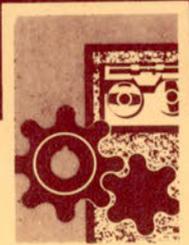


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NIOSH



A TECHNICAL REPORT

**VINYL FLUORIDE and
VINYL BROMIDE
INDUSTRIAL HYGIENE
SURVEY REPORT**

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

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VINYL FLUORIDE AND VINYL BROMIDE
Industrial Hygiene Survey Report

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Contract No. 210-75-0064

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
Division of Surveillance, Hazard Evaluations, and Field Studies
Cincinnati, Ohio 45226

November 1978

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ABSTRACT

This report consolidates the findings of industrial hygiene surveys conducted at a vinyl fluoride manufacturing plant, a vinyl fluoride polymerization plant, and a vinyl bromide manufacturing plant. The surveys were conducted over 8-hr. periods of the three work shifts in each plant.

Plant operator exposure levels for normal vinyl fluoride (VF) production operations were found to be less than 2 ppm VF for 7 of 8 samples taken. One sample was measured to be 21 ppm VF for a plant operator during the start-up shift.

Polymer operator exposures for vinyl fluoride for the polymer operation varied from 1-5 ppm vinyl fluoride for 11 samples. The average TWA exposure was 1.9 ppm vinyl fluoride.

Worker exposures at the vinyl bromide manufacturing plant were found to be less than 0.5 ppm VBr and less than 0.2 ppm ethylene dibromide for the VBr plant operators based on 4 samples; less than 0.6 ppm VBr based on 2 samples and 0.26 ppm ethylene dibromide based on one sample for the lab technician; and 1.2 ppm VBr and 0.57 ppm ethylene dibromide for the shipping crewman based on one sample. A one-hour sample indicated an exposure level of 6.3 ppm VBr while a shipping crewman was loading a tank car.

This report was submitted in fulfillment of Contract No. 210-75-0064 by Tracor Jitco, Inc., under the sponsorship of the National Institute for Occupational Safety and Health.

CONTENTS

Abstract	iii
Introduction	1
Authority	1
Purposes of Study	1
Survey Limitations	1
Criteria for Evaluations	2
Study Description	5
Types of Plants, Processes, and Operations Surveyed	5
Worker Job Descriptions and Job Titles	7
Observations at Work Sites	11
Sampling Procedures and Analytical Methods Employed	13
Study Results and Data Analysis and Evaluation	14
Worker Exposures to Vinyl Fluoride and Vinyl Bromide	14
Worker Exposures to Other Materials and Agents	14
Evaluation of Exposure Level Measurements	14
Exposure Control Efforts	18
Summary of Hazard Experience and Potential	19
Recommendations	20
References	22

TABLES

Table 1.	Acute Toxicity of Vinyl Fluoride	3
Table 2.	Results of Air Sampling; Vinyl Fluoride Manufacture-Plant A .	15
Table 3.	Results of Air Sampling; Vinyl Fluoride Polymerization- Plant B	16
Table 4.	Results of Air Sampling; Vinyl Bromide Manufacture-Plant C .	17

FIGURES

	<u>Page</u>
Figure 1.	Vinyl Fluoride Process - Block Diagram 6
Figure 2.	Vinyl Fluoride Polymerization Process 8
Figure 3.	Vinyl Bromide Production - Process Flow Diagram 9

INTRODUCTION

AUTHORITY

NIOSH has been granted the authority and responsibility under the "Occupational Safety and Health Act of 1970" to conduct field research studies in industry, evaluate findings, and report on these findings (1). Section 20(a)7 of this Act states that NIOSH shall conduct and publish industrywide studies of the effects of chronic or low-level exposure to industrial materials, processes, and stresses on the potential for illness, disease, or loss of functional capacity in aging adults. Section 20(b) authorizes NIOSH to make inspections and question employers and employees as provided in Section 8 of this Act in order to carry out the functions and responsibilities under this Section. Section 22(e) further states the authority to enter into contracts, agreements, or other arrangements with appropriate public agencies or private organizations for purposes of conducting studies relating to responsibilities under the Act. For this purpose NIOSH established a contractual agreement with Tracor Jitco, Inc. to perform an industrywide study of worker exposure to vinyl fluoride and vinyl bromide.

PURPOSES OF THE STUDY

There are many chemicals used in industry for which there are insufficient data and experience to determine the extent of worker exposure and the long term biological effects on exposed workers. Additionally, there is a need to determine the effectiveness of control measures presently in use by industry, and to identify work practices and other control methods which would limit worker exposures to the lowest possible level.

The primary purposes of this industrial hygiene study are to determine worker exposures to the vinyl fluoride and vinyl bromide and to document engineering controls, work practices, administrative controls, and biological and environmental sampling requirements being used by the companies. For each plant, individual industrial hygiene survey reports were prepared and submitted to NIOSH, company management, the national and local union, and the NIOSH and OSHA regional office.

SURVEY LIMITATIONS

The industrial hygiene surveys represent singular evaluations of worker exposure to vinyl fluoride and vinyl bromide and, therefore, do not reflect possible variations in exposure due to seasonal or operational changes. Since the plant operators have the greatest potential for routine exposure, TWA exposure measurements for plant operators were predominant. Other workers, in more remote work locations, or who may have occasional or lower exposures, were not necessarily included in exposure measurements. The air samples were collected during periods of normal operations. Therefore, the resulting exposure measurements are considered to characterize normal operating conditions.

The surveys do not generally include exposure measurements during maintenance operations since maintenance is intermittent. On-stream maintenance or repair work may result in significant short-term exposures to process materials unless precautionary work procedures are followed.

CRITERIA FOR EVALUATIONS

The existing permissible concentrations (2) or threshold limit values (3) for two of the materials of potential exposure at the time of this study are listed below:

	<u>Permissible Conc. (2)</u>	<u>TLV(3)</u>
Vinyl Bromide	---	250 ppm (1100 mg/m ³)
Ethylene Dibromide	20 ppm*	20 ppm (145 mg/m ³)

*(30 ppm ceiling and 50 ppm peak for 5 min.)

No threshold limit value or permissible concentration for vinyl fluoride or difluoroethane has been established. The following summarizes reported toxicologic information for vinyl fluoride and difluoroethane:

Acute inhalation LD₅₀ and Approximate Lethal Concentration (ALC) values reported for vinyl fluoride are given in Table 1. Lester and Greenberg (5) exposed adult white rats to varying concentrations of vinyl fluoride in a gassing chamber for periods up to 12½ hours and determined the effect on postural, righting, and corneal reflexes. There were no deaths. Adequate oxygen was provided in each test and carbon dioxide produced was removed by soda lime. Loss of the postural reflex was taken as an indication of moderate intoxication; disappearance of the righting reflex, as severe intoxication; and loss of the corneal reflex, as deep anesthesia.

According to the authors, "before the postural reflex was lost at 60% VF, the rats were slightly intoxicated at 30% with evidence of hind leg instability. At 80%, the animals were dyspneic, but they recovered fully after breathing room air for 1 minute. Some rats were kept at 80% for 12½ hours, at which time the corneal reflex was still present. These, too, recovered their reflexes immediately on being removed to room air. The rats were killed with carbon monoxide and their lungs showed no evidence of irritation." No liver damage (gross or microscopic) was observed.

Kopecny et al. (6), in an acute inhalation toxicity test, were unable to confirm a narcotic effect of vinyl fluoride reported in the literature. The authors indicated, however, that at levels of 66.6-71 vol. % vinyl fluoride, there was insufficient free oxygen in their test mixture (as low as 6.2 vol. %).

Table 1. Acute Toxicity of Vinyl Fluoride (5,6,7)

Animal	Administration	Toxicity LD ₅₀ or Other
Rat, Adult (White)	Inhalation	LD ₅₀ = 80% by vol. (12½ hr)
Mouse (White)	Inhalation	LD ₅₀ = 69 vol. %*
Rat	Inhalation	ALC=800,000 ppm (12½ hr)**

* Insufficient free oxygen available, however, in test mixture (6.2 vol. %).
Exposure period not given in abstract.

ALC = Approximate Lethal Concentration

** 80% CH₂=CHF, 20% O₂.

Du Pont's Haskell Laboratory for Toxicology and Industrial Medicine (8) reported that rats exposed to 100,000 ppm vinyl fluoride seven hours a day five days a week for a total of thirty exposures, showed no evidence of toxicity according to clinical observations, weight gain, gross and micropathology, and organ weights.

No human volunteer studies or medical reports on the effect of vinyl fluoride on human beings were found in the literature search. Lester and Greenberg (5) suggested, as the maximum allowable concentration for single short exposures of human beings to vinyl fluoride, 20% by volume, on the basis of their results in experiments with adult white rats. In arriving at this value, according to the authors, the limiting factor was the appearance of symptoms of intoxication.

The du Pont Company (8) stated, that, "it would appear that vinyl fluoride does not constitute much of an inhalation hazard." They indicated that the American Conference of Governmental Industrial Hygienists recommended no Threshold Limit Value for vinyl fluoride but if one was established, "It would probably be 1,000 ppm like the common fluorinated propellants and refrigerants."

Clayton (7) reports for difluoroethane ($\text{CHF}_2\text{-CH}_3$) the effects of repeated exposures to 10% (100,000 ppm) concentration 16 hours per day for 60 days on rats to be "no toxic signs; no gross pathological change; mild round cell infiltration in lung; and normal liver histology."

STUDY DESCRIPTION

TYPES OF PLANTS, PROCESSES, AND OPERATIONS SURVEYED

Three plants were surveyed for this report. One is a manufacturer of vinyl fluoride; one, a user of vinyl fluoride; and one, a manufacturer of vinyl bromide. The surveys were conducted from March to June, 1977. Exposures to vinyl fluoride, vinyl bromide, and associated chemicals were evaluated.

Plant Descriptions

Plant A is the sole producer of vinyl fluoride on a commercial scale. Located in the southern U.S., in a complex of 17 chemical manufacturing plants, Plant A is primarily engaged in the manufacture of neoprene rubber and chlorodifluoromethane. This plant and others began production of synthetic rubber (neoprene) in 1942 as a result of government efforts to provide a substitute for the natural rubber needed for the war efforts. At present, about 1,400 employees are engaged in manufacturing, primarily the production of elastomers. Production of vinyl fluoride began in 1962. The production of vinyl fluoride has been below capacity but quite constant since start-up.

Plant B, located in the northeastern U.S., is currently engaged in the production of polymerized vinyl fluoride in a variety of product formulations and forms as well as the manufacture of methyl methacrylate plastic, polyolefin, polypropylene netting, and flat polyethylene porous pipe. The plant was originally a producer of rayon and cellophane which have been discontinued in favor of the other products. The plant work force at that time was over 3,000; the plant now employs 470. The production of polymerized vinyl fluoride products began in 1962; the process has remained essentially unchanged.

Plant C manufactures vinyl bromide as well as bromine and chlorobutyronitrile. The plant is located in the southern U.S. where subterranean brine has significant bromine content. Brine is pumped from wells in the area and elemental bromine is produced by chlorine displacement. The bromine is a primary product and also serves as a raw material in the production of brominated hydrocarbons. Vinyl bromide is produced continuously from ethylene dibromide in a small, separate processing plant on the property. The plant was started up in 1971 and has been operated unchanged since that date; production has been steady. Current employment at this facility is 140.

Process Descriptions

Process information at Plant A is closely guarded because patent rights have expired on the basic process. However, the process involves a pressurized reaction of hydrofluoric acid and acetylene. Difluoroethane is formed as an intermediate product that is cracked to yield ethylene fluoride and hydrogen fluoride (Figure 1). The reaction products are refined by distillation; the off-products are recycled to process streams. On occasion an excess pressure may result in a venting of process gases to the atmosphere through a stack which extends above the top of the process tower. The product, liquid vinyl fluoride, is piped to an insulated and cooled storage tank and from there to connecting hoses which couple to the pressure tank trucks. The vinyl fluoride at this point is maintained at -80° F and 300 psi. The truck tanks are insulated to maintain safe pressures during transport. Most of the product is shipped to Plant B for vinyl fluoride polymerization.

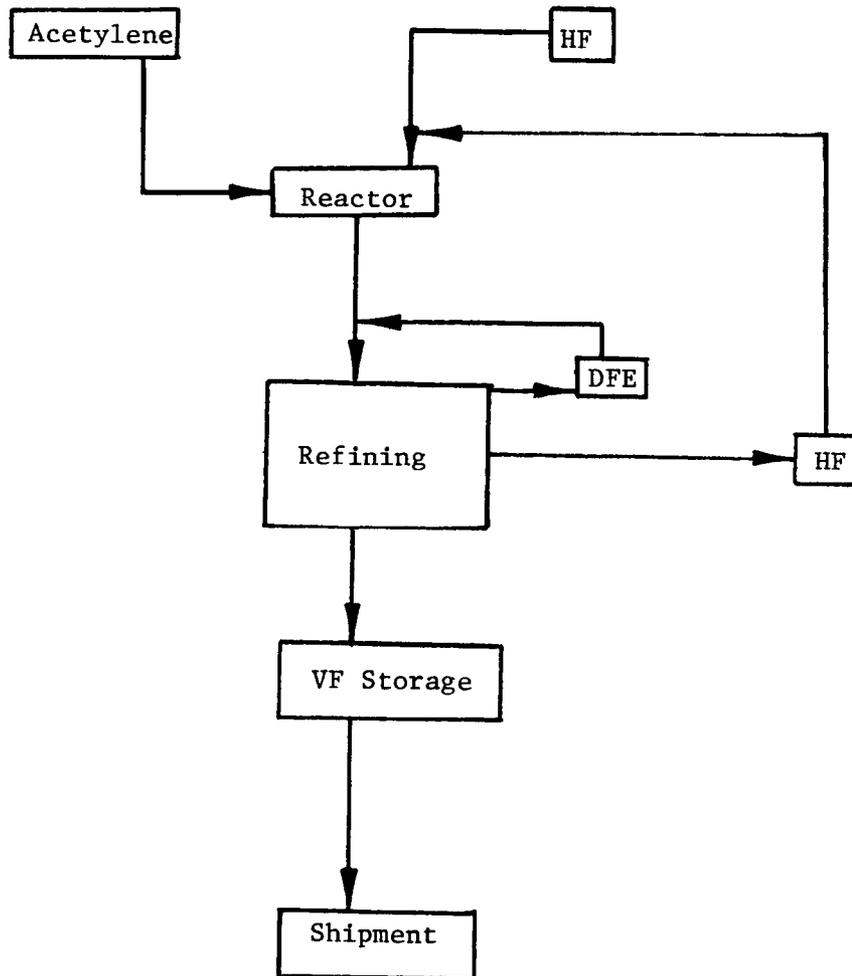


Figure 1. Vinyl Fluoride Process - Block Diagram

The vinyl fluoride is transported by tank truck to Plant B, transferred out-of-doors to storage tanks, and piped to the vinyl fluoride polymerization building. The vinyl fluoride is maintained cold and under pressure during transportation and storage and contains a small percentage of an inhibitor (d-limonene) which prevents premature polymerization. The vinyl fluoride is continuously pumped to the processing building where the vinyl fluoride is distilled off and fed to a supply tank (Figure 2). It is injected into water and pumped to a reactor to which an aqueous solution of a reaction initiator (an azo compound) is simultaneously pumped. The reactor is barricaded from the remainder of the processing area since the polymerization reaction is carried out under high pressure and the reaction must be carefully controlled. The reacted vinyl fluoride produces a finely divided precipitate, polyvinyl fluoride, which is separated from the reactor aqueous liquor. Unreacted vinyl fluoride is recycled to the supply tank. The finely divided polymer is stored as a 5% aqueous slurry which is fed to a continuous rotary filter. The process is in a closed system until the slurry is fed to the rotary filter. No unreacted vinyl fluoride is present at this stage. The resulting filter cake of the polymer is a white product with no noticeable odor. After drying, it is collected in bag filters, classified, and stored in bins for further processing.

Ethylene dibromide, manufactured from ethylene and bromine at Plant C, is continuously fed to a reactor in the vinyl bromide plant where caustic dehydrobrominates the dibromide and yields vinyl bromide (Figure 3). The bromide is recycled and the unreacted ethylene dibromide is removed by distillation and recycled. The vinyl bromide is pumped to storage tanks adjacent to the railroad siding where it is transferred to a railroad car for shipment. Vinyl bromide production is an enclosed process; the plant structure is open and out-of-doors. The process control instrumentation is located in a separate nearby building. The plant operators constantly monitor the process parameters from the control room.

WORKER JOB DESCRIPTIONS AND JOB TITLES

About 25 operators, 10 foremen, and 4 supervisors are engaged in the production of vinyl fluoride at Plant A. Vinyl fluoride operators average about 3 years in the production area, ranging from 2 months to more than 5 years. Promotional policies foster movement between departments within the plant. Thus, perhaps 75 men have had any appreciable work experience in the vinyl fluoride plant. General plant maintenance workers do repair and maintenance work in the vinyl fluoride plant on a scheduled as well as on an as-needed basis. Since the process is normally operated continuously, operators work in the plant for standard 8-hour shifts, 24 hours per day, predominantly in the centrally located control room monitoring the process and occasionally inspecting or adjusting the plant process equipment.

Personnel records are maintained by the plant. Records do not contain information of prior employment history. Place and date of death would be known only if the employee was retired by the company, i.e., long time company

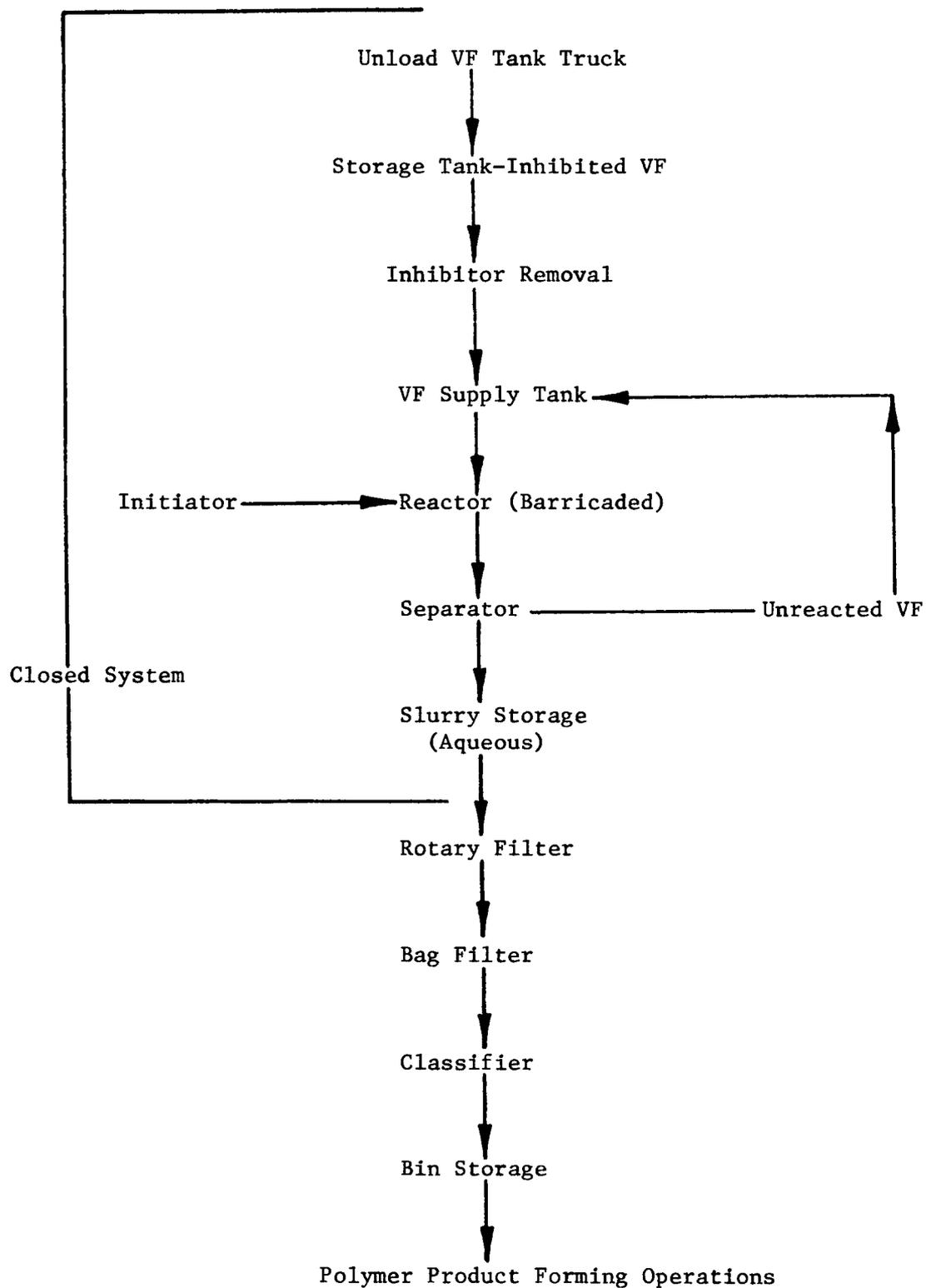


Figure 2. Vinyl Fluoride Polymerization Process

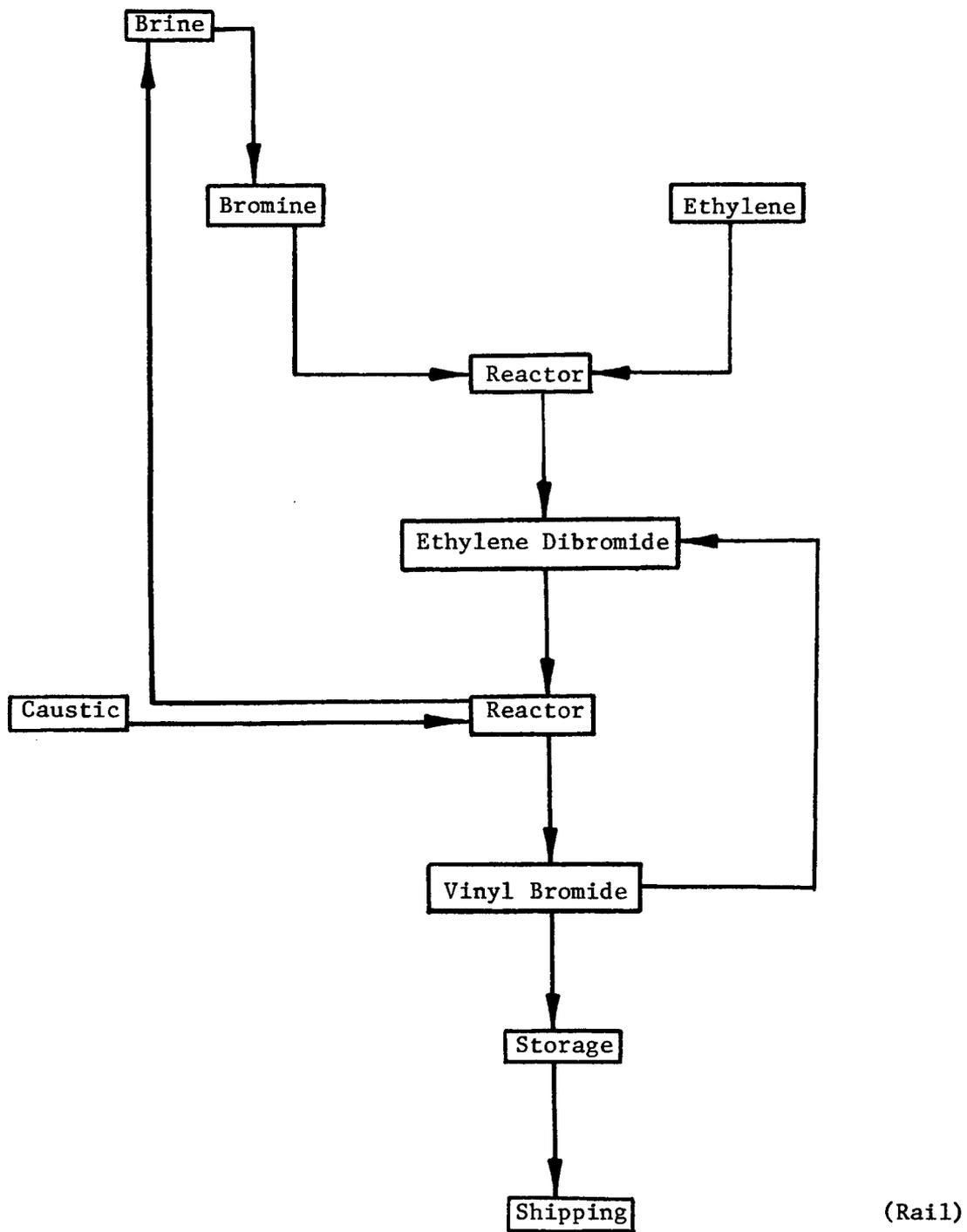


Figure 3. Vinyl Bromide Production - Process Flow Diagram

employees only. Usual personal identification data are contained in records. Job classifications are broadly defined, i.e., a "chemical operator" may work at many different locations and have many different duties. The plant work force is represented by a local independent union which has been active since 1960.

Plant B has two chemical operators and a shift foreman operate the vinyl fluoride polymer plant on four shifts; two relief operators are also available. The plant is operated continuously 24 hours per day. Thus the polymer plant personnel total 10 chemical operators, 4 shift foremen, one area supervisor, and one assistant area supervisor. Also, 4 maintenance workers are in the polymer process area intermittently, two of these are engaged in instrument maintenance. About 150 are employed in the polymer product area.

In the vinyl fluoride processing area, the operating and supervisory personnel work primarily in or adjacent to the process control room which is centrally located in the processing plant. Remote monitoring and operation from this location is the rule. Work in the processing area is limited to the need for inspection, maintenance, or sample collection. The finished product slurry is sampled from a process port twice per shift for quality control purposes.

During the 15 years that the vinyl fluoride polymerization process has been in operation about 50-55 persons have been employed in this processing area. The plant maintains personnel and medical records for all employees and can identify employment and transfers within the plant. Records of long term employees and retirees include vital statistical information beyond employment records. A local independent union has represented the plant employees for over 30 years. An occupational health committee is active in the union.

Plant C has 4 chemical operators who run the plant continuously from the vinyl bromide operations control room with occasional short periods out-of-doors attending or inspecting the process equipment. The maintenance personnel, loading and shipping personnel, and the laboratory personnel are not solely involved with vinyl bromide manufacture but work generally for all production facilities. Personnel turnover rate is very low. The records for company retirement benefits are retained in all instances, i.e., no options by employees. Therefore, a record is maintained of all past employees with address and mortality data. The plant is not unionized.

OBSERVATIONS AT WORK SITES

Medical Program

Plant A has one physician employed full time, and a nursing staff that maintains around-the-clock medical clinic service for employees. This program has been active since 1942. Medical records have also been maintained since 1942. Routine medical exams are conducted annually for employees over 40 and biennially for employees less than 40 years of age.

At Plant B a physician has responsibilities for maintenance of the plant medical program and is employed part time to provide in-plant medical services. A nurse is on duty full time in the plant during the day shift. The medical department employed 2 physicians full time when employment numbered 3,000. The corporate medical department provides medical advisory services to the plant site on a routine basis.

At Plant C a local physician is employed part-time as plant physician and provides medical services for plant personnel including physical examinations, and for some employees, routine biological sampling, e.g., blood specimen samples. The medical records are maintained in the physician's office. The Corporate Medical Department advises and coordinates the medical program.

Industrial Hygiene Program

No organized plant industrial hygiene program is in operation at Plant A. The central plant laboratory provides the air sampling and analyses for vinyl fluoride in the vinyl fluoride plant. The laboratory superintendent and a chemist have conducted the vinyl fluoride air analyses.

Environmental monitoring including industrial hygiene in-plant area monitoring as well as source monitoring for control purposes has been conducted for about 3 years in the vinyl fluoride polymerization area of Plant B. Corporate industrial hygiene services, generally advisory, are routinely available; engineering assistance is available from the Central Engineering Department.

Plant C has an active safety committee. Industrial hygiene services are provided on a routine basis (quarterly since November, 1976) by the Corporate Toxicology and Industrial Hygiene Department. At the time of this vinyl bromide survey, the Supervisor of Environmental Monitoring, and an assistant were conducting routine industrial hygiene surveys of the facility.

Past Exposures

Before December, 1975, only limited area samples had been collected at Plant A. Personal monitoring is presently conducted once every three months since December, 1975, using teflon air sampling bags worn by the vinyl fluoride plant operators. The company has reported an average exposure level of 0.55 ppm VF with the highest level being 2.2 ppm for 20(TWA) personal samples taken on production employees. Air monitoring data have been collected for various purposes at Plant B since 1974. Initially, evacuated cans were used to collect instantaneous air samples which were analyzed by gas chromatography.

Since last year, a portable MIRAN 101 A infra-red analyzer has been used to monitor the polymer plant areas and detect vinyl fluoride leakage. The air concentrations encountered in the polymer plant vary in the approximate range of 2-10 ppm vinyl fluoride. Exposure levels (TWA) for plant personnel would probably fall in the lower part of this range because of the work patterns described.

Air monitoring of vinyl bromide personal exposures has been performed by Plant C industrial hygiene teams on several occasions, e.g., Jan. 19-23, 1976, and August 23-27, 1976. The monitoring results provided by the Director of Toxicology and Industrial Hygiene of Plant C showed the following:

<u>January 19-23, 1976</u>	<u>No. of Samples</u>	<u>TWA Range (ppm)</u>	<u>TWA Mean (ppm)</u>
VBr Control Room Operator	6	0.01-1.0	0.7
Tank Car Loader (A)	5	0.01-12.2	3.25
Tank Car Loader (B)	5	0.05-15.9	4.1
Chemist	3	0.1-0.4	0.23
 <u>January 19-23, 1976</u>			
Lab Technician	1	-	0.4
Fixed Station (VBr Unit)	3	0.5-8.1	3.1
 <u>August 23-27, 1976</u>			
VBr Control Room Operator	6	0.2-4.7	1.6
Tank Car Loader (A)	5	0.02-3.25	0.8
Tank Car Loader (B)	4	0.14-1.9	0.6
Lab Technician	2	0.29-0.73	0.5
Fixed Station (VBr Unit)	4	0.6-4.3	2.15

Operations and work procedures have been constant since start-up. It is probable that these exposure levels would be representative of the exposure levels experienced by the workers since 1971.

Potential Exposures

Workers in the vinyl fluoride production area of Plant A are potentially exposed to the raw materials, acetylene and hydrofluoric acid; the intermediate product, difluoroethane; and the final product, vinyl fluoride.

Potentially, both inhalation and skin and eye contact hazards are present. Immediate to the vinyl fluoride production plant is the chlorodifluoromethane production plant using CHCl_3 as the primary raw material. Thus, potential exposure in the area includes CHCl_3 and chlorodifluoromethane.

In the vinyl fluoride polymerization area of Plant B, the potential exposures are primarily to vinyl fluoride and minimally to the inhibitor and the final product, vinyl fluoride polymer.

Potential exposures in the vinyl bromide area of Plant C are primarily to vinyl bromide and ethylene dibromide. Workers such as those in maintenance or shipping spend much of their work time in other plant areas of the facility and therefore would have potential exposure to other products such as chlorine, bromine, and chlorobutyronitrile.

SAMPLING PROCEDURES AND ANALYTICAL METHODS EMPLOYED

NIOSH validated sampling and analytical methods were not available for vinyl fluoride and vinyl bromide at the time of this study. The best available techniques were employed in conducting sampling and analysing results. Air samples were collected to evaluate worker exposures to vinyl fluoride in Plants A and B. A 7.7 liter teflon bag (Alltech Associates, Inc., 202 Campus Drive, Arlington Heights, Ill. 60004) in a backpack worn by the worker was used to collect the individual air samples (4). Each worker also wore a personal air sampling pump equipped with teflon and glass sampling lines. Air samples were collected at flow rates of 14 to 100 cc/min for each of four consecutive work shifts. Sipin Model P personal air sampling pumps (Anatole J. Sipin Co., Inc., New York, N.Y) and du Pont Model P200 Constant Flow Samplers were used. Measurements of two prepared samples of VF at 10 ppm in teflon bags were made to determine the potential loss with time. Decay occurred at 10% in four days and 50% in two weeks.

During the industrial hygiene survey at Plant C air samples were collected using personal sampling pumps worn for the duration of a work shift or a selected portion of a work shift. Samples were collected at a flow rate of 50-75 cc/min for each of the four consecutive shifts. The sampling media was the standard 150 mg Pittsburgh PCB charcoal tube and the analytical method was desorption with carbon disulfide and gas chromatography (NIOSH P & CAM #127). SKC (SKC, Inc., Environmental Sciences Division, Post Office Box 55, Venetia, Pennsylvania, 15367) charcoal adsorption tubes (Lot 105) were used for sampling. The air sampling pumps used were SKC Model 222-351 Personal Pump and du Pont (E.I. du Pont de Nemours and Co., Inc., Applied Technology Division, Wilmington, Delaware, 19898) Model P200 Constant Flow Sampler.

All samples were analyzed by gas chromatography in the Analytical Section, Kettering Laboratory, University of Cincinnati Medical Center.

STUDY RESULTS AND DATA ANALYSIS AND EVALUATION

WORKER EXPOSURES TO VINYL FLUORIDE AND VINYL BROMIDE

Plant operator exposure levels (TWA) for normal vinyl fluoride production operations were less than 2 ppm vinyl fluoride (Table 2). Potentially, much higher exposures are possible during plant start-up. However, respiratory protection as well as protective clothing and a face shield are worn by operators during in-plant start-up operations. Thus, actual exposure during this period is reduced by some factor depending upon effectiveness of the respirator. The measured TWA exposure to an operator during start-up was 21 ppm vinyl fluoride.

In the vinyl fluoride polymerization plant, the measured levels of TWA exposures to vinyl fluoride for the polymer operators (i.e., operators, auxiliary operators, trainee operator, and supervisor) varied from 1-5 ppm vinyl fluoride (Table 3). The average air concentration of twelve samples collected over three shifts was 1.9 ppm vinyl fluoride. The TWA exposure for the polymer operators, averaged over three shifts, was also 1.9 ppm vinyl fluoride for 7 samples.

In the vinyl bromide manufacturing plant, the median TWA exposure for VBr plant operators was 0.27 ppm VBr; for a laboratory technician 0.4 ppm VBr; and for a loading crewman 1.2 ppm VBr (Table 4). The measured exposure of a loading crewman for a 61-minute period (only while in the loading area during tank car loading) was 6.3 ppm VBr.

WORKER EXPOSURES TO OTHER MATERIALS AND AGENTS

In the manufacture of vinyl fluoride, difluoroethane (DFE) is normally an intermediate product. At the time of this survey, DFE was being supplied to the vinyl fluoride production process from storage tanks. For this operating condition the measured TWA exposures to DFE for plant operators were all less than 3 ppm. One general area sample collected in the control room showed 5 ppm DFE (Table 2).

In the manufacture of vinyl bromide, ethylene dibromide is an intermediate product. The median TWA exposures to ethylene dibromide were 0.08 ppm for VBr operators, 0.26 ppm for a lab technician, and 0.57 ppm for a loading crewman.

EVALUATION OF EXPOSURE LEVEL MEASUREMENTS

In the manufacture of vinyl fluoride, plant operator TWA exposures were measured to be less than 2 ppm vinyl fluoride and less than 3 ppm difluoroethane. These levels are comparable to the sample results of previous measurements reported by the plant management (average of 0.55 ppm VF based on 20 TWA samples with a maximum TWA level of 2.2 ppm VF). An exposure of 21 ppm VF (TWA) was measured during one shift when plant start up operations were being performed. This demonstrates that during a work shift with abnormal or

Table 2. Results of Air Sampling:
Vinyl Fluoride Manufacture - Plant A

No.	Sample Job/Location	Shift Time	Air Concentrations (ppm)	
			Vinyl Fluoride	Difluoroethane
5/31/77				
1	Maintenance Crewman - Repair of VF process (not operating)* Reactor Vent System	2nd (1356-1539)	<2 ^b	<3
2	Vinyl Fluoride Plant Operator	3rd (1530-2340)	<2	<3
3	Vinyl Fluoride Plant Control Room (GA) ⁺	3rd (1640-2340)	<2	--- ^a
6/1/77				
4	Vinyl Fluoride Plant Operator	1st** (2340-0800)	21	---
5	Vinyl Fluoride Plant Control Room	1st (0110-0800)	<2	<3
6	Vinyl Fluoride Plant Operator	2nd (0745-1545)	<2	---
7	Vinyl Fluoride Plant Control Room (GA)	2nd (0745-1545)	<2	5
8	Vinyl Fluoride Plant Operator	3rd (1625-2330)	<2	<3

* Note: Plant production shut down on 5/30. Start-up operations for vinyl fluoride production (using difluoroethane from storage tank supply to vinyl fluoride reactor) performed by operators during second and third shifts on 5/31/77.

** Vinyl fluoride production started during first shift 6/1/77. Continuous operation second and third shifts. (difluoroethane production start-up scheduled for following shift 6/2/77.)

⁺ GA - general area sample

^a Not analyzed: ^b Interference from DFE prevented better definition of VF data.

Table 3. Results of Air Sampling:
Vinyl Fluoride Polymerization - Plant B

No.	<u>Sample</u>	Shift Time	<u>Air Concentrations (ppm)</u>
	Job/Location		Vinyl Fluoride
1	Polymer Operator	5/4/77 2nd (1220-1539)	1
2	Auxiliary Polymer Operator	2nd (0920-1247)	2
3	Day Supervisor's Office (GA)* (Adjacent to Control Room)	2nd (1015-1307)	1
4	Auxiliary Polymer Operator	2nd (1249-1550)	1
6A	Polymer Trainee	3rd (2118-2340)	4
7	Auxiliary Polymer Operator	3rd (1614-2346)	1
8	Day Supervisor's Office (GA)	5/5/77 1st (2359-0028)	2
9	Polymer Operator	1st (2359-0740)	2
10	Polymer Operator	1st (0402-0725)	2
11	Pump Room (GA)	1st (0457-0845)	5
12	Day Supervisor's Office (GA)	2nd (0507-1109)	2

* General Area Sample

TWA Exposure, Polymer Operators, 3 shift average = 1.9 ppm VF

Table 4. Results of Air Sampling:
Vinyl Bromide Manufacture - Plant C

No.	Sample Job/Location	Shift Time	Air Concentrations (ppm)	
			Vinyl Bromide	Ethylene Dibromide
3/23/77				
1	Vinyl Bromide Operator	1st (0635-1405)	0.21	0.07
2	Laboratory Technician	1st (0803-1642)	0.29	0.26
3	Vinyl Bromide Operator	2nd (1407-2200)	0.10	0.08
3/24/77				
4	Vinyl Bromide Operator	3rd (2155-0608)	0.43	0.15
5	Laboratory Technician	1st (0826-1631)	0.51	---
6	Loading Crewman (Loading VBr Tank Car/only while in Loading Area)	1st (0855-0928) (1110-1138)	6.3	0.28
7	Vinyl Bromide Operator	1st (0613-1406)	0.32	0.05
8	Loading Crewman	1st (0850-1507)	1.2	0.57

Summary of Exposure Levels For Job Types

- VBR Operators - Median TWA = 0.27 ppm VBr and 0.08 ppm Ethylene Dibromide for 4 samples.
- Lab Technician - Median TWA = 0.4 ppm VBr and 0.26 ppm Ethylene Dibromide for 2 and 1 sample respectively.
- Loading Crewman - TWA = 1.2 ppm VBr and 0.57 ppm Ethylene Dibromide for 1 sample (Exposure level during 61 min. VBr loading period = 6.3 ppm VBr).

unusual work operations, the potential for greater exposure exists. With continued caution on the part of the operators and the use of respiratory protection as well as protective clothing and face shields during these operations, the actual exposures will be minimized.

In the vinyl fluoride polymer plant, the plant operator TWA exposure, averaged over 3 shifts, was 1.9 ppm VF. The highest single TWA measurement was 4 ppm VF. No adverse health effects would be expected.

In the manufacturing of vinyl bromide, the measured TWA exposures to vinyl bromide and ethylene dibromide were below existing permissible levels.

No adverse health effects were reported at the time of this study from the stated exposure levels. However, this industrial hygiene evaluation of exposure levels does not propose to evaluate adverse health effects from continued exposure to these levels. Rather, it is recognized that exposures should be controlled and minimized.

EXPOSURE CONTROL EFFORTS

The primary control of vinyl fluoride in Plant A is the total enclosure of the process materials. Continuous maintenance checks reduce the chance for leakage to occur from the pressurized process equipment, piping, and storage. When dangerous excess pressures occur, the gases are vented to the top of the process tower and to the atmosphere at a considerable elevation above ground level. Also, operators are housed in a separate control building and the process itself is located out-of-doors in a process tower. Operators wear self-contained emergency air supply respirators in the processing area when a serious leakage problem exists. Respirators with cannisters capable of removal of organic vapors and acid gases are used routinely by plant operators while performing tasks in the processing areas of the plant.

Vinyl fluoride at Plant B is maintained within the processing equipment, i.e., storage tanks, piping system, pumps, distillation units, and reactor. Leakage from the pressurized system is held to a minimum. Operators control and monitor the process remotely from a room in the plant that houses the instrument control panels. Closed circuit monitors with zoom lenses allow remote visual inspection of process equipment. Equipment design and maintenance minimize vinyl fluoride leakage. Total enclosure of the process is the primary measure for the control of vinyl fluoride. The polymer is pumped as a slurry to rotary filters and a wet filter cake is produced in the polymer plant, thus no polymer dust is generated. Air monitoring with a portable, direct reading infra-red detector (MIRAN 101 A infra-red analyzer mounted on a cart) has been found to be very useful for monitoring the plant areas for VF monomers. With a tube extension on the inlet for detecting leak points in the process equipment, this procedure has been effective in directing maintenance and repair efforts to minimize vinyl fluoride leakage.

Worker exposure to vinyl bromide at Plant C is controlled primarily by the containment of the process and the process materials. An effort is made to minimize process leakage and consequent material losses. Physical separation of the plant from the process control room reduces the potential for exposure to process materials since the operators spend the majority of the work time in the control room. Also, workers recognize the potential toxic nature of process materials and tend to avoid exposures as well as continuously maintain the integrity of the process systems. Samples are routinely collected from a product process line for process control testing and daily for quality control analysis. At the time of sample collection some vinyl bromide is wasted and a brief exposure may result depending upon the wind direction. The sample is contained and transported immediately to the laboratory for analyses where conventional ventilated chemical laboratory hoods are used. Transfer of vinyl bromide to tank cars occurs several times a week. A vapor return line is used during the filling operation, thereby minimizing vapor loss in the tank filling area. Emergency respiratory protection is available for use when a process leak necessitates emergency action for repair or evacuation.

SUMMARY OF HAZARD EXPERIENCE AND POTENTIAL

In the manufacturing of vinyl fluoride and vinyl bromide, as well as in the polymerization of VF, the integrity of the process systems are maintained sufficiently to present minimal exposure hazards to plant workers. This control, which is a result of design and maintenance, in conjunction with safe work procedures, remote process control rooms, and use of personal protection equipment in certain potential exposure situations (such as during sample collection, coupling/decoupling of tank lines, or when leaks develop or process equipment is opened for inspection or repair) has resulted in low exposures to the plant personnel. Thus, for normal operations the health hazards are minimized.

The potential for high exposures and relatively great hazard is ever present since large quantities of very volatile materials as well as toxic or flammable materials are contained in pressurized process equipment. During occasional periods of plant start-up or when on-stream repair work is being done the potential hazard is comparably much greater.

RECOMMENDATIONS

Continued and improved good industrial hygiene practices are warranted for controlling worker exposure to vinyl fluoride and vinyl bromide. Although acute health effects are not normally encountered at the exposure levels reported in this study, the chronic health effects from continued exposure at these levels are not yet well defined. It is prudent to minimize exposures by employing preventive measures. The following general recommendations are made:

- (1) The plants should maintain their present control measures. The plants should institute a surveillance program. An industrial hygiene surveillance program should include regularly scheduled personal sampling of potentially exposed personnel and the installation of leak detecting alarm systems in production areas or the use of portable organic vapor analyzers to locate the source of leakage. Where measurements indicate deficiencies, steps should be taken to effect corrective measures.
- (2) The design and installation of enclosed process systems that are leak resistant and routine maintenance of process equipment should continue to be the primary control effort.
- (3) In all tank car filling operations, vapor return lines should be installed and used. Improved shaft seals, gaskets, flangers, and pumps should be considered on a replacement maintenance basis.
- (4) Respiratory protection and protective clothing should be made available to employees for use when potential exposures and emergency conditions warrant additional protection. The short-term exposures experienced by tank car loaders when coupling and decoupling tank car lines, opening and inspecting tanks or valves, venting tanks or collecting samples should require appropriate respiratory protection. Similarly, process operators and maintenance crewmen should be equipped with appropriate respiratory protection for use in performing product sampling and process maintenance as well as for unusual operations and emergencies.
- (5) Instruction of employees, especially new employees, in the toxic nature of process materials and the need for proper and timely use of protective equipment and clothing should be conducted on a routine periodic basis. Training is essential to effectively minimize worker exposures. Safe work procedures and practices aimed at minimizing worker exposure should be developed. They should be understood and followed by all employees.
- (6) To prevent irritation and frostbite types of burns, skin and eye contact with airborne vinyls should be avoided. Eyewash fountains and emergency showers should be located near all vinyl exposure areas. Employees should wear safety goggles, glasses with side shields, rubber gloves, and boots for operations where contact with these chemicals would be possible. One vinyl bromide manufacturer has recommended that neoprene gloves and boots be worn by employees opening process lines and repairing pumps and that a one-piece nylon suit, vinyl-coated on both sides, with

attached neoprene boots and gloves be worn by employees entering reactor vessels or tanks.

- (7) The vinyl halides are highly flammable at a wide range of air concentrations. Contact with ignition sources should be avoided; smoking should be permitted only in designated areas.

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