FIELD SURVEY OF DOW CHEMICAL COMPANY

CHLOROMETHYLETHER FACILITIES

MIDLAND, MICHIGAN

September 8, 1972

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16. Abstract (Limit: 200 words)

A field survey was conducted at the chloromethylmethylether (107302) (CMME) facilities of the Dow Chemical Company (SIC-2869) in Midland, Michigan, on September 8, 1972. The production process, exposure potential, and protective measures practiced by the company and its workers were considered. The company employed approximately 12,000 to 16,000 persons. Approximately 4,000 blue collar workers were involved with chemical production. The production system was self contained within the processing equipment, ventilation was provided at potential leak sites, and respiratory protection was provided for emergency access. The number of personnel was kept minimal in production areas. Laundered clothing and paid shower time was provided by the company when necessary, and medical services were provided by 4 or 5 industrial hygienists, 10 technicians, 10 safety advisers, 4 physicians, and 50 full or part-time nurses. The company collected personal and area air samples for CMME and an impurity, bis(chloromethyl)ether (542881) (bis-CME), from 1949 to 1972. The current continuous monitoring system utilized an infrared analyzer. The highest time weighted average (TWA) exposures to CMME and bis-CME during August, 1972 were 0.838 parts per million (ppm) and 0.610 parts per billion (ppb), respectively. TWA exposures to CMME for seven operators and to bis-CME for 4 operators ranged from 0.10 to 0.43ppm and 0.082 to 0.201ppb, respectively.

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FIELD SURVEY

OF

DOW CHEMICAL COMPANY

CHLOROMETHYLETHER FACILITIES

MIDLAND MICHIGAN

I. BACKGROUND

In the near future, NIOSH will be responsible for development of criteria and the recommendation of a standard for occupational exposures to bis(chloromethyl) ether (bis-CME). Recent evidence has implicated this by-product as a possible potent lung carcinogen. To develop in-house expertise regarding methods of production, exposure potential and protective measures, necessary for the formulation of a criteria package, brief field surveys have been arranged for Division personnel of facilities involved in the use and manufacture of chloromethylether (CME).

On September 8, 1972, representatives of DFSCI and personnel from New York University conducted one such study of the Dow facilities at Midland, Michigan. The visit included discussions with plant personnel concerning our areas of interest, and a walk-through of the plant CME operations, research labs, and monitoring apparatus.

II. MANAGEMENT

Management personnel were extremely cooperative and helpful throughout the visit. Dr. Ralph Langner of the Industrial Hygiene

Department directed the discussion. Appended are a list of participants. Each Dow representative at the meeting discussed his particular area of expertise as related to the CME operations and led us on a tour of his facilities. Accompanying us on the tour and with us in the discussion were Roy Albert and Morton Lippmann of New York University.

III. THE PLANT

Dow was founded in 1897 for the purpose of recovering halogens from the brine wells located in the Midland area. From this modest beginning, the company has grown to be a major manufacturer of a diversified line of organic and inorganic chemicals, plastics, pharmaceutical, agriculture chemicals and magnesium metal.

At Midland, Dow has about 13,000 acres, 800 buildings and a total of 12,000-16,000 employees. This includes sales and international service people. Of these about 8,500 employees are associated with the chemical manufacturing and activities that directly concern the Midland facilities. The company is unionized and represented by the United Mine Workers.

Since there is much research activity and activities of a professional nature at Midland, the 8,500 employee population consists of about 50% white and 50% blue collar workers, a much larger percentage of white collar workers than is usually found in most industries.

IV. PLANT PROCESSES INCLUDING CME

Dow utilizes chloromethylether as an intermediate in the production of two different types of resins: anion exchange resins made at Building #458 and an electroconductive resin (DOW ECR) manufactured at Building #441. There is a batch reactor at each location to produce the chloromethylether necessary for internal use only at each work site. This system avoids

any shipping of CME within or outside the plant. Dow uses methyl alcohol, hydrochloric acid, and paraformaldehyde as the raw materials to produce CME. They are currently experimenting with different reactor conditions in order to produce as little of the bis-chloromethylether by-product as possible in the CME reactors.

In building #458 the vessels are arranged vertically to use a gravity feed system. At the top level the CME, a catalyst, and divinylbenzene-styrene copolymer beads are agitated together to chloromethylate the beads. After washing in a tank one floor below, the mixture travels down to another reaction vessel where hydrochloric acid and either a secondary or tertiary amine are added to aminate the beads. In the bottom two vessels the product is washed and filtered. The anion exchange resin beads are then ready to be packed and shipped.

The manufacture of the electroconductive resin uses CME in a similar manner to that of the anion exchange resin, with minor modifications which are of a propietary nature.

V. INDUSTRIAL HYGIENE AND SAFETY PROGRAM

At Midland, the company has a Safety and Industrial Hygiene program which includes 4-5 industrial hygiene people, plus 10 technicians, 10 safety people, 4 medical doctors, and about 50 full and part time nurses who give round the clock medical service.

Though the company has many safety committees and both management and employees take their safety effort very seriously, there is no union-management safety committee, since the union is apparently well satisfied with the company program.

Clothing is furnished on some operations, and where they are furnished they are laundered by the company. Where showers are required the men are paid shower time, however, they are available in most facilities to all employees on an optional basis.

Safety shoes are not generally required, thereby, their use is encouraged. Where safety shoes are required they are furnished.

The Dow CME facility can be considered to be typical of operations in a modern well designed chemical plant, which contains a minimum of partitions and in many cases grilled floors and windows that may be opened or closed depending on the season of the year.

The industrial hygiene philosophy employed is to completely contain the product inside the process equipment and to have local exhaust ventilation at points of potential leakage, such as around seals on rotating shafts. This allows the worker to be in the production area without having to rely upon respiratory protection. An additional safety feature is the presence of self contained Scott Air Packs placed in strategic locations in the plant areas where CME is used. In case of an unexpected discharge of CME into the room, this material would be readily detected in very small concentrations because of its acrid odor. In such a case fresh air masks would be donned. The potential for exposure to the toxic substance is further reduced by improving the engineering on the process so as to require fewer people. In addition to that, these workers spend most of their time in a pressurized control room which is isolated from the process equipment.

Another approach we have seen applied to this same problem is to stress the isolation of the worker rather than the complete containment of the hazardous material. The man works most of the shift inside a control room, sealed off from the process. For the small amount of time the worker normally spends by the equipment, he is required to wear a fresh air mask to insure that he is not being exposed.

Done properly, either philosophy works, but the approach that Dow uses has the advantage of not hampering their employees by burdening them with safety equipment which is made unnecessary by good engineering techniques.

Dow first started working with chloromethylether in the 1940's. Due to its irritating properties, the company has tried to restrict exposure to CME to the TLV for chlorine of 1 ppm. This was strictly on its irritating properties and prior to any knowledge of its carcinogenic properties.

It is estimated that there have been about 120 people who have worked with CME at Dow. Research started on this material prior to 1949 and production started in the early 1960's. At the present time about 20 people are working on the production and manufacture involving the use of chloromethylether.

VI. MONITORING SYSTEM

The monitoring system for CME and BCME is described by Richard Kupel of the Physical and Chemical Branch. This report is appended along with selected monitoring data shown to us and supplied to us by Dow.

VII. MEDICAL DATA

The basic medical program is voluntary and is performed annually in a 12' x 56' trailer. An interval medical questionnaire is filled out by the employee and reviewed by an R.N. Height, weight, and blood pressure are determined; and laboratory tests include CBC, urinalysis (dipstick), and a biochemical screening battery. Other examinations include a vitalometer, 14" x 17" PA chest x-ray, and EKG.

A comprehensive occupational medical clinic is staffed by four physicians in addition to nursing staff.

Workers with past and current exposure to bis(chloromethyl)ether receive the same basic periodical examinations as other workers. Carcinogenic hazards of bis(chloromethyl)ether reportedly have been explained to these workers by their supervisors and not by medical staff. The implementation of a sputum cytology program is being considered by Dr. Holden, who is concerned about potential iatrogenic problems associated with false positive cytology.

In 1948, the one and only case of pulmonary edema and bronchitis occurred secondary to exposure to CME.

Only one lung cancer case is known among workers with exposures to BCME. A male, heavy smoker in his 50's, developed lung cancer and no pathology is apparently available. Only approximately 120 workers reportedly have been exposed to BCME in this facility since production began in 1949.

Management has attempted to control CME exposures to 1 ppm because mucosal membrane irritation occurs at greater concentrations. The following odor limits have been experienced:

No odor	0.5 ppm
Barely detected	1.5 ppm
Easily noticed	23.0 ppm
Strong	100.0 ppm

A P P E N D I X

MEMORANDUM

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
HEALTH SERVICES AND MENTAL HEALTH ADMINISTRATION
National Institute for Occupational Safety & Health
1014 Broadway, Cincinnati, Ohio 45202

TO : Director, DLCD, NIOSH

DATE: Sept. 20, 1972

Through: Chief, Physical & Chemical Analysis Branch

FROM : Assistant Chief, P&CA Branch

SUBJECT: Report on Trip to Midland, Michigan

1. Travel Order No. PHS-090330, August 31, 1972

2. Departed Cincinnati, Ohio at 4:44 PM(EDT) on Sept. 7, 1972.

3. Arrived Saginaw, Michigan at 6:40 PM(EST) on Sept. 7, 1972.

4. Purpose of Visit: To attend a meeting with representatives of NIOSH and Dow Chemical Company, Midland, Michigan to discuss the manufacturing and analytical procedures for air sampling and monitoring for Bis-chloromethyl ether (Bis-CME). Those in attendance were:

DOW CHEMICAL CO.	NYU
Dr. Ralph Langner	Dr. Roy E. Alben
Dr. Stewart L. Bender	Mr. Morton Lippmann
Mr. G. E. Socha	
Mr. Harold Hoyle	NIOSH
Mr. Dick Deline	
Mr. V. K. Rowe	Dr. Joseph K. Wagoner
	Dr. William M. Johnson
	Mr. Harry M. Donaldson
	Mr. Patrick J. Shuler
	Mr. Richard E. Rupel

The plant process was explained in detail by Drs. Ralph Langner and Stewart L. Bender. Both men continually pressed the point that Dow Chemical believes in containing a chemical during processing rather than require workmen to wear protective equipment.

The analytical procedure used to monitor chloromethylmethyl ether (CMME) was explained by Mr. G. E. Socha. He explained that CMME was the major product used and that bis-CME was an impurity. The

CMME was monitored continuously using an infrared analyzer with a 10 meter gas cell. The CMME was controlled to <1 ppm. Twenty-four-hour atmospheric samples collected on column packing material is analyzed for bis-CME using gas chromatography and mass spectroscopy procedures. The level of bis-CME is maintained at <1 ppb. The data from the IR analyzer is fed into a computer and a daily print-out is obtained.

We were conducted on a tour of the two buildings where CMME is being used. The philosophy is quite different between Dow Chemical and Rohn and Haas. Rohn and Haas has inclosed the processing line completely and require fresh air breathing equipment to be used whenever anyone enters the processing area. On the other hand, Dow Chemical believes it is more important to contain the process so that there are no leaks and thus reduces the need for protective breathing apparatus. They do have "Scott Air Packs" available throughout the plants for emergency use. Dow Chemical does not monitor for bis-CME as such on a continuous remote basis as does Rohn and Haas.

A tour was conducted of the Toxicology Laboratories, the Analytical Laboratories and the Medical Facility. Animals are currently being exposed to various concentrations of bis-CME to determine the long term effects. The study was just recently started with no data available to date.

5. Returned: September 8, 1972.

Richard E. Kupel

cc: Mr. J. V. Crable
Mr. Harry Donaldson

DOW CHEMICAL COMPANY
Midland, Michigan

Attendance List

Roy E. Albert, M.D.	NYU Medical Center	
Stuart L. Bender	Dow	Midland
Dick Deline	Dow	Midland
Harry M. Donaldson	NIOSH	Cincinnati
Harold Hoyle	Dow	Midland
William M. Johnson, M.D.	NIOSH	Cincinnati
Richard E. Kupel	NIOSH	Cincinnati
Ralph Langner	Dow	Midland
Morton Lippmann	NYU Medical Center	
V. K. Rowe	Dow	Midland
Patrick J. Shuler	NIOSH	Cincinnati
G. E. Sochā	Dow	Midland
Joseph K. Wagoner, S.D. Hyg.	NIOSH	Cincinnati

CHLOROMETHYLETHER AND BISCHLOROMETHYLETHER

EXPOSURE DATE

(1949-1972)

SUPPLIED BY

DOW CHEMICAL COMPANY
Midland, Michigan

TABLE I

CMME EXPOSURES, ANCIENT HISTORY,

WORK AREA CONCENTRATIONS NOT TIME-WEIGHTED AVERAGES

DATE	NO. OF SAMPLES	AVG. (PPM)	RANGE (PPM)
1949	7	5.2	2.2-9.7
1952	3	1.1	<0.15-2.65
1957	230	0.7	0-12
1961	8	2.5	<1-8

SUMMARY OF BIS-CME DATA IN 441 BUILDING

	TWA CONC. (PPB) BY JOB CLASSIFICATION			
MONTH	ECR #1 Operator	ECR #2 Operator	ECR #3 Operator	ECR #4 Operator
11/71	0.816	0.884	0.257	1.587
12/71	1.559	1.786	0.420	2.907
1/72	1.244	1.412	0.326	2.251
2/72	1.557	1.668	0.404	2.442
3/72	3.270	3.600	1.212	4.353
4/72	0.380	0.384	0.119	0.486
5/72	0.121	0.140	0.049	0.157
6/72	0.194	0.231	0.080	0.255
7/72	0.164	0.191	0.071	0.194
8/72	0.169*	0.201*	0.082*	0.175*

*Through August 24, based on 20 days of data.

TABLE II

TIME-WEIGHTED AVERAGE EXPOSURE TO CDME (PPM)

JOB	1966	1970	1971	1972
OPERATOR #1	0.5			
OPERATOR #2			2.4	0.29
OPERATOR #3			1.8	0.3
OPERATOR #4			0.6	0.1
OPERATOR #5				0.43
OPERATOR #6		0.34	0.08	0.24
OPERATOR #7			0.04	0.10
OPERATOR #8			0.04	0.24

TIME WEIGHTED AVERAGE EXPOSURES (PPM) OF 458 BUILDING OPERATING PERSONNEL TO CMME AS DETERMINED BY INFRARED ANALYSIS

Month	Days of Data	Operator #5	Operator #6	Operator #7
6/72	27	0.333	0.248	0.137
7/72	25	0.219	0.156	0.087
8/72	26	0.182	0.133	0.074

SUMMARY OF BIS-CME DATA IN 458 BUILDING

MONTH	TWA EXPOSURE (PPB) #5 Operator	#6 Operator	#7 Operator
11/71	0.287	0.177	0.054
12/71	0.810	0.669	0.219
1/72	5.519	5.797	1.214
2/72	1.839	2.609	0.345
3/72	0.353	0.271	0.088
4/72	0.046	0.061	0.138
5/72	0.085	0.061	0.031
6/72	0.118	0.150	0.028
7/72	0.133	0.073	0.036
8/72	0.610*	0.058*	0.249*

*Through August 21, 1972 based on 12 days of data.

TIME WEIGHTED AVERAGE EXPOSURES (PPM) OF 441 BUILDING OPERATING PERSONNEL TO CMME AS DETERMINED BY INFRARED ANALYSIS

Month	Days of Data	ECR #1 Operator	ECR #2 Operator	ECR #3 Operator	ECR #4 Operator
6/72	29	0.375	0.543	0.168	0.357
7/72	29	0.358	0.486	0.154	0.355
8/72	27	0.648	0.838	0.285	0.634

COMPOUNDS KNOWN TO INTERFERE WITH THE INFRARED ANALYSIS OF CMME IN AIR

A. METHYLAL $CH_3-O-CH_2-O-CH_3$

B. DIMETHYL ETHER CH_3-O-CH_3

C. TRIMETHYL AMINE