certain circumstances.(54) The Soviet experience must have been similar, as demonstrated by a 1957 report which quotes exposure levels ranging from 8 to over 16,000 parts per million with average exposures of 20 to 300 ppm. Some of the problems mentioned in this Soviet study included charging vinyl chloride to the reactor through open manholes, leaks in the drying ovens, lack of vents, and inadequate local and general ventilation. (23)

Some other problems described in the literature were leaking reactor seals, charging of initiator and suspending agents through open manholes, venting of reactors into the workroom air, and, most of all, reactor cleaning. Reactors have the problem of polymer clinging to the interior surfaces, which must be periodically removed, the frequency of such cleaning varying with the process, and reactor size and operating conditions. In the past, the standard procedure was to drain and purge the reactor, then open one of the manholes and attach a blower to exhaust the remaining gases into the reactor floor area. After a suitable time, a man would enter the reactor and hand-chip the polymer from the interior. Since this was considered an undesirable job, it was generally rotated among the most junior operators in most plants. Measurements made in one study where ample ventilation was supplied before and during manual reactor cleaning revealed

breathing zone concentrations of 30 to 100 parts per million, with levels close to the work of 600 to 1000 parts per million.(16) Other reports make it quite clear that levels in such operations were often orders of magnitude higher, even to the point, in at least one case, of causing death by cardiac arrest.(19)

In the very late 1950's and early 1960's certain chronic effects such as acroosteolysis and angioneurosis were beginning to be recognized. Not all manufacturers recognized any need to take action, but a few at least initiated some controls and monitoring. About 1960, for example, Dow Chemical established a company standard for a limit of 50 parts per million measured as a time-weighted average. They were generally successful in reducing exposures to about the 25 parts per million level in most of their operations, however, operators were exposed at up to 80 parts per million with excursions to 500 parts per million. About the same time, they also initiated continuous sampling with a multipoint remote sampler. Exposure levels were routinely calculated by matching work patterns to the measured levels in the air.. (54)

The control picture changed drastically when the revelation of vinyl chloride's probable carcinogenicity came in January, 1974. The epidemiological and experimental data

which followed prompted the Occupational Safety and Health Administration to set an emergency temporary standard of 50 parts per million on April 5, 1974.(49) Hearings and further studies have since been conducted which resulted in the promulgation of a "permanent" standard on October 4, 1974. The basic requirements of the standard are:(51)

1. The standard applies, in effect, to all industries handling vinyl chloride monomer, and to those fabricators whose operations involve heating the polymer such that the residual monomer might be released.

2. The maximum 8-hour time-weighted average (TWA) shall be 1 parts per million, with a maximum excursion (no longer than 15 minutes in any one day) level of 5 parts per million.

3. Monitoring is required to determine what levels exist.

4. If levels are determined to be consistantly less than the "action level" of a TWA of 0.5 parts per million, no further monitoring program is required.

5. If levels are between TWA's of 0.5 and 1.0 parts per million, then quarterly monitoring must be continued until levels of less than 0.5 ppm are consistantly obtained. Also a medical surveillance program must be established, and medical records must be maintained.

6. If levels exceed TWA's of 1.0 part per million, in

addition to the above requirements, regulated areas must be established, and rosters of persons entering and leaving must be maintained. Additionally, respirators must be provided.

7. Workers were allowed to decline to use the respirators at levels below 25 parts per million, until April 1, 1976.

8. A worker education program must be developed.

9. Containers must bear a warning of the suspected cancer hazard.

10. The regulation was to become effective on January 1, 1975.(52)

The regulation was challenged on several points by some industries and the Society of the Plastics Industry. However, it was upheld by all courts, up to and including the U.S. Supreme Court. The court battle resulted in the delaying of the effective date until April 1, 1975.(17,68,69)

B. METHODS OF CONTROL IN THE VINYL CHLORIDE MONOMER INDUSTRY:

The problem of controlling vinyl chloride can be better appreciated if one realizes the very small quantity which is necessary to exceed the concentrations allowable under the new Occupational Safety and Health Administration regulations. For example, in Table I it was shown that the 1 part per million limit would represent only 0.00256 mg/liter. Thus, in a typical reactor of 4500 gallon capacity only about 0.22 milliliters (ml) of liquid monomer would need be present to

exceed the 5 parts per million excursion limit. Or, a single milliliter of the liquid would raise the concentration to one part per million in an unventilated room 30 by 45 feet with a 10 foot ceiling. Thus, extremely slow leaks such as at pipe joints or valve stems could result in excessive exposures.

Ironically the monomer industry, where the pure vinyl chloride monomer is originally synthesized has less of a problem controlling industrial exposures than does the polymer industry. There are several reasons for this, the most basic being the process itself. The equipment for producing the monomer provides fewer opportunities for losses than does that used in polymer production. Also, the monomer industry uses outdoor, unenclosed structures for the process, whereas most polymer facilities are enclosed by conventional buildings.(48,50,73)

The main losses of vinyl chloride in the monomer industry were from tank car loading and process equipment vents. Fugitive losses, such as from valve stems, pump and compressor seals, leaks, and spills, were also a prime source.(75,76) The losses from the vents probably have little effect of the concentrations in the work area, since they are usually remotely located well above or away from occupied areas. Since these are primarily significant to the general environ-

ment, a detailed discussion of the vent losses and their control will be presented in the next Chapter of this work.

According to some industrial sources interviewed, the employment of sampling equipment has been the single most effective factor in the development of their control practices and techniques. The approach taken by B. F. Goodrich was a combination of fixed and portable instruments. Studies concerning the capabilities of various instruments had been initiated prior to the determination of the more serious health hazards of vinyl chloride. The instruments selected in this study were of the flame ionization detection type. The fixed system consisted of a Bendix 8401 Total Hydrocarbon Analyzer with a six point sampling system and a multipoint recorder and programable calculator. The portable instrument chosen was a Century Organic Vapor Analyzer (OVA).(18) When the effort to achieve a significant reduction was begun in 1974, this combination of instruments was successfully applied to control leakage. The OVA's were used to make measurements at numerous points throughout the plant. The data were statistically examined to determine the best location for the fixed sampling points. Once the fixed samplers had been installed it was possible to use an alarm system to alert operators to the presence of leaks. The leaks could then be pin pointed by surveying the area

with a portable OVA. This allowed the detection and repair of defective equipment such as flanges, gaskets, seals or packings. As the standards were further decreased, it became necessary to increase the sensitivity and selectivity of the instruments, since a flame ionization detector does not differentiate between the various organic compounds which might be in the sample. Thus, the fixed instruments were replaced with gas chromatographs that are sensitive to levels below one part per million and able to distinguish the vinyl chloride from other contaminants. The OVA's were not changed, since they were still being used for spot checks when leaks were detected by the fixed system.(48,56) Such monitoring systems are in excess of the requirements of the OSHA regulations,(51) but would be required under the proposed Environmental Protection Agency regulations.(75)

These fixed sampling systems are also the basis for administrative procedures for reacting to leaks or other unexpected releases. The B. F. Goodrich vinyl chloride monomer plant in Calvert City, Kentucky has four gas chromatographs, one for the tank farm area, and one for each production unit. Each of these has a ten-point sampler which checks each point every thirty minutes. Each sampling point has a "spider" arrangement of pickups to give representative sampling from each location. These samplers are integrated by small computers into an alarm system which

gives warnings at levels of 1, 5 and 100 parts per million, indicating increasing degrees of hazard and urgency of action. The one part per million level corresponds to the maximum continuous concentration allowable under the OSHA standard. The five parts per million level is the maximum excursion limit under OSHA standards and indicates a significant leak requiring immediate attention. The 100 parts per million level was selected as one half the emergency level designated by Kentucky's regulations and indicates the occurrence of a major release. This level requires immediate corrective action, and also the use of self-contained breathing apparatus and the evacuation of all non-essential persons. When the alarms indicate a leak, the area of the leak is checked with an OVA and the leak is thus located and promptly repaired.(48)

Two other useful administrative measures for exposure control are designated by the OSHA regulations. The first of these is the establishment of regulated areas, which OSHA defines as areas where vinyl chloride levels exceed the one part per million limits. Some manufacturers have also chosen to establish regulated areas wherever there is a significant potential of occasionally exceeding the limits.

Entry into regulated areas is restricted to those workers whose duties require it. All those entering are logged in and out, and their times in such areas are recorded. The

second measure is that all jobs where there may be a high potential for concentrated vapor or liquid releases are designated as "hazardous operations". Workers engaged in such operations are assumed to be at risk of high exposure and are normally required to wear proper respirators and protective clothing.(48,51)

The OSHA vinyl chloride regulation is rather unique in its approach to respiratory protective devices. Ordinarily OSHA has not recognized respiratory protection as a legitimate means of protecting the worker. In this regulation, however, such equipment is allowed when "feasible engineering methods" are inadequate to sufficiently reduce the vinyl chloride levels in the work area. Specifically, OSHA's reasoning is, "Where feasible engineering and work practice controls will reduce exposures below the permissible levels, they must be instituted. Where such controls will not reduce exposures below the permissible level, they must nonetheless be implemented to reduce exposures to the lowest practical level, and be supplemented by the use of respirators to provide the necessary protection."(50) The definition of "feasible" is not precise in this guidance, but it is generally interpreted that if one manufacturer is able to employ a particular technique, then that technique is feasible. A technique would be considered unfeasible if it would not

apply to a particular process, or if engineering knowledge was not available for its implementation. It is to be expected that significant controversy will result in determinations of what may or may not be economically feasible. (50,56)

Permissible respirators for various concentrations are clearly specified in the regulation. These specifications are reproduced in Table V.

Respirator use, regardless of type, presents certain problems. For example, the canister and cartridge masks allowable at lower concentrations present a significant problem in the form of short service-life. Table VI gives typical performance of some cartridges tested by the National Institute for Occupational Safety and Health.

Canister-type masks give longer service-life, but also are not very long-lived, as shown in the typical performance figures in Table VII.

Since cartridges are used in pairs, it can be seen that a single worker might consume two canisters or over a dozen cartridges in a single day. Since canisters cost about ten dollars each, it can be seen that using these devices could prove quite expensive.(56) Because of this, it has been desirable to bypass these type respirators and go directly to the type "c" supplied air respirators which are required

TABLE V

RESPIRATORY PROTECTION REQUIREMENTS (51)

Atmospheric concentration of vinyl chloride		*Required apparatus*
(i) Unknown, or above 3,600 ppm		Open-circuit, self-contained breathing apparatus, pressure demand type, with full facepiece.
(ii) Not over 3,600 ppm	(A)	Combination type C supplied air respirator, pressure demand type, with full or half facepiece, and auxiliary self-contained air supply; or
	(B)	Combination type C, supplied air respirator continuous flow type, with full or half facepiece and auxiliary self-contained air supply.
(iii) Not over 1,000 ppm		Type C, supplied air respirator continuous flow type, with full or half facepiece, helmet or hood.
(iv) Not over 100 ppm	(A)	Combination type C supplied air respirator demand type, with full facepiece, and auxiliary self-contained air supply; or
	(B)	Open-circuit self-contained breathing apparatus with full facepiece, in demand mode; or
	(C)	Type C supplied air respirator, demand type, with full facepiece.
(v) Not over 25 ppm	(A)	A powered air-purifying respirator with hood, helmet, full or half facepiece, and a canister which provides a service life of at least 4 hours for concentrations of vinyl chloride up to 25 ppm, or
	(B)	Gas mask, front- or back-mounted canister which provides a service life of at least 4 hours for concentrations of vinyl chloride up to 25 ppm.
(vi) Not over 10 ppm	(A)	Combination type C supplied-air respirator, demand type, with half facepiece, and auxiliary self-contained air supply; or
	(B)	Type C supplied-air respirator, demand type, with half facepiece; or
	(C)	Any chemical cartridge respirator with an organic vapor cartridge which provides a service life of at least 1 hour for concentrations of vinyl chloride up to 10 ppm.

TABLE VI

RESPIRATOR CARTRIDGE TEST DATA FOR 50 PARTS PER MILLION VINYL CHLORIDE (64)

Manufacturer	Grams Charged Per Cartridge	10% Breakthrough Time in Minutes
1	49.7	54.4
2	35.7	28.1
3	35.0	29.2
4	36.1	32.6

Test run by NIOSH at 50% relative humidity and 30 liters per minute.

TABLE VII

RESPIRATOR CANISTER TEST DATA FOR 100 PARTS PER MILLION VINYL CHLORIDE (64)

Manufacturer	Grams of Charcoal Per Canister	10% Breakthrough Time in Minutes
1	436.8	356
2	318.4	284
3	463.8	276.5
4	311.2	208.5

Tests run by NIOSH at 50% relative humidity and at 60 liters per minute.

above 25 parts per million in any case. These masks use a continuous supply of air under slight pressure to insure that any leaks around the mask will result in clean air leaking out instead of contaminated air leaking in. The disadvantages of this kind of mask include the requirement for an air supply, the interference from hoses and difficulties in fitting all workers. Since the mask requires a supply of clean, pressurized air, some kind of system for providing this air is needed. One may use plant air as a source if an adequate means of decontaminating and checking it is used. Such a system was installed by General Tire and Rubber Company at their Astabula, Ohio polyvinyl plant. This system uses vapor absorbers with activated carbon to remove contaminants. To protect the carbon from saturation, the carbon bed is preceded by a special ceramic filter which eliminates unwanted moisture, dirt and oil from the air stream. This system is sized such that the carbon requires changing only twice per year. The system employs four water sealed compressors, thus protecting against system failure through redundancy and also humidifying and cooling the air. Vinyl chloride levels in the air are routinely tested with a gas chromatograph and have been found to average about 0.10 parts per million vinyl chloride (with a range of 0.01 to 0.31 parts per million). This system is connected through receivers (holding tanks) and pipes to quick

connect fittings throughout the plant. This, then, provides workers with a convenient air supply for their respirators wherever needed. This system costs about $60,000.(6) Goodrich has a similar system in both their Louisville and Calvert City plants, the primary difference being that rather than using an air purifying system, air is drawn from an area which is consistantly very low in vinyl chloride. They initially used the same system that supplies compressed air for pneumatically activated control valves and instruments. This has since been replaced by a system with a separate compressor for breathing air, backed up by the older instrument air compressor.(48,56)

The final type of respiratory protection is the self-contained breathing apparatus, with a pressure-demand regulator. This, too, maintains a positive pressure within the respirator to preclude any leakage of contaminated air into the facepiece. This unit, however, uses a tank of compressed air as its supply rather than a system requiring pumps and hoses. While this system provides excellent protection, it is very heavy and is good for only a very short while between tank changes. This is, thus, best suited for escape use or for emergency maintenance during spills or major releases. Goodrich has placed these in strategic locations throughout their plants for such use.(48)

The maze of different respirators for different vinyl chloride levels has led some manufacturers to use a system of only two such devices, namely the supplied-air type and self-contained type. For example, Goodrich uses the supplied-air respirators in all cases up to 100 parts per million which they have designated the emergency level. Above 100 parts per million, they go to the self-contained type. This eliminated the need for each man to be fitted with and trained in the use of various masks and also eliminated the need for multiple alarms to indicate which level had been exceeded and which respirator should be used.(48)

Attempts to reduce worker exposures have also resulted in changes in equipment and work practices. For example,quality control sampling procedures used to result in significant discharges. The sampling bomb was a cylinder with a valve on either end which was constructed to withstand the pressure exerted by the vinyl chloride. Samples were collected by attaching one end of the sample bomb to the sampling valve and flushing it by venting gases from the valve on its opposite end. Once a sufficient amount had been vented to assure representative sample, the vent valve was closed and the sampler filled to the pressure in the system, then valved-off and taken to the lab. Exposures in this process have been reduced by a combination of less sampling, on-

stream product analysis and closed sampling loops.(48)

An example of the operation of a closed loop sampling system is shown in Figure 9. In this system, the sampling bomb is attached into the system with tubing fittings at either end, and the pressure of the downstream side of the pump is used to force the material through the sampler back to the low pressure side of the pump. When the sampler has been flushed and filled, valves one, two, three, and four are closed, and valves five, six, seven, and eight are opened. This discharges the few ounces of monomer in the lines to a remote vent (or air cleaner) and purges the lines. Then all the valves are closed and the sampler is removed. Once at the lab, the sampler is placed in a hood, and connected for analysis by tubing. The sampler is then stored in a special cabinet away from any occupied area. When the sampler is next used, the remaining vinyl chloride in it is returned to the system.(8)

Tank car loading has been another large source of emissions, amounting to several hundred pounds per day at some locations. (73) In the past, the primary method of determining when the tank car or barge was full was through the use of a gauge rod through which the liquid overflowed when the tank was full. Vapors released from tank cars or storage tanks were vented to the atmosphere as the material was transferred. As shown

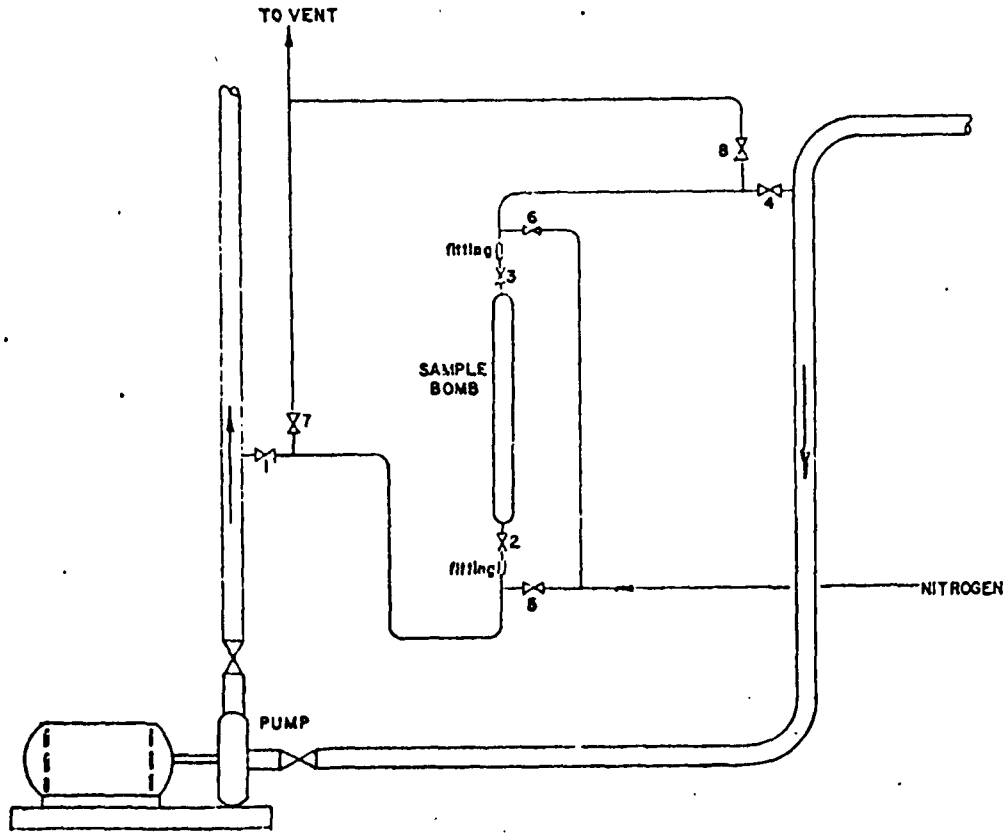

FIGURE 9: Closed Loop Sampling System (8).

in Figure 10, the loss of vapors is eliminated by attaching an equalizing line between the vents of the storage tank and the tank car. Losses from gauging may be eliminated by replacing the slip tube (gauge rod) with a magnetic float gauge or by weighing techniques. Another alternative is that shown in Figure 10 in which the overflow is connected through a "bullseye" to a remote vent or recovery system. The "bullseye" provides a transparent port in which liquid flow can be observed when the tank is full. Before any lines are disconnected, the system is drained and blown down with nitrogen, with the contaminated gases being vented remotely or fed to a recovery system.(8)

In equipment maintenance, such as filter or pump replacement, another simple protective system has been devised (see Figure 11). Fittings are installed as shown with hose couplings on them. First the item to be maintained is cleared of liquid by injecting high pressure nitrogen at the top and driving the vinyl chloride into the process piping. The inlet and outlet block valves are closed and the item is purged through a second hose which leads to a remote vent or recovery system. After maintenance has been completed, the item is purged, and the vent hose is attached to the uppermost outlet. The block valve is opened and the vinyl chloride displaces the nitrogen. The vent line is then purged and the item returned to service.(8) Larger items, such as

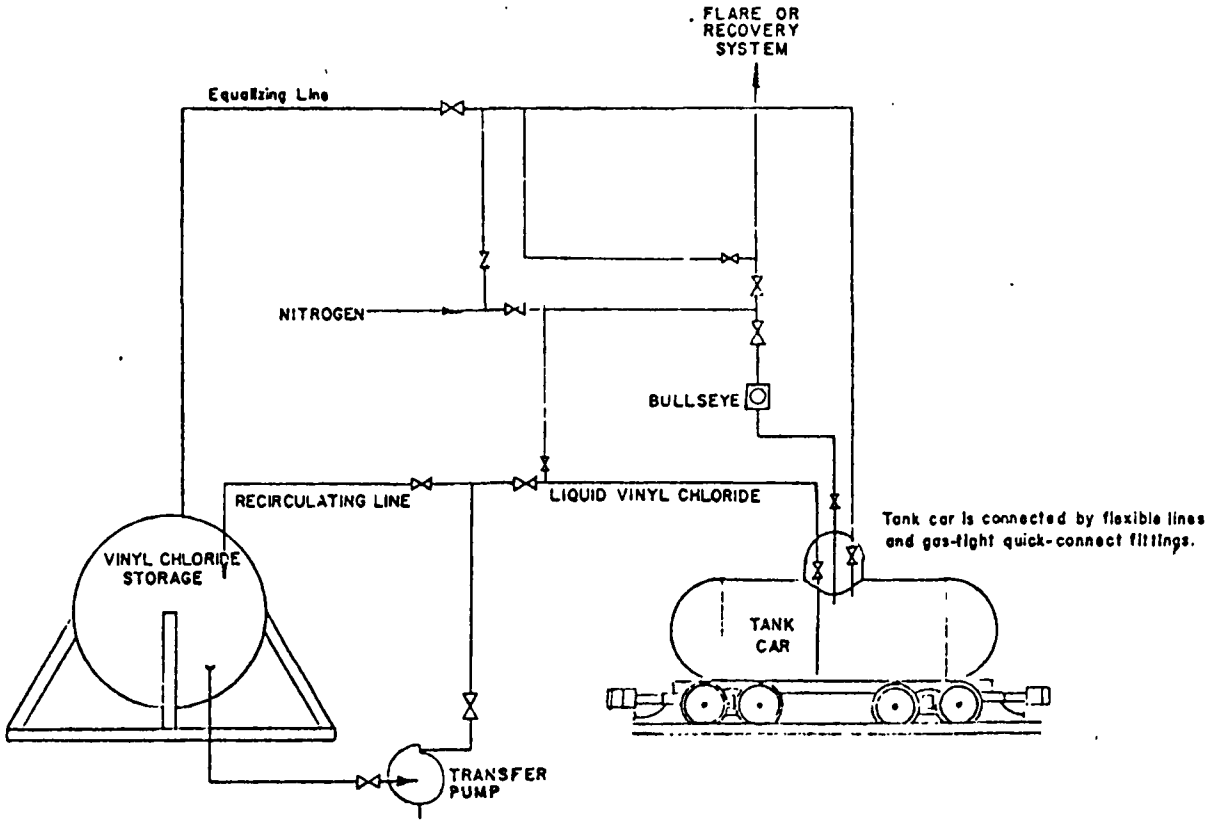

FIGURE 10: Closed System for Tank Car Loading (8).

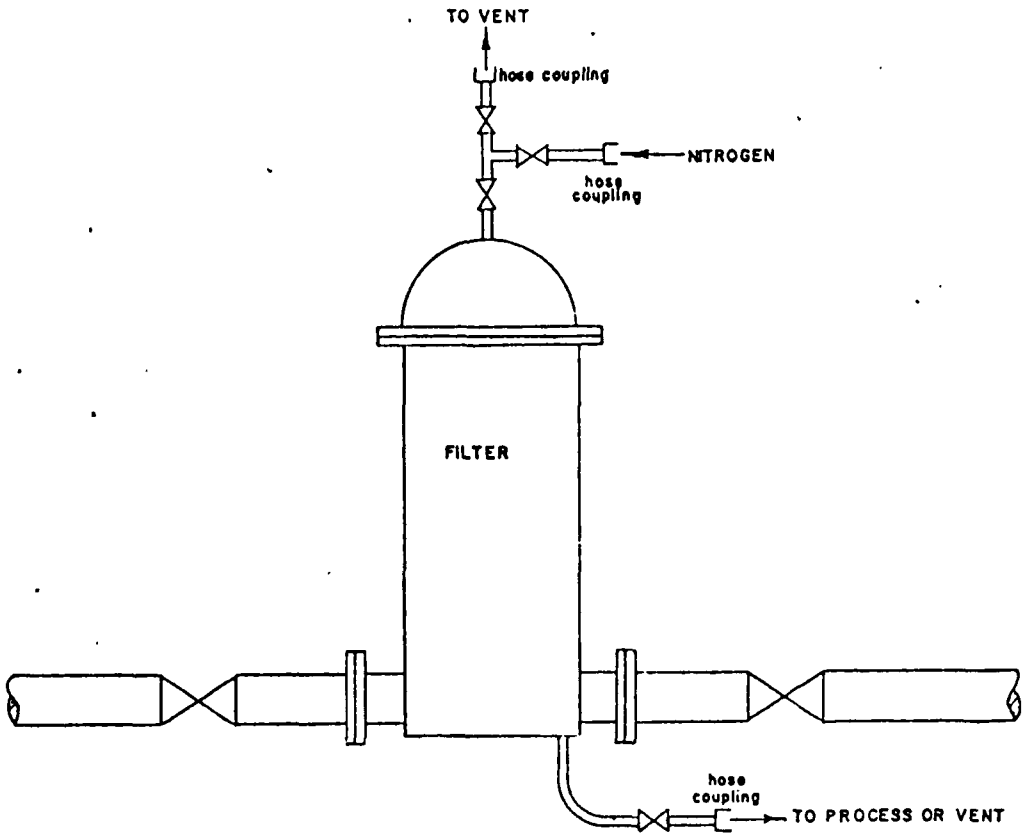

FIGURE II: Equipment Maintenance Clearing System (8).

condensers or reboilers being opened might require even more extensive preparation. For example, carbon and polymer tends to build up in reboiler tubes making periodic cleaning necessary. Since vinyl chloride could be trapped in such a system, it is desirable to first flush it out with a suitable solvent such as ethylene dichloride, and then purge it with nitrogen prior to opening.(48)

Fugitive losses from equipment such as piping joints, seals on rotating shafts, and valve items have been found to be a very significant source of vinyl chloride emissions in most plants, and are estimated to account for an average of 27% of the total emissions in vinyl chloride monomer plants. (75)

The pipe joints which would present the greatest problem would be threaded joints. Such joints cannot be tightened to stop leaks in most cases, since tightening doesn't eliminate the potential pathway for leakage. The simplest expedient way to eliminate leakage would be to seal-weld such joints (see Figure 12), but this would eliminate the possibility of disassembly for maintenance. A more satisfactory solution has been the installation of flanged joints which can be easily tightened to prevent or correct leakage, and easily disassembled when necessary (see Figure 13). This technique is also applicable to joints at valves and pumps

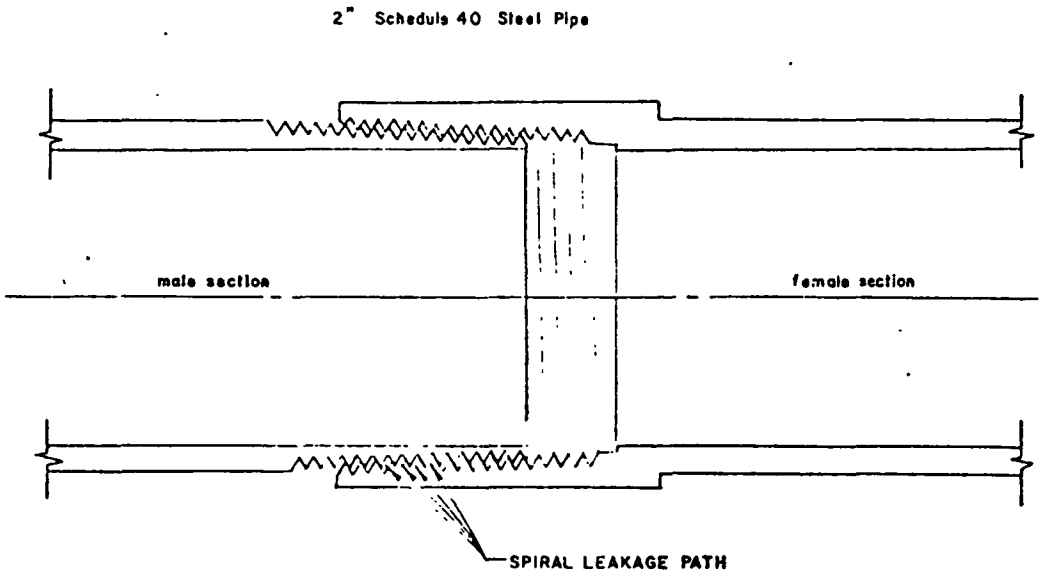

FIGURE 12: Tapered-Thread Pipe Joint (57).

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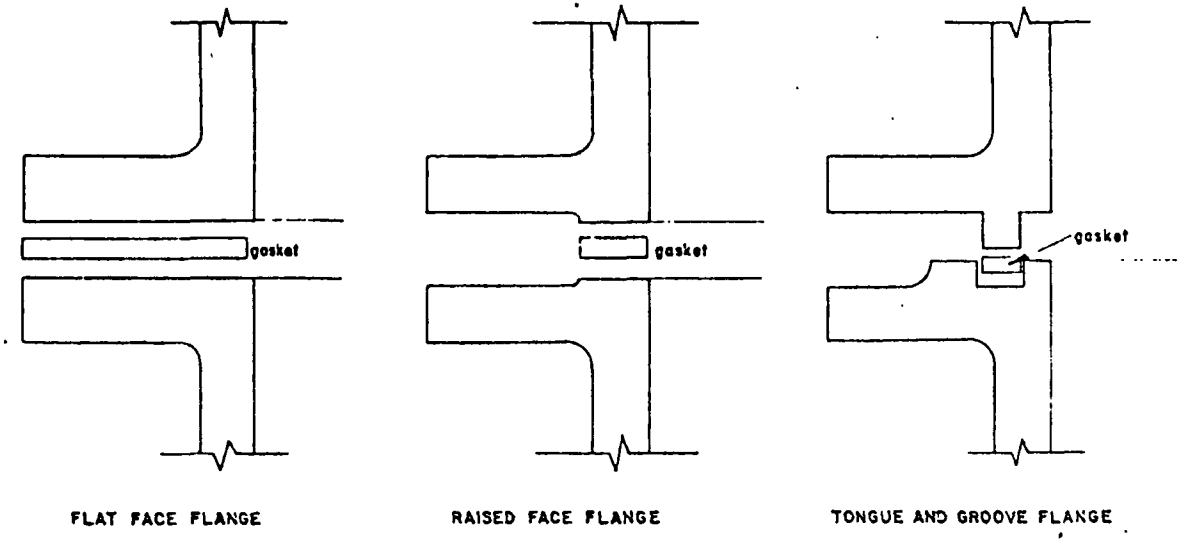
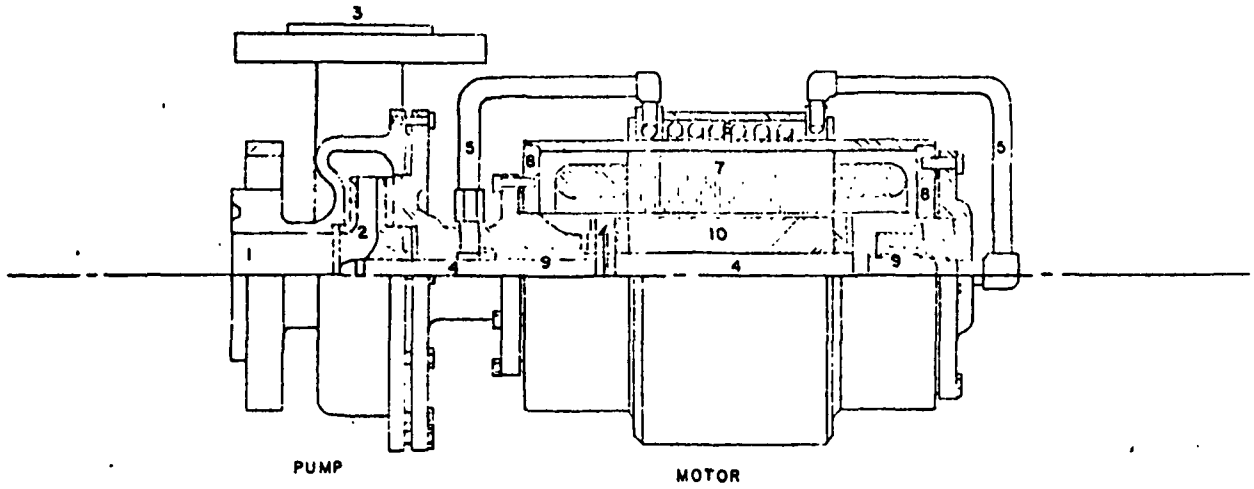


Note: The flanges illustrated above are for low pressure. High pressure flanges have the face or flange adapted to allow longer bolts.

FIGURE 13: Examples of Flanged Pipe Joints (57).

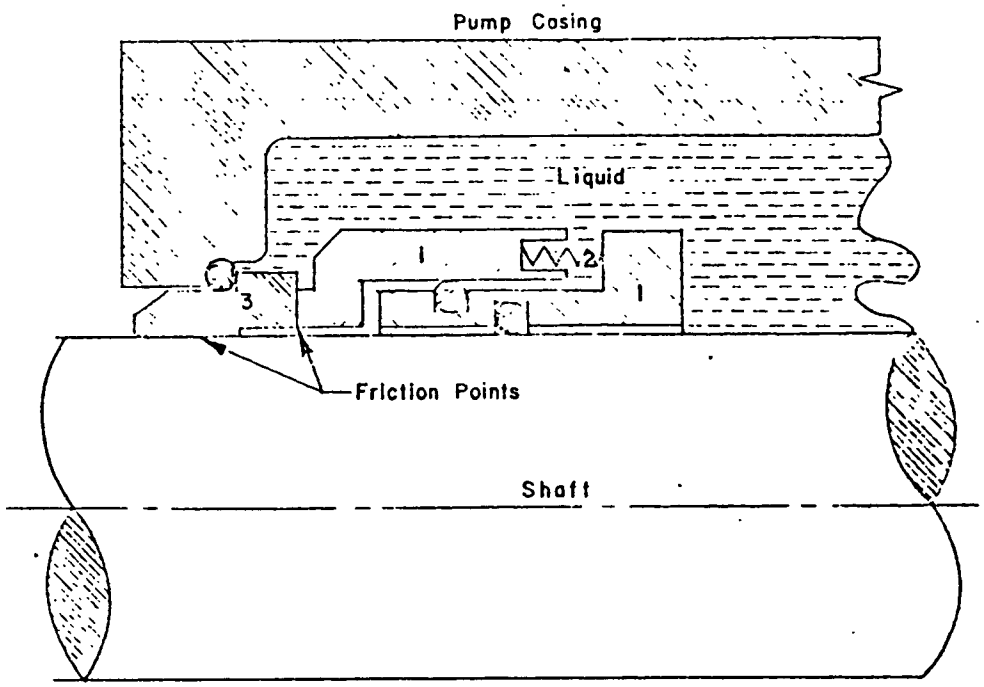
since these are commonly available with flanged fittings in almost all sizes.(57,77)

The control technique used on rotating shafts is dependent largely on the type of equipment. For pumps, the ideal solution would be the substitution of a "canned-motor" pump, in which the pump casing and motor housing are all made in one piece. As a result, there are no seals required, and the bearings derive their lubrication directly from the fluid being pumped (see Figure 14). Another alternative which would eliminate pump seals would be the use of a magnetic coupling between the motor and pump, but this system would necessarily be limited to applications where low torque was required, and thus would have very few applications in the vinyl chloride industry.(57) The technique which is proving the most useful is the installation of double mechanical seals. These are applicable to rotating shafts on pumps, compressors, or agitators. A slightly different type can be used on reciprocating pumps or compressors. Since the pumps originally installed were not specifically selected for emission control, most had standard single mechanical seals as shown in Figure 15. These normally depended on wetting of the seal surfaces by the liquid being pumped for lubrication, thus, some leakage was inherent and expected. Replacing these with double mechanical seals as shown in Figure 16 has been troublesome in many cases since



1. Intake
2. Main Impeller
3. Discharge
4. Shaft
5. Circulating Tubes
6. Integral Heat Exchanger
7. Stator
8. Stator Liner
9. Bearings
10. Rotor

FIGURE 14: Chempump Canned-Motor Pump (57).



1. Rotating Element of Seal (attached to shaft).
2. Compensating Spring.
3. Fixed Element of Seal (attached to casing).

= "O" Ring Seal

Impellor is to the right.

FIGURE 15: Standard Single Mechanical Seal for Rotating Shaft (57).

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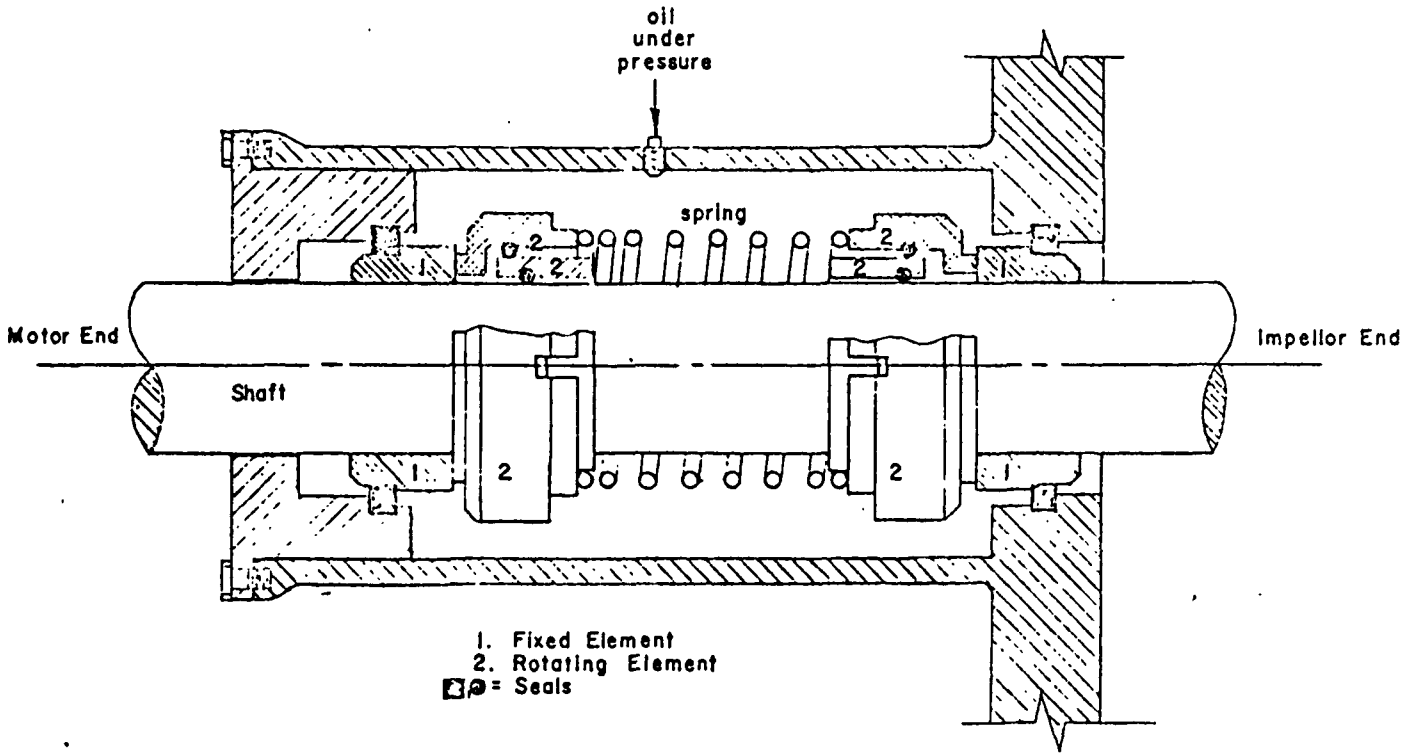

FIGURE 16: Typical Double Mechanical Seal for a Rotating Shaft (57).

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the equipment had to be modified for the new seal. Other equipment requires the machining of custom-made seals since the manufacturer never anticipated a requirement for double seals, and thus never produced any. In a few instances, it has not been possible to install double seals because the design of the equipment does not provide adequate clearance for the larger seals.(48,56,57) The inherently better sealing of the double mechanical seal would be further enhanced by either venting the space between the seals to a remote vent or by injecting a seal lubricant at sufficient pressure to ensure that the direction of any leakage past the seals would be into the process.(75)

Control of leakage around valve stems presents a slightly more difficult problem since there does not appear to be any readily applicable way to improve sealing. Such leakage will be very slight if the packing around the stem is properly maintained. Thus, the best method of control has been to frequently test for leakage with a portable instrument and then tighten or replace the packing as necessary.(75) Another alternative would be the use of diaphragm valves, such as is illustrated in Figure 17. This type valve entirely separates the valve stem from the fluid through the use of an elastomer diaphragm, which also acts as the control element of the valve. Such valves, however, are

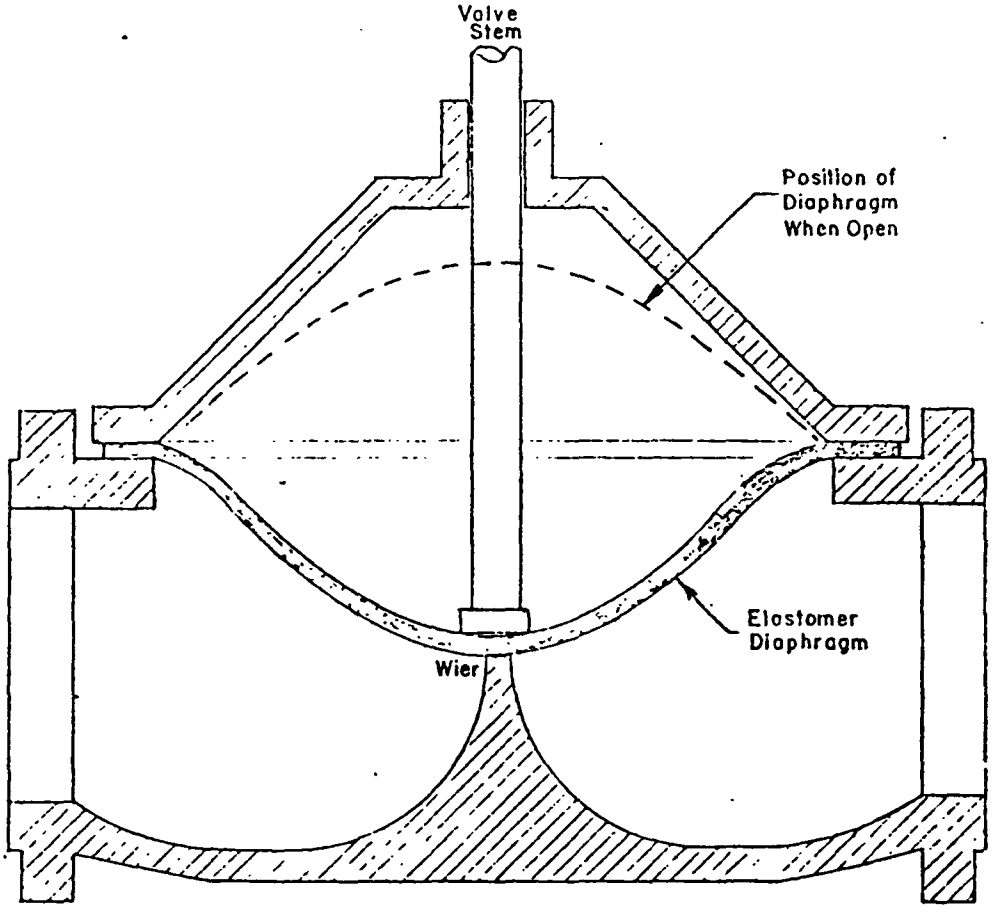

FIGURE 17: Typical Diaphragm Valve (57).

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subject to problems of erosion, attack of the elastomer diaphragm by the process fluids and failure at higher pressures.(57)

Another control for fugitive losses is the use of a "scavenging" system. In this system, all vinyl chloride sources such as pump or compressor seals, process vents, relief valves, and storage tanks are attached to a header and fed to a recovery system. The design of such recovery systems is discussed in the third Chapter of this paper.

One unusual control technique which is being investigated by Goodrich and Mine Safety Appliances Companies is an air purifier for the air conditioning systems of the control rooms. Levels of vinyl chloride in such areas have been described as extremely low already, but this project is being pursued in an effort to prove the feasibility of such a system. This would make the area where the operator spends most of his working day a "clean area" and thus further reduce his overall time-weighed exposure.(48)

Since the ultimate purpose in the entire control effort is to protect the worker from harm, it is logical that medical monitoring of the workforce should be a part of the control program. The current regulation requires all those exposed to ambient levels (without regard to respirator use) of above 0.5 parts per million to receive initial and annual

physical examinations. In addition, those with over ten years in vinyl chloride work are required to be provided with semi-annual examinations. The current requirement includes a physical examination, a medical history, and certain blood tests. The physical is intended specifically to detect enlargement or disfunction of the liver, spleen or kidneys, and to check for injury to the skin or connective tissues and to check for respiratory problems. The history must include alcohol intake, past incidents of hepatitis, work history, blood transfusions, and hospitalizations. The blood tests required are tests of the serum for total bilirubin, alkaline phosphatase, serum glutamic oxalacetic transaminase (SGOT), serum glutamic pyruvic transaminase (SGPT) and gamma glutamyl transpeptidase (GGTP).(51) The National Institute for Occupational Safety and Health (NIOSH) also recommends tests for lactic dehydrogenase (LDH), serum proteins, serum protein electrophoresis and a platelet count. (47) Many industries are offering their employees more extensive physicals, by including even more extensive tests than are required. For example, Goodrich performs a more extensive blood test and also provides chest x-rays. In addition, they offer the physicals to all of their employees, regardless of their exposure, even including clerical and staff employees. Their PVC workers are also frequently

given liver scans. The cost of such physicals is about $300.00 per person, and these are given on company time. (48,56) The extent of this commitment to medical investigation is further reflected by the providing of funding for research on liver cancer by the University of Louisville's Health Sciences Center.(38) If, as a result of the medical examination, any employee found to be at increased risk from further vinyl chloride exposure, he is reassigned to avoid exposure.(51,56)

C. METHODS OF CONTROL IN THE POLYVINYL CHLORIDE INDUSTRY:

The polymerization industry has had considerably more difficulty in reducing vinyl chloride levels to meet the requirements of the new regulations. Levels very close to the standard are now being achieved. For example, Sweden's Kema Nord reported in early 1975 that they had achieved levels of 1.5 parts per million measured as an eight-hour time-weighted average.(77) By the end of 1975 many U. S. manufacturers were operating below 2 parts per million.(46) By March of 1976, B. F. Goodrich Company had operating levels in its Louisville plant mostly below one part per million, with most workers exposed to less than that when measured on a time-weighted average.(56) The levels of the standard seem now to be eventually attainable, but not without considerable effort. For example, B. F. Goodrich Company stated

that controlling vinyl chloride had been the most ambitious research and development project in the company's history, costing over $34 million and consuming almost a half million man-hours by December, 1975.(46)

The methods described in the previous section for use in the monomer industry are also applicable to the polymer industry, where overall monomer losses averaged 4.5 to 7.5 percent, depending on the process and the condition of the plant. Fugitive losses have accounted for up to 50 percent of some plant's losses.(12)

As in the monomer industry, the use of sampling equipment of both the fixed and the portable type have proven very useful. In polymerization it is customary to locate the sampling points throughout the area where the reaction vessels are located. The system shown in Figure 18 is that used by Air Products Company in their Calvert City, Kentucky, polyvinyl chloride plant. In this system, the red flashing warning lights are triggered by the analyzer anytime that a concentration over 1 part per million is detected in the area which it serves. That is, the lights will come on in a particular area only if levels in that area exceed 1 part per million. These stay on as a warning until the sampler determines that the levels are below 1 part per million. There is no alarm for the 5 parts per million excursion

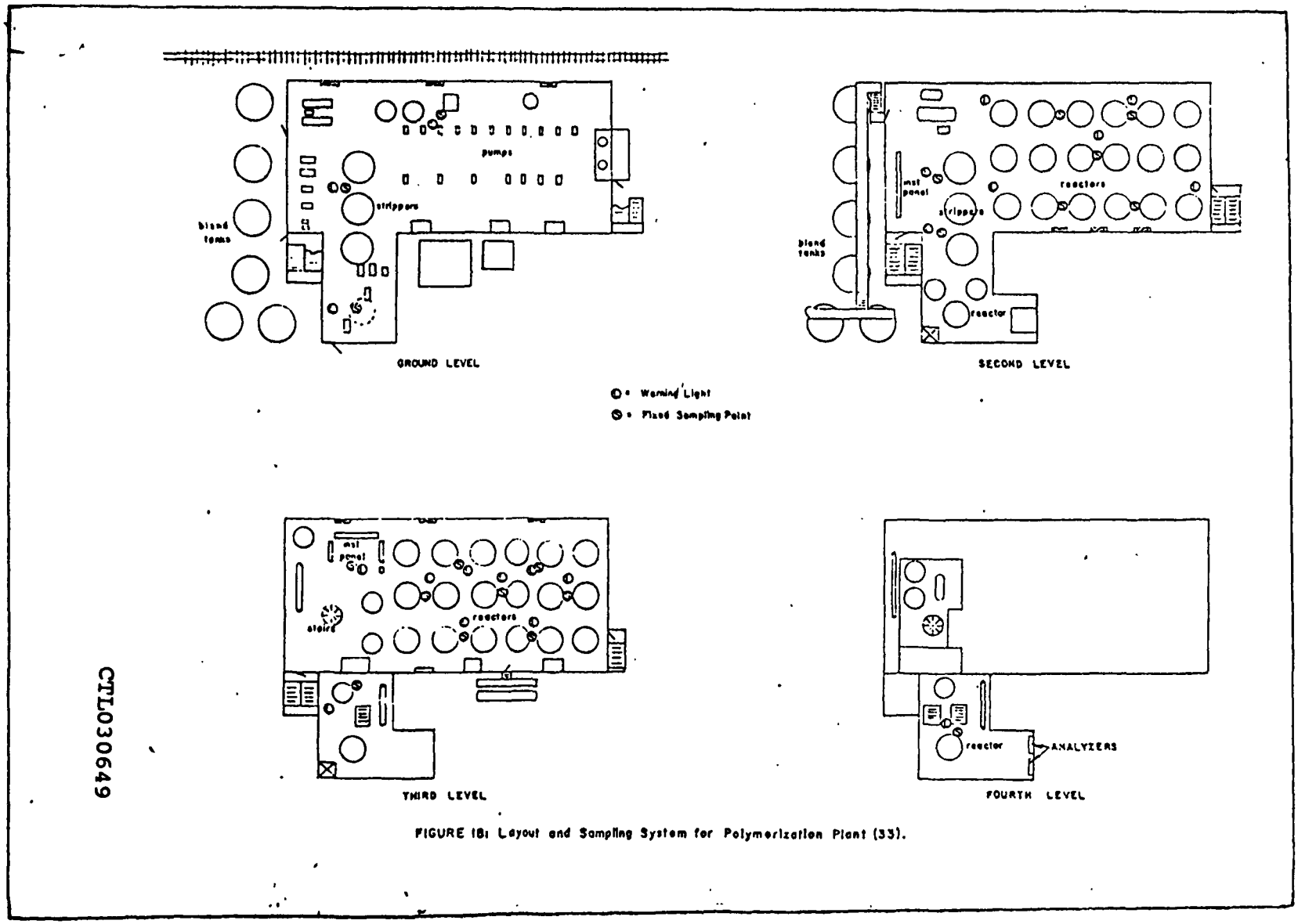

FIGURE 18: Layout and Sampling System for Polymerization Plant (33).

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limit, since respirators are worn above 1 part per million anyway. Alarms are to be set at 25 parts per million and at 100 parts per million to warn of a leak and a major release (requiring immediate attention) respectively. Another alarm will be set at 1000 parts per million, which will also trigger blue rotating beacons throughout the work area to signal workers of the need for self-contained breathing apparatus and evacuation of all non-essential persons. (33)

Other administrative procedures are much the same as for the monomer industry, especially emergency procedures and regulated area designations, since these are largely dictated by the OSHA regulation.(51,56) The requirements and use of respirators are also much the same, although, there are differences in the levels at which different manufacturers switch from supplied-air respirators to self-contained breathing apparatus.

While equipment modifications, such as closed loop sampling, double mechanical seals, and housekeeping and maintenance improvements have been important in reducing overall exposures in the polyvinyl chloride industry, probably the most significant advancement in protecting the workers' health has been in changing procedure used for cleaning reactors. Reactor cleaners have had the worst

record of injury and illness due to vinyl chloride, and thus any improvement in this area can be expected to yield substantial health benefits. As of January, 1975, fourteen of the sixteen American workers who died of angiosarcoma were ex-reactor cleaners.(14) There are currently three general procedures which are being used in the industry.

The first procedure is an interim type, since it still requires the worker to enter the reactor. Prior to entry, the reactor would be washed down one or more times and then purged with inert gas. When the vinyl chloride has been sufficiently reduced, the worker enters and manually scrapes the polymer residue off the walls of the vessel. He uses a supplied air respirator (Type "C") with a full-facepiece. With such a device inhalation of vinyl chloride should be essentially zero.(44) In addition to the respirator, he would also be required protection against direct contact with the liquid since it is injurious to the skin. Although absorption through the skin is only 0.1% as rapid as through the lungs (31), there is a danger of skin injury from direct contact with the liquid.(43) This protection would typically be foul weather gear including both rubberized jacket and pants, with a cloth cap and rubber boots and gloves. While in the vessel he would be constantly monitored by another qualified worker similarly equipped.(33)

The second process was developed by Goodrich and is actually a combination of two sets of technology which they refer to as Hydraulic Reactor Cleaner and Clean Reactor Technology. The Clean Reactor Technology is a technique for coating the interior of the reactors to prevent build-up of polymer on the walls and also a revised formulation for the reactants to curb the tendancy for forming deposits. The Hydraulic Reactor Cleaner is a very high pressure water cleaning devise. To use it, the reactor is first flushed and purged. Before opening, the reactor is placed under vacuum, so that no gases from within it will escape into the reactor floor area. After opening the reactor is continuously exhausted, such that air flows from the work-room into the reactor and is then exhausted to a remote area. The cleaning device is then attached through the man-hole opening. The high pressure water nozzles are mounted on arms which are guided by a cam-activated programmer to completely cover the interior of the reactor. If any points are missed, they are manually cleaned by a long-handled tool by an operator outside the reactor.(25,35,46,56) Although this technology is considered proprietary by Goodrich, it has been leasing it to any company desiring it.(25)

The final process is a solvent cleaning process in which the reactor is sprayed with a proprietary solvent.

This process has been publicized by the GAF corporation, using a solvent called M-Pyrol (N-methyl-2 pyrolidone). The solvent is injected into the reactor at about 100°C through nozzles at the top. It dissolves the polymer buildup, which is then carried away out the bottom of the vessel with the solvent. The solvent may then be distilled off and condensed for reuse. The nozzles may be permanently mounted in the reactor, which would eliminate the need for a worker to ever enter the vessel at all. The total solvent cleaning system would, therefore, be like that shown in Figure 19. (24,76)

Ventilation systems have also been generally more important for polymerization plants than for monomer plants, since many polymer plants are indoors. One method of control is to set up a sweep-type ventilation system through out the building, which is an application of simple dilution ventilation. This method was particularly desirable where many of the sources were fugitive sources which would not be precisely located and where there were a great many small sources that made local exhausts for each impractical. The older, indoor plant of Goodrich's in Louisville has this system and supplements it with auxiliary fans and automatic louvers which came into operation whenever there is a major release.(56) Several companies are also employing spot ventilation consisting of a separate duct

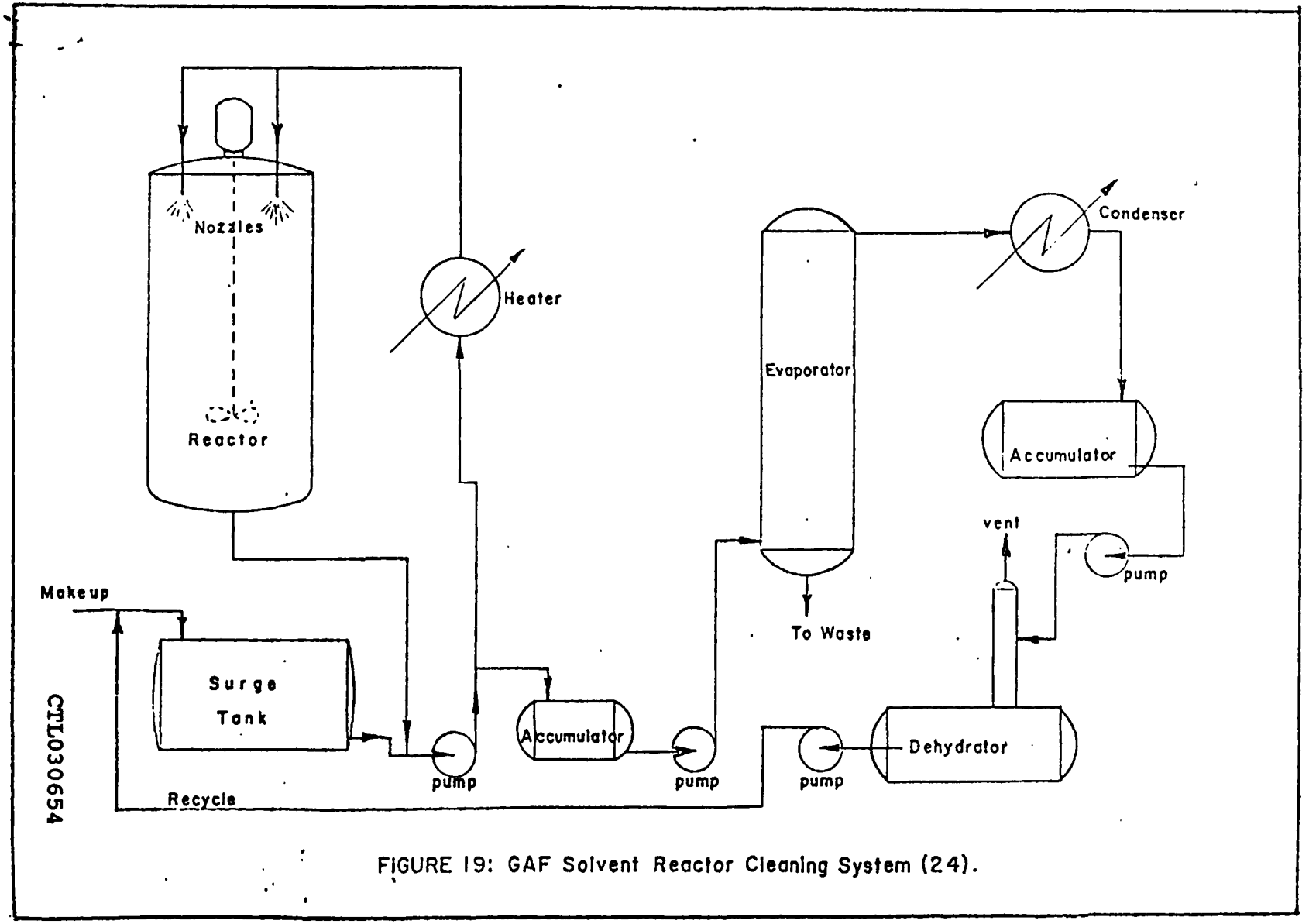

FIGURE 19: GAF Solvent Reactor Cleaning System (24).

which is located immediately adjacent to a known or potential source to remove the contaminant before it spreads throughout the room air.(56,77) Such spot exhaust systems are also useful for preventing the occurrence of excessive levels throughout the work area when a piece of equipment such as a pump or even a reactor is opened. In these instances, the flexible duct is located in or adjacent to the source and captures the monomer as it is evolved.

Another consideration in the polymerization industry has been prevention and management of upset conditions in reactors. Prevention of upsets is best achieved through proper operator training, and is being included in training programs of most companies. Reactors are protected from damage in such upsets by either rupture discs or relief valves, both of which present certain advantages, and disadvantages. If a reactor is equipped with rupture discs only, then, when an upset occurs, the entire contents of the reactor will normally be lost out the vent. Since the rupture disc does not reclose, the reactor is vented to atmospheric pressure, at this pressure vinyl chloride is a gas. Thus, if a relief valve is used instead of a rupture disc, the valve will reclose when the pressure drops below that for which it is set. However, because most such valves do not have a distinct activating pressure, there will

normally be some leakage below the pressure level where full opening is obtained. Also fouling of the valve seat may prevent complete closure. Thus, the optimal system is a relief valve with a rupture disc between it and the reactor. Thus, during normal operations, the disc would give a gas tight seal, and after any upset, the relief valve would close to prevent volatilization of all the vinyl chloride in the reactor.(56,75,76)

Another area of improvement has been the application of improved stripping technology for removing residual monomer from the polumer. This technique can be generally applied to all the various type resins, although with less success to dispersion resins. The great majority of any residual monomer is normally released from the resin in the stages downstream of the reactor, thus contributing to the overall problem in the workplace. However, this technological renovation is even more relevant to environmental protection and this will be discussed in detail in the next Chapter.(76)

D. METHODS OF CONTROL IN POLYVINYL CHLORIDE FABRICATION:

Recent developments in polymer technology have greatly improved and simplified control techniques in the control of vinyl chloride monomer in the fabrication industry. In Tribukh's 1949 study, it was recognized that a simple point of operation ventilation could control the health hazard

fairly well, even though the hazard itself was not clearly recognized.(46) An example of the controls which he recommended is shown in Figure 20, which demonstrates an exhaust hood for a mixer.(72) This approach, however, is inefficient since it allows the vinyl chloride to escape and then attempts to collect it, thus, requiring large air volumes and risking release due to interfering crossdrafts.

Another method, however, has been introduced that goes closer to the source in eliminating the vinyl chloride. In nearly all fabrication processes it is necessary to first blend and soften or melt the polymer powder or pellets. The mix is normally heated in this process to a point where a large percentage of the residual monomer is driven off, therefore, what has been done is to enclose and aspirate the blender, as shown in Figure 21. The process is further enhanced if air is introduced at the bottom of the blender and used to strip monomer from the blend. The exhausted air is run through a cyclone then through a cloth filter to remove any entrained polymer for recovery, then exhausted to a remote vent. An air cleaning device such as will be discussed in the following Chapter can be used to prevent the discharge of the vinyl chloride to the atmosphere. Table VIII demonstrates the effectiveness of this technique in reducing monomer residuals. Reduction of this extent

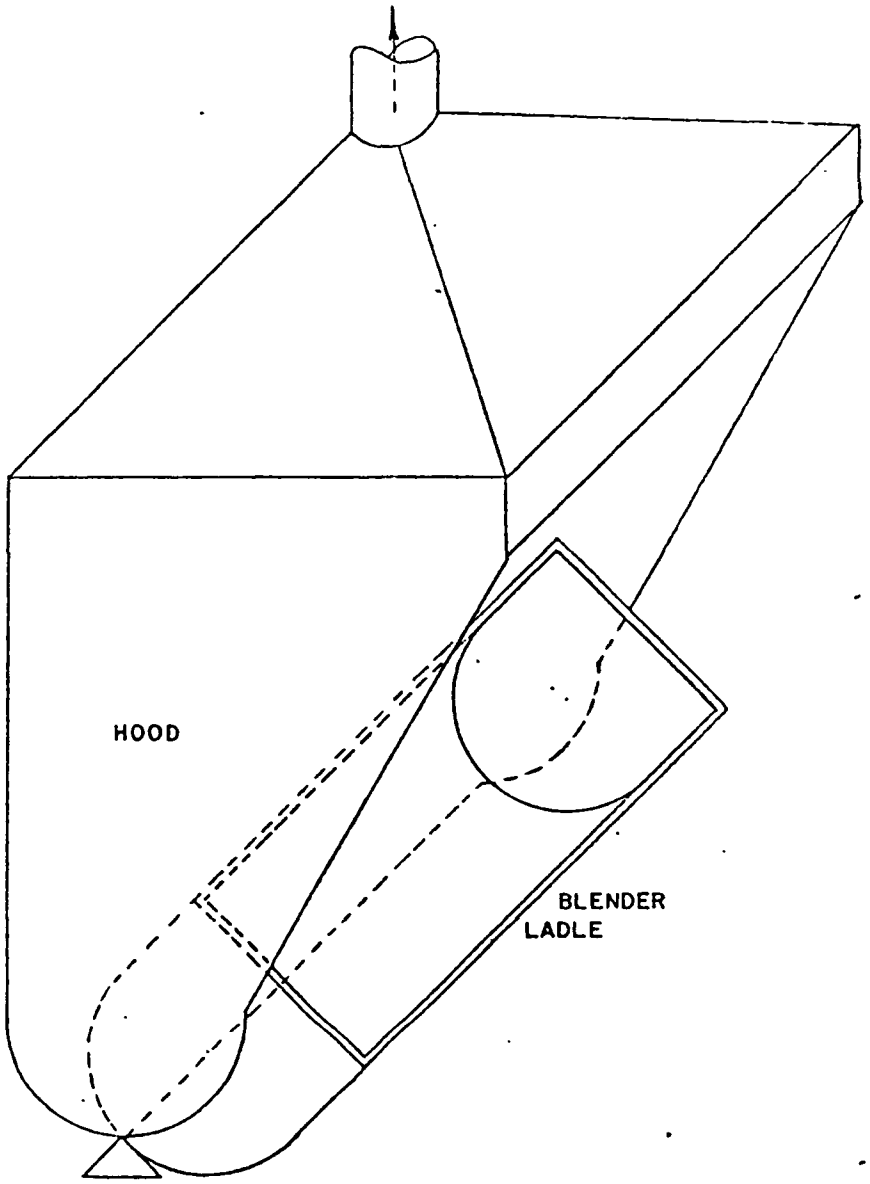

FIGURE 20: Exhaust Hood for Blender as Recommended by Tribukh (72).

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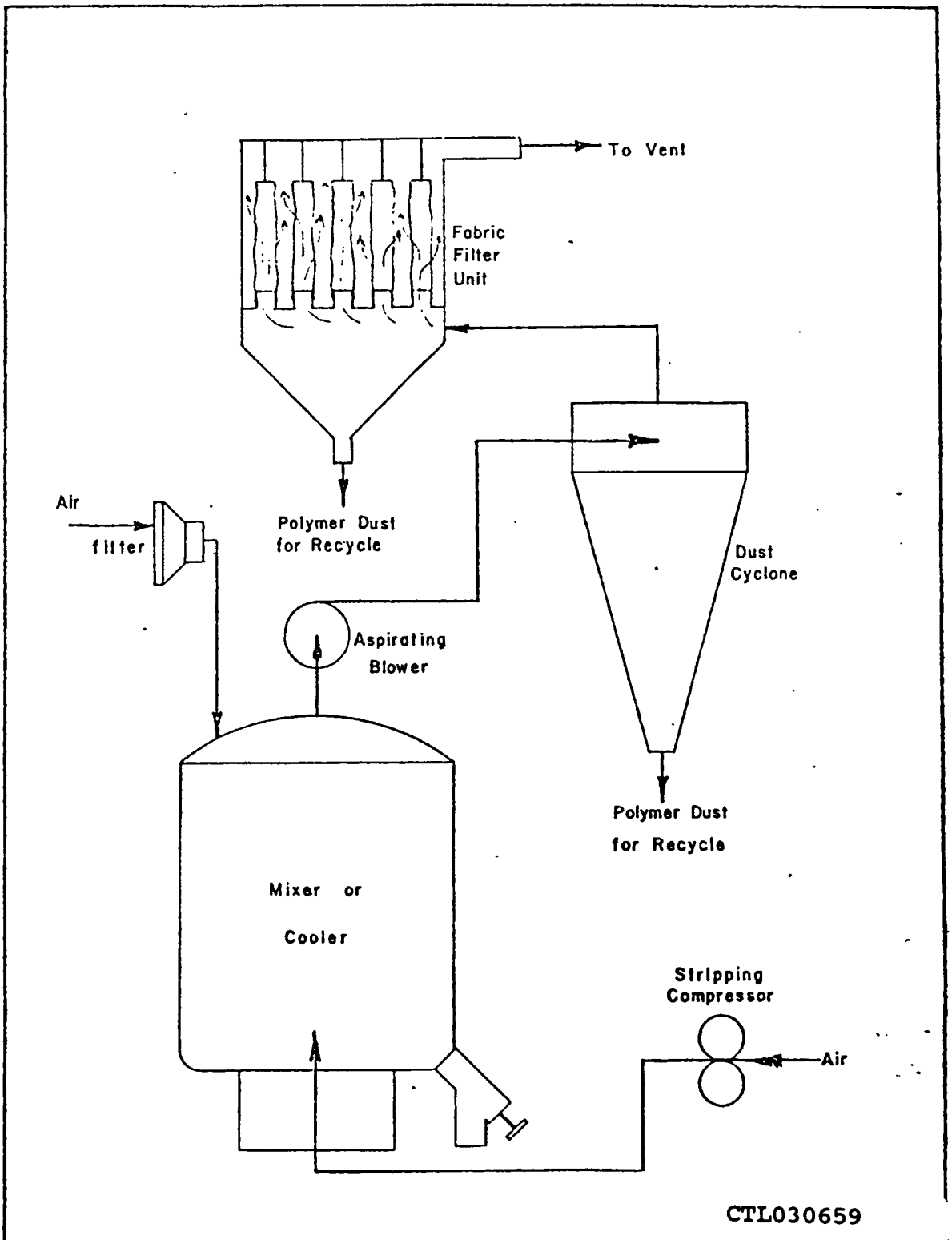

FIGURE 21: Aspiration System for Dry Blender (39).

TABLE VIII

EFFECTS OF ASPIRATION AND AIR STRIPPING IN REDUCING VINYL CHLORIDE RESIDUALS (39)

Type Resin	Mix Temperature	Process Used	Residual from Blender	Residual from Cooler
Rigid PVC	120°C	None	565 ppm	160 ppm
Rigid PVC	120°C	Aspiration	205 ppm	36 ppm
Rigid PVC	130°C	Aspiration	54 ppm	3 ppm
Rigid PVC	120°C	Aspiration and Air Stripping	68 ppm	11 ppm
PVA/PVC Copolymer	100°C	None	260 ppm	230 ppm
PVA/PVC Copolymer	100°C	Aspiration	170 ppm	140 ppm
PVA/PVC Copolymer	110°C	Aspiration	71 ppm	20 ppm
PVA/PVC Copolymer	120°C	Aspiration	18 ppm	5 ppm
PVA/PVC Copolymer	130°C	Aspiration	14 ppm	3 ppm
PVA/PVC Copolymer	100°C	Aspiration and Air Stripping	77 ppm	14 ppm

essentially assures that no significant concentrations will exist in the work areas.(39,44)

A more important development has occurred in the last few months, with the commercialization of improved stripping processes which have achieved significantly lower monomer residuals. B. F. Goodrich led in this development, announcing in May of 1975 that they had developed a technique using continuous steam stripping, which was compatible with all the production processes used by the company. Monomer residuals announced at that time were below 10 ppm.(15) Within a few weeks, Tenneco Chemical Company also announced achieving residuals of less than 10 ppm in twelve of their thirty grades of resins.(22) A survey by the Environmental Protection Agency has shown that technology is now generally available to achieve residuals below 400 parts per million for all bulk, suspension, and solution resins. The practical limit for dispersion (emulsion) resins currently seems to be about 2000 parts per million.(42,76) The lowest residuals attained in any resin at this time would appear to be those of B. F. Goodrich's compounds for plastic bottles for the food industry. It was announced near the end of 1975 that improved compounding and stripping consistantly resulted in residuals of less than one part per million in these compounds.(25)

The primary result of these residual reductions is that the quantity of monomer which might potentially be released during fabrication is lessened by several orders of magnitude. Thus, fabricators are spared the need for extensive control and disposal measures which might be necessary for resins with higher residuals. If aspiration and air stripping of blenders were combined with the use of low residual monomers, it would appear certain that any fabricator could consistantly stay below OSHA's 0.5 parts per million "action level".

CHAPTER III

ENVIRONMENTAL CONTROLS

A. CONCERN FOR POSSIBLE EFFECTS ON THE COMMUNITY:

Almost simultaneously with the finding of the relationship between vinyl chloride and the occurrence of angiocarcoma in workers, there was a greatly increased concern for the effects that vinyl chloride might have on the general population. Aside from the general hysteria that usually surrounds the subject of cancer, there are grounds for genuine concern for the community. The main basis for this concern is that it is not known at this time whether there is a "threshold" effect for carcinogens. For ordinary toxic materials, there is a certain quantity which the body is able to detoxify, eliminate, compensate for or otherwise overcome without any ill effects. When this safe amount, or threshold, is exceeded, injury results. For carcinogens, however, it is not known whether a threshold phenomenon can be defined. This dilemma comes from the assumption that only one cell need be transformed to a cancerous cell to result in the eventual formation of a full-blowm cancer, and there is some chance that any quantity, no matter how small, could cause this transformation. There is a counter argument that,

even for carcinogens, there is still an amount that can be safely handled by the body, or that if only one, or a very few cells are transformed, the body's natural defenses can overcome it and prevent the formation of an injurious cancer growth. Still another argument stems from the observation that the phenomenally long incubation period for cancer becomes progressively greater at lower concentrations. Thus, some contend that at some point the incubation period exceeds man's lifespan. Finally there is the problem of the lack of fundamental knowledge necessary to project animal data to man or even to relate cancer in man to his total, complicated environment for which there is seldom any detailed history of exposures.(13,76) While this controversy rages on, the Occupational Safety and Health Administration and the Environmental Protection Agency have opted to slide by the no-safe-level theory since it provides the most certain means of protecting the workforce and the public.(45,51,75) This conservative philosophy has been tested and upheld in court, where it was held that the agency had the obligation to act in the best interest of the public "even in circumstances where existing methodology or research is deficient." (17) In addition to the concern for vinyl chloride's carcinogenicity, recent reports have suggested that it might have mutagenic or teratogenic potentials. Tests in bacterial

systems have shown the mutagenic potential, but this has not been shown in higher animals.(60) Preliminary results of teratogenesis tests on mammals have been negative, but these are not yet conclusive.(66) There has been no documentation of injury to plants, although vinyl chloride has been experimentally shown to affect plants in a manner similar to ethylene.(74)

A survey performed for the Environmental Protection Agency indicates that there are some 4.6 million people living within a five-mile radius of plants emitting vinyl chloride.(20) The extent to which these people are exposed is largely dependent on the type of plant, the distance they live from the plant and the direction and velocity of the winds. Those living in the immediate vicinity of vinyl chloride and polyvinyl chloride plants are generally exposed to average concentrations of less than one part per million, with occasionally higher concentrations for short periods. (76)

B. EPA SURVEYS FOR VINYL CHLORIDE IN THE VICINITY OF PLANTS:

In early 1974, shortly after the revelation of vinyl chloride carcinogenicity, the Environmental Protection Agency initiated surveys of airborne concentrations in the vicinity of several plants. The maximum measured in any survey was 33 parts per million, however, this was a grab sample taken only 0.5 kilometers (1640 feet) from the center

of the plant, and may have been much closer than this to the actual release point. Levels about one part per million were found in only 10% of samples in residential areas adjacent to plants handling vinyl chloride, with the great majority of these being measured very close to the plant itself. A summary of the samples made in these surveys is shown in Tables IX and X. Regardless of the relatively low levels found in most of the samples, there is significant cause for concern when one realizes that total vinyl chloride emissions in the United States are estimated to be some 137,000 tons per year (124 million kilograms).(74)

The Environmental Protection Agency also gathered data on the primary sources of these emissions. Although there are great variations from plant to plant depending on factors such as the process in use, types of equipment used, pre-existing abatement measures, and housekeeping and maintenance practices, it was found that the primary emission sources could be categorized by the process used.

In the production of vinyl chloride by the hydrochlorination of acetylene, the primary source of emissions is the main reactor vent, accounting for about 60% of the total. Fugitive emissions and tank car loading account for a further 25%.

In the production of vinyl chloride by the ethylene

TABLE IX

RESULTS OF GRAB SAMPLES TAKEN BY THE ENVIRONMENTAL PROTECTION AGENCY NEAR VINYL CHLORIDE PLANTS (74)

EPA Region	Site Designation	Distance From Plant in Kilometers	Number of Samples	Maximum Concentration in ppm	Mean Concentration in ppm	Number of Samples Over 1 ppm
I	A	0.3	17	6.0	0.52	2
I	B	0.2	16	0.30	0.06	0
I	C	0.3	9	0.22	0.06	0
I	D	0.2	9	0.90	0.15	0
I	E	0.6	11	0.60	0.14	0
I	F	0.6	9	0.24	0.19	0
I	G	0.8	8	0	0	0
I	H	0.8	10	0	0	0
I	I	1.1	12	0.40	0.05	0
I	J	1.6	8	0	0	0
I	K	1.9	7	0.24	0.06	0
I	L	9.8	8	0	0	0
I	M	1.0	6	0	0	0
I	N	1.0	4	0	0	0
I	O	1.1	5	0	0	0
I	P	0.8	6	0.32	0.11	0

TABLE IX (continued)

EPA Region	Site Designation	Distance From Plant in Kilometers	Number of Samples	Maximum Concentration in ppm	Mean Concentration in ppm	Number of Samples Over 1 ppm
IV	A	0	6	2.2	0.84	2
IV	B	0.6	3	0.58	0.40	0
IV	C	0.6	4	1.26	0.33	1
IV	D	0.6	6	0.29	0.12	0
IV	E	0.8	3	0.24	0.16	0
IV	F	0.8	15	0.39	<0.17	0
IV	G	0.8	2	NR	<0.17	0
IV	H	0.5	1	NR	<0.17	0
IV	I	1.3	1	NR	<0.17	0
IV	J	1.0	1	NR	<0.17	0
IV	K	1.0	2	NR	<0.17	0
IV	L	1.3	1	NR	<0.17	0
IV	M	4.8	2	NR	<0.17	0
IV	N	1.0	1	NR	<0.17	0
IV	A*	0.0	6	1.7	0.33	NR
IV	B	0.6	21	5.6	1.6	NR
IV	C	0.6	21	5.8	0.71	NR
IV	D	0.6	19	2.8	0.54	NR
IV	E	0.8	2	0.10	0.07	0
IV	H	0.5	3	1.2	0.50	NR
IV	I	1.3	2	1.6	1.00	1

TABLE IX (continued)

EPA Region	Site Designation	Distance From Plant in Kilometers	Number of Samples	Maximum Concentration in ppm	Mean Concentration in ppm	Number of Samples Over 1 ppm
IV	L	1.3	2	0	0	0
IV	N	1.0	1	0	0	0
IV	P	0.6	8	0.08	0.06	0
IV	Q	0.8	12	1.7	0.34	NR
IV	R	0.5	83	33.0	3.15	NR
IV	S	0.6	1	1.2	1.20	1
IV	T	1.0	3	0.57	0.21	0
IV	U	1.0	3	0	0	0
IV	V	0.2	1	0	0	0
VI	A	0.0	8	7.8	1.75	3
VI	B	0.8	4	0.34	0.08	0
VI	C	1.2	5	0.17	0.03	0
VI	D	1.6	2	0.002	0.002	0
VI	E	3.2	5	0.18	0.08	0
VI	F	4.0	1	0	0	0
VI	G	4.8	3	0.002	0.002	0
IX	11	2.4	12	0.53	0.12	0
IX	12	1.8	12	0.48	0.18	0
IX	13	2.4	12	0.85	0.16	0
IX	14	4.5	12	0.32	0.12	0
IX	15	4.3	12	1.2	0.28	1

TABLE IX (continued)

EPA Region	Site Designation	Distance From Plant in Kilometers	Number of Samples	Maximum Concentration in ppm	Mean Concentration in ppm	Number Samples Over 1 ppm
IX	16	5.0	12	1.4	0.25	1
IX	17	5.0	12	3.4	0.53	1
IX	18	1.8	12	2.7	0.41	1
IX	19	3.1	12	1.7	0.26	1
IX	20	1.1	12	2.1	0.36	2
IX	21	1.4	12	0.45	0.14	0
IX	27	0.8	12	1.1	0.30	2
IX	23	1.0	12	0.50	0.15	0
IX	24	1.0	12	1.3	0.33	3
IX	25	2.1	12	0.48	0.12	0

*S cond set of sites for Region IV are at a different plant.

Distance is reported as kilometers from the center of the plant.

NR = data not reported.

TABLE X

RESULTS OF INTEGRATED SAMPLES TAKEN BY THE ENVIRONMENTAL PROTECTION AGENCY NEAR VINYL CHLORIDE PLANTS (74)

EPA Region	Site Designation	Distance in Kilometers	Mean Concentration in ppm	Number of Samples
I	A	0.3	0.445	3
I	B	0.2	0.008	3
I	C	0.3	0.013	3
I	D	0.2	0.080	3
IV	MSD	0.6	0.16	NR
IV	NFL	0.6	0.007	NR
IV	SOP	0.3	0.55	NR
IV	DPT	0.2	0.10	NR
IV	CP	1.0	0.01	NR
IX	1	1.1	0.08*	3
IX	2	1.3	0.07	3
IX	3	3.1	0.04	3
IX	4	4.3	0.04	3
IX	5	4.5	0.40	3
IX	6	5.3	0.05	3

*12 hour samples, all others are 24 hour samples.

Distance reported in kilometers from center of plant.

NR = data not reported.

based processes, the prime sources of emissions are the distillation column vents. The vent from the ethylene dichloride light ends column accounts for from 9 to 20% of the total, while the vent from the ethylene dichloride heavy ends column contributes another 18%. Ten to thirteen percent of the emissions originate from the vent of the vinyl chloride light ends column. Tank car loading contributes 10 to 20% while the oxychlorination reactor vent contributes 6 to 10%.

In polymerization by the suspension process, the fugitive emissions account for nearly half the emissions. Another 35% of the total comes from the drier, conveyor and storage vents. Emissions from solution polymerization, though not well characterized, are expected to be similar to those of the suspension process.

In the dispersion (emulsion) process, vents from the drier, conveyor, storage and wastewater systems contribute up to 85% of the total emissions. Fugitive losses may be as high as 17% of the total loss, and the blind surge tank may contribute up to another 6%.

For polymerization by the bulk process, the major loss is again from fugitive losses, which account for about 35% of the total. The main reactor vent contributes another 25%, while vents of the resin receiver, collector, and

storage areas contribute another 20%.(12,74,76)

C. METHODS FOR ABATING EMISSIONS:

Unlike the Occupational Safety and Health Administration, the Environmental Protection Agency has not yet completed the promulgation of its standards for vinyl chloride. They have, however, published a proposed standard (75) and considerable supporting information. They have classified the potential control techniques into the following four categories:(76)

1. Improved design of valves and of seals for pumps, compressors and other reciprocating or rotating equipment.

2. Improved maintenance and maintenance procedures, and adoption of standard operating procedures resulting in lowered emissions.

3. Reducing emissions by process alteration, especially reduction of post-reactor stage emissions in polymerization through improved stripping.

4. Collection and "cleaning" of contaminated gas streams by add-on systems.

The first of these techniques has been described in detail earlier in this paper in the section on control techniques for the vinyl chloride monomer industry. The second technique has also been partially described in earlier sections, for example, in the procedures for clearing

vinyl chloride from process equipment prior to opening, closed loop sampling procedures, and closed systems for loading and unloading monomer. One procedure which is being given emphasis, however, requires further elaboration here, and that is abatement of losses from reactor openings. The EPA has proposed in its notice of intended rule making to control losses from all equipment openings other than reactors, by imposing a limit on the amount of vinyl chloride which may be emitted in each instance. This limit is proposed at 110 liters of gaseous vinyl chloride (at standard temperature and pressure) or two percent by volume of the item being opened, whichever is larger. However, losses from reactor openings would be limited to one gram of vinyl chloride per one hundred kilograms of polymer produced (dry weight). This policy is intended to reduce both the frequency of openings and the loss from each.(75)

In the past it was necessary to open the reactor after each batch to clean the accumulated polymer from the reactor walls. The number of such entries has been greatly reduced by several techniques. For example, the B. F. Goodrich Company has extended the number of batches between cleanings through their "Clean Reactor Technology", which involves pretreating the reactor walls and reformulating the reactants.(25) The trend toward larger reactors, less sub-

ject to fouling, and also the solvent cleaning process described earlier also could reduce the frequency of reactor openings. When reactors are opened, vinyl chloride losses could be further reduced by several methods. One of the simplest systems is to displace the remaining monomer to a collection system by filling the reactor with water. An alternate technique would be the use of a vacuum system to remove the monomer. Improved stripping techniques would also be useful where stripping is done in the reaction vessel. Also any combination of these methods would be useful in abating reactor opening losses.(76)

The only process changes which currently appear promising are improved stripping for the polymer industry and substitution of oxygen for air in the oxychlorination process of monomer production. The latter is already in use by one company and has been found to have two advantages over oxychlorination with air (see Figures 3 and 4). First the product stream from the reactor is greatly reduced, since the inerts (mostly nitrogen) are eliminated, thus reducing the size and increasing the efficiency of control measures required. At the same time, this produces a vent stream which can be incinerated with little or no supplemental fuel, whereas large volumes of supplemental fuel are required to incinerate the vent stream when air

is used in the process.(75)

Improved stripping is intended primarily to reduce the emissions from equipment such as conveyors, driers, and storage bins which are downstream of the reactor in polymerization processes, although it indirectly is of benefit in solving control problems for fabricators. As related earlier, the polymerization process is normally run to 85 to 90 percent of completion, thus leaving a large amount of unreacted monomer which is distributed in the liquid (except in bulk process), gaseous and solid phases of the reactor contents. Previous practice has frequently been to vent the gaseous phase and possibly strip the economically recoverable monomer from the other phases. The monomer which remained was largely released in subsequent processing or storage, or at the fabricator's plant when the resin was worked. It is possible to use containment and control processes on these downstream sources, and it appears that this would be permissible, however, the most effective, and the most economical, method is removal at the earliest opportunity after the reactor.(76)

The majority of the entrained monomer is trapped in the polymer particles, thus, the stripping process must be tailored to remove this residual without damage to the product. Since the monomer is a volatile substance,

stripping is favored by increased temperature and decreased pressure. Thus, the typical operation might involve steam injection to achieve a temperature of about 75 to 80°C while a vacuum is applied to reduce the absolute pressure to about 0.52 to 0.60 atmospheres. A typical procedure is shown in Figures 22 and 23 where it can be seen that the key factors are temperature, pressure, and residence time.(42,76)

Emissions of greater than ten parts per million vinyl chloride would require some means of control to be applied under the proposed Environmental Protection Agency standard. The standard also specifies that releases from relief valves, wastewater, and other such sources are also to be controlled. Most of these can be vented without pretreating to a control system for gaseous contaminants. The wastewater will require stripping to remove the vinyl chloride, which would then be vented through a collection header to a control system. Because of the large volume which could be emitted in a reactor upset, it would be necessary to provide a large capacity gas holder to contain such releases until the control system is able to recycle or destroy the vinyl chloride so released.

There are basically four systems which are currently under study for "cleaning" effluent gas streams. These are adsorption, absorption, incineration and refrigeration.

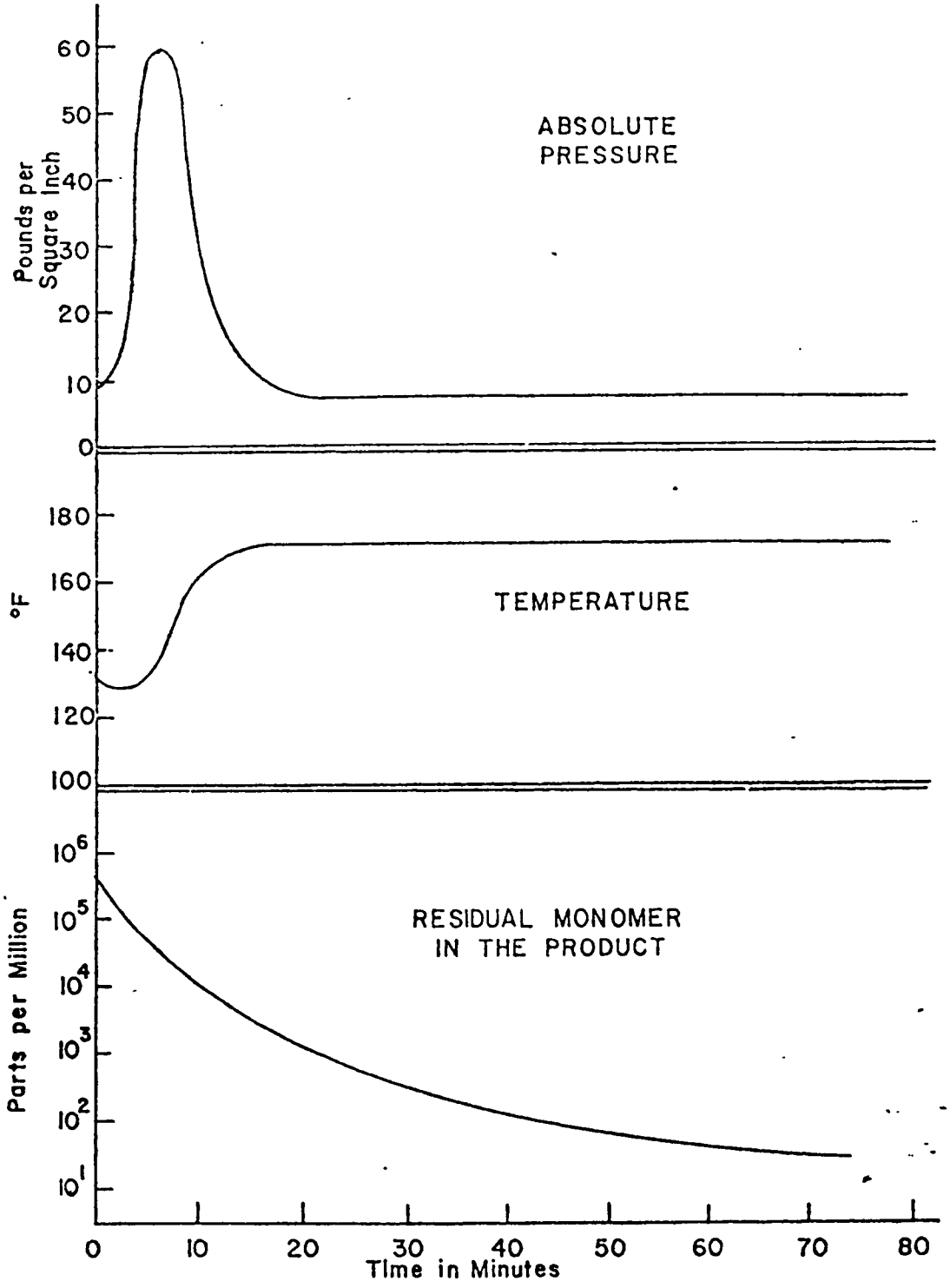

FIGURE 22: Typical Improved Stripping Process Parameters (42).

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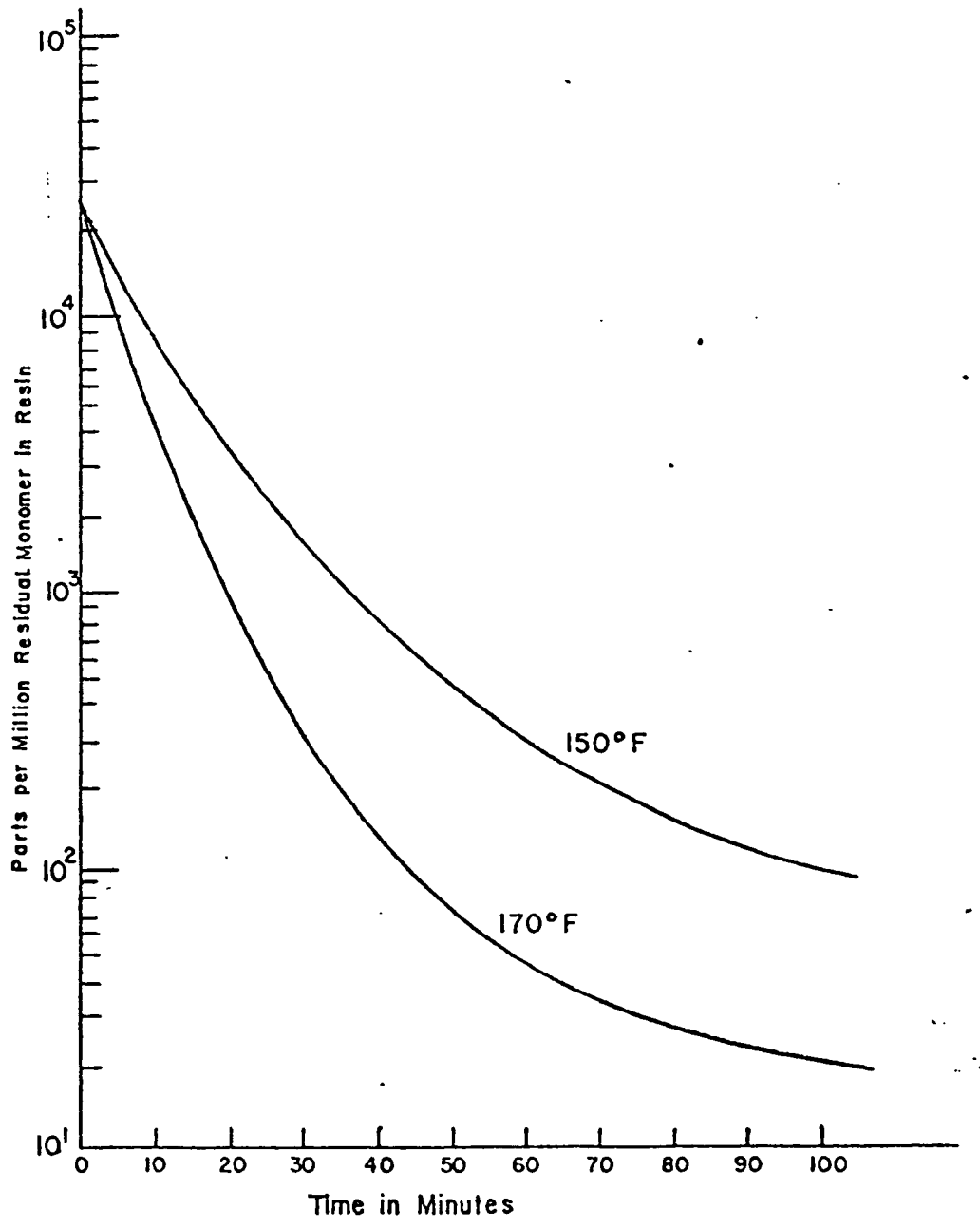

FIGURE 23: Effect of Temperature in Stripping of Polyvinyl Chloride Resins (42).

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(76). Each of these processes has advantages and disadvantages, and it is expected that various combinations will eventually be chosen which will allow each manufacturer to most economically meet the new standards.(12,73)

The adsorption process would use parallel beds of activated carbon which would alternately be used, then regenerated with steam or hot inert gas, as shown in Figure 24. If the gas stream is kept concentrated at or above one percent, the process would seem attractive. At this vinyl chloride concentration, the activated carbon can be expected to adsorb 99% of the monomer out of the gas stream up to a saturation of about 12% of its own weight. Once the carbon was saturated, the vinyl chloride may be desorbed with either hot inert gas or steam, and recovered for return to the process or incinerated. The main problem arises if the gas stream is not concentrated, for then the saturation point of the carbon drops drastically. For example, at ten parts per million, the carbon contains only one percent vinyl chloride by weight at the time the vinyl chloride breaks through the carbon bed. Other disadvantages would be that the beds would require constant operator attention to insure proper operation, and that water in the gas stream could seriously reduce the capacity of the carbon bed. Finally, when the bed is regenerated, the desorbed vinyl

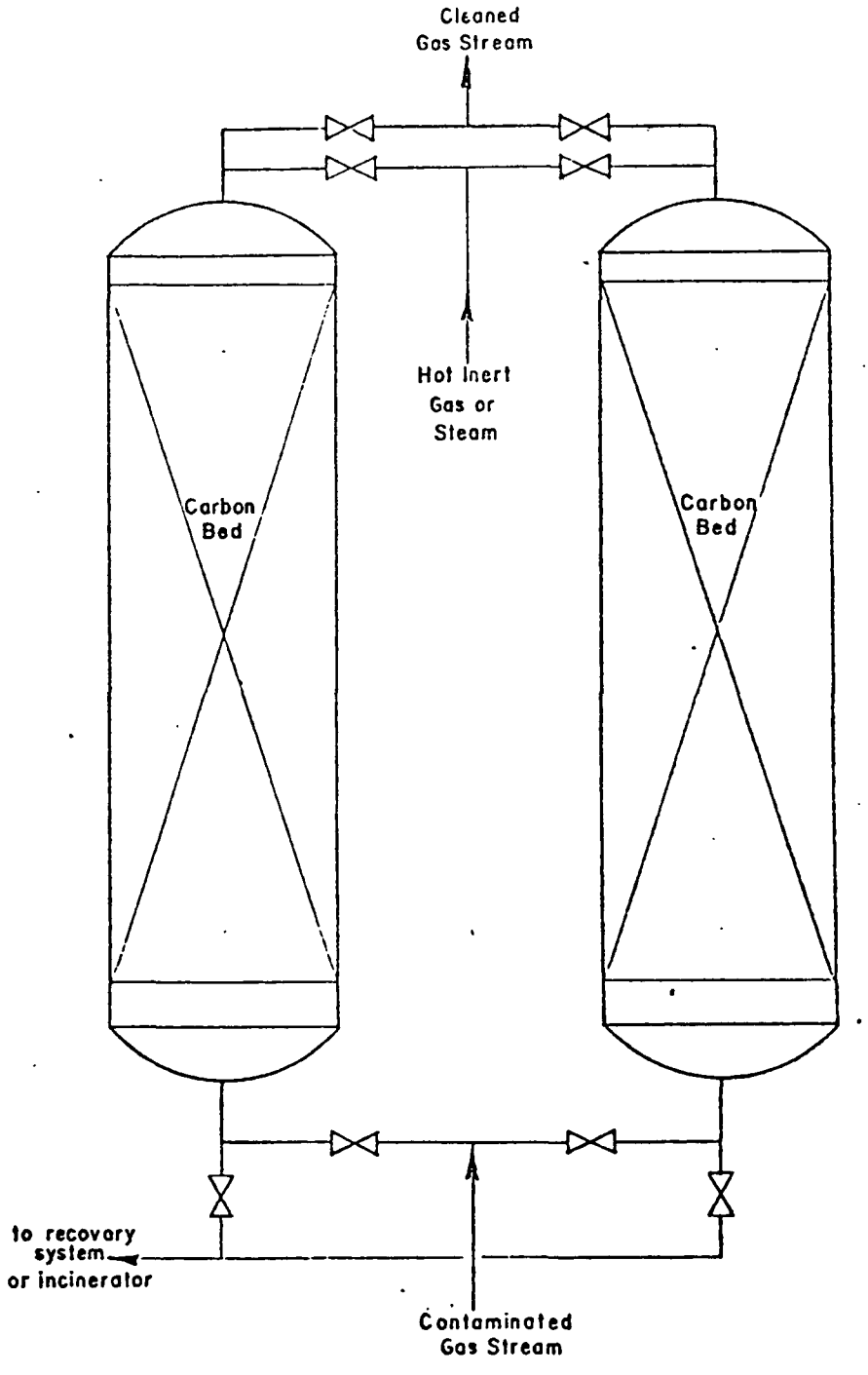

FIGURE 24: Simplified Flow Sheet for Activated Carbon Adsorption System (12).

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chloride must still be disposed of. If hot inert gas is used for regeneration, it might be necessary to use incineration, absorption, or refrigeration to remove the desorbed vinyl chloride. If steam is used, the aqueous portion could be condensed, leaving the monomer for compression and cooling for recycling.(10,66,76)

The absorption process would probably use a packed column scrubber in which a suitable solvent was used to extract the vinyl chloride from the gas stream in countercurrent flow. The solvent would then be pumped to a stripper where the vinyl chloride would be separated for recovery or disposed of as is shown in Figure 25. The solvent would then return to the absorber for reuse.(76)

The solvents currently being studied include alcohol, ethylene dichloride, and N,N-dimethyl formamide (DMF). The DMF offers the highest efficiency (99%), but is also very expensive, and would require emission controls itself due to its high toxicity. Ethylene dichloride would be desirable for its ready availability in the monomer industry, and also offers a very high efficiency. The need for a separate stripper might also be eliminated by returning the solvent to the process in the quench column. The most likely choice for the polymer industry would seem to be alcohol, since it is relatively non-toxic, and would still offer absorption

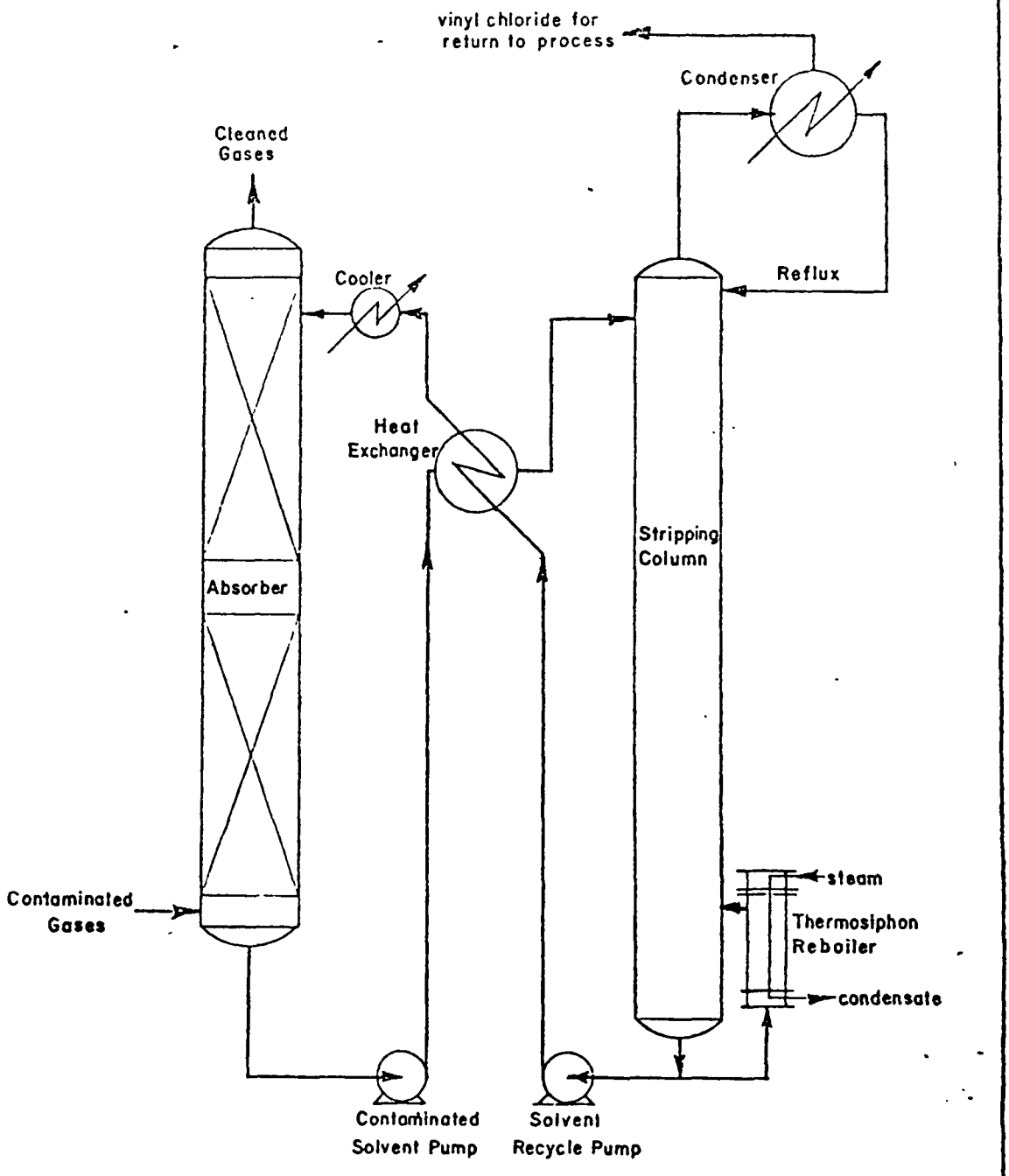

FIGURE 25: Solvent Absorption System for Vinyl Chloride Control (79).

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efficiencies of 95% at a fraction of the cost of the other solvents.(76)

The third system being studied is an incineration system. At present, some plants are successfully using flares to destroy vented vinyl chloride, but the procedure is undesirable due to the hydrogen chloride which is emitted in doing so. Studies have shown that the combustion products of vinyl chloride at over 600°C are essentially hydrogen chloride, carbon monoxide, carbon dioxide, and water. (53) Other researchers have stated that higher temperature, in the neighborhood of 1000°C would be necessary to ensure complete combustion.(76) Because of the presence of vinyl chloride in the combustion products, it would be necessary to scrub the exhaust before it is discharged to the atmosphere, and to take measures to prevent corrosion of the exposed parts of the burner. Two systems have been proposed to handle corrosive combustion gases of this nature. In one instance, the burner is arranged to exhaust below the surface of the scrubbing liquid. This system is currently being used for the incineration of chlorinated hydrocarbon wastes.(61) An alternative system is to pass the exhaust through a counter-current packed column. For high concentrations where it is desirable to neutralize the hydrogen chloride as it is absorbed, it is possible to add a little calcium carbonate or sodium hydroxide to the wash water. It

may also be desirable to immediately quench the combustion gases after the desired residence time, as is currently in experimental use at the University of Cincinnati's Kettering Laboratory.(59) Several manufacturers are also successfully applying incineration as a successful control measure.(76)

The final control system is the one currently enjoying the greatest popularity, and that is refrigeration. This system normally combines pressure and cooling to condense the vinyl chloride for recovery. The system shown in Figure 26 is typical of those currently in use by at least twenty-five plants for vinyl chloride recovery. The system is very useful for handling highly concentrated streams, but suffers the drawback that the gases leaving the heat exchanger will still be saturated at the temperature and pressure being used. For example, at 7°C and 4.4 atmospheres, the gas stream would still contain 50% vinyl chloride, while even at -26°C and 5.8 atmospheres, the vinyl chloride content would still be ten percent by volume.(76,79) This system, however, would be particularly useful for pretreating highly concentrated streams prior to one of the previously described systems.

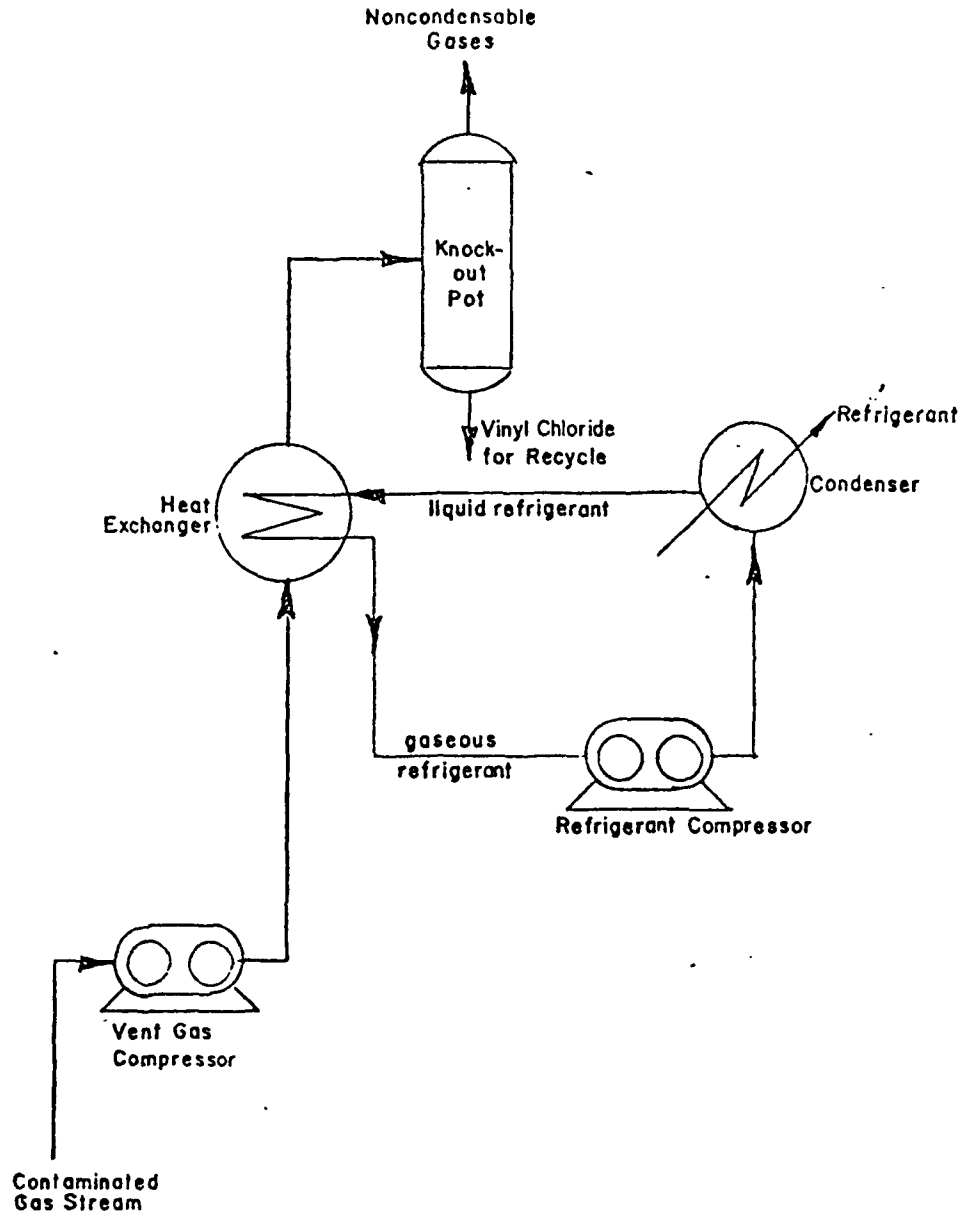

FIGURE 26: Refrigerated Vent System for Vinyl Chloride Control (79).

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CHAPTER IV

SUMMARY

A. REVIEW OF THE CURRENT STATE-OF-THE-ART FOR VINYL CHLORIDE CONTROL:

As was stated earlier in this paper, the problem of controlling vinyl chloride has presented industry with an unprecedented situation. Between January and April, 1974, the standard for allowable exposure in the workplace dropped from 500 to 50 parts per million, and in October, 1974, it was announced that concentrations were to be down to one part per million by the first day of 1975 (although this last target date was later delayed to April 1, 1975). (49,51,52)

The approach taken in meeting this challenge has been one of common sense, applying some well known principles of industrial hygiene and sound engineering. Since most monomer production facilities are outdoor structures, improved ventilation was not particularly applicable. However, most polymer plants, especially the older ones, are enclosed by buildings, thus making improved ventilation the first step. As one engineer put it, "The first thing we did was to open all the windows".(56) This was followed-up by

design of improved general and local exhaust ventilation. (56,77)

Once the steps to remove contamination had been taken, the sources were sought. One very useful procedure has been the use of portable organic vapor analyzers to detect leaks from valves, packings, seals of agitators, pumps and compressors, man-head covers, flanges, and pipe joints. The use of these instruments proved especially valuable for very small leaks, for they were found to be capable of detecting leaks which went unnoticed using conventional test methods. Once these leaks were detected, they were attacked by engineering control methods. For example, pumps and agitators were given double seals, while man-heads were given double "O" ring seals set in machined retaining and aligning grooves.(56)

Once these existing leaks had been found and controlled, the fixed monitoring systems came into its own. As related earlier, some experimental and industrial systems were already in existence before the vinyl chloride problem became a crisis. These early systems have been adapted and improved for application as "instantaneous" monitors of the workplace. They have since served two very important functions. First, they rapidly detect any increase in the vinyl chloride levels in the plant air, and warn the

operators so that corrective action may be taken. Second, since it has not been possible to constantly remain below one part per million, these samplers warn the worker of times when respiratory protection is needed. It is possible that some manufacturers may be allowed to substitute a combination of area monitoring and time studies for personal monitoring. They would prefer to use this method based on the area samplers due to its elimination of the second sampling system and, also, for its essentially real-time analysis of exposures.(18,33,48,56)

Respiratory protection has been a part of the control procedure since the outset. For example, one of Goodrich's first reactions was to purchase cartridge-type organic vapor respirators which were used at concentrations above 25 parts per million. These were known to be of very limit d effectiveness, but since there was no respirator at the tim specifically designed for vinyl chloride protection, they were the only thing available. They later went to canister masks which were intended for vinyl chloride service, and which are still acceptable up to 25 parts per million under the OSHA regulations. These respirators were heavy, and required frequent replacement of their expensive cartridges, and were consequently dropped in favor of supplied-air (pressure-demand) respirators which are supported by a

plant-wide system of headers with convenient plug-in air hose connections for the masks. Self-contained pressure-demand respirators are prepositioned for emergency use throughout plants, with extras available for use by emergency teams. The self-contained units have extremely short useful time limits (30 minutes or less in most instances) and are, therefore, impractical for routine use. (33,48,56,64)

The industry has also initiated changes in equipment and work practices with the intention of abating emissions at the source. To date, there have been no drastic process modifications, such as new routes of production, and currently published research does not reflect any reasons to expect such changes. One trend that is apparent is the preference for much larger polymerization reactors which result in lowered emissions by way of having a better ratio of capacity for throughput to sources for emissions than do smaller reactors. (22,75,76)

The only major process change which appears applicable to the monomer industry would be to substitute oxygen for air in the oxychlorination process. This would be a very difficult process modification for most manufacturers, however, since the reactor and considerable downstream equipment would require redesign or possibly replacement. (75,76)

Two process changes have proven valuable and generally applicable to the polymer industry. The first of these has been the development of improved techniques for cleaning reactors, or for extending the time between reactor openings. The second has been the development of improved stripping procedures, which has been partially backed by improved blending to form resins more easily stripped. Both of these improvements were extensively discussed in earlier sections of this work (22,25,48,56,75,76).

In the fabrication industry, two major developments have been those of aspirating blend tanks to remove residual monomer, and development of low residual polymers for most uses. These improvements should be sufficient to assure that fabricators are able to comply with the standards without other systems for ventilation or the use of respiratory protection.(39)

Environmental protection currently depends primarily on refrigeration processes, which were mostly installed for recovery of as much vinyl chloride from vent systems as economically desirable. Some plants have added or increased utilization of flares to burn the residual monomer. This system results in the emission of hydrogen chloride, but the hazard of such emissions is deemed much less than that of vinyl chloride. Other systems are being used on

various scales experimentally and in pilot plant studies, but none have yet reached the point of industry-wide recognition.(48,75,76)

B. EFFECTIVENESS OF CONTROLS:

Much has been said about the feasibility of attaining of the one part per million standard set forth by the Occupational Safety and Health Administration. The need for such a low standard has been questioned on various grounds, including, for example, the fact that cases of angiosarcoma have been found in only three of the eight plants which have produced polyvinyl chloride for more than twenty years.(50) Other arguments against the standard include the lack of animal or human data for exposures below 50 parts per million (50) and the lack of a clear understanding of the metabolism of vinyl chloride and its relation to cancer induction.(32) The reasoning which prevailed, however, was that where human cancer was concerned the limit must be set as low as possible without destroying the industry.(50)

As to actually attaining this level, there is also considerable debate. It has now been generally agreed that fabricators should be able to maintain compliance by engineering means alone. It was claimed by industry, however, that neither the polymer nor monomer industries

could do so. The Occupational Safety and Health Administration believes that although it is not currently feasible for these industries to achieve the one part per million level by engineering means alone, that they will be able to do so in a few years.(50)

Since the determination of the severe health risk from vinyl chloride, and the promulgation of the OSHA standards, the vinyl chloride industry has made great progress in reducing occupational exposures. The problems of acro-osteolysis and angioneurosis have been eliminated.(71) Levels in the monomer industry have been most successfully controlled. For example, average concentrations at B. F. Goodrich's Calvert City, Kentucky, monomer plant were reduced from about five or six parts per million two years ago to levels of about 0.2 parts per million as of March, 1976. Personal monitoring, without regard to respirators, shows that the vast majority of exposures are below the one part per million limit, with most higher exposures due to excursions during which the worker would be wearing a respirator.(48)

The polymer industry has also had considerable success in reducing exposures, however, they are experiencing difficulty in consistently staying below the one part per million limit. Area monitoring results were generally

down to the one to three parts per million range at Goodrich's polymerization plants by the end of 1975, (26) and have been further reduced at the 34 year-old Louisville plant by March, 1976, such that operation below one part per million was frequently possible. (56) Worker exposures, as measured by personal monitoring, have been lower than this. (26,56) The newer polymer plants, with their larger reactors and outdoor structures, promise even lower exposures.(22,56)

In both the monomer and polymer industry, respiratory protection will continue to be a necessary exposure control technique for the foreseeable future. This is partly due to minor leaks raising ambient levels within the plant, but is primarily because of the so-called hazardous operations, which may involve exposure to liquid vinyl chloride or its concentrated vapors. This includes operations such as removal of pumps or filters for servicing or entry into tanks or reactors for repairs or inspections. There will also remain the threat of spills or other accidental releases.(22,56)

Environmental controls thus far have been in the form of "fallout" from attempts to reduce occupational exposures. Monomer plants had reduced their emissions such that their downwind levels were already in the parts per billion range, (48) even before the imposition of the new Environmental

Protection Agency requirements. Ambient levels due to polymer plants have also been reduced, especially where improved stripping is used. For example, one company employing improved stripping was able to report at the end of 1975 that vinyl chloride levels at the plant property line were a "few hundreths of a part per million", and were "virtually undetectable a short distance from the plant". (25,26)

Unfortunately, it would be impossible to judge the effectiveness of these improvements for many years to come. This is because cancer in man has an incubation period estimated to be as long as twenty years. Thus, there may be more cases of angiosarcoma occurring within the next few years, and it could be twenty to thirty years before any effect or reduced exposures could be demonstrated. Also, if the occupational cancer is eliminated, it will not be possible (nor necessarily desirable) to know if it would also have been controlled by a less stringent limit.

Still, regardless of the financial hardships of the new control measures, the vinyl chloride industry has remained a healthy and growing one. The industry was estimated to have produced over $3 billion worth of finished products in 1974 (71) with an annual capacity of some 4-65 billion pounds. Despite the cost of personal and environmental

protection it is still estimated that it will grow to over 8.5 billion pounds by 1980.(58)

BIBLIOGRAPHY

1. Albright, L. F. "Manufacture of Vinyl Chloride." Chemical Engineering, 74 (1967), 218-226.

2. Albright, L. F. "Vinyl Chloride Processes." Chemical Engineering, 74 (1967), 128-138.

3. Albright, L. F. "Vinyl Chloride Polymerization by the Suspension Process Yields Polyvinyl Chloride Resins." Chemical Engineering, 74 (1967), 145-152.

4. Albright, L. F. "Polymerization of Vinyl Chloride." Chemical Engineering, 74 (1967), 151-158.

5. Albright, L. F. "Vinyl Chloride Polymerization by Emulsion, Bulk, and Solution Processes." Chemical Engineering, 74 (1967), 85-92.

6. Allen, T. L. "VCM in Respirable Air Cut to 1/10th The OSHA Standard." Chemical Processing, Dec. 1975, 88-89.

7. Anderson, L. A., Jr. "Threshold Limit Values for Vinyl Chloride: A Critical Review of the Literature Used To Establish Standards for Industrial Exposure to Vinyl Chloride." Unpublished Master's Thesis, University of Cincinnati, 1975.

8. Bell, Z. G., et al. "Control Methods for Vinyl Chloride." Chemical Engineering Progress, 71 (Sept. 1975), 45-53.

9. Berk, Paul D., Martin, James F., and Waggoner, Jeanne G. "Persistance of Vinyl Chloride-Induced Liver Injury After Cessation of Exposure." Annals of the New York Academy of Sciences, 2246 (Jan. 31, 1975), 70-77.

10. Calgon Corporation. "Controlling Vinyl Chloride Emissions with Activated Carbon." Company Bulletin Number 23-200.

11. Cantow, Manfred J. R. "Poly(vinyl chloride)." Kirk-Othmer Encyclopedia of Chemical Technology. 2nd ed. Vol. XXI. New York: John Wiley and Sons, Inc. 1970.

12. Carpenter, B. H. "Vinyl Chloride - An Assessment of Emission Control Techniques and Costs." Washington, D.C.: U.S. Environmental Protection Agency, Sept. 1974.

13. Cassarett, Louis J. and Doull, John, ed. Toxicology, the Basic Science of Poisons. New York: Macmillan Publishing Company, 1975.

14. Clark, G. " The Best Available Evidence." Job Safety and Health, 3:1 (Jan. 1975), 4-12.

15. "Continuous Stripping of Vinyl Chloride Monomer from Polyvinyl Chloride Resins." Chemical Engineering, 82 (Sept. 15, 1975), 67.

16. Cook, W. A., et al. "Occupational Acroosteolysis II: And Industrial Hygiene Study." Archives of Environmental Health, 22 (Jan. 1971), 74-82.

17. "Court Upholds Vinyl Chloride Standard, Delays Effective Date." Occupational Safety and Health Reporter, 4:36 (Feb. 6, 1975), 1175-76.

18. Crider, L. B. "An Instrumental System for Monitoring of Vinyl Chloride Monomer in Plant and Laboratory Work Environments." Avon Lake, Ohio: B. F. Goodrich Chemical Company, January, 1974.

19. Danziger, H. "Accidental Poisoning by Vinyl Chloride - Report of Two Cases." Canadian Medical Association Journal, 82 (Apr. 1960), 828.

20. Environmental Health Hazards Project of the American Public Health Association. Population Residing Near Plants Producing Vinyl Chloride. Washington, D.C.: United States Environmental Protection Agency, August 1975.

21. Faith, W. L.; Keyes, D. B.; and Clark, R. L. Industrial Chemicals. 3rd ed. New York: John Wiley and Sons, Inc., 1965, 805-810.

22. "A 50-fold Decrease in the Usual Residual-Vinyl-Chloride Content of PVC Resins." Chemical Engineering, 82:10 (May 12, 1975), 37.

23. Filatova, V. S., and Gronsberg, Y. S. "Sanitary Hygiene Working Conditions in the Production of Polyvinyl Chloride Resins and Measures for Improving These Conditions." Giga. Sanit., (1957), 38-42.

24. GAF Corporation. "Reactor Cleaning System Reduces Downtime." Chemical Processing, (July 1972).

25. Goodrich Chemical Company, B. F. "Progress in Vinyl Chloride Containment." Akron, Ohio, B. F. Goodrich Company, December 4, 1975.

26. "Goodrich Expands PVC Production, While Complying With OSHA Standard." Occupational Safety and Health Reporter, 5:28 (December 11, 1975) 983.

27. Griffith, M.E., and Wheeler, T. N. "Odor Threshold for Vinyl Chloride." Study Prepared for the Manufacturing Chemists Association, August, 1974.

28. Hardie, D.W.F. "Vinyl Chloride." Kirk-Othmer Encyclopedia of Chemical Technology. 2nd ed. Vol. V. New York: John Wiley and Sons, Inc., 1964.

29. Hawley, Gessner G. Condensed Chemical Dictionary. New York: Van Nostrand Reinhold Company, 1971.

30. Heath, Clark W., Jr.; Falk, Henry; and Creech, John L., Jr. "Characteristics of Cases of Angiosarcoma of the Liver Among Vinyl Chloride Workers in the United States." Annals of the New York Academy of Sciences, 246 (Jan. 31, 1975), 321-236.

31. Hefner, R. E.; Watanabe, P. G.; and Gehring, P. J. "Precutaneous Absorption of Vinyl Chloride (VCM) Gas in the Rhesus Monkey." Study Prepared for the Manufacturing Chemists Association, August, 1974.

32. Hefner, R. E.; Watanabe, P. G.; and Gehring, P. J. "Preliminary Studies of the Fate of Inhaled Vinyl Chloride Monomer (VCM) in Rats." Study Prepared for the Manufacturing Chemists Association, July, 1974.

33. Herbig, Thomas W. Letter. Air Products and Chemicals Company, Inc., Calvert City, Kentucky, March 9, 1976.

34. "Hygenic Guides Series - Vinyl Chloride." American Industrial Hygiene Association Journal, 25 (July/Aug. 1964), 421-423.

35. Jones, Jay. Presonal Communication. March 5, 1976.

36. Levinson, C. "The Malevolent Workplace." Ambio, 4 (1), 24-29.

37. Lilas, Ruth, et al. "Prevalence of Disease Among Vinyl Chloride and Polyvinyl Chloride Workers." Annals of the New York Academy of Sciences, 246 (Jan. 31, 1975), 22-41.

38. "Louisville Health Sciences Center Organizes Research on Liver Cancer." Occupational Safety and Health Reporter, 3:43 (March 28, 1974), 1356-7.

39. Mack, W. A. "Vinyl Chloride Monomer Reduction and Control." Chemical Engineering Progress, 71 (Sept. 1975), 141-144.

40. Maltoni, Cesare, and Lefemine, Giuseppe. "Carcinogenicity Bioassays of Vinyl Chloride: Current Results." Annals of the New York Academy of Sciences, 246 (Jan. 31, 1975), 195-218.

41. Maltoni, Cesare. "The Value of Predictive Experimental Bioassays in Occupational and Environmental Carcinogensis. An Example: Vinyl Chloride." Ambio, 4 (1), 18-23.

42. Mantell, G. J.; Barr, J. T.; and Chan, R. K. S. "Stripping VCM from PVC Resins." Chemical Engineering Progress, 71 (Sept. 1975), 54-62.

43. Marsteller, H. J., et al. "Unusual Splenomegalic Liver Disease as Evidenced by Peritoneoscopy and Guided Liver Biopsy Among Polyvinyl Chloride Production Workers." Annals of the New York Academy of Sciences, 246 (Jan. 31, 1975), 95-134.

44. Naitove, Matthew H. "Living with VCM, How PVC Processors Can Cope." Plastics Technology, (December, 1974).

45. National Institute for Occupational Safety and Health. "NIOSH Recommended Standard for Occupational Exposure to Vinyl Chloride," Cincinnati: Office of Technical Publications, National Institute for Occupational Safety and Health, 1974.

46. New York Times. "How Polyvinyl Chloride Met Health Rules." December 28, 1975.

47. "NIOSH Issues Medical Surveillance Supplement to VC Document." Occupational Safety and Health Reporter, 3:43 (March 28, 1974), 1356.

48. O'Brien, William C. Interview, B. F. Goodrich Chemical Company, Calvert City, Kentucky, March 28, 1976.

49. Occupational Safety and Health Administration. "Emergency Temporary Standard for Exposure to Vinyl Chloride." Federal Register, 39 (April 5, 1974), 12342-12344.

50. Occupational Safety and Health Administration. "Preamble to the OSHA Permanent Standard for Exposure of Employees to Vinyl Chloride, Occupational Safety and Health Reporter, 4:19 (October 10, 1974), 545-551.

51. Occupational Safety and Health Administration. "Standard for Exposure to Vinyl Chloride." Federal Register, 39 (October 4, 1974), 35890-38898.

52. Occupational Safety and Health Administration. "Standard for Exposure to Vinyl Chloride: Effective Date." Federal Register, 40 (March 25, 1975), 13211.

53. O'Mara, M. M., et al. "Combustion Products from Vinyl Chloride Monomer." American Industrial Hygiene Association Journal, 32 (March, 1971), 153-156.

54. Ott, Marvin G.; Langer, Ralph R.; and Holder, Benjamin B. "Vinyl Chloride Exposure in a Controlled Industrial Environment: A Long-Term Mortality Experience in 594 Employees." Archieves of Environmental Health, 30 (July, 1975), 333-339.

55. Patty, Frank A. Industrial Hygiene and Toxicology. Vol. II. New York: John Wiley and Sons, Inc., 1963, 1303-1305.

56. Pember, Ken, et al. Interview, B. F. Goodrich Chemical Company, Louisville, Kentucky, March 11, 1976.

57. Perry, Robert H., et al., ed. Chemical Engineers' Handbook, 4th Edition. New York: McGraw Hill Book Company, 1963.

58. "PVC Growth Outlook Looks Good." Chemical Engineering, 81:13 (July 8, 1974).

59. Radike, Martha and Brown, Phillip. Presentation on Control of Carcinogens in the Laboratory. Environmental Health Seminar, Kettering Laboratory, University of Cincinnati, May 26, 1976.

60. Rannug, E., et al. "Mutagenicity of Vinyl Chloride After Metabolic Activation." Ambio, 3 (5), 194-7.

61. Santoleri, J. J. "Chlorinated Hydrocarbon Waste Disposal." Chemical Engineering Progress 69:1 (January, 1973), 68-74.

62. Selikoff, I., and Waggoner, J. "Vinyl Chloride: The Canary in the Coal Mine." Job Safety and Health, 3 (January, 1975), 27-30.

63. Schneiderman, Marvin A.; Mantel, Nathan; and Brown, Charles C. "From Mouse to Man - or How to Get From the Laboratory to Park Avenue and 59th Street." Annals of the New York Academy of Sciences, 246 (January 31, 1975), 237-248.

64. Smith, David L., and Giesler, William S. "An Evaluation of Organic Vapor Respirator Cartridges and Canisters Against Vinyl Chloride." Cincinnati: National Institute for Occupational Safety and Health, October, 1974.

65. Steenberg, L. R. "Air Pollution Control Costs for Vinyl Chloride Monomer and Polyvinyl Chloride Processing." Study Prepared for the U. S. Environmental Protection Agency, February 28, 1975.

66. Schwitz, B. A., et al. "Vinyl Chloride-Teratology - Study in Mice, Rats and Rabbits." Study Prepared for the Manufacturing Chemists Association, August, 1974.

67. Suciu, I., et al. "Clinical Manifestations of Vinyl Chloride Poisoning." Annals of the New York Academy of Sciences, 246 (January 31, 1975), 53-69.

68. "Supreme Court Declines Review of Second Circuit Court Ruling in VC Case." Occupational Safety and Health Reporter, 4:52 (May 29, 1975).

69. "Suprene Court Denies Stay of VC Standard." Occupational Safety and Health Reporter, 4:44 (April 3, 1975) 1439.

70. Tabershaw/Cooper Associates. "Epidemiological Survey of Vinyl Chloride Workers." Study Prepared for the Manufacturing Chemists Association, May 3, 1975.

71. Torkelson, Theodore R. "Statement of the Manufacturing Chemists Association Before the Subcommittee on the Environment of the Senate Committee on Commerce on Vinyl Chloride." August 21, 1974.

72. Tribukh, S. L., et al. "Working Conditions and Measures for Their Sanitation in the Production and Utilization of Vinyl Chloride Plastics." Giga. Sanit., 10 (1949), 38-45.

73. U. S. Environmental Protection Agency. Preliminary Assessment of the Environmental Problems Associated with Vinyl Chloride and Polyvinyl Chloride. Washington, D.C.: U. S. Environmental Protection Agency, September, 1974.

74. U. S. Environmental Protection Agency. Scientific and Technical Assessment Report on Vinyl Chloride and Polyvinyl Chloride. Washington, D.C.: U. S. Environmental Protection Agency, 1975.

75. U. S. Environmental Protection Agency. "Proposed Standard for Vinyl Chloride." Federal Register, 40 (December 24, 1975), 59531-59552.

76. U. S. Environmental Protection Agency. Standard Support and Environments Impact Statement: Emission Standard for Vinyl Chloride. Washington, D.C.: U. S. Environmental Protection Agency, October, 1975.

77. "Unusually Low Concentrations of VC in Workplace Ambient Air." Chemical Engineering, 82:8 (April 14, 1975).

78. Veltman, G., et al. "Clinical Manifestations and Course of Vinyl Chloride Disease." Annals of the New York Academy of Sciences, 246 (January 31, 1975), 6-17.

79. Wheeler, R. N. and Sutherland, M. E. "Control of In-Transit VCM." Chemical Engineering Progress, 71:9 (September, 1975), 48-53.

80. Wyatt, Robert H., et al. "An Epidemiological Study of Blood Screening Tests and Illness Histories Among Chemical Workers Involved in the Manufacture of Polyvinyl Chloride." Annals of the New York Academy of Sciences, 246 (January 31, 1976), 80-87.