

SHELL CHEMICAL COMPANY

A DIVISION OF SHELL OIL COMPANY

ONE SHELL PLAZA

P.O. BOX 2463

HOUSTON, TEXAS 77001

March 6, 1974

The Firestone Tire & Rubber Company
1200 Firestone Parkway
Akron, Ohio 44317

Attention Mr. W. P. Bray

Gentlemen:

Attached for your information and use within your company is a copy of the statement presented by Shell at the OSHA hearing on VCM manufacture and use February 15, 1974.

During the hearing, expert testimony was given by Dow Chemical Company, and by Professor Cesare Maltoni, Instituto di Oncologia, Bologna, Italy as to the effects observed in sophisticated tests of animals exposed long term to various levels of VCM. B. F. Goodrich testified also as to the discovery of angiosarcoma in livers of certain polyvinyl chloride workers at autopsy. Some follow-up reports on the incidence of angiosarcoma are found in the Wall Street Journal February 19, 1974 page 6, Chemical Engineering News February 25, 1974 and Chemical Week February 27, 1974. We would urge you to make arrangements with the OSHA recorder to receive a copy of the full testimony at the hearing when available.

Enclosed is a copy of our vinyl chloride safety data sheet which we have revised, based on testimony given at the hearing, to give more explicit warning of the potentialities associated with exposure to VCM. In this version of the safety data sheet, we specifically reference the information from Professor Maltoni that cancer development has been noted in rats down to VCM exposures of 250 ppm and also the information that exposure to VCM may be implicated in development of liver cancer in some polyvinyl chloride workers. In view of this information, we now rate VCM as a health hazard 3 (using the National Fire Protection Association rating system) and recommend air pack or supplied air respirator for personnel protection where such protection is required.

We are now preparing for external distribution an expanded description of the sampling and analytical techniques we have been using to determine VCM concentration in workers' breathing zones. When this description is ready (probably about March 15, 1974) we shall send you a copy. As you know, we have adopted an internal working level of 50 ppm.

OCC 017675

maximum VCM exposure over eight hours for our operations. We believe that the periodic use of breathing zone analyses has helped considerably in keeping significantly below this level.

Very truly yours,
SHELL CHEMICAL COMPANY



R. J. Reynolds
Manager, Vinyl Chloride

Attachment

SHELL CHEMICAL STATEMENT
TO OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION
CONCERNING POSSIBLE HAZARDS OF VINYL CHLORIDE MANUFACTURE AND USE

Mr. Chairman:

My name is Richard J. Reynolds, Manager Vinyl Chloride, Shell Chemical Company. I am accompanied here by Mr. Howard L. Kusnetz, Manager of Industrial Hygiene, Shell Oil Company and Dr. R. L. Maycock, Manager Environment and Safety, Shell Chemical Company. The Shell Oil Company and its division, the Shell Chemical Company, are pleased to be able to participate in this fact-finding hearing on the possible hazards of vinyl chloride manufacture and use. We are especially appreciative that the U. S. Department of Labor called this hearing before publishing any proposed regulation.

Shell Chemical Company manufactures vinyl chloride monomer (VCM) at Deer Park, Texas (near Houston) and at Norco, Louisiana (near New Orleans). We entered the vinyl chloride industry only recently and produce only the monomer. Our remarks will be limited to this segment of the industry only.

Shell's facilities comprise large, continuously operating process units closely integrated and requiring minimal manual attention or exposure to feed and product streams. Production in the unit at Deer Park, Texas was started in August 1971. Production in the Norco unit was started in October 1973. Design production capacity is about 1,200 tons VCM per day at Deer Park and about 1,000 tons VCM per day at Norco. At Deer Park about twenty persons are involved directly in the day-to-day operation of the VCM unit. Approximately twenty-five additional employees are involved less continually with VCM manufacture during the regular performance of their duties in maintenance, shipping and supervision. Thus, at Deer Park, about 45 workers out of a total chemical plant staff of 1,300 are concerned with VCM manufacture on a regular basis. At Norco, a similar number of direct VCM workers are required but fewer shipping personnel so about 25 workers of a total chemical plant staff of about 370 are involved on a regular basis with VCM manufacture.

The principal raw materials used in our VCM production units are ethylene and chlorine. At both Houston and Norco the ethylene is received by

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pipeline. Chlorine at Houston is received by pipeline and at Norco by railroad tank car. Small quantities of dichloroethane are received at both locations by barge to supplement these primary feeds. At Houston small supplemental quantities of hydrogen chloride feed are received via pipeline and tank truck.

The process technology employed at both Shell VCM units was licensed from Stauffer Chemical Company. In this process, about half of the ethylene and all of the chlorine fed are reacted to form the main intermediate which is 1,2-dichloroethane. After purification, the 1,2-dichloroethane is heated in a furnace to form product VCM and the main byproduct, hydrogen chloride. The product VCM is purified to greater than 99.9% purity by distillation and stored as a liquid under its own vapor pressure. The byproduct hydrogen chloride is recovered by reaction with the remaining half of the ethylene feed and with air to form additional 1,2-dichloroethane. Minor byproducts of the process include: carbon oxides, chloroform, carbon tetrachloride, ethyl chloride, the isomeric dichloroethylenes, the isomeric trichloroethylenes and trichloroethanes, tetrachloroethanes, and the isomeric chlorinated butanes.

The process is a continuous one. The reactants, intermediates, byproducts and product VCM are contained within the process equipment in a closed system except for a continuous stream of waste process nitrogen which is vented from a high stack after water scrubbing. Occasionally there may be minor vents such as from loading arm drainage or leaks. The process equipment is opened only for maintenance, and then only after washing followed by purging of feed, product, or byproducts contents. Maintenance operations are generally infrequent (maintenance shutdowns are scheduled only once or twice a year). The general precautions for containing and purging organic materials in large chemical process equipment are well known to us as a result of our long history of manufacture and handling of flammable materials and chlorinated compounds.

When the process technology was licensed, a substantial compilation of toxicological information on VCM and associated feed and byproduct compounds was received from the Jitensor. Also we had available considerable other toxicologic information dealing with compounds already handled by Shell Chemical

such as chlorine, ethylene and ethyl chloride. This information is available to the public in toxicologic reference works; therefore, we will avoid re quoting it here.

Initial review of the VCM process toxicology information available to us in 1969 and 1970 led us to conclude that additional studies of our own were not required. Thereafter, in a paper delivered at the 1970 International Congress on Cancer by Viola et al., ⁽¹⁾ it was reported that tumor development was observed in rats exposed repeatedly to high concentrations of VCM. The exposure levels in the Viola work (30,000 ppm) were grossly in excess of published standards. Nevertheless, the report raised a new concern as to what hitherto unknown effects might be expected with exposure to lower levels. Thus, we accepted an invitation by the Manufacturing Chemists Association to participate with others in the industry in sponsoring an exposure study to elucidate the possible effects of VCM at much lower levels and to participate in an epidemiology study. These programs were described in detail to you by the Manufacturing Chemists Association today. Shell Chemical has provided financial support and has participated actively in these programs from the outset.

From the time our Deer Park unit began VCM production in August of 1971 until early 1973, periodic spot measurements were made of the ambient plant air in the operating unit using standard colormetric VCM detector tubes. All measurements were well below the OSHA 500 ppm ceiling level and the 200 ppm time weighted average Threshold Limit Value set by the ACGIH in June 1972. From previous experience with other volatile and flammable materials, we were confident that the plant ambient air contained less than 200 ppm VCM but this could not be verified because the detector tubes are not sensitive to much lower values. It was apparent that a new analytical method would be required to measure low levels of VCM and also that improved sampling techniques would be required to compensate for the greater effect of variances introduced by weather conditions and sampling location at low levels. Therefore, a sensitive gas-chromatographic analytical technique for VCM in air was developed and

(1) P. L. Viola, A. Bigotti and A. Caputo, Cancer Research, Vol. 31 p. 516 (1971)

sampling was modified to meet the needs of the situation. A copy of the method is appended.

Based on a developing concern and with the new analytical tools, our company elected to establish an internal working level of 50 ppm (eight hour time weighted average) maximum exposure to VCM concentrations in air. This level and the possible implications and incentives for minimizing exposure indicated by the Viola work were discussed with our employees in July-August 1973. On August 15, 1973 we formally advised all of our customers of our new working level and the reasons for it (copy appended). Along with the new sensitive analytic technique we had our workers periodically wear an improved device for taking a continuous sample over eight hours of the air in worker's breathing zone. Results with the improved sampling and measurement technique showed no values in either VCM plant location exceeding the 50 ppm VCM eight hour time weighted average. Special tests were also made to ascertain the maximum VCM exposure a worker might receive under abnormal conditions at the job site. Under some of these conditions, we found values of 100 ppm - 200 ppm VCM but these concentrations persisted only for a short time. Based on these tests, additional precautions and directions were put into practice.

In 1973 we began a program of medical surveillance of VCM workers who would be regularly assigned to jobs involving potential or regular exposure to VCM. Twenty-five workers at Norco were given the examination described below. Forty-two examinations will have been given at Deer Park when the current examination cycle is complete.

The annual examination provides for:

- (1) Medical history
- (2) Physical examination by a physician
- (3) Laboratory blood studies including RBC, hematocrit, hemoglobin, WBC, differential count, and platelet count
- (4) SMA-12 blood chemistry including serum bilirubin
- (5) Routine urine examination
- (6) 14 X 17 P-A Chest X-ray

Based on existing knowledge, with the very low accumulated exposure of our workers to VCM we would not expect these examinations to provide any data beyond that establishing a baseline for subsequent medical history. In fact, to date,

we have found no liver damage or cancer among the Shell participants. Although we have not been onstream long enough to have meaningful epidemiological data of our own, Shell Chemical is a financial supporter of the Manufacturing Chemists Association epidemiology study contracted to Tabershaw Cooper Associates and described to you today.

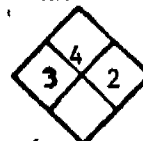
In addition to the above actions, we continue efforts to locate and curtail emissions, should they be found, throughout our process units and associated loading areas.

With respect to item 6 in the notice of this hearing, Shell Chemical would favor the route of the regular rulemaking under Section 6(b) of the Occupational Safety and Health Act for a VCM standard, as opposed to an Emergency Temporary Standard. The rulemaking procedure would allow the orderly development of data.



SHELL OIL COMPANY
SHELL CHEMICAL COMPANY
SHELL DEVELOPMENT COMPANY
SHELL PIPE LINE CORPORATION

RATING



MATERIAL SAFETY DATA SHEET

Information on this form is furnished solely for the purpose of compliance with the Occupational Safety and Health Act of 1970 and shall not be used for any other purpose. Use or dissemination of all or any part of this information for any other purpose may result in a violation of law or constitute grounds for legal action.

SECTION I	
MANUFACTURER'S NAME Shell Chemical Company	EMERGENCY TELEPHONE NO. (713) 473-9461
ADDRESS (Number, Street, City, State, and ZIP Code) P.O. Box 2463, Houston, Texas 77001	
CHEMICAL NAME AND SYNONYMS Vinyl Chloride, Chloroethylene, Chloroethene	TRADE NAME Vinyl Chloride Monomer (VCM)
CHEMICAL FAMILY Vinyl Halide	FORMULA

SECTION II HAZARDOUS INGREDIENTS*	
COMPOSITION	2
Vinyl Chloride	100
Extended exposure of rats to known concentrations of VCM vapor ranging from 30,000-250 ppm has resulted in cancers of a variety of organs, including a rare cancer of the liver. No cancers or other effects have been reported in animal exposed to 50 ppm. After years of exposure to unreported concentrations of VCM and other chemicals associated with PVC production, some workers have developed degeneration of the ends of the finger bones. A larger than normal percentage have shown some degree of liver abnormality. A few have developed the same rare form of liver cancer found in the rat studies. Where the human exposure levels are known (160 ppm average over 17 years), no clinical illness or overt condition attributable to VCM was found. Some blood test values appeared to be altered, however. Detailed reports of the toxicological studies are available for examination in the Plant Safety Office. In view of the above, VCM must be accorded the precautions appropriate for a cancer-suspect agent.	

SECTION III PHYSICAL DATA			
BOILING POINT (°F)	7	SPECIFIC GRAVITY (H ₂ O=1) 20° C.	0.91
VAPOR PRESSURE (mmHg) @ 68° F.	2580	PERCENT VOLATILE BY VOLUME (%)	100
VAPOR DENSITY (AIR=1)	2.15	EVAPORATION RATE (_____=1)	
SOLUBILITY IN WATER	Slight		
APPEARANCE AND ODOR Colorless, sweet, smelling gas. Odor threshold about 250 ppm, but olfactory fatigue occurs, so odor cannot be relied upon to provide warning of hazardous levels.			

SECTION IV FIRE AND EXPLOSION HAZARD DATA			
FLASH POINT (Method used)	-108° F., T.O.C.	FLAMMABLE LIMITS	
		at ordinary temperature	3.6 33.0
EXTINGUISHING MEDIA	CO ₂ , dry chemicals		
SPECIAL FIRE FIGHTING PROCEDURES	Do not use water except as a spray or fog.		
	Wear self contained breathing apparatus.		
UNUSUAL FIRE AND EXPLOSION HAZARDS	Handle as an extremely flammable liquid and gas. Material is under pressure.		

SECTION V HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE	OSHA - 500 ppm (ceiling); ACGIH - 200 ppm (TWA); Shell - 50 ppm (TWA)
EFFECTS OF OVEREXPOSURE	See Section II Also, exposure to very high concentrations may cause asphyxiation, persistent irregular heartbeat, unconsciousness, nausea, or dizziness. Liquid on body or clothing may cause freezing or lead to above symptoms via overexposure from inhalation or systemic absorption.
EMERGENCY AND FIRST AID PROCEDURES	Remove victim to area free of vinyl chloride vapors. Give artificial respiration if necessary. Remove contaminated clothing. Notify supervisor immediately of spills. Remove from eyes with large amounts of water. or leaks.

SECTION VI REACTIVITY DATA

STABILITY	UNSTABLE	X	CONDITIONS TO AVOID Avoid sunlight and/or heat and exclude all oxygen
	STABLE		
INCOMPATIBILITY (Materials to avoid)	air, oxygen		
HAZARDOUS DECOMPOSITION PRODUCTS	H Cl; CO and phosgene on combustion		
HAZARDOUS POLYMERIZATION	MAY OCCUR	X	CONDITIONS TO AVOID air, sunlight and/or heat
	WILL NOT OCCUR		

SECTION VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN WHEN MATERIAL IS RELEASED OR SPILLED	Remove all sources of ignition. Remove all personnel not wearing protection equipment shown in Sect. VIII. Use forced ventilation from explosion-proof equipment. Allow to evaporate slowly.
WASTE DISPOSAL METHOD	Do not permit material to enter sewers. Use controlled evaporation. Guard against fire and explosion hazards.

SECTION VIII SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify type)	Air pack or supplied air respirator as required.
VENTILATION	LOCAL EXHAUST Highly recommended (Use explosion proof equipment)
	MECHANICAL (General) OTHER
PROTECTIVE GLOVES	Rubber
OTHER PROTECTIVE EQUIPMENT	Chemical goggles and/or face shields
To prevent all contact with body as required.	

SECTION IX SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING	Prevent any leakage. Provide sufficient ventilation to prevent high concentrations. Keep away from all sources of ignition. Handle as an extremely flammable material which is stored under pressure.
AVOID BREATHING VAPOR	

D. M. Sheets, Supervisor
Regulatory Affairs - Chemical Products
Shell Chemical Company

D. M. Sheets
February 1974

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