from process leaks. Also due to the location of the exhaust fans, leaks in one area do not usually exert a large contaminating influence on other areas due to the overall direction of the flow.

Ventilation systems are designed so as to avoid inadvertant recirculation of

VCM. Typically, the vent stack outlet is located well above (e.g., 80 ft.) the top of the process building in order to prevent vented VCM from re-entering any process 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 can be performed.

WORK PRACTICES

Work practices are an essential adjunct to the extensive engineering control "hardware" which has been previously discussed. Specific examples of effective work practices are given below.

Reactor and Autoclave Degassing and Cleaning

Effective, safe work practices have been important in preventing employee exposure to VCM during routine maintenance and cleanup operations on the inside of autoclaves and reaction vessels.

Typical procedures for bulk polymerization processes are as follows:

Prepolymerizer Degassing Operation --

The degassing procedure for this vessel is dependent on whether operator entry is planned following the cycle. If entry is not required, a single vacuum to 2.6 psia is pulled by the two-stage recovery compressor and the residual VCM goes to the recovery system. If operator entry is required (approximately once per day), a multiple degassing sequence is required. First, the recovery compressor draws a vacuum to 2.1 psi, first breaking the vacuum with nitrogen, then with air. The manhole is opened and a flexible duct exhaust is immediately inserted. Prior to entry, the vessel air is checked for VCM escape when the manway is opened for entry. Employees who enter the vessel are required to wear respiratory protection; minimizing VCM concentrations reduces the exposure potential for these employees also.

Autoclave Degassing Operation --

A three-stage degassing procedure is used to remove residual VCM from the vessel vapor space and the PVC resin. First, the vent line valves are opened, allowing the autoclave pressure to force VCM vapor to the recovery condenser. This process continues until the pressure has been reduced to 70 psi, at which time the recovery compressor is started. The compressor pulls vacuum to 2.6 psia and the steam stripping operation is begun. After a time, the vacuum pump is activated and the autoclave pressure is reduced to 2.1 psia (depending on the resin, the steam may be cut off prior to the vacuum pump activation). Nitrogen is used to break the vacuum to slightly below atmospheric pressure and the resin is then ready for transfer. Prior to operator entry, the nitrogen is removed by airflow induced by the resin transfer operation.

This process removes virtually all VCM from the autoclave vapor space and reduces residual VCM in the resin to below 400 ppm. The VCM in the resin diffuses very slowly over a long period of time so that VCM concentrations around all downstream operations are greatly reduced and the potential for further exposure is essentially eliminated. As with the propolymerizer degassing process, potential exposure to VCM when employees open and enter the vessel is reduced substantially.

Typical procedures for suspension or dispersion polymerization are as follows:

Reactor Degassing and Cleaning Procedure --

After the fully reacted PVC slurry is transferred from the reactor to the stripper, it is necessary to remove VCM from the reactor air space prior to opening the vessel for cleaning. The recovery compressor pulls suction on the reactor for about 1 hour to a vacuum pressure of 22 inches of mercury (previously 30 minutes and a vacuum pressure of 20 inches of mercury). Next, the reactor is purged with nitrogen, which is vented to the atmosphere. The exhaust system is hooked up at the bottom of the reactor and the manway is unbolted and lifted slightly to check the airflow. If there is no inward flow, the exhaust duct is checked for plugs and cleared and airflow is again checked. The manway is never opened fully until the airflow is assured. Next, the manway is removed and the reactor is purged with the ambient air. After approximately an hour, a high pressure water lance is inserted into the top of the reactor and connected to a water hose inserted at the bottom of the reactor. (Prior to the use of the water lance, operators had to manually clean the reactor walls after each batch). Finally, the cleaning water is drained from the reactor. Once a week the reactor bottom is cleaned with a 3D jet nozzle. This has eliminated yet another manual cleaning operation.

Housekeeping

General housekeeping is important in maintaining workplace VCM levels, particularly in the disposal of VCM-laden PVC scrap or process waste water. In one bulk polymerization process, PVC crust and residual powder cleaned from the autoclaves were previously put into a drum which was usually left in the reactor area. It was common to record VCM levels greater than 100 ppm in areas around the drum. This problem was alleviated by insisting that employees move the scrap outdoors immediately after the autoclave has been cleaned. This example illustrates the importance of good housekeeping, which is well recognized by plant personnel responsible for reducing VCM exposure levels. For this purpose, there are two full-time employees whose sole responsibility is assuring good housekeeping in the reaction and resin classification areas.

In a dispersion polymerization process, prior to 1975, VCM contaminated process liquids were drained to open sewers in the buildings. In most cases this procedure was modified to transport these liquids outside of the plant to open pits. However, this caused periodically high VCM excursions outside and frequently the VCM drifted into buildings and created employee exposure. Presently, most of the process liquids are piped to a closed, holding tank for treatment and recycle or disposal. This change has effected a substantial decrease in the frequency and severity of VCM excursions.

Work Practices in Maintenance Operations

Good work practices are necessary to minimize the potential for employee exposure during maintenance operations. Maintenance operations present a particularly serious potential for exposure to VCM in suspension and dispersion polymerization processes because of frequent equipment plugging and failure associated with slurry handling and transport. Several specific examples of good work practices for maintenance operations in suspension/dispersion polymerization processes are given below.

One example concerns gasket usage. In 1975, the leak detection program identified a recurring problem with reactor manway gasket leakage which often led to VCM concentration in excess of 100 ppm. First, all new gaskets were examined and many were found to be defective. The problem was discussed with the vendor and subsequent shipments were satisfactory. Also, a significant portion of the leakage was determined to be a result of improper securing techniques by the reactor operators. A re-emphasis and retraining program was initiated and the frequency of leakage was subsequently diminished.

Another significant source of employee expsoure for both dispersion and suspension polymerization processes was the frequent maintenance operations necessary to clean the high pressure recovered VCM filter. When the filter was neglected until totally plugged, extensive time was required for maintenance and exposure to VCM was very high. This problem has been reduced by cleaning the filters on a routine basis; that is, before they become totally plugged. A hot water (71°C - 160°F)) injection system was installed to reduce the amount of vinyl chloride in the filter prior to opening. This has appreciably reduced the exposure potential associated with changing the filters.

A third example involves maintenance procedures on cuno filters (used for removing oversized particles from the PVC slurry). Piping modifications have been made to cuno cartridge filters such that they may be drained and flushed with water before opening for cleaning. Although employees must still wear respiratory protection during the cleaning operation, vinyl chloride escape is substantially reduced. Filter opening and cleaning no longer causes high vinyl chloride concentrations in areas remote to the filters.

Process-Worker Interaction

The optimum use of work practices as a method of control for PVC plants requires a substantial amount of process-worker interaction. Mechanical control devices have the advantage of being programmed to perform a given task in exactly the same manner each time, with the associated disadvantage of inflexibility in exercising judgement to respond to particular situations. Trained operators can exercise judgement, but are sometimes subject to inadvertant errors. Ideally, the reliability of mechanical control devices should be used to backup the operators, and the judgement of the operators should supplement the mechanical control devices. A number of applications of this concept are used in PVC plants.

In some cases, mechanical stepping switches are used to control valve operations, pressure switches, weight set points, analog controller set points and other sequential operations. The mechanical sequencer will not proceed until clearance is received from process condition sensors or from a switch triggered by the operator. The operators are thus required to interact with the control system in certain critical process steps. The potential for large releases of VCM by avoiding manual operation of process equipment. It also reduces the number of operators necessary to run the process.

In one bulk polymerization plant, each prepolymerizer and autoclave has a warning light system to warn the operator of possible error and thus reduce VCM emissions. When the light is red, vessel manways cannot be opened, spectacle valves cannot be changed and degassing filter spool pieces cannot be removed. A green light indicates that there is no pressure on the system and lines or vessels are clear of VCM.

Other typical types of process-worker interactions involve step-by-step check lists. Each step has to be signed off and the critical steps have to be double-checked and signed. For example, any spectacle valve change is a two person operation; i.e., one operator will change it and one will verify that it has been changed.

Another important area of process-worker interaction involves the leak detection and prevention procedures used by PVC plants.

Rapid leak detection is critical to the success of vinyl chloride control programs, since (1) it allows the timely containment and/or repair of leaks soon after they occur (since most leaks develop slowly, they may be contained before large emissions of vinyl chloride develop) and, (2) it assists in reducing exposure by activating visual alarms when hazardous concentrations of vinyl chloride exist and respiratory protection is necessary.

The basis of the system is a VCM-specific workplace gas chromatograph monitoring network consisting of a number of strategically placed air sampling heads. Air samples are typically taken every 10 to 20 minutes. The system is generally tied into the process control computer so that any level from 1 to 5 ppm will set off alarm lights, requiring that respirators be used or that employees evacuate the area to the control room.

Once a warning light is activated, an employee will use a portable hydrocarbon detector to determine the exact location of the leak(s). The local exhaust system is then used to contain the leak until repairs can be made and a maintenance work order is made out. The nature and location of each leak is recorded and these records are periodically analyzed for trends and planned engineering needs.

Many plant engineers involved in the vinyl chloride control program consider rapid leak detection the most important control technique other than the VCM stripping process. On a regular schedule, an employee uses a portable hydrocarbon detector to check all potential leak sources. VCM leaks can thus be detected early when they are small and the resulting exposure area is not extensive. Many leaks are detected and repaired or contained well before the automatic monitoring system would be alerted. Work orders resulting from the search and secure program carry priority status. Each month, these records are analyzed and summarized by top management and either new control goals are established or ongoing ones are followed up.

PERSONAL PROTECTIVE EQUIPMENT

Typical respiratory protection programs follow the requirements of the OSHA regulations for vinyl chloride. Implementation of protective equipment measures is activated by the workplace gas chromatograph monitoring system. Employees are required to use a half-face supplied air line system when the amber warning light (vinyl chloride reading greater than 1 ppm) is activated. This type of respiratory protection is also required when employees perform specific job tasks which are suspected of releasing vinyl chloride. A flashing red light (vinyl chloride greater than 5 ppm) also dictates the use of the half-face supplied air line system. The difference between the two alarms is that the flashing red light means that employees must use the air line respirator when moving from one air plug to another. If the monitoring system detects a "disaster" (vinyl chloride concentration in excess of 900 ppm), an alarm is sounded and the building must be evacuated. A self-contained air pack is required for re-entry into the building.

When employees enter a reactor for cleaning or other maintenance, protective clothing is required to prevent skin contact with vinyl chloride contaminated liquids. The clothing includes a cotton (or Tyvex) work uniform, gloves, a head covering and impervious boots. A full-face supplied air respirator is also required. Work uniforms are provided daily for all employees and showers are generally encouraged but not required.

WORKER ISOLATION

Worker isolation is achieved in most PVC plants through the use of centralized process control rooms.

Process controls are typically located in an enclosed control room under positive pressure from an independent air handling system. As an average, employee time distribution is as follows for one bulk polymerization plant:

JOB TITLE	PERCENT TIME IN CONTROL ROOM
Superintendent	75%
Foreman	75%
Operators	95%
Assistant Operators	75%
Autoclave Cleaners	10%
Utility Employees	15%

Since the VCM concentration is essentially zero in the control room, most employees are isolated from the exposure area for a large segment of the shift. Employee time distributions for most other plants should be roughly comparable to the above figures.

WORKPLACE MONITORING SYSTEMS

Two types of workplace monitoring systems as used in PVC plants are discussed below.

Monitoring Systems with a Gas Chromatograph Sensor

Gas chromatographs have been used in industrial applications for monitoring process streams and controlling the performance of process equipment in refineries and chemical plants for over 18 years. Much of the technology developed for the monitoring and control of industrial processes is directly applicable for area monitoring of workplace environments in PVC manufacturing plants. Gas chromatographic monitoring instrument systems similar to the one described here have been used for a number of industrial applications for monitoring workplace air. A block diagram for a typical system is given in Figure 11.

Workplace samples are collected by a series of sensor probes which are located in work area breathing zones near known potential emission points. The probes are equipped with dust deflecting screen filters and are connected to the sample selector system by means of thin-walled 1/4-inch diameter tubing. The sample selector system transfers the desired sample flow directly to the chromatographic analyzer for analysis. Air is continuously drawn through each probe to assure that a fresh sample is available for each sample point when needed at the sample selector.

The samples are analyzed by a chromatographic analyzer which has a temperature-controlled oven containing the sample valves, GC columns, column switching valves, heaters and detector cell. The area outside the oven contains the pressure regulators for gas flow control and the electronics for the temperature control and detector operation. The unit is designed for extended operation without maintenance or manual calibration. The instrument companies with equivalent analyzers are Bendix, Beckman, Honeywell, and Process Analyzers, Inc.

The sampling sequence is dictated by a programmer, which is designed to operate the valve switching operations within the chromatographic analyzer and the sample selection, and to interface with the output from the detector electronics located in the chromatographic analyzer. The signal output from the programmer is transmitted to a computer and a strip chart recorder that displays a bar graph readout. Instrument companies that manufacture comparable programmers are Bendix, Beckman and Honeywell.

Each plant which employs a gas chromatographic monitoring system uses the central computer in a somewhat different manner. The most sophisticated users also utilized the computer for process control, time and motion study, statistically analyzing various alerts caused by human errors by plant operators, and for printing out data required by Federal Regulations. The analysis of causes of various VCM leaks gives the plant industrial engineers, industrial hygienists and management a measure of how effective the various employee training may be and which employees, if any, may be accident-prone. Also, this analysis gives an indication to plant management where to direct engineering talent and capital investment to protect the workers in hazardous environments.

Monitoring System With A Fourier Intereferometer Sensor

A recent development in monitoring instrument systems is the use of an area monitoring system for computing time weighted average exposure in real time. This monitoring instrument system consists of a Fourier Infrared Composition Sensor for measuring VCM concentration levels in air samples, a sample collection manifold, a digital computer, output equipment and software that combines a data processing algorithm and a statistical model of a time and motion study of plant operators' activities. This system was installed in a PVC resin manufacturing plant employing a suspension process. A block diagram of the system is shown in Figure 12.

The sampling manifold collects the samples and makes them available for analysis by the infrared intereferometer sensor. An on-line computer activates the sampling manifold to deliver desired area samples of breathing air to the sensor. The sensor output is analyzed by the on-line computer, the exposure data is printed out when requested, and the annunciators are activated when permissible exposure levels are exceeded.

The sample transport system consists of a 48 point sample manifold and a pumping and valving arrangement that delivers air samples to the sensor sample cell. The computer selects the point to be sampled and the air sample is "pulled" by the sample pump through the sample cell. All sample lines not being monitored are under a constant vacuum to assure that fresh samples are available when needed for analysis.

The 48 sample probes are connected in split probe arrangements of 2 or 3 to 23 sample lines. This split probe arrangement averages the VCM level reading and typically reduces the analysis time per probe. For example, if the concentration of VCM in the split probe arrangement is less than 1/3 of the permissible VCM level when the samples are averaged, the computer will select another probe arrangement for analysis. However, if the reading is greater than 1/3 of the permissible VCM level, the computer will command that VCM analysis be performed on air samples from individual probes within the arrangement in order to identify the zone where VCM concentrations are excessive. The manifold of the sample transport system is located centrally between the two plants so that the sample lines have lengths varying between 30.48 and 182.9 meters (100 and 600 feet).

The composition sensor is a rapid-scan Michelson Intereferometer. Its electrical output is coupled to a high-speed digital computer. The air sample can be scanned for several components in about 15 seconds. Software performs classical

Fourier transforms on selected frequencies in real time. The above system is marketed as the Fourier Infrared Air Monitor. The system used at this plant is manufactured by Eocom Corporation (Fourier Multiplex Spectrometer System Model 7200).

Additional software was developed to meet the following requirements for an intelligent multi-level sampling system:

- Determine the frequency and level of sampling to be initiated at each station.
- Isolate the alarm level excursions and display the results.
- Provide the data for the computation of accurate employee TWA's.
- Update the internal data file to reflect the general changes in vinyl chloride levels at the points being monitored.

A sampling algorithm was developed to sample groups of stations over a period of time in proportion to their probabilities of having points with extremely low probability of excursion. The sampling algorithm and the statistical model of time and motion study are used to compute the employee time weighted average exposures.

A plant report listing the following information is printed every 15 minutes:

- Number of blue alarms (5 - 24 ppm)
- Number of yellow alarms (25 - 1000 ppm)
- Number of red alarms (>1000 ppm)
- Average TWA of the process areas over the report interval
- TWA dosage of each operator over the report interval

Also, at the end of eight hours, the following reports are generated:

- Long-term TWA

- Average length of each alarm
- Probability of each alarm level

Initial start-up and definition of plant configuration requires manual operation. Hereafter, the system will define the plant profile, calculate TWA's, initiate alarms and update its data files.

This intelligent monitoring system has the following distinct advantages over fixed-point monitors:

- The monitoring system responds to the plant environment.
- Sampling frequency is determined by the probabilistic history of the point in question,, using data accumulated over the previous eight hours.
- The system hunts for excursions using its probabilistic intelligence.

The following tests were carried out to establish the equivalency with fixed point monitoring systems:

- Charcoal tubes changed once per hour monitor at one of the area probes and the results were compared with the TWA data from the area monitor.
- Monitoring four employees with personal monitor using charcoal tubes for one hour intervals for a total of 21 eight-hour work shifts.

A comparison of the data from the first test shows a good agreement of both methods with the expected log normal distribution curve. Readings from the second test show the area monitor data follows the log normal distribution curve. Readings from the second test show the area monitor data follows the log normal distribution curve while the charcoal tube data does not. This is accounted for by the fact that employees are not always in the plant. Figures 13 and 14 demonstrate these needs.

EFFECTIVENESS OF CONTROL

The control measures described in the previous sections are effective in meeting the 1 ppm, 8-hour TWA PEL for VCM. Workplace monitoring systems indicate that most parts of most plants are consisently below 1 ppm of VCM. Actual worker exposures (as indicated by charcoal tubes) are somewhat better than the area monitors indicate, since employees are required to avoid high exposure areas when possible (process/worker isolation). The use of respirators makes the amount of VCM inhaled by workers even less than is indicated by charcoal tubes, since the charcoal tubes are mounted on clothing in the breathing zone outside of respirators. Respirators are mandated in cases of high workplace VCM levels.

In summary, the control technology exists and is being applied to protect workers from occupational exposure to VCM at the 1 ppm TWA level. This technology relies primarily on containment of VCM in enclosed, isolated processes, but the combination of all available control measures is required to meet the challenge of controlling VCM.

RECOMMENDATIONS

CRITIQUE OF THE PLASTICS AND RESINS STUDY

In retrospect, a number of other considerations could have been included which would add considerably to the value of the present study. One key area is the cost (installation, maintenance and operation) for the controls that are discussed. A second area involves consideration of the environmental pollution implications of the controls. A control system which meets occupational health standards without meeting environmental health standards (or vice versa) is not satisfactory. A third area is the identification of technology which would be appropriate if a new plant were to be constructed with current/future occupational health standards in mind.

FOLLOW-UP

NIOSH is attempting to address the above deficiencies in many of the current control technology studies of other industries. The budgets for these studies have been increased to five to six man-years, compared to two man-years for this plastics and resins study. An evaluation of the need for further studies on control technology for chemical processes is planned. Further studies will probably be restricted to unit operations in order to minimize redundancy.

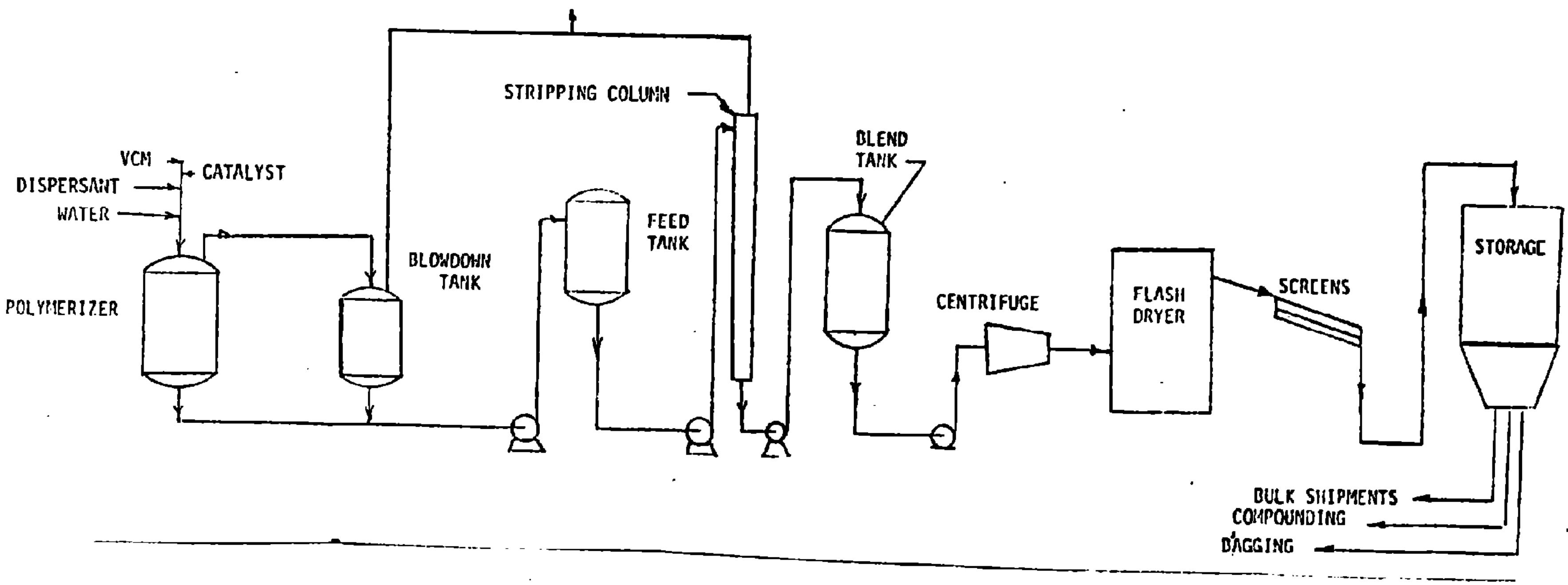


Figure 1. Typical PVC Suspension Polymerization Process

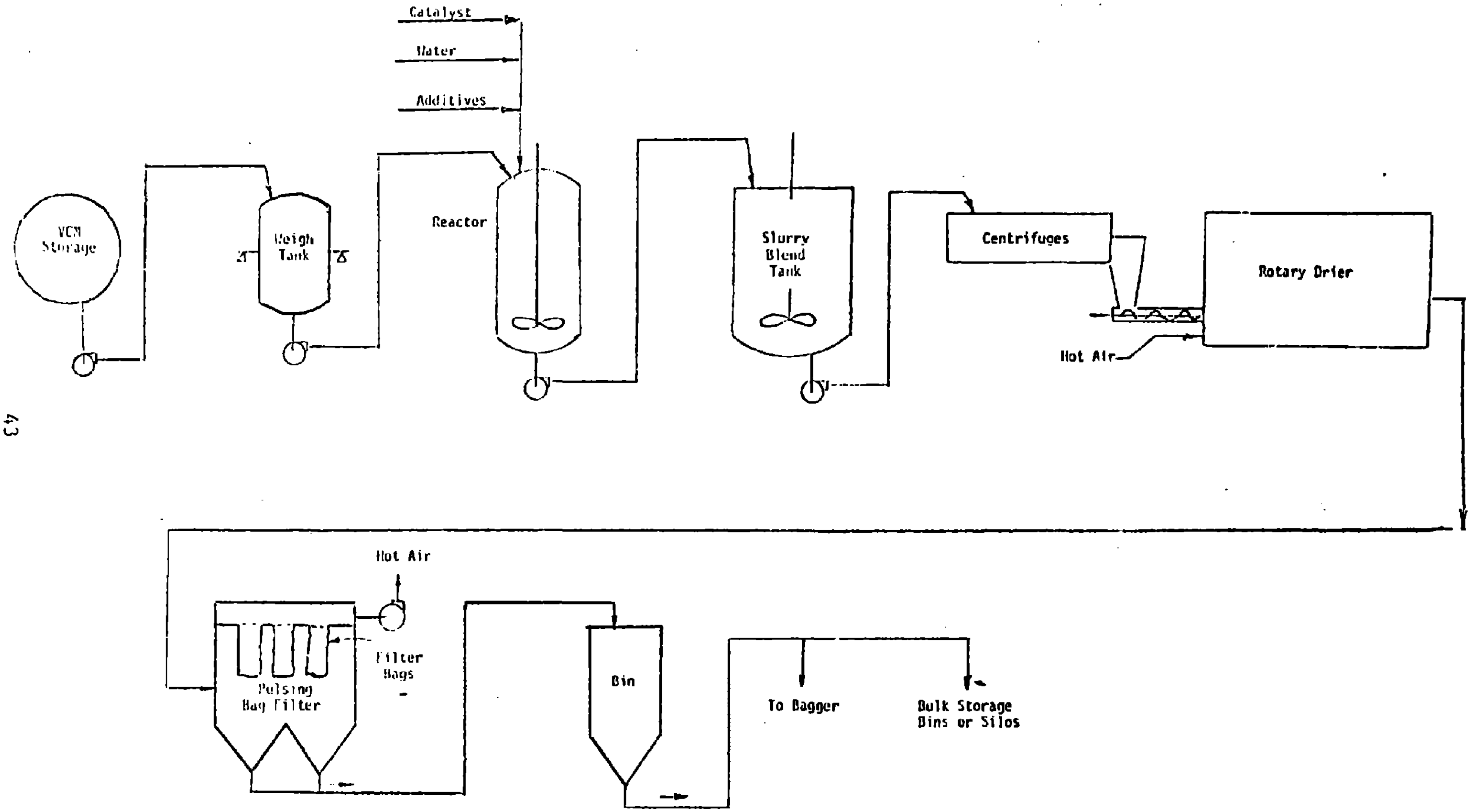


Figure 2. Typical PVC Suspension Polymerization Process

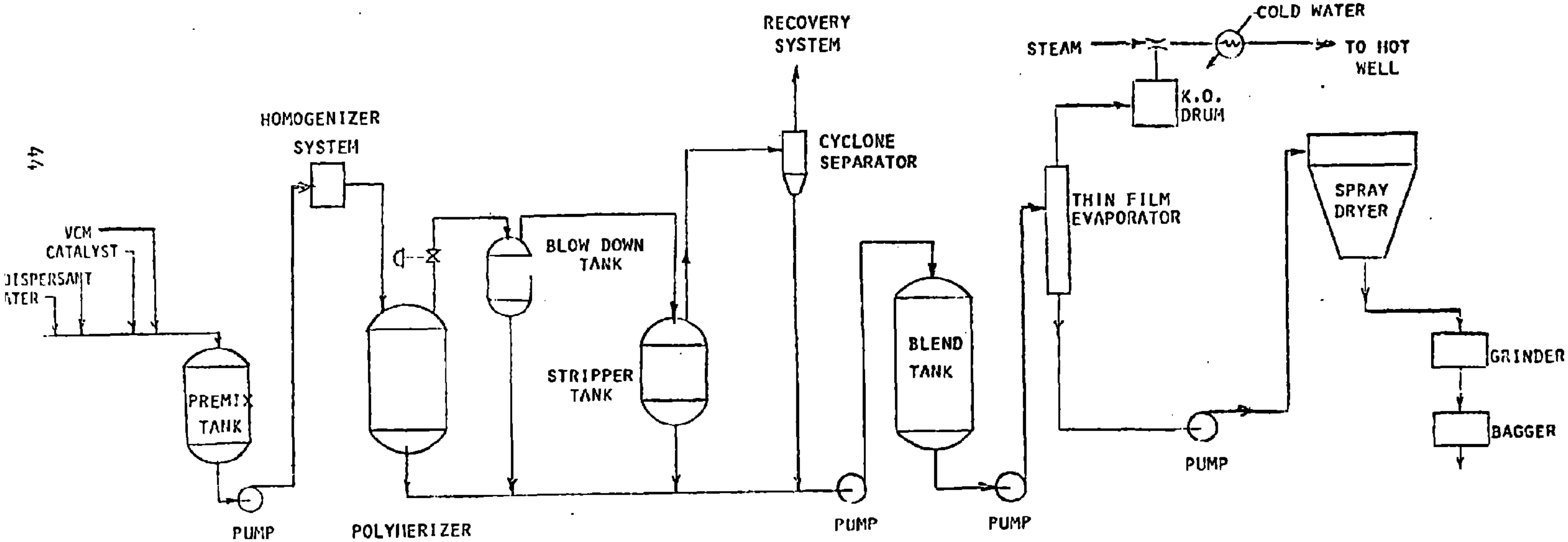


Figure 3. Typical PVC Dispersion Polymerization Process

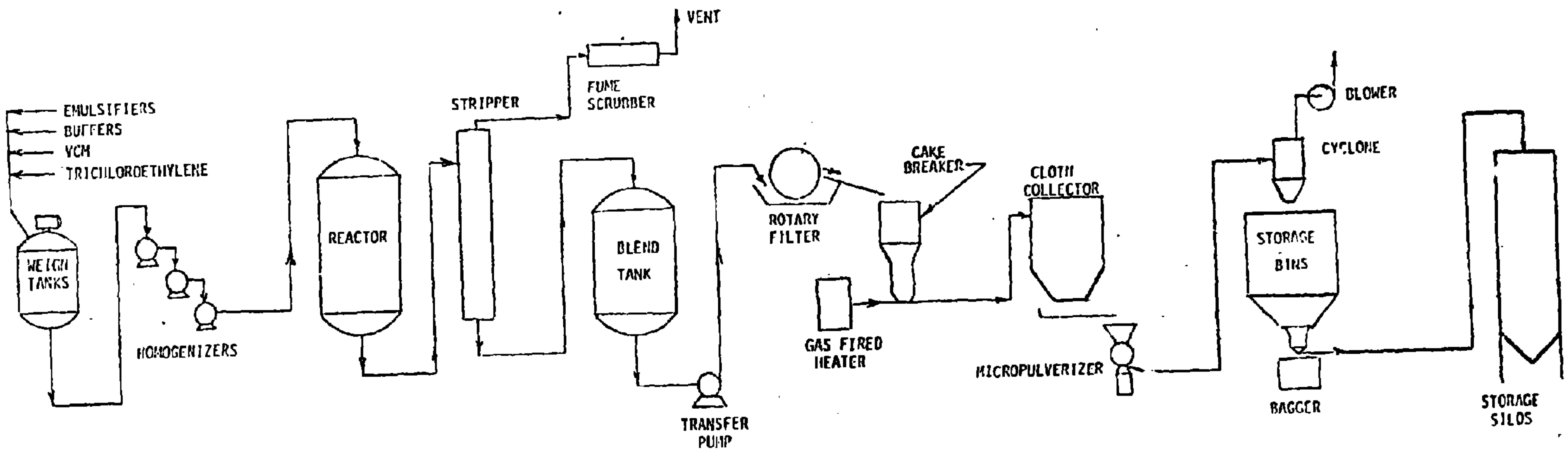


Figure 4. Typical PVC Dispersion Polymerization Process

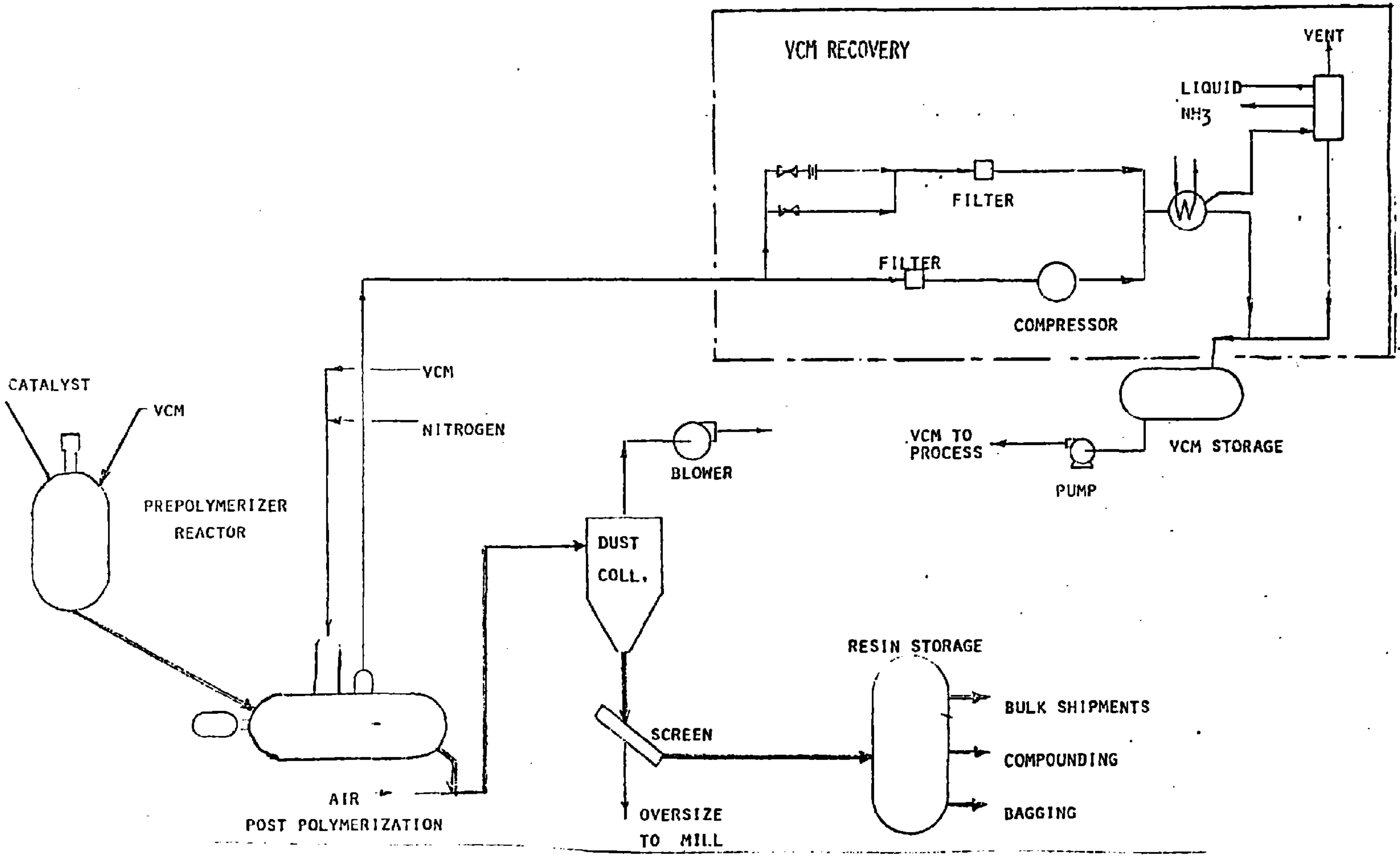


Figure 5. Typical PVC Bulk Polymerization Process

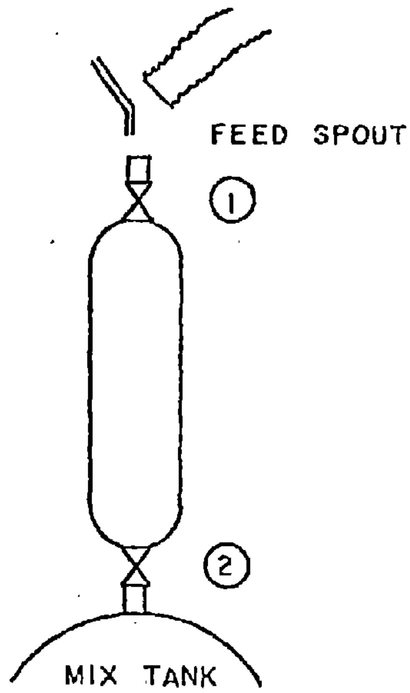


Figure 6. Additives Entry Air Lock

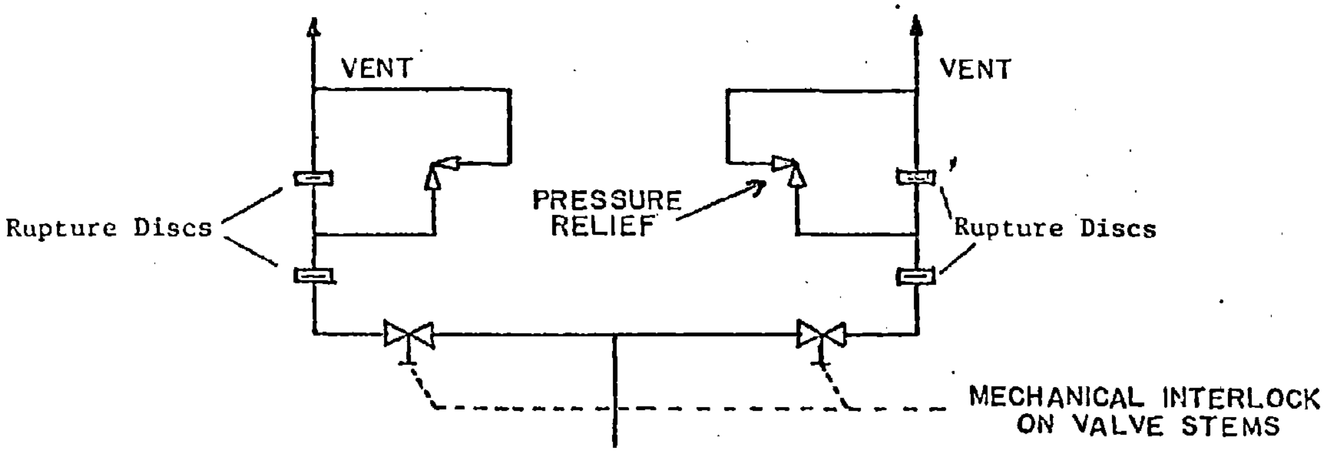


Figure 7. Dual Rupture Discs on Bulk Polymerization Vessels

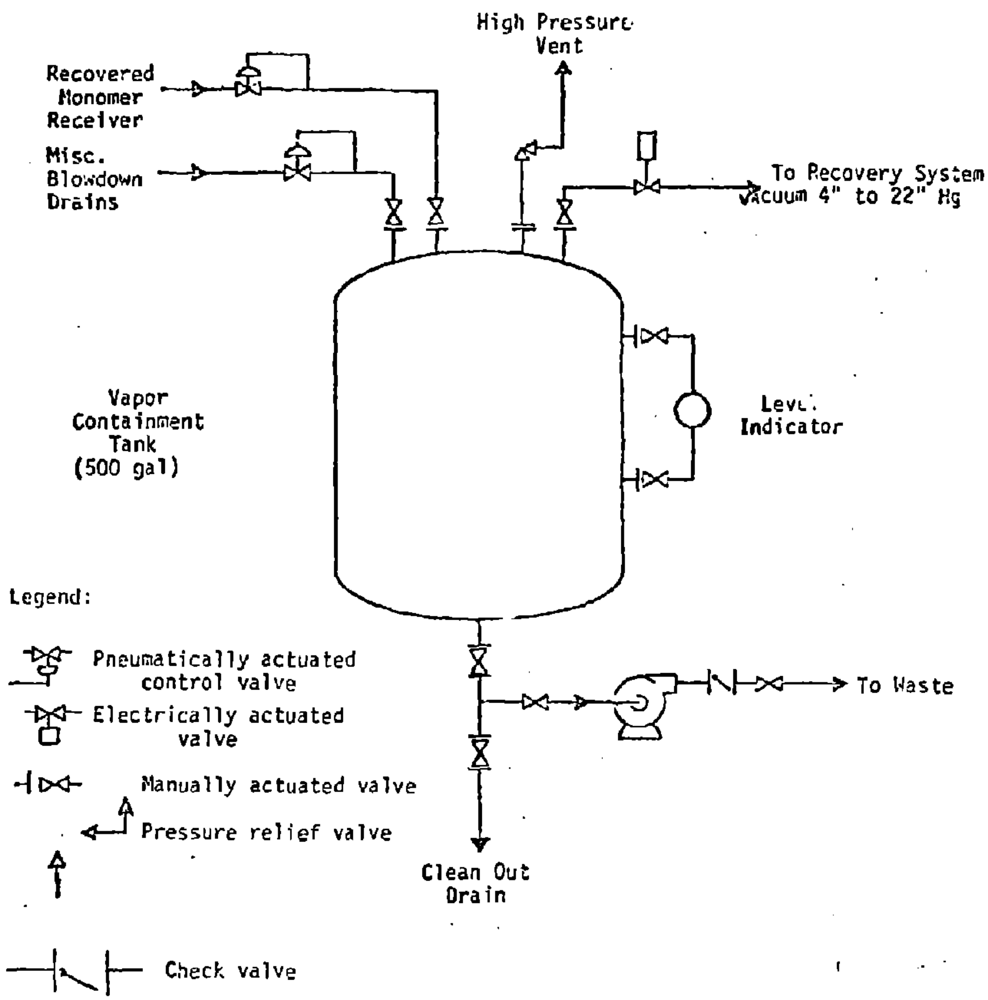
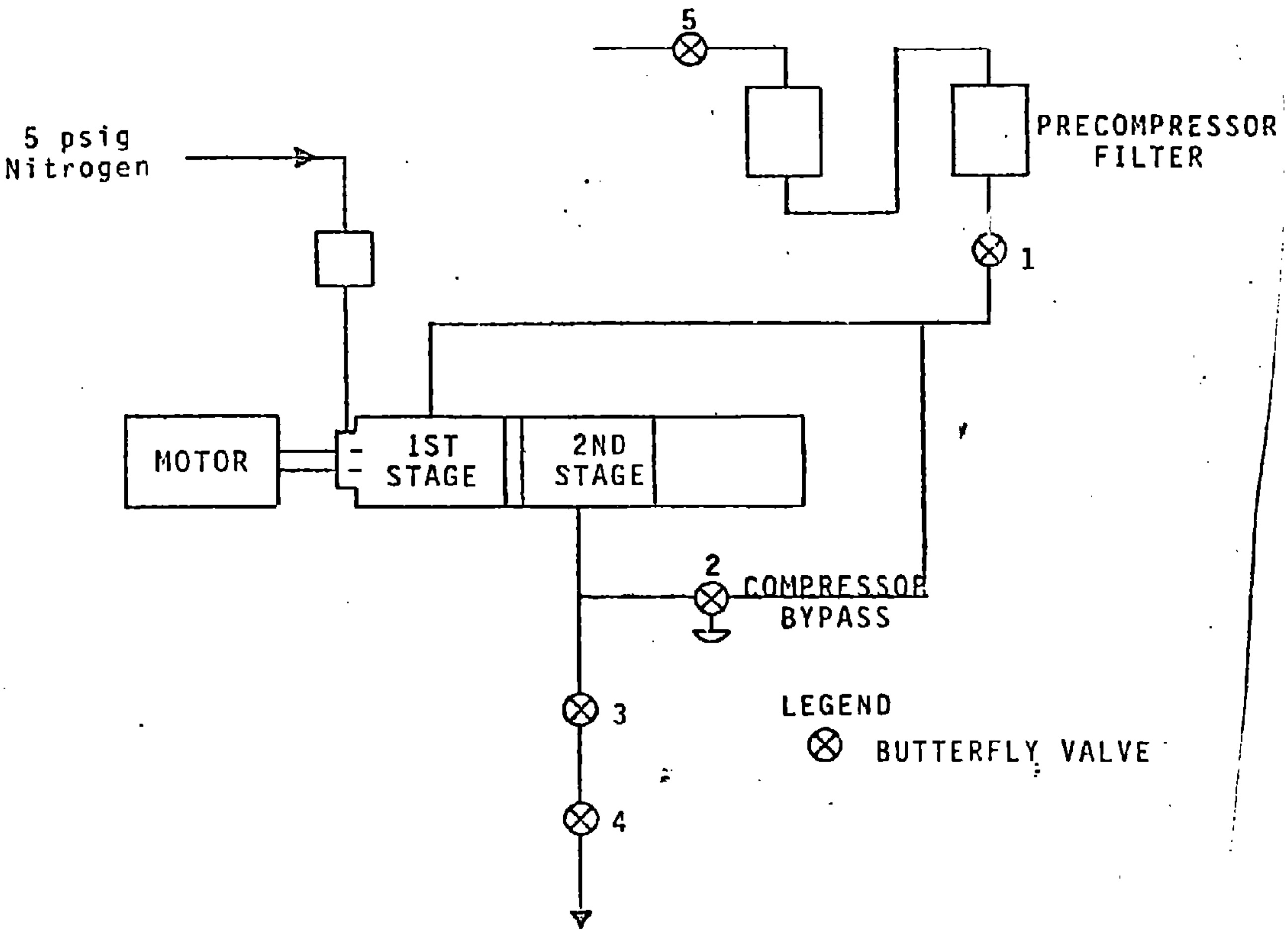


Figure 8. Waste Water Vapor Containment System



Operation sequence:

a. When compressor starts, valves 1, 2, 3 and 5 are open and system recirculates for 30 seconds.

b. Valve 2 is closed.

c. When the compressor stops, valves 3 and 1 close and valve 2 opens.

Figure 9. Vent Compressor System (Wharton Compressor)

Fan	Winter	Air Flow m³/s Summer	Emergency
RV29	0	3.30	3.30
RV30	0	3.30	3.30
RV32	0	1.75	1.75
EF42	0	0.654	0.654
EF46	1.75	1.75	1.75
EF39	3.30	6.61	6.61
EF40	3.30	6.61	6.61
EF41	0	6.61	6.61
EF45	0	6.61	6.61
EF54	6.61	6.61	6.61
EF55	6.61	6.61	6.61
Louvers	closed	open	open
Air change /hour	19	37	37

EF = exhaust fan

RV = roof ventilation

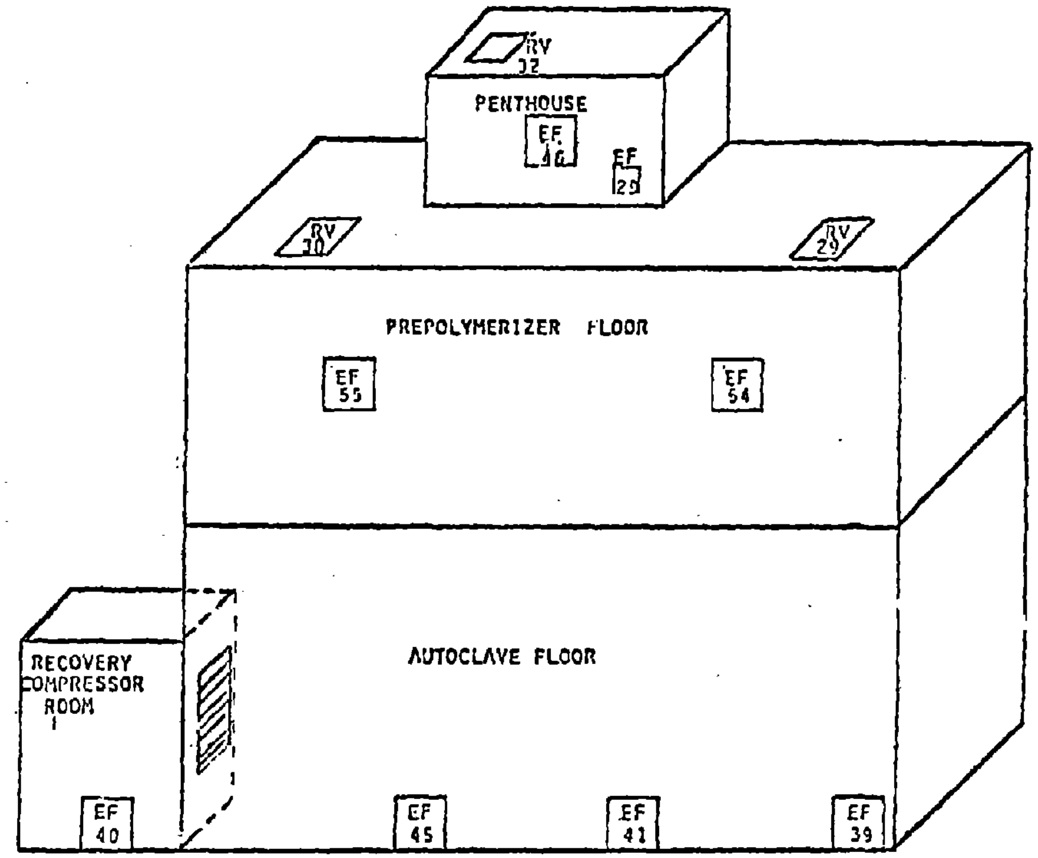


Figure 10, Typical General Ventilation Scheme For A PVC Plant

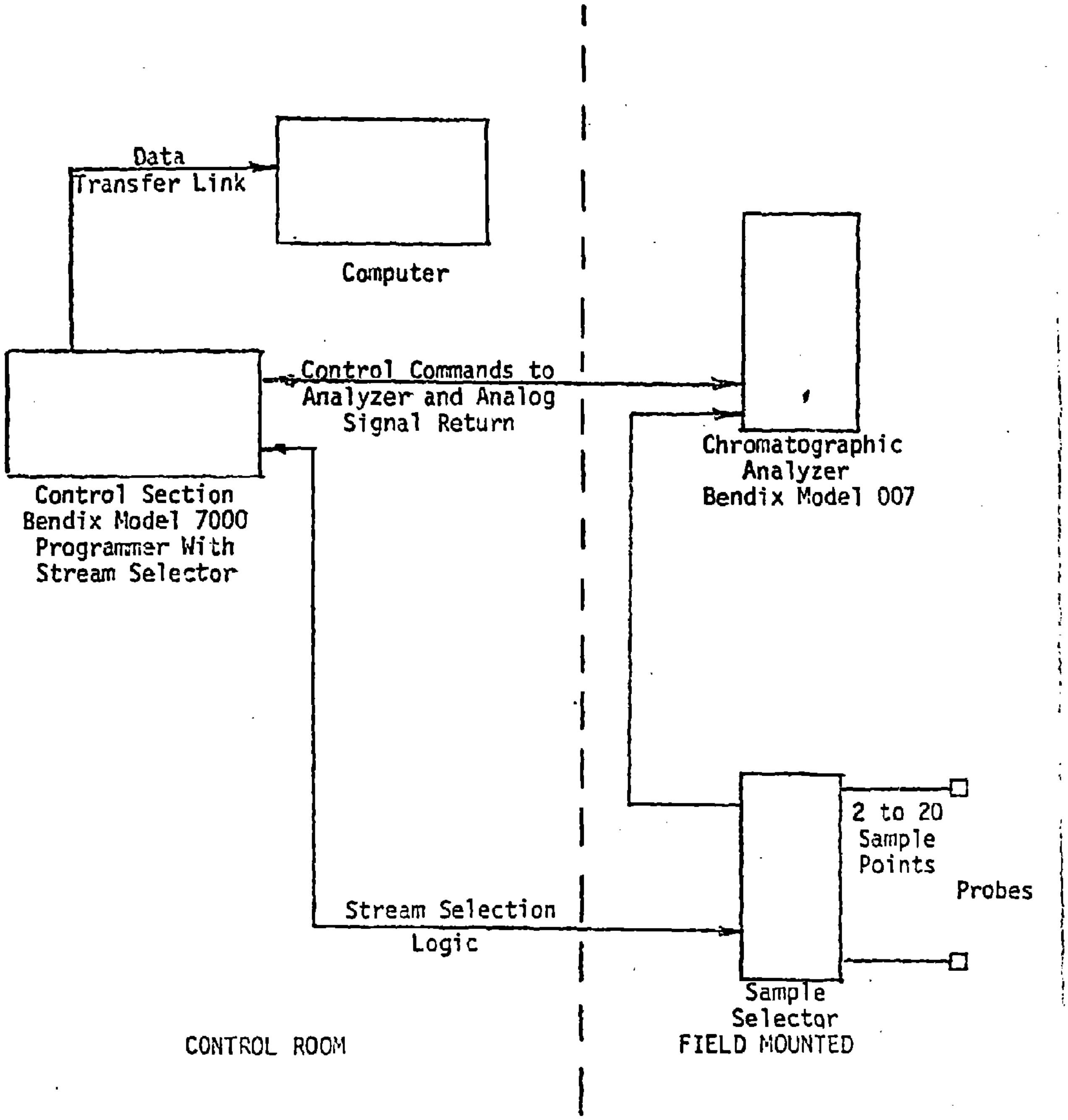


Figure 11. Instrument Monitoring System Employing a Process Gas Chromatograph - Block Diagram

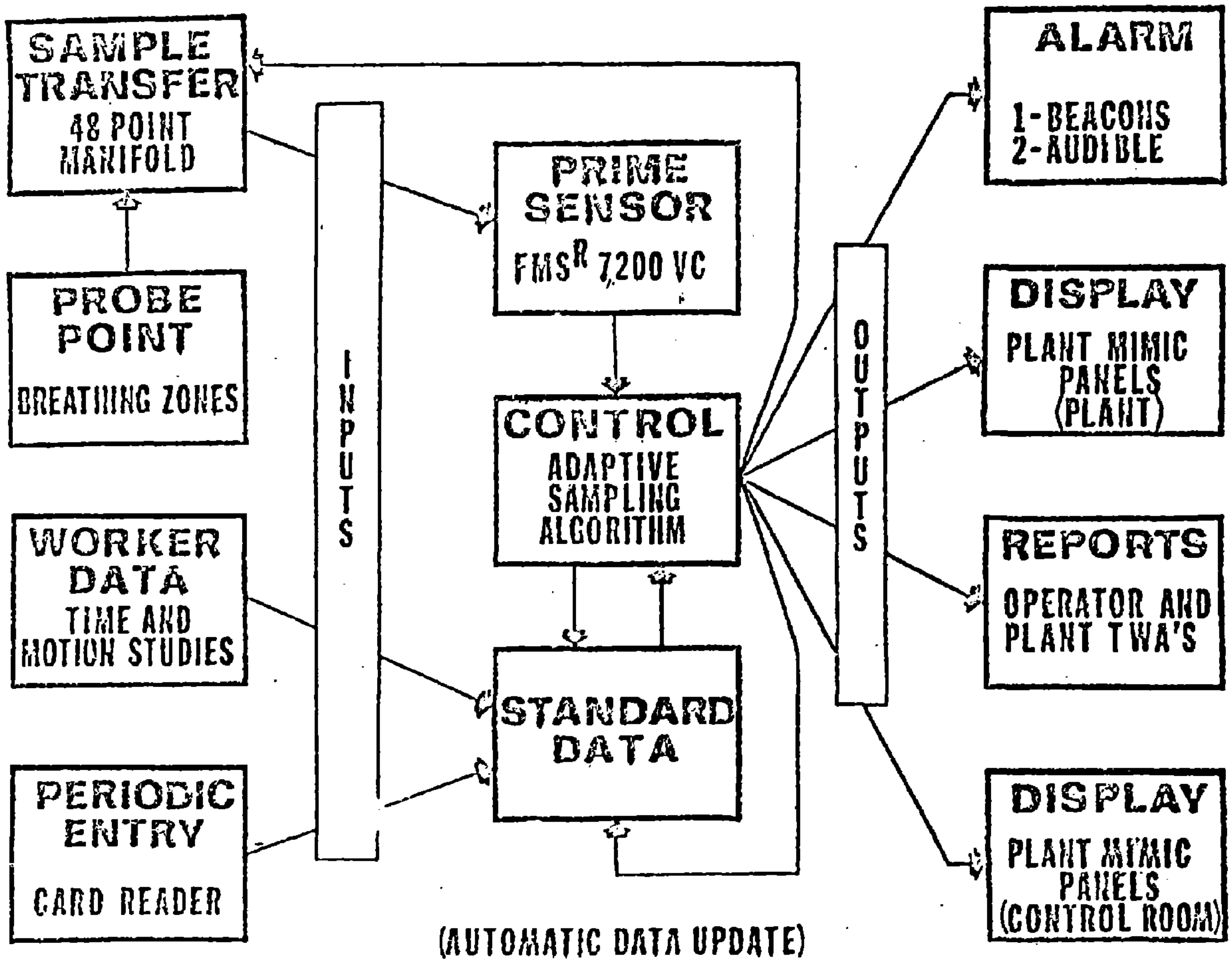


Figure 12. Block Diagram - VCM Monitoring System

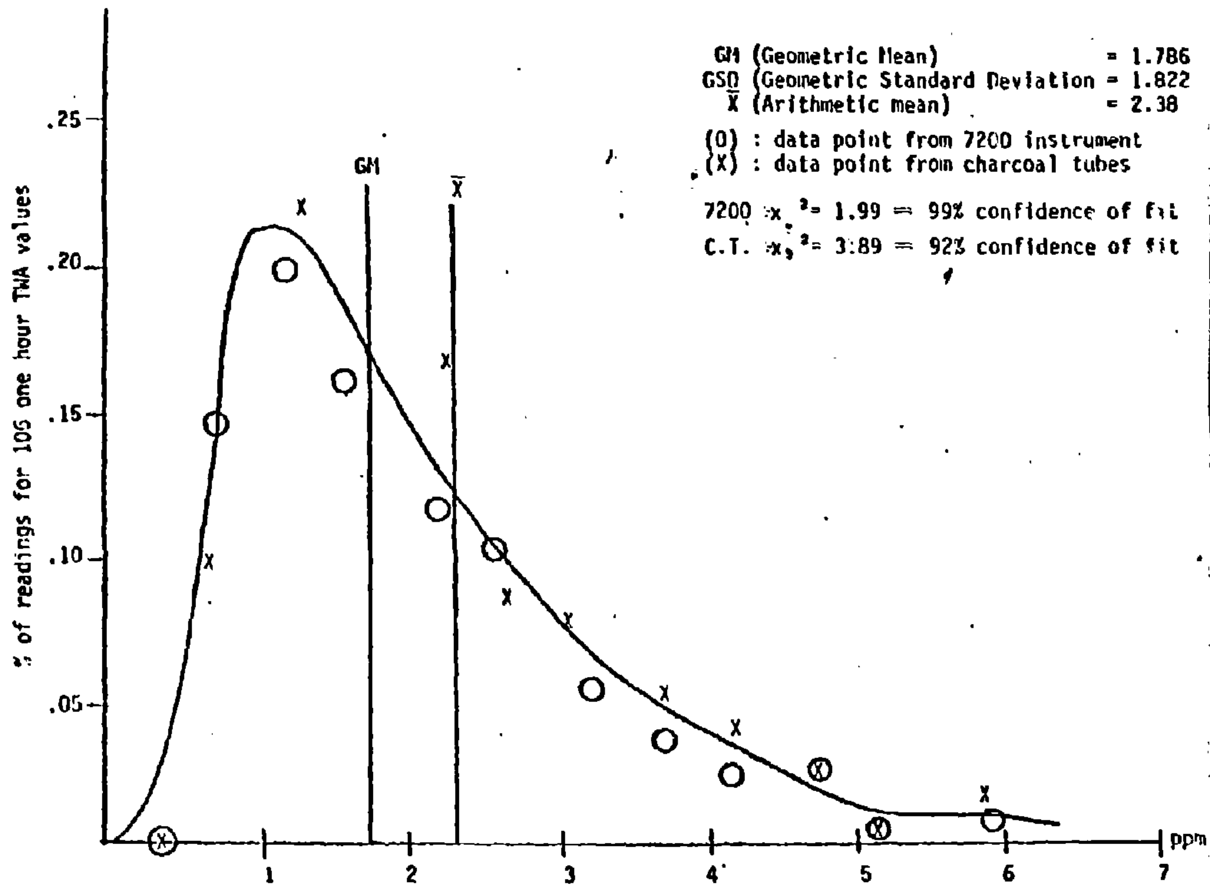


Figure 13. Observed Airborne VCM for a Fixed Point in the Plant

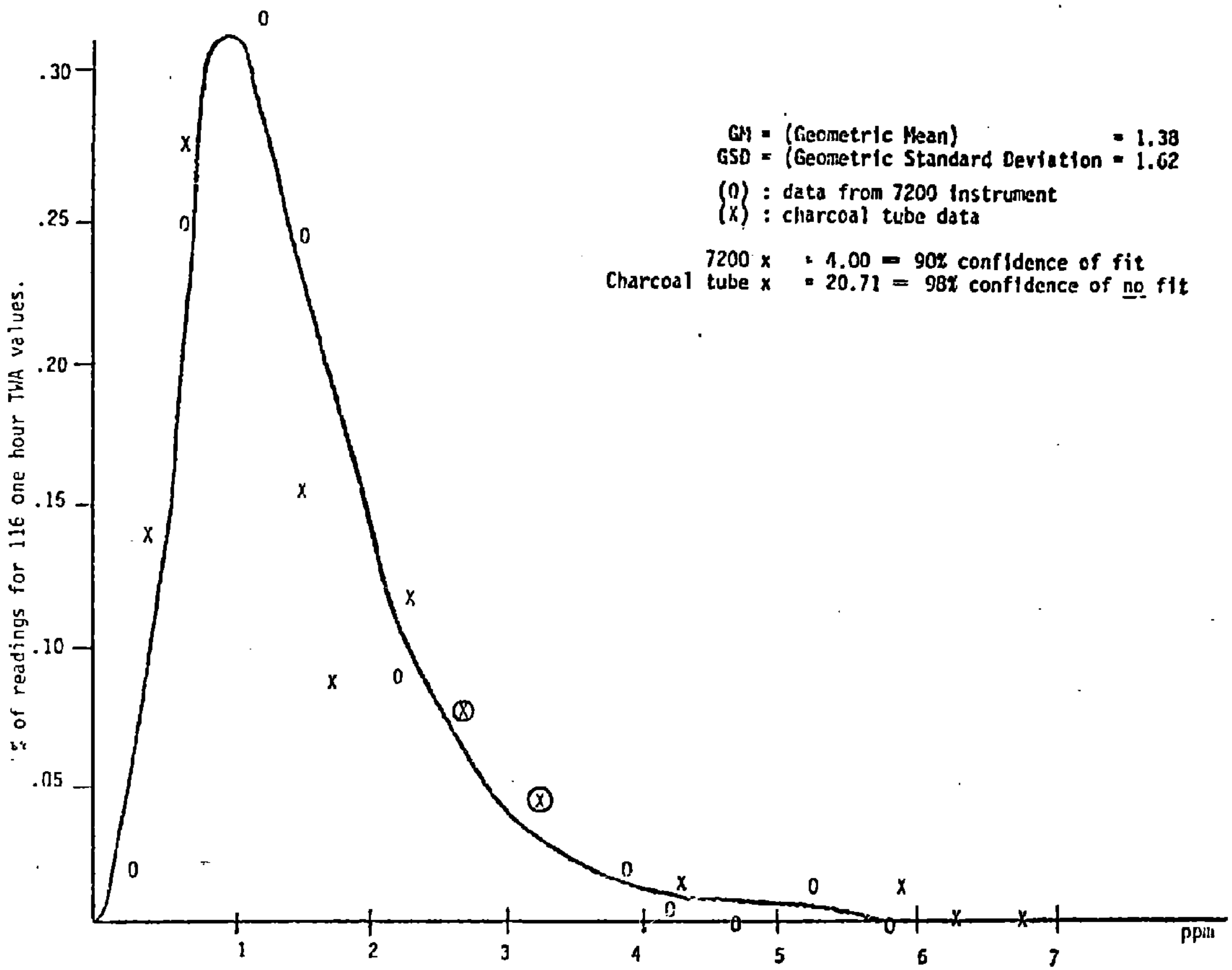


Figure 14. Employee VCM Exposure for Typical Month