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February 7, 1975

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Control of Vinyl Chloride Emissions in Distribution Operations

M. E. Sutherland and R. N. Wheeler, Jr.
Union Carbide Corporation, South Charleston, West Virginia



Control of vinyl chloride emissions in vinyl chloride monomer transportation operations is a difficult problem. The primary control objective is to protect the health of employees and the general public from damage by excessive vinyl chloride exposure. With this objective in mind, the Occupational Safety and Health Administration has issued a standard for workers. This standard will be followed by regulations from the Environmental Protection Administration, the Department of Transportation, and the Coast Guard. The OSHA permissible exposure limits of one part per million by volume for workers and the rumored EPA limit of 90 parts per billion by volume for plant fence-line concentration are hard to conceive in an industrial environment. Gauging a tank car with a slip tube releases several pounds of vinyl chloride to the atmosphere. One pound of vinyl chloride raises the concentration of 6 MMCF of air to one part per million or 70 MMCF of air to 90 parts per billion. While the subjects of safe vinyl chloride concentration and the health problem resulting from vinyl chloride exposure may be debatable, governmental regulations in regard to worker and public exposure are here to stay. There are no easy solutions to emission control; thus, the scope of this discussion is limited to a brief review of vinyl chloride transportation operations, defining some major problems, and proposing some ways of approaching the solution to those problems.

Vinyl chloride distribution facilities generally consist of large storage tanks such as refrigerated spheres or buried tanks located at some distance from the production facility, smaller horizontal storage vessels located in or adjacent to the production facility, pipelines, shipping containers, and shipping container loading or unloading facilities. Some vinyl chloride monomer is moved by tanker, by truck, and by barge but, in the main, vinyl chloride is transferred from producer to user via tank cars or pipelines.

Figure 1 shows a flow sheet of a representative vinyl chloride distribution system. The VCM producer transfers the product from plant to a storage sphere from which tank cars, trucks, or ships are loaded. The shipping containers and the storage tanks are pressured by the vapor pressure of vinyl chloride contained. Theoretically, a tank car containing only vinyl chloride gas can be loaded without venting. On a more practical basis, these containers are vented either to the air or back to the storage tank from which ultimately some inert gases must be released. The loaded tank car is then valved in, loading hoses are removed, and the car is moved via the railroad to the consumer. At the consumer, unloading hoses are attached, pressure in the car is raised above that generated by ambient temperature with vapors from a vinyl chloride vaporizer, and the car contents are pumped to a storage tank. At the end of the unloading operation, the

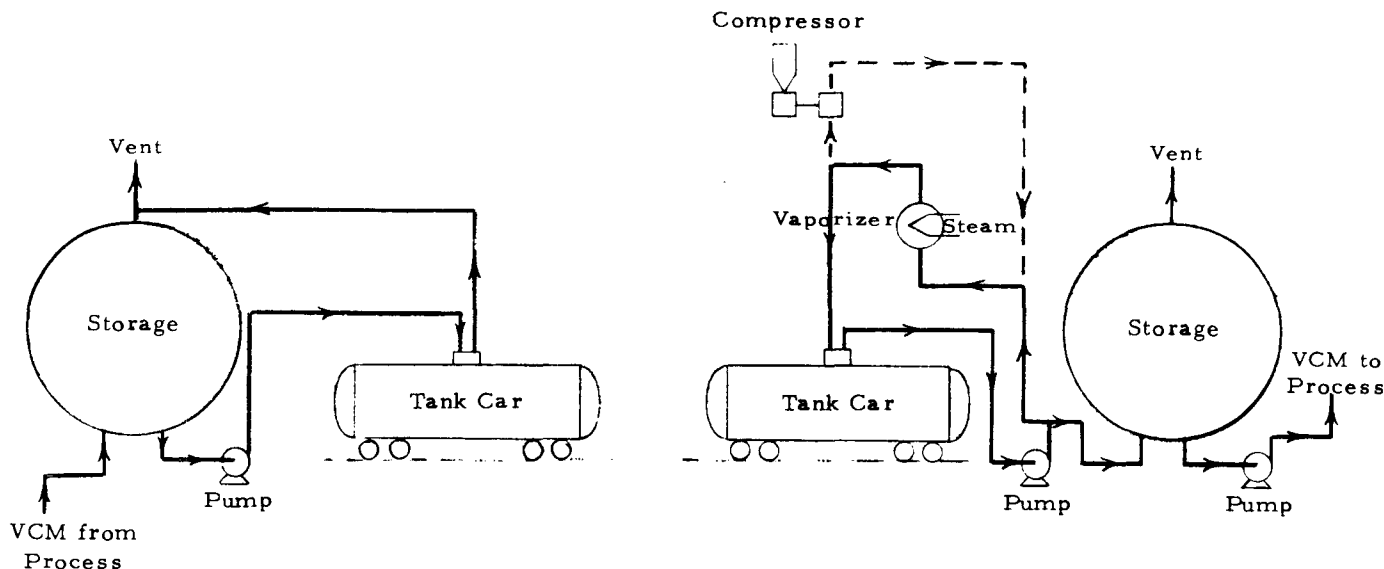


FIGURE 1 VINYL CHLORIDE DISTRIBUTION SYSTEM

pressure in the car is reduced by a compressor to 1 to 5-lb. gauge. The car is valved in and the hoses removed. The consumer's system is also pressured by the vapor pressure of vinyl chloride; but again some venting of inert gases is required. For normal distribution operations, major emissions result from slip-tube gauging of the tank car, removal of loading and vent hoses, and any venting required to maintain the storage tank pressures at the pressure of saturated vinyl chloride vapor. Vapor compression and condensation are often used for tank cooling. The presence of large amounts of uncondensable gases would preclude the operation of such a cooling system. The plant usually has a remote vent stack or a flare for handling these vents.

Formerly, when equipment maintenance was required, the item was emptied of liquid vinyl chloride if possible, the pressure released to a vent system or to the air, and the equipment purged with inert gas to remove the contained vinyl chloride gas. The inert gas was then removed by a thorough airing of the equipment. On completion of the maintenance work, the equipment was purged with inert gas followed by displacement of the inert gas with vinyl chloride. Gases released were vented to a flare stack or simply released to the ambient air. Maintenance work on a tank car could result in release of 500 pounds of VCM while a simple pump repair might release 1 to 10 pounds. Design of storage systems often stressed vapor conservation for operational emissions, but only rarely was provision made to control emissions resulting from maintenance work.

The various governmental safety regulations will

require changes in distribution equipment and operations to control vinyl chloride monomer emissions. Reducing emissions to achieve the permissible levels of exposure required is arduous, expensive, and time-consuming. A thorough detailed discussion would require more time than is available; therefore, only certain useful items will be covered.

Gauging devices that permit no product emission must be installed on tank cars, tank trucks, and barge tanks. A common past practice in loading a shipping vessel was to pull the slip tube out to the desired liquid level and open the valve slightly. When the vessel was filled to the desired level, the spurting of liquid was readily visible to the loader from a distance, and loading was terminated. This procedure also took care of any air or other non-condensable gases that might be in the car. As a result of the OSHA regulation, various ventilation hoods and sight-flow indicators are being used in loading and unloading operations. A gauging device that has worked well on tank cars is a float that is magnetically coupled to a tape system in a pipe isolated from the product. In the event of a failure of the mechanical tape system, it can be removed for repair without emptying the car. The tape sight-glass simply protects the tape assembly from the weather. The tank can be gauged by reading the tape and measuring the tank temperature. Adaptation of this or similar devices to all shipping containers is the most direct approach to control of gauging emissions.

Tank car size is being limited to 25,500 gallons for all new cars in vinyl chloride service. The car must either be insulated or have steel safety shields

on the ends of the car to reduce the possibility of tank punctures in derailments. Cars that are not insulated or do not have the safety shield must be switched individually by engine in the rail yards. Major industry use of a poorly-designed, 38,000-gallon tank car for vinyl chloride transport has caused much of the railroad transportation hazard and the resulting regulations. These cars with their six-wheel trucks were unable to round a normal railroad curve properly. As a result, they derailed frequently, especially when empty. The couplings often did not match properly with other cars in switching; thus, in switching and train make-up, the coupler missed connection and the tank car was punctured when it struck the car being coupled. Limitations on car size and handling procedures are highly regressive steps and fail to directly approach the problems of proper tank car design and of failure by the railroads to maintain their road beds. For an industry changing to 30,000-gallon reactors, the proper tank car for minimum emissions is the 48,000-gallon tank car equipped with float gauging and insulation. In requiring the small tank car, the Department of Transportation has reduced some of the danger of the individual accident at the risk of increasing the cost of transportation and of increasing the frequency of accidents by requiring more tank cars for vinyl chloride transportation.

Pipelines offer the ultimate potential reduction in emissions for VCM distribution, but pipelines carrying suspected carcinogens will be subject to a new set of rules. Above-ground pipelines can be properly labeled and monitored regularly for leaks. Emergency procedures could be instituted quickly before any leak became significant. Buried pipelines will require above-ground warning signs, a foolproof system for leak monitoring, and cathodic protection. The only foolproof system for leak monitoring in a buried pipeline appears to be a pipeline within a pipeline. The outside pipeline would provide the basis for leak detection and disposition. In either the above-ground or buried pipeline, the number of

flanges, valves, and pumps should be minimized while provisions for prompt isolation of leaking sections and disposition of their contents must be planned with great care. In-plant pipelines impose little or no regulatory problems, but the likelihood of getting a permit to install a vinyl chloride pipeline on public property appears remote.

Vinyl chloride scavenging systems will need to be installed or expanded so that each pipeline, heat exchanger, pump, tank, or tank car can be stripped of vinyl chloride liquid or vapor in the event of failure, prior to maintenance work, or prior to routine disassembly. Figure 2 shows a flow sheet of such a system. Where there is access to a plant monomer recovery system, an additional compressor, a condenser, and a collection tank are not needed. In remote facilities, this scavenging system could consist of a small compressor, such as the Corken built by Pump Service Company. This compressor requires 30 horsepower and will pump 40 to 54 ACFM from 0 to 105 pounds without lubrication. If the compressor discharge system has the ability to absorb heat, then the condenser is unnecessary. This compressor has been used to evacuate unloading hoses, tank cars, and other equipment at a tank-car unloading station. The compressor may be discharged into the liquid vinyl chloride transfer pipeline without cooling if the system has adequate heat dissipation capacity. In an emergency, it has been simply discharged into an empty tank car. When such a scavenging compressor is used intermittently, provision must be made to keep it from filling up with liquid vinyl chloride. On this installation, electric heaters were installed in the compressor suction trap to vaporize any liquid that collected during the out-of-service time. Activation of the heaters for a preset time is required before the compressor will start. The scavenging system must be designed to fit the operation involved. The most important criteria to consider in such a design is to be sure all eventualities requiring scavenging have been considered, and to be sure that air is excluded from such a system.

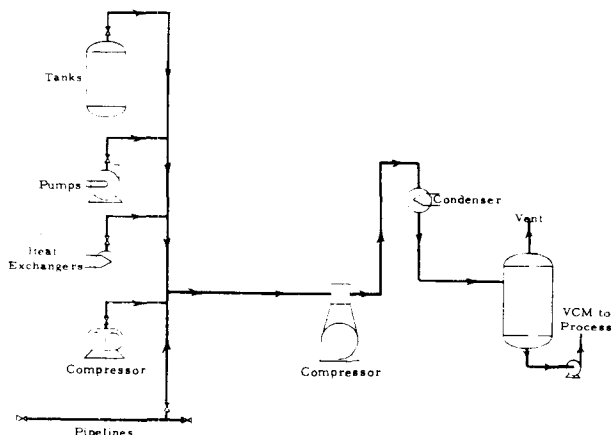


FIGURE 2 VINYL CHLORIDE SCAVENGING SYSTEM

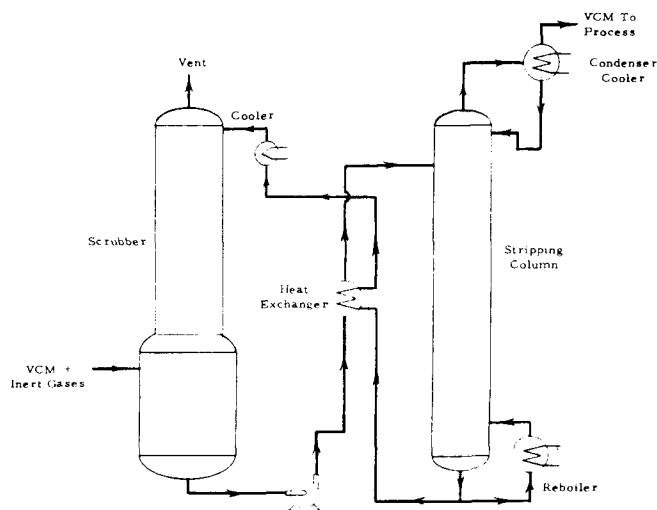


FIGURE 3 SOLVENT VENT SCRUBBING SYSTEM

Inert gas purging of equipment that has been scavenged of its available vinyl chloride monomer is necessary to reduce the explosion hazard and to remove the last traces of vinyl chloride monomer. A tank-car unloading hose that has been scavenged contains several tenths of a pound of vinyl chloride. A tank car contains several hundred pounds. This material has to be removed and the VCM concentration in the equipment reduced. One tank-car shop has already notified owners it will not accept tank cars for servicing containing more than 25 ppm VCM. Depending on the equipment configuration, it may be swept out by blowing inert gas through the system or it may be diluted by alternately pressurizing the tank with inert gas and venting it down. In any case, sweeping the last traces of vinyl chloride out of equipment prior to maintenance generates a large volume of inert gas contaminated with vinyl chloride. A rule of thumb for the pressurizing and venting technique is 15 to 20 cubic feet of inert gas per cubic foot of vessel capacity. The inert gas must then be removed by airing, if vessel entry is required. When maintenance work is complete, the process must be reversed with inert gas purging out the air and then vinyl chloride purging out the inert gases. Maintenance of distribution facilities and transportation equipment will require a supply of inert gas and the equipment to dispose of the VCM contaminated inert gas.

Refrigerated solvent scrubbing of inert gas streams, as shown in Figure 3, represents the most reliable and economical means of removing vinyl chloride from inert gas. The choice of solvent is largely a matter of which ones are readily available, the conditions chosen for stripping the dissolved vinyl chloride from the rich solvent, and limiting the loss of solvent with the vent gas stream. Solvents that have been used successfully are acetone, methyl ethyl ketone, ethylene dichloride, butyl acetate, and heptyl butyl ketone. Absorber temperatures of 0 to -20°C are effective. To keep equipment sizes down, a solvent scrubber is normally operated under pressure in conjunction with the vinyl chloride scavenging system. Vinyl chloride recovery efficiencies of 99.5% are readily obtained. Solvent rates of 4 pounds per pound of gas at 100 psig and 10°C yield essentially vinyl-chloride-free vent gas.

Refrigerated vent coolers are useful only where the volume of inerts is very low or more efficient recovery equipment is not available. Figure 4 shows an inert gas purge system that operates in conjunction with a large refrigeration system to rid a storage sphere of inert gases. This unit requires two horsepower to cool inert gases to -29°C and discharge heat at 6°C. The inert gas discharged to the air contains 13% VCM by volume. The storage sphere using this unit is remote from other operations and receives little or no operating supervision. In this case, the amount of vent gas is essentially insignificant and, due to remoteness, no personnel exposure is involved; thus, a relatively poor system is acceptable.

Decontamination of vent gases by other methods,

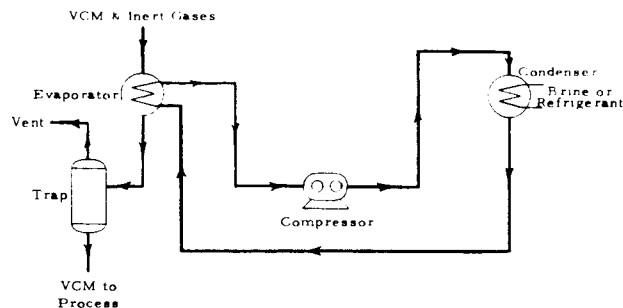
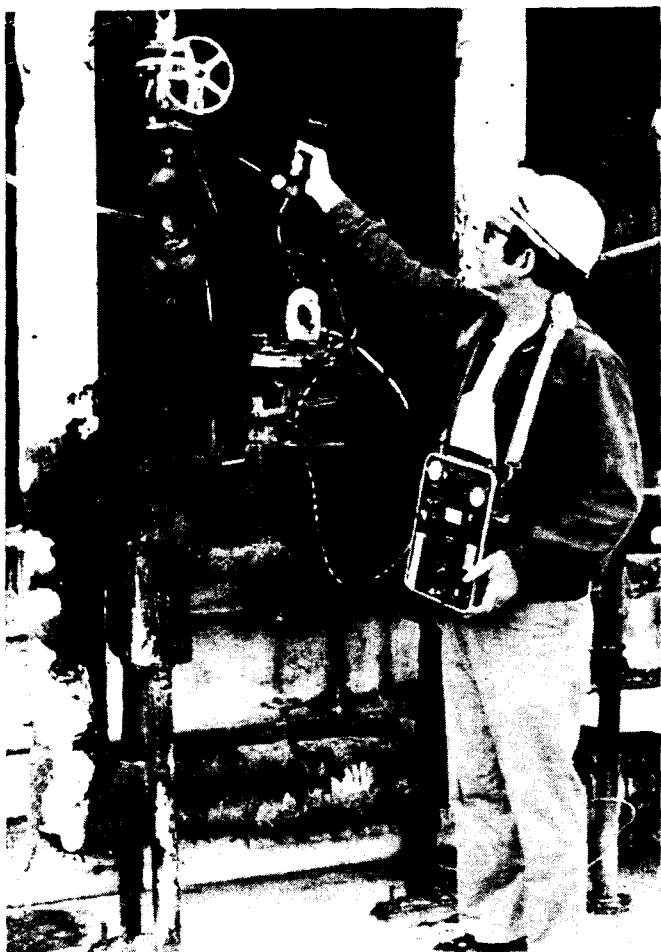


FIGURE 4 REFRIGERATED VENT SYSTEM

such as carbon adsorption or incineration followed by scrubbing the incinerated gas with water, are being considered by many companies. In the case of carbon adsorption, the technology is not fully defined and proven in practice. Operation of the adsorbers is cyclic, requiring more operating labor; the formation of polymer and peroxides on the carbon could be problems. Incineration or flare stacks are widely used for disposal of flammables, and should be used as a final cleanup technique for even solvent-scrubbed vent gases. Use of incineration to dispose of relatively large amounts of vinyl chloride would entail removal of the hydrogen chloride generated by water scrubbing and subsequent disposal of acid formed. Disposal of quantities of salt, muratic acid, or hydrogen chloride is a pollution problem not lightly considered by EPA.

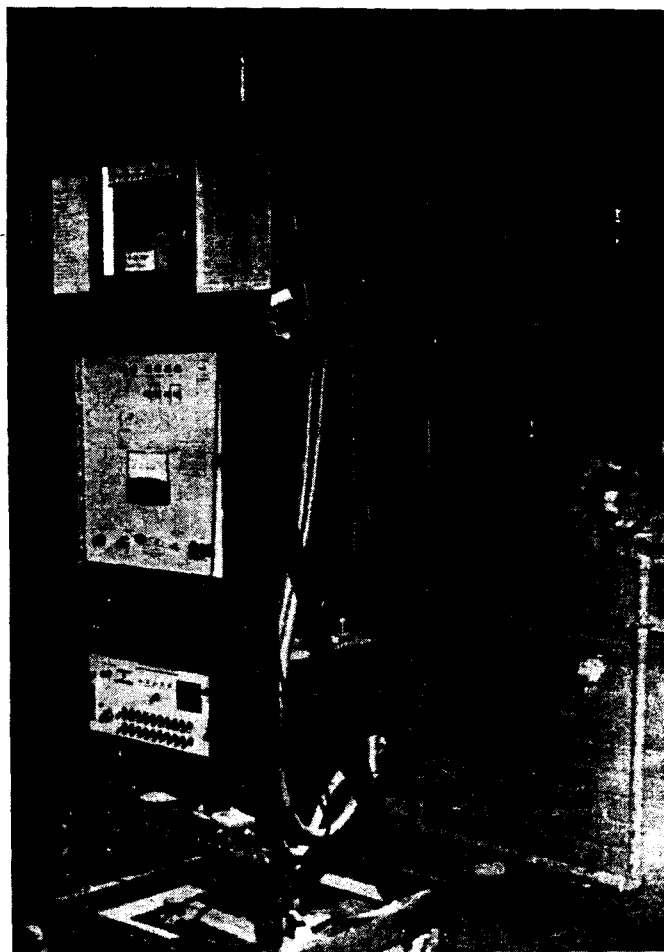
Monitoring of vinyl chloride concentrations in distribution operations is necessary to determine sources of emissions and to protect personnel and the public from excessive exposure to vinyl chloride in their breathing air. For general troubleshooting and survey work, one of the most adaptable instruments is the Century Organic Vapor Analyzer with or without the chromatographic column attachment. This instrument is portable and is direct reading in terms of organic vapor. If there is a question as to whether the organic vapor is vinyl chloride, then the chromatographic column attachment has value. In addition to locating leaking pump seals, valves, and other fixed equipment, it should be used to carefully check each loaded tank car or other shipping container for leakage prior to shipment. Admittedly, a shipping container can develop a leak in transit but, in most cases, the container was leaking when shipped since this was the last time the container's mechanical equipment was operated. For large, fixed distribution facilities, a fixed area monitor with alarms, such as the multipoint automatic chromatograph, is valuable. Fixed distribution facilities are usually remote from plant operations and may not even be manned full time. This lack of supervision plus the potential for massive VCM releases makes automatic detection a primary protective device. The pictured automatic chromatograph



Manual VCM monitoring with a portable organic vapor detector

analyzes 19 points within a remote vinyl chloride tank-car unloading and storage system every 40 minutes, and will sound an alarm if a preset concentration is exceeded. Automatic analyzers, unfortunately, provide more data than can be readily assimilated by the operating supervisor; therefore, a data processing system is worthwhile. These systems compile and correlate results so that problems, other than emergencies, can be identified.

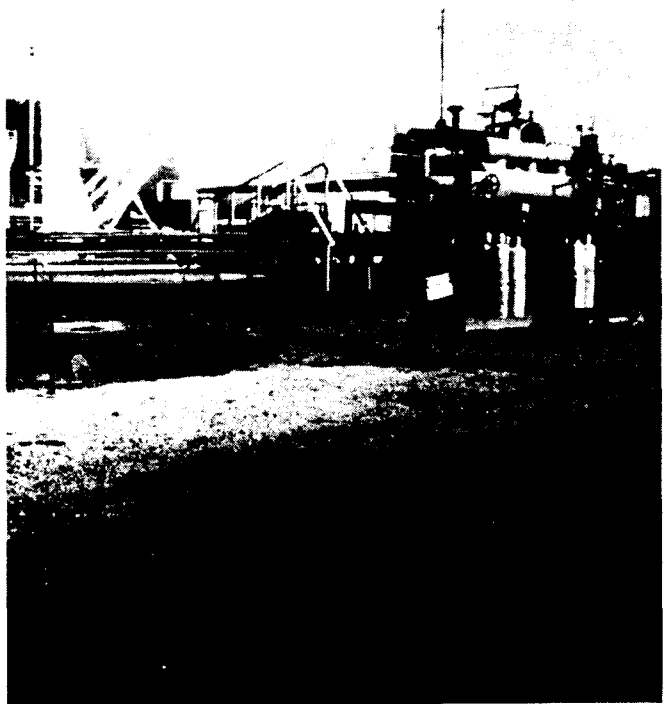
Regardless of the technique or the equipment for monitoring, it should be done frequently and thoroughly. The monitoring data should be carefully evaluated and kept on file for up to 30 years, if personnel exposure is involved. If the evaluation identifies a problem, then prompt action must be taken. Monitoring provides the basis for demonstrating compliance to governmental regulations and, as such, is required. In addition, it is the means by which equipment is improved, faulty work practices are corrected, emergency situations are controlled, problems are identified and, above all, personnel are protected from excessive exposure to vinyl chloride. Monitoring is the means one uses to see the situation and, as such, it is the most important action to be taken in the control of vinyl chloride emissions. Timely data from monitoring, though expensive in terms of equipment, is less costly than using yesterday's data on today's problems.



Automatic chromatograph for fixed installation VCM monitoring

Automation is the final approach to control of personnel exposure to vinyl chloride. Regardless of the system design, the potential for personnel exposure to vinyl chloride exists; thus, removal of personnel from that operation via automation reduces hazards as well as cost. Vinyl chloride storage tank areas may be barricaded and never entered in normal operations. Tank-car unloading or loading can be designed so that the only human intervention is the unloading hose coupling or uncoupling. Equipment for these kinds of operations are valves with position indicators, pipeline flow indicators, remote-operated pumps, remote-control valves, and programmed controllers. The pictured vinyl chloride sphere with attendant pumps, refrigeration equipment, and pipelines is operated entirely by remote control from a central control room. The tank car unloading system requires manual hookup and disconnections of the unloading hoses and operation of the shutoff valves on the car and at the hose ends. All other operations are controlled from a control building.

The foregoing discussion is intended to show some of the ways to reduce vinyl chloride emissions and control personnel exposure to VCM in distribution operations. No implications of governmental approval for the techniques involved should be drawn. While the various procedures will lead to minimum



VCM storage sphere equipped with remote-controlled valves and pumps

exposure to vinyl chloride, the ability to meet the various regulations is not implied through use of the same. In controlling vinyl chloride emissions and reducing personnel exposures, interaction of regulations and goals from OSHA, EPA, DOT, and the Coast Guard must be considered; i.e., ventilation of the work space may please OSHA while creating EPA problems. The only sure thing concerning vinyl chloride regulations is that they are here to stay and the latitude available to the vinyl chloride monomer and polymer industry, with regard to employee safety and to plant procedures, will be minimal.

Pictures were made available by Union Carbide Corporation.

The authors

M. E. Sutherland joined Union Carbide Corporation in 1942 upon receiving his B.S.Ch.E. Degree from West Virginia University. He has spent most of his career in the production of vinyl chloride monomer and resins and has held a number of supervisory positions in these operations. Since 1969 he has been associated with the Chemicals and Plastics Safety Group and presently holds the position of Process Safety Program Manager.

R. N. Wheeler, Jr., Assistant Production Manager for Vinyl Resins at Union Carbide Corporation, is a graduate chemical engineer from Virginia Polytechnic Institute. Mr. Wheeler has been associated with vinyl resins manufacture for thirty years and has represented Union Carbide Corporation in various aspects of the vinyl chloride health problem.

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