

INDUSTRIAL HYGIENE SURVEY REPORT ON VINYL CHLORIDE

AND POLYVINYL CHLORIDE MANUFACTURING FACILITIES

BY

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MARCH 1974

ASI 00023463

SUMMARY

1. Five vinyl chloride monomer (VCM) and two polyvinyl chloride (PVC) manufacturing facilities in the New Orleans - Baton Rouge area have been visited by the staff of the Office of Standards Development during a fact-finding survey.
2. The PVC manufacturers have a more serious problem of VCM exposure than the VCM producers because most of the polymerization process equipment are in enclosed areas and ventilation is inadequate.
3. Leaks from the process equipment, vessel entry, VCM tank car loading, unloading, and process sampling, PVC reactor cleaning and compounding and packaging are the major potential sources of VCM exposure found during this survey.
4. Engineering technology for the control of VCM exposure is available and has been implemented by the industry.
5. The observed practices relative to equipment maintenance, monitoring medical examination and surveillance and training are considered to be inadequate to control the employee's exposure to vinyl chloride.
6. The fact-finding survey was found to be very useful in the development of proposed rulemaking of health standards.

INDUSTRIAL HYGIENE SURVEY REPORT ON VINYL CHLORIDE MANUFACTURING AND POLYMERIZATION FACILITIES

- Introduction

A fact-finding survey of several vinyl chloride (VCM) and polyvinyl chloride (PVC) manufacturing facilities has been conducted by the staff of the Office of Standards Development during the week of March 11. Five VCM Plants and two PVC Plants in the New Orleans and Baton Rouge area were visited during this survey. A list of all plants is presented in Table 1.

Process

The VCM is either produced by the direct chlorination or oxychlorination of ethylene to ethylene dichloride (EDC) and pyrolysis of EDC to VCM or by the reaction between acetylene and hydrogen chloride. The crude VCM is purified by distillation to yield a product having purity of 99.99%.

The PVC is produced by either wet or dry polymerization process. The wet process is carried out by reacting VCM in aqueous solution containing dispersing or emulsifying agents and catalyst. The dry process produces PVC by direct reaction between VCM and catalyst in a two-stage reactor. The unreacted VCM is separated from the PVC and the raw PVC is ground to desirable size. Block diagrams of various processes are presented in Figure 1 through 4.

Potential Area of VCM Exposure and Its Control

Based on observations of this survey the areas where exposure to VCM is likely in a VCM plant during normal operations are:

1. Sampling and analysis of VCM for quality control.
2. Loading of VCM for shipping.
3. Entry of VCM containing vessels for maintenance and repair work.
4. Leak of VCM in the process area.

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The areas of VCM exposure in a PVC plant can be summarized as the following:

1. Unloading of incoming VCM.
2. Reactor cleaning.
3. Entry of VCM containing vessels for maintenance and repair work.
4. Entry of PVC storage silos.
5. Compounding of PVC into molding powder.
6. Shipping or packaging of PVC.
7. Leak of VCM in the process area.

The VCM plant is operated around the clock and usually five or less employees are worked on each shift. One or two of these employees have to stay outside for one or two hours per shift to take samples, check gages and handle minor maintenance or repair work. About ten VCM samples are collected per shift by one employee. The VCM is collected in a sampling bomb with the time of collection being about one minute. The sampling port can be modified to reduce the exposure of VCM during such operation.

Loading or unloading of VCM is another area of possible VCM exposure. Most loading is done on day shift only and the employee is loading eight or less tank cars at one time. Each loading operation takes about ten minutes. However, if more than one tank car is being loaded at one time the employee may spend as much as six hours on the loading deck every day. One company official claimed that they are installing a system to reduce the emission of VCM during loading. Since the loading deck is located in open space and ventilation is good and if the emission control system is installed and the employee is standing at the upwind director with gloves and face shield, the exposure to VCM is insignificant unless the wind is strong.

The reactor cleaning is probably the area where VCM exposure is highest among VCM and PVC plants. The manufacturing of the PVC is still a batch process and the reaction time is about eight hours. The agitator and the bottom part of a wet process reactor is cleaned after two or three batches were made. The whole reactor of the dry process is

cleaned after each batch was made. The average cleaning time is 30 minutes and usually two employees are performing the task. The dry process reactor is cleaned by using scraper and chisel under local exhaust ventilation. It is a dusty operation and no personal protective equipment of any kind is being used. A filter head which separates unreacted VCM from the PVC is cleaned by compressed air. The operator also uses compressed air to blow dust off his body. The cleaning should be performed by vacuuming or by using scraper equipped with local exhaust ventilation. In addition, the operator should wear coveralls, face shield and gloves with or without supplied air respirator depending on the residual concentration of VCM in the reactor. After the reactants and products have been removed from a wet process reactor vessel, it is filled with water and rinsed one time before cleaning. The cleaning is under local exhaust ventilation. Chisel and scraper are also used for cleaning of this type of reactor. Since the reactor surface is wet, dust exposure is not a problem. However, the exposure to VCM may be likely because cold water rinse is not effective to remove the residual VCM absorbed on the walls of the reactor and steam purging is preferred. No test for VCM concentration in the reactor was made prior to entry. It is a good practice to require the use of supplied air respirator for any reactor cleaning work.

Most employers indicated that they have established procedures for vessel entry and in some companies a permit is required prior to initiation of such operations. It is questionable whether these procedures are enforced, especially regarding VCM exposure. A requirement containing details regarding entry of VCM containing vessel for maintenance or repair work should be included in the proposed standard.

There is no information available to date regarding the desorption of VCM from the surfaces of the PVC particles during storage and handling. However, it is preferable to establish a procedure for the entry of PVC storage silos and require local exhaust ventilation systems be installed in all PVC compounding and packaging and loading operations where PVC dust can be released. Although the manufacturing of VCM and PVC is under pressure in a closed system, exposure to VCM is unlikely during normal operation. However, inadequate maintenance and wear of packings and seals of process equipment can results in leaks of VCM.

Nearly all the VCM exposures are outdoors in the VCM plants while most PVC manufacturing operations except in the deep south and west coast where winter climate is mild, are enclosed. The exposure of VCM from equipment leaks can be significant in a PVC plant. We found that most

of the plants do not have maintenance crews on all three shifts and preventive maintenance program is inadequate or non-existent. We should ask the employer to implement a maintenance program to insure that the leakage of VCM is unlikely during normal operations. An equipment check list should be prepared and the frequency of inspection should be based on the probability of failure or malfunctioning of equipment, piping or fittings. The equipment maintenance and repair record should be included in the OSHA record keeping requirements.

The VCM samples collected in the bombs are analyzed by gas chromatography in a quality control laboratory. If the bomb is stored in an exhaust hood with good ventilation and the sample is withdrawn from the hood, no exposure of VCM is expected during such operations.

Monitoring

Before the outbreak of liver cancers in the Goodrich PVC plant, the VCM was considered a fire hazard and less precise sampling and analytical methods were used for monitoring. This still appears to be the case from the observations gathered on this survey. We obtained some monitoring data from several VCM plants. Only one PVC manufacturer promised us to send us monitoring data on PVC operations. Another PVC plant uses a combustible vapor tester for monitoring VCM exposure and this type monitoring is neither accurate, specific nor sensitive to low concentrations of VCM.

Gas chromatograph (GC) appeared to be a common instrument used for the analysis of VCM. The VCM is either collected as grab or time-weighted-average (TWA) samples in gas-tight syringes, plastic bags, or activated charcoal tubes.

By reviewing the monitoring data submitted by two VCM plants (Table II & III) though the data is limited, however, it does indicate that VCM loader, process sample man and maintenance personnel are most likely exposed to higher levels of VCM than other employees in these plants. The method of control of VCM exposure for these employees are discussed in the previous section.

There is wide difference between the sampling method and analytical techniques for VCM. Standardized sampling and analytical procedures should be established for the monitoring of VCM. This may be obtained through NIOSH. Most plants indicated that they are acquiring fixed continuous monitoring stations and more sophisticated portable monitoring for VCM in their facilities. A guideline should be laid out to get the maximum benefit for the use of such instruments.

VCM can be detected by the GC techniques in the order of 1 ppm. The detectable range of two most promising portable direct reading VCM detector, the Century Organic Vapor Analyzer (OVA) and the Wilks Miran infrared spectrophotometer (MIRAN) are in the order of 1 ppm. The accuracy of these instruments at such low concentration may be $\pm 50\%$. The accuracy of GC is dependent on the preparation and calibration of the standard. The reliability of a prepared standard at 1 ppm may also pose a problem. A 2 ppm concentration may be the lowest limit at which we can have reasonable confidence on these instruments.

The required method of monitoring is dependent on the permissible limit on the proposed standard. If a limit is set, the VCM exposure for each job classification should be monitored on a TWA basis. Personal breathing samples should be collected on a sampling device having a collection efficiency of at least 95%. Sufficient number of area samples should also be collected to pin point high exposure areas for the implementation of control measures. The sensors of a continuous VCM monitoring system can be located at high exposure areas of VCM. The initial monitoring of the workplace should take abnormal operating conditions such as hot weather into consideration and monitoring should be repeated on a periodic basis or after process modifications and repairs.

If no exposure limit is being proposed, the initial monitoring is still required for the implementation of engineering controls. The use of direct reading and continuous monitoring instruments are more imperative since no leaks can be tolerated under such circumstances. The monitoring should be conducted on a daily basis at predetermined sampling points.

Medical

All plants have preplacement physical examination programs. However, periodic physical examination is not a common practice. Two of the six plants have a physician and nurse staff on duty, the others have a physician and nurse on the part time basis. Most supervisors and selected employees have trained in first aid.

Since the outbreak of the Goodrich liver cancer, more companies have started providing SMA-12 or other tests to employees who are handling VCM. However, few of the companies indicated that they are conducting medical surveillance of their employees as a routine program.

Because Dow Chemical Company is the leading producer of chlorinated hydrocarbons in this country, they have put more emphasis on liver function testing of their employees. The medical surveillance program as presented to us by Dow (Table IV) can be used as a basis for the medical requirement in our proposed vinyl chloride standard.

Engineering Control

Ventilation is still an effective method to control the VCM exposure. The control rooms in all the VCM and PVC plants are air conditioned, however, the air is withdrawn from the process area and discharged outdoors without any purification. Both the inlet and outlet air to the control room should be treated if a standard with very low or no permissible limit is proposed.

Engineering control methods are available for the control of VCM exposures, during sampling and loading operations. However, a reasonable time should be allowed for the implementation for such measures. This is also true for the installation of local exhaust ventilation systems. It may be more practical to allow time for the implementation of engineering control measures or an interim standard could be set to give employees some protection while the employer is provided with time for implementation of such controls. Usually, a time period of six months may be sufficient to install VCM emission control system and one year for ventilation systems.

Personal Protective Equipment

All plants visited have self contained breathing apparatus (SCBA) or Gas Mask for emergency use and they indicated that every employee is trained to use such equipment. Two plants use canisters made for acid gases or ammonia other than organic vapor to equip their gas masks which is not considered to be suitable and one plant uses a quarter facepiece emergency escape respirator as a standard accessory for every employee and visitor in the process area containing hydrocarbons. This practice may give an employee a false sense of security and he may be exposed to high concentrations of VCM and still believe he is adequately protected.

Supplied air respirators, either in continuous flow or pressure demand mode should be used for reactor cleaning or maintenance and repair work inside of a vessel containing VCM. One plant used supplied air for cleaning of reactors, however, no pressure reducer nor contaminant filtering device were found in the adjacent air supply. The present OSHA standard on breathing air quality is based on the recommendation of the Compressed Gas Association (CGA) which has higher tolerance for the common contaminants in the compressed air such as oil, carbon monoxide, etc. A low tolerance of these air contaminants and VCM in the breathing air and more specific, accurate and frequent monitoring methods should be proposed to insure that the quality of the breathing air is acceptable.

The use of gas masks equipped with activated charcoal adsorbent for the VCM will depend on whether we propose a standard with or without a permissible limit. Based on a test conducted by Gary Nelson of the Lawrence Livermore Laboratory, he indicated that the activated charcoal in a organic vapor canister or cartridge is not a good VCM absorbent. From his results, the time to reach 1% breakthrough of VCM at a concentration of 1,000 ppm, 50% relative humidity, 22° C and a breathing rate of 53.3 lpm is 3.8 minutes against 77 minutes for carbon tetrachloride. The present problem with organic vapor adsorbent is there is no indication of the life of such substance. The manufacturer's common practice is to set a shelf life of about three years from the date of manufacture with the assumption that the seal of the canister or cartridge is remained intact. Once the seal is broken, the useful life will be one year.

Use of gas masks give an operator more freedom of movement than with a supplied air respirator or SCBA. This is particularly true for the process sample man and tank car loader. If gas masks are permitted to be used with a permissible limit of 5 or 10 ppm is proposed, the requirements for periodic renewal of canisters on different levels of VCM exposures should be specified in the proposed standard.

Safety glasses, goggles, hard hat and gloves are commonly used in all plants visited. Since liquid VCM is an irritant to skin and mucous membranes, the use of eye protective devices and gloves should be made mandatory for employees who may contact liquid VCM. The VCM vapor or gas is not considered to be absorbed through the skin at the present time, the use of ordinary protective clothing is useless and the need for an air supplied impervious suit is questionable in operations involving VCM exposure. The PVC reactor cleaning can be a dusty task and a cloth coverall or whole body covering is a good personal hygiene practice. If VCM is not found to be absorbed through the skin then the requirement for shower facilities may not be necessary.

Housekeeping

Except for one plant, the general impression on housekeeping is that it is inadequate. This problem is more evident in the FVC plant since particulate material is involved. More effort is needed on immediate clean up spills and keeping the work environment in a cleaner, more orderly fashion.

Maintenance is another problem area. Preventive maintenance seems nonexistent and most of the plants have maintenance staff on day shift only. Since the leak of VCM from the process equipment, pipelines and fittings may be the significant source of unnecessary exposure in the industry, a more stringent maintenance program is imperative.

Most of the plants visited have either written or informal procedures regarding operations where VCM exposure is likely such as process sampling, tank car loading, reactor cleaning and vessel entry. We may issue mandatory work practice procedures on these operations. A written procedure and checklist should be prepared for these operations and reactor cleaning and vessel entry should be performed by permit only and signed by the employer or his representative to insure that all precautionary measures regarding minimizing employee's exposure to VCM during such operations are enforced.

Quite a few chemicals are used in the manufacturing of VCM or PVC, some of them can be very toxic such as hydrogen chloride, chlorine or mercury salt and the toxic properties of some raw materials are not available at this time. It should be a safe practice to require the employer to evaluate the toxicity of every raw material he uses and establish written procedures for the safe handling of such substances.

Training

Most employers indicate that they have training courses for VCM operators and regular safety meetings to educate their employees. Some companies use the word-by-mouth training techniques and such training are conducted by foreman. The success of such type of training is dependent on the quality of the instructor. In general, a written training manual should be preferred and should include items such as the Hazards of VCM and other toxic raw materials, work practices, use and care of personal protective equipment, first aid, emergency procedures, fire fighting and safe handling of the VCM. It is imperative that an untrained employee should not be permitted to work in the VCM or PVC process area and refresher courses on these subjects should be given on a periodic basis. A monitoring system should also be established to insure that an employee is benefiting from such training.

Waste Disposal

Both of the PVC plants claimed that the unreacted VCM is recycled back to the process. The off specification VCM is reprocessed to meet the requirement. One PVC producer discharges the scraps from reactor cleaning into a pond and another collects the waste into boxes for sale to a scrap dealer. One plant loads the PVC in box cars under pneumatic force. It is a closed system, any powder released from loading is sent back to the storage silos.

Since the toxic effect of PVC is not known to date, it may seem unreasonable to require the manufacturers to dispose of the PVC waste in impermeable bags since the bags probably made from PVC or to require the incineration of PVC or VCM as a means of disposal because the decomposition product is toxic. We may require procedures to be established for the destruction of these substances by a safe chemical method or just leave this paragraph open until we get more information.

Conclusion

The exposure to VCM is less of a problem to the VCM producers than to the PVC producers because all the process equipment of the former are located outdoors with fewer employees and control is less expensive to implement. Most of the PVC manufacturing facilities are enclosed and more employees are involved in the production. Engineering Control is more expensive because of the high volume of air to be ventilated. However, control technology is readily available and the cost of compliance may not be prohibitive.

Lack of maintenance programs, monitoring activities, inadequate employee training, medical examination and surveillance, and poor housekeeping are the common observations found during this survey. We may put emphasis on these areas on our proposed standard on the VCM.

All manufacturers were very cooperative during this survey. They answered all questions we asked and gave us the information we needed. From this survey, we were given the chance to communicate with the production people, to find out which areas present potential exposures to VCM, what the producer has accomplished to control the exposures at each area, and at which areas further control of the problem and what enforcement is required. We sincerely believe that this type survey should be included in our regular rule-making procedures so far as health standards development is concerned.

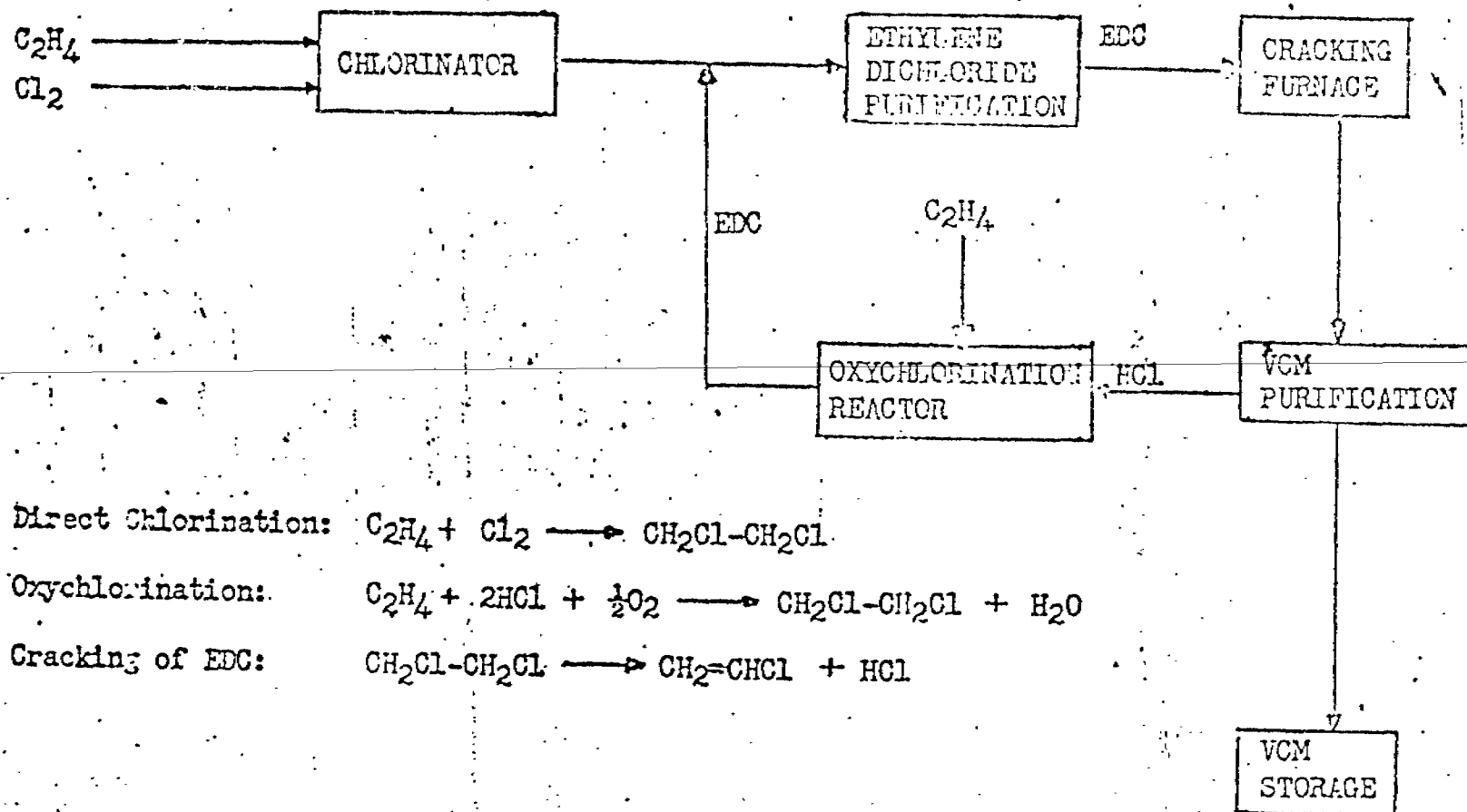
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1. Manufacturing of VCM by Direct Chlorination and Oxychlorination of Ethylene
2. Manufacturing of VCM by Direct Chlorination of Acetylene
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FIGURE 1.. MANUFACTURING OF VCM BY DIRECT CHLORINATION AND OXYCHLORINATION



Direct Chlorination: $C_2H_4 + Cl_2 \longrightarrow CH_2Cl-CH_2Cl$

Oxychlorination: $C_2H_4 + 2HCl + \frac{1}{2}O_2 \longrightarrow CH_2Cl-CH_2Cl + H_2O$

Cracking of EDC: $CH_2Cl-CH_2Cl \longrightarrow CH_2=CHCl + HCl$

FIGURE 2. MANUFACTURING OF VCM BY DIRECT CHLORINATION OF ACETYLENE

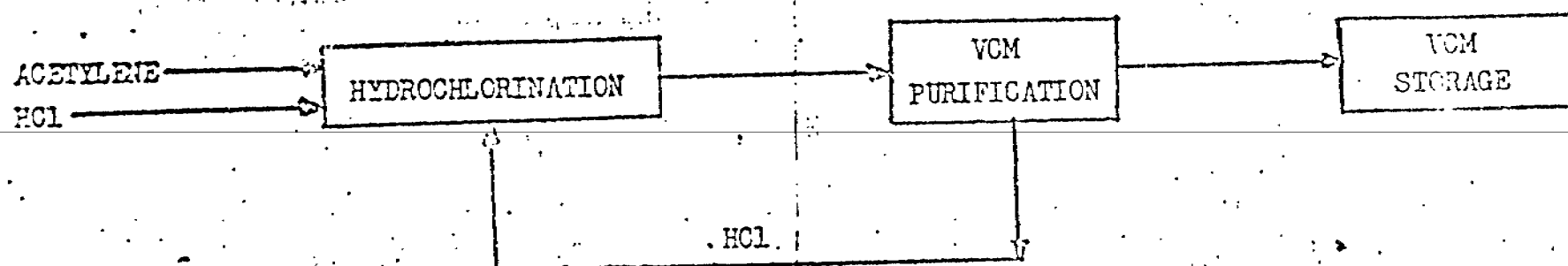


FIGURE 3. MANUFACTURING OF PVC BY SUSPENSION
OR EMULSION POLYMERIZATION

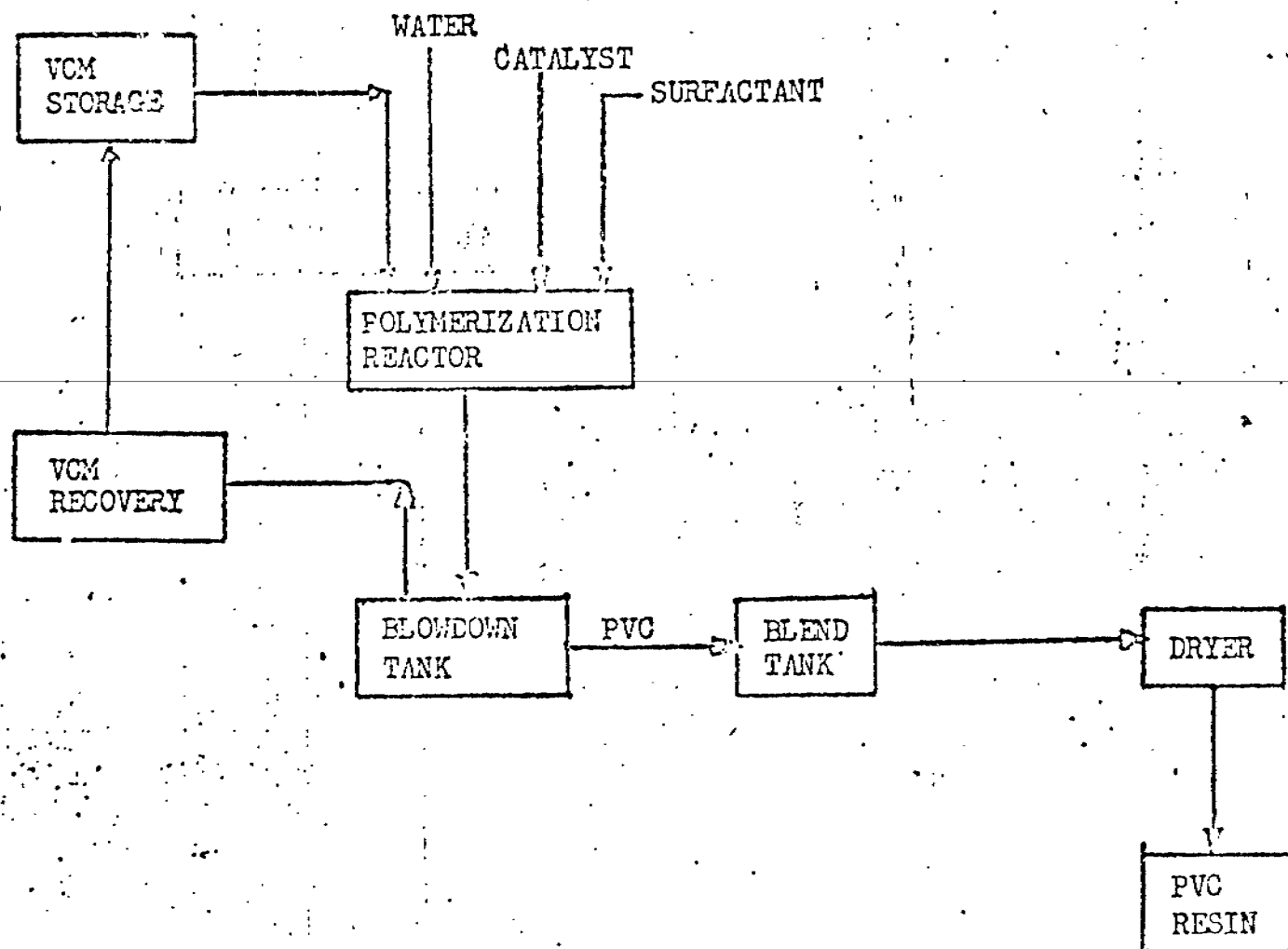


FIGURE 4. MANUFACTURING OF PVC BY BULK POLIMERIZATION

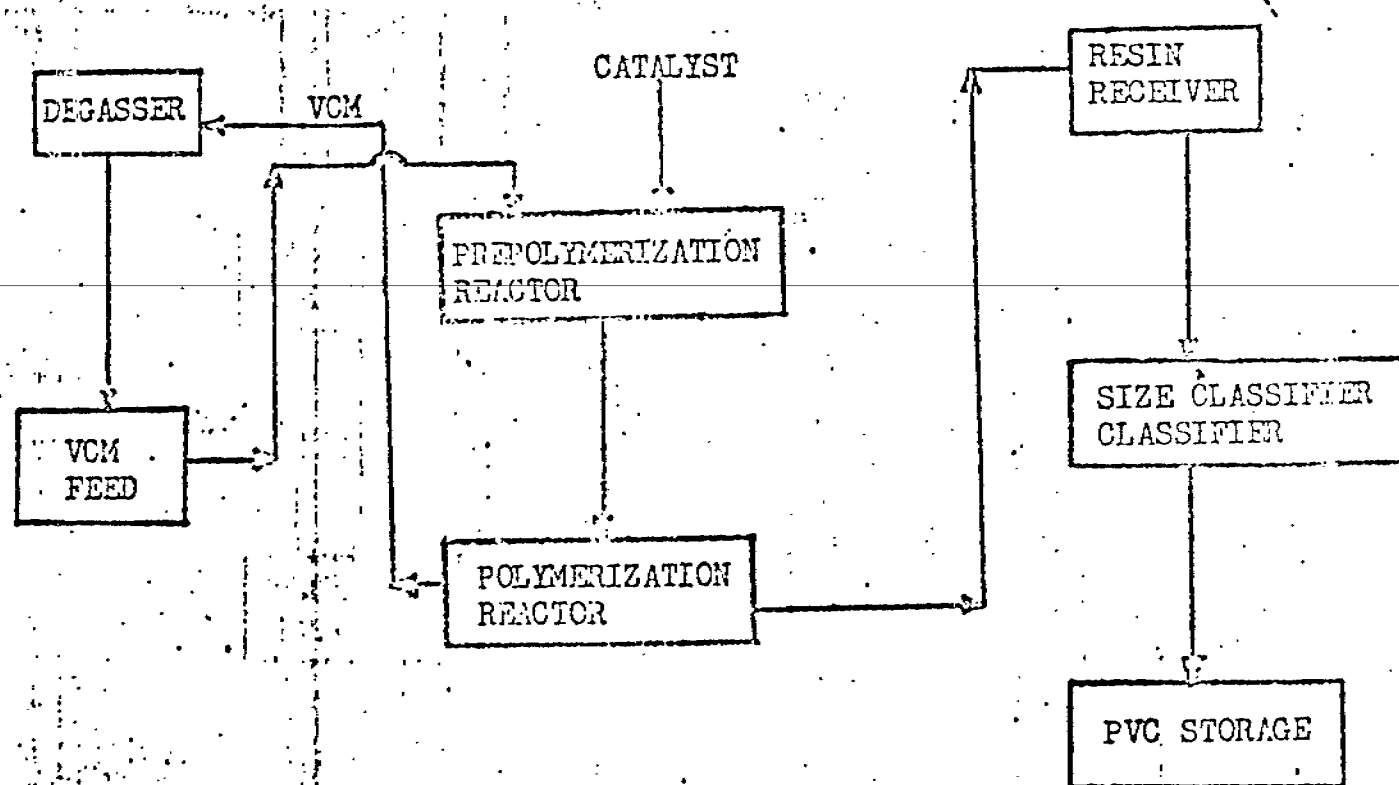


TABLE 1
MANUFACTURING FACILITIES OF VINYL CHLORIDE
and
POLYVINYL CHLORIDE

<u>Plant</u>	<u>Location</u>	<u>Process</u>
Ethyl Corp.	Baton Rouge, LA	VCM- Direct and oxychlorination of ethylene PVC- Suspension and emulsion polymerization
Shell Chemical Co.	Norco, LA	VCM- Direct and oxychlorination of ethylene
Dow Chemical Co. U.S.A.	Plaquemine, LA	VCM- Direct chlorination of ethylene
Allied Chemical Co.	Baton Rouge, LA	VCM- Direct and oxychlorination of ethylene
Goodyear Chemical Co.	Plaquemine, LA	PVC- Bulk polymerization
Monochem Corp. (Borden and Uniroyal)	Geismar, LA	VCM- Direct chlorination of acetylene

TABLE II

INITIAL VCM MONITORING

DATA FROM PLANT A

Sampling Periods

November 1973

Job Classification	Sampling Time hr.	VCM Concentration ppm
VCM Operator	7.5	1.3
VCM Operator	7.5	1.7
EDC Operator	7.5	0.8
EDC Operator	25 min.	
OXY Operator	7.5	0.3
VCM Loader	3.0	8.7
CM Loader	25 min.	16.0
VCM Loader	3.5	13.4
VCM Loader	45 min.	43.0
Lab Technician	10 min.	3.2

TABLE III

VCM MONITORING DATA FROM PLANT B

Sampling period: September 1972, March & April 1973

VCM Concentration: ppm (v/v)

Job classification	Samples range		Number of samples taken	TW
	high	low		
Shift supervisor	3.7	0.1	10	0.
VCM boardman	3.6	0.03	18	0.6
EDC boardman	5.5	0.07	10	2.4
Sample man	13.0	0.1	12	0.7
VCM loader	158.0	0.05	30	4.2
VCM loader	13.5	0.05	30	2.9
Shift supervisor	13.0	0.03	20	0.4
Junior operator	13.5	0.03	32	2.3
Q.C. specialist	32.1	0.05	28	3.0
Lab technician	158.1	0.06	26	10.3
Lab technician	229.0	0.1	30	15.0
Material controller	0.3	0.05	10	0.1
Instrument technician	13.0	0.03	30	1.9
Pipefitter	13.0	0.03	10	4.5
Millwright	13.0	0.03	10	4.4
Electrician	13.0	0.03	10	3.5
Laborer	13.0	0.03	12	4.5

TABLE IV. MEDICAL SURVEILLANCE PROGRAM
DOW CHEMICAL U.S.A.

March 12, 1974

LOUISIANA DIVISION
PLAQUEMINE, LOUISIANA 70754
504 687-4321

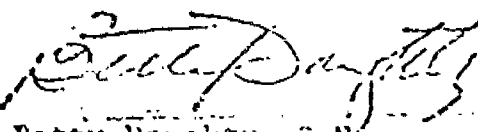
MEDICAL SURVEILLANCE

All contractor and Dow employees working in areas where chemicals may have toxic effect on liver have been included in plant medical surveillance program for several years. Originally tests obtained to determine liver toxicity were S.G.O.T., Thymol Turbidity, Cephalin Flocculation, and Bilirubin. We began obtaining SMA-12 in 1969. Approximately 300 to 350 employees are tested yearly. Several thousand persons have been tested over the years. We have never found any indication of liver toxicity due to chemical exposure. Plants included in this testing program are Glycol #1, Chlorinated Solvents, Vinyl, Chlorinated Methanes, Marine Tank Car Cleaning, Waste Disposal workers, and selected R & D personnel.

In 1971 we began a more comprehensive testing program on all employees engaged in operations. Medical history is taken as well as smoking history, any indication of weight loss or gain during past year is recorded - hemoglobin and urinalysis is done. Urinalysis includes blood, glucose, ketone, P.H., specific gravity, bilirubin and urobilinogen.

Additional procedures on those employees working in Vinyl Chloride area have been proposed, including EPA of chest, x-ray of hands, microscopic urinalysis, S.G.P.T., CBC, platelet count, forced expiratory volume and Fev₁. Physical examinations have been recommended and we are now in the process of securing these procedures.

In event of single exposures breath sample for analysis is secured, physical examination by physician, SMA and other tests as indicated are secured.


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ASI 00023483