DOCKET #1964

FEBRUARY 15 HEARINGS ON
VINYL CHLORIDE
FOR DR. CUMMIN

BOOK #2 (of 3)

Exhibit 1C

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, continously 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

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 ~~from~~ 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 licensor. 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 requoting 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 etal, [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

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(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 ~~standard~~ working level of 50 ppm (eight hour time weighted average) maximum exposure to VCM concentrations in air. This ~~standard~~ 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 ~~standard~~ 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 CHEMICAL COMPANY
A DIVISION OF SHELL OIL COMPANY
ONE SHELL PLAZA
HOUSTON, TEXAS 77002

INDUSTRIAL CHEMICALS DIVISION

August 15, 1973

Gentlemen:

The necessity for limiting and controlling human exposure to high concentrations of vinyl chloride has been long recognized by industry. A 500 ppm ceiling value is specified by the Department of Labor, under the Occupational Safety and Health Act, as the permitted employee exposure level to vinyl chloride. The most recent Manufacturing Chemists Association safety data sheet for vinyl chloride reports this value. A copy of this data sheet is enclosed for your information.

In June of 1972, the American Conference of Governmental Industrial Hygienists (ACGIH) adopted an eight hour time weighted average Threshold Limit Value (TLV) of 200 ppm (vol/vol) for vinyl chloride. Documentation covering the considerations leading to the adoption of this value may be obtained by request to the Chairman, TLV Committee, American Conference of Governmental Industrial Hygienists, P. O. Box 1937, Cincinnati, Ohio 45201.

While the ACGIH adopted a 200 ppm level for vinyl chloride, the TLV Documentation cites studies which recommend levels from 50 ppm to 500 ppm. As you may be aware, the Manufacturing Chemists Association has contracted with independent consultants, on behalf of a group of vinyl chloride producers and consumers to conduct animal exposure studies and a comprehensive epidemiology study of vinyl chloride workers. It is hoped that results from these studies will aid in clarifying what exposure limitation would be most appropriate. However, until these results are available and in view of the range in recommendations, we considered it prudent in our operations to establish a vinyl chloride TLV of 50 ppm; further, measurements indicate that this is a feasible level for us. We urge you to give consideration to the vinyl chloride exposure levels which may be appropriate for your operations.

We would be pleased to make available our techniques for measuring low concentrations of vinyl chloride if you would consider them helpful.

Very truly yours,
SHELL CHEMICAL COMPANY

R. J. Reynolds
Manager, Vinyl Chloride
Business Center

Attachment: MCA Safety Data Sheet SD-56 (1972 Version)

DETERMINATION OF

VINYL CHLORIDE MONOMER IN AIR

Gas Chromatographic-Flame Detector Method

SCOPE

1. This method is intended for the determination of traces of vinyl chloride monomer (VCM) in air in the range from 5 to 1000 ppm v/v.

METHOD SUMMARY

2. A one-ml sample of air is analyzed by gas chromatography on either of two columns, having quite different selectivity, using a flame ionization detector. If a significant concentration is observed the identification of VCM is confirmed on another type of column. Results are calculated by comparison with a known standard.

Note 1. *CAUTION.* VCM is toxic and flammable and should be handled in a hood away from sources of ignition. The liquid should be kept cool to avoid polymerization. No copper or copper alloy should be used in contact with VCM.

APPARATUS

3.(a) *Chromatographs* with flame detector, sensitive enough to detect 10 ppm of VCM in one ml of air with at least 10% scale deflection on the recorder, under the conditions of the method.

(b) *Columns*, five feet long by 1/8-inch O.D., 0.012" wall, stainless steel tubing, one packed with 80-100 mesh Durapak Carbowax 400/Porasil C and the other with Durapak n-octane/Porasil C.[1]

(c) *Accessories*, one-ml gas-tight syringe, 50-microliter gas-tight syringe, 100-ml glass sample cylinders, vacuum pump for evacuating these; or a bottle can be used which can be flushed with the air to be analyzed and then septum capped. If glass sample cylinders with stopcocks are used, the syringe needle must reach through the stopcock into the storage chamber.

Note 2. A coulometric detector in the chloride mode would provide specific response for organic chlorides, eliminating the risk of interference from non-chloride atmospheric contaminants. An electron capture detector would probably also be satisfactory but has not been tested for this

1 Available from Waters Associates, Framingham, Mass.

Published in 1973 Shell Development Company
Printed in U.S.A.

application. Since the non-specific flame detector is used in this method two different types of column are employed to reduce materially the probability of an erroneous finding of VCM.

REAGENT

4. VCM, Matheson Company[2] or equivalent. A lecture bottle is convenient.

PROCEDURE

5. Set up the chromatograph as described in Table 1. Prepare a 100 ppm v/v VCM in air sample by adding 10 microliters of VCM vapor per 100 ml of air to a glass sampling vessel or to a serum capped bottle of known volume. The vapor can be obtained from the gas cap over the VCM liquid in the supply cylinder by venting the material at a moderate rate through a short length of tubing and sampling the exit end of the tubing with the 50 m croliter syringe. Mix the blend by rotating the vessel in a random manner or by shaking with previously enclosed glass beads. Analyze one ml of this blend using either column and note the retention time and the peak height. Repetitive analyses should agree within about ± 5 ppm. Obtain samples of the air to be analyzed and analyze them in the same way. If VCM is found in significant concentrations repeat the calibration and analyses on the other column to confirm or refute the identification of VCM.

Table 1. Conditions for Gas Chromatography

Helium Carrier Gas: flowing 30-40 ml/minute.
Hydrogen: 30 ml/minute, adjusted for optimum response.
Air: 350 ml/minute.
Injector and detector temperatures: 50-150°C.
Column temperature: Isothermal in the range 20-25°C.

CALCULATION

6. Calculate the VCM content of the unknown air sample, using peak heights corrected for the attenuation, as follows:

$$\text{VCM, ppm v/v} = 100 \times \frac{\text{Peak height of unknown}}{\text{Peak height of standard}}$$

PRECISION

7. Limited data indicate that the precision is about ± 5 ppm at 100 ppm and about ± 2 ppm at the 10 ppm level.

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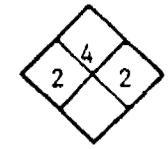
[2] Matheson Company, La Porte, Texas 77571

ADAPTED FROM USDL
FORM NO LSB-005-4-MAY 1969

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

HAZARD 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	EMERGENCY TELEPHONE NO.
Shell Chemical Company	(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, Chloroethane	TRADE NAME: Vinyl Chloride Monomer (VCM)
CHEMICAL FAMILY: Vinyl Halide	FORMULA

SECTION II HAZARDOUS INGREDIENTS*

COMPOSITION	%	SPECIES	LD_{50} ORAL	LD_{50} DERMAL	LC_{50} CONCENTRATION	LC_{50} HOURS
Vinyl Chloride	100					

Vinyl chloride has anaesthetic properties at high concentrations (80,000-120,000 ppm). Cardiac arrhythmias have been found in dogs at these levels. Liver changes have been reported in rabbits at 200 ppm, but not in rats, guinea pigs or dogs. Studies on exposed workers over a 17 year period at a mean air concentration of 160 ppm failed to reveal any overt condition attributable to VCM. One Italian report in 1970 indicated tumor development in rats at 30,000 ppm.

SECTION III PHYSICAL DATA

BOILING POINT (°F)	7	SPECIFIC GRAVITY (H_2O=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		

SECTION IV FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method used)	FLAMMABLE LIMITS	Lel	Uel
-108° F., T.O.C.	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.

*Modified by Shell Oil Company

SECTION V HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE	OSHA - 500 ppm (ceiling); ACGIH - 200 ppm (TWA); Shell - 50 ppm (TWA)
EFFECTS OF OVEREXPOSURE	See over. Also prolonged contact with skin results in freezing.
EMERGENCY AND FIRST AID PROCEDURES	Remove victim to area free of vinyl chloride vapors. Give artificial respiration if necessary. Remove contaminated clothing to prevent freezing. Remove from eyes with large amounts of water.

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 IN CASE 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.
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 organic canister mask as required.		
VENTILATION	LOCAL EXHAUST: highly recommended	SPECIAL	
	MECHANICAL (General): Highly recommended - use explosion-proof equipment	OTHER	
PROTECTIVE GLOVES	Rubber	EYE PROTECTION	Chemical goggles and/or face shields
OTHER PROTECTIVE EQUIPMENT	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.

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

DATE July 1973