U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE CENTER FOR DISEASE CONTROL NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH CINCINNATI, OHIO 45202

HEALTH HAZARD EVALUATION DETERMINATION REPORT NO. 73-160-206

## GLYCO CHEMICALS, FINCORPORATED WILLIAMSPORT, PENNSYLVANIA JULY 1975

#### TOXICITY DETERMINATION

It has been determined that employees at the reactor station were exposed to toxic concentrations of 1,3-dichloro-5,5-dimethylhydantoin (DCDMH). This determination is reached because high air concentrations of contaminant were measured during an evaluation of the workplace conducted on January 16-17, 1975. These levels exceeded both the ACGIH TLV and the OSHA standards for 8-hour time weighted average concentrations and also the State of Pennsylvania's short term (15 minute period) maximum exposure limit. Associated with the high concentrations of DCDMH measured were complaints of cough and chest discomfort in a reactor operator. The major cause of the overexposure was an accidental over reaction during the aereation process causing 100-150 pounds of 1,3-dichloro-5,5-dimethylhydantoin to overflow from the reaction vessel.

During previous visits on December 12, 1973, and May 6-7, 1974, visual observations of the work area indicated that the drum packaging operation was not well controlled. Verbal recommendations were made concerning work practices and engineering. These recommendations were accomplished prior to the January 1975 visit, resulting in a good housekeeping program and improved local exhaust ventilation at the packaging operation.

Detailed information concerning environmental and medical results are contained in the body of the report.

## II. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are available upon request from the Hazard Evaluation Services Branch, NIOSH, U.S. Post Office Building, Room 508, 5th and Walnut Streets, Cincinnati, Ohio 45202.

Copies have been sent to:

- a) Glyco Chemicals, Incorporated
- b) Authorized Representative of Employees
- c) U.S. Department of Labor Region III
- d) NIOSH Region III

Page 2 - Health Hazard Evaluation Determination 73-160

For the purposes of informing the approximately 15 "affected employees" the employer will promptly "post" the Determination Report in a prominent place(s) near where effected employees work for a period of 30 calendar days.

## III. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S. Code 669(a)(6) authorizes the Secretary of Health, Education, and Welfare, following a written request by any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The National Institute for Occupational Safety and Health (NIOSH) received such a request from management and from an authorized representative of the employees regarding exposures to 1,3-dichloro-5,5-dimethylhydantoin during the manufacturing and packaging operations.

#### IV. HEALTH HAZARD EVALUATION

A. Description of Process - Conditions of Use

The areas evaluated were buildings 3 and 26. In building 3, dimethylhydantoin, soda ash and chlorine gas are made into a slurry. After a prescribed time of reaction, the slurry which now is, 1,3-dichloro-5,5-dimethylhydantoin (DCDMH), is aereated.

This compound is then dropped into a centrifuge where the water is removed. The semi-dry material is then fed into a fluid bed dryer. After the material is dried, it is transported to building 26 into a cyclone receiver.

The DCDMH is fed onto a vibratory screen and packaged in drums as a coarse or fine product. Local exhaust ventilation is supplied at the packing, centrifuge and cyclone receiving stations.

### B. Study Progress and Design

On December 12, 1973, an initial environmental and medical survey was conducted at Glyco Chemicals Inc. On May 6-7, 1974 an atmospheric evaluation was conducted by a NIOSH industrial hygienist and medical interviews were conducted by a NIOSH medical officer. Analysis of air samples was carried out, but the results were inaccurate because of insensitivity of the analytical method. The NIOSH laboratory was requested to develop an analytical method more sensitive Page 3 - Health Hazard Evaluation Determination 73-160

to the contaminant. Subsequently on January 16-17, 1975, a second atmospheric evaluation and non-directed interviews with employees were conducted before and after the work shift to determine if any adverse health effects were experienced from exposure to the contaminated air.

C. Evaluation Methods

1. Medical evaluation encompassed the following:

(1) Questionnaire interviews and examinations. These were conducted with individuals who had long term work exposures to DCDMH. A medical history and physical examination were carried out with emphasis on those systems which have been known to be adversely affected by DCDMH or related hydantoin compounds (eg. diphenyl hydantoin) - i.e. eyes, ears, nose and throat; respiratory; gastrointestinal; reticuloendothelial; and neurologic systems.

(2) Review of blood test results which men exposed to DCDMH have had performed by the company.

(3) Review of the health status of men who had worked with DCDMH in past years.

2. Environmental Methods

Employee exposure samples and general air samples were collected in impingers containing an alkaline solution and utilizing personal air sampling pumps. The DCDMH concentrations were determined utilizing its chlorinating properties. The free chlorine liberates iodine from an acidified solution and the liberated iodine is measured spectophotometrically.

Ventilation determinations and air flow patterns were measured utilizing Alnor Jr. velometer and Kitagawa air flow indicator tubes.

D. Evaluation Criteria

Environmental

The occupational health standard promulgated by the U.S. Department of Labor (Federal Register, June 27, 1974, Title 29, Chapter XVII, Subpart G, Table G-1)<sup>1</sup> and the American Conference of Governmental Industrial Hygienists (ACGIH) applicable to this evaluation are as follows:

Substance

8-Hour Maximum Average Exposure

 $0.2 \text{ mg/M}^{3}$ \*

1,3-Dichloro-5,5-dimethylhydantoin

Pennsylvania's Rules and Regulations, Chapter 201, Places of Employment, Subchapter A, Threshold Limits, Table III<sup>2</sup>

Page 4 - Health Hazard Evaluation Determination 73-160

Substance

15 Minute, Maximum Average Exposure

1.3-Dichloro-5,5-dimethylhydantoin

 $0.5 \text{ mg/M}^{3}$ \*

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\*denotes - milligram of substance per cubic meter of air.

Medical

Some comment regarding the toxicity of DCDMH is appropriate. DCDMH was first manufactured commercially in the late 1930's but did not find a large market until World War II when it was used as a bacterial decontaminating agent, dissolved in tetrachloroethane.<sup>3</sup> In the late 1940's it was introduced as a laundry bleach and has since found use as an organic bleaching agent in the textile industry, a chlorinating agent for swimming pools, as well as other uses.<sup>4</sup> Despite apparent widespread use, DCDMH has undergone little toxicologic<sub>3</sub>study.<sup>5,6,7</sup> The present federal standard (TLV) for DCDMH is listed as 0.2 mg/M° over an 8-hour time weighted average period. The basis for this standard comes primarily from a communication to the TLV committee in February, 1964, describing the onset of acute irritant nose and throat symptoms at concentrations greater than 0.2 mg/M<sup>3</sup> per cubic meter. Although not extensively studied, its toxicologic and irritation properties can be predicted from the corrosive effects this agent has when it comes into contact with moist surfaces, namely burning of the eyes, burning and watering of the mucous membranes of the nose and throat, and contact irritant dermatitis. Toxic systemic effects have not been noted with DCDMH, but the medical literature is replete with information regarding another hydantoin, specifically 5,5-diphenylhydantoin (DilantinR) as well as 3-methyl-5,5-diphenylhydantoin (Mephenytoin<sup>R</sup>). Adverse effects from these drugs (which are used generally as antiarrhythmics and anticonvulsants) include: gingival hyperplasia, various exanthemas, hematologic abnormalities, lymphadenopathies, hepatitis, dyscollagenosis, endocrine and neurologic abnormalities.8,9,10,11 It must be emphasized that, although they are related structurally, DCDMH and diphenylhydantoin differ considerably in their chemical composition. Consequently adverse effects associated with diphenylhydantoin ingestion may have no relationship to DCDMH exposure. Furthermore, usual diphenylhydantoin exposure is by ingestion whereas DCDMH is by inhalation and skin contact.

E. Results

1. Environmental

During the atmospheric evaluation conducted on January 16-17, 1975, six(6) personal samples and general air samples were collected at the fluid bed drier, reactor and packaging stations. Employee exposure at the reactor station for an 8-hour time weighted average(TWA) period was 2.23 milligrams per cubic meter. During the over-reaction, one sample of 50 minutes duration was taken.

## Page 5 - Health Hazard Evaluation Determination 73-160

Air concentrations during this period reached 6.62 milligrams per cubic meter of air. The Pennsylvania Department of resources in their short term limit values lists a permissible level of 0.5 milligram per cubic air, maximum average exposure for a 15 minute exposure.

Time weighted average exposure at the packaging station was 0.166 milligram per cubic meter of air. This did not exceed the ACGIH or federal health standards.

Air velocity measurements taken at the packaging station on May 6-7, 1974, were 50 to 75 feet per minute. Recommendations were made at that time to make alterations in the local exhaust ventilation design. Following the completion of the alterations, on January 16-17, 1975 air velocity measurements at the above stations were 225-250 feet per minute.

2. Medical

(1) Questionnaire interviews and examinations Medical questionnaire interviews and physical examinations were carried out at the time of the first NIOSH visit. Eight men were interviewed and examined. Seven of the men whose jobs involved processing and packaging of DCDMH were exposed to it for approximately 12 hours/week. Their average duration of exposure to DCDMH was 15 years. The other employee was an electrician (maintenance department) who occasionally had close contact with DCDMH in the maintenance of the processing equipment. The primary complaints which the men had when they received a "dose" (i.e. a concentrated exposure) of DCDMH were a runny nose (6/8), burning or "scratching" sensation in the eyes (5/8), and a sore throat (4/8). Other complaints included cough, shortness of breath, sneezing, and chest pain. These symptoms subsided usually several hours to a day or two after exposure and occurred several times per month. A number of the men also mentioned skin irritation particularly during the summer months when they perspired to a greater extent. Nearly all men said they could avoid nose, throat, and chest symptoms with the use of respirators and no one experienced such symptoms when gas masks were used. The chief complaint about use of a respirator or gas mask was the occasional skin irritation where the mask had contact with the face. Except for these complaints, no other system (i.e. gastrointestinal, reticuloendothelial or neurologic) elicited positive findings.

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Physical examination involved the following areas: oropharynx, lymph nodes, lungs, heart, reflexes, and peripheral sensation (pin prick vibration, position sense). All examinations were considered within normal limits with two exceptions: (a) one individual had mild decrease in sensation to pin prick in one extremity, but this was readily explained by a history of a cervical disc compression some years before, which had left his entire hand numb at the time; (b) one individual had diminished vibration sensation in both lower extremities with pin prick and position sensation being normal; no easy explanation was afforded in this instance.

# Page 6 - Health Hazard Evaluation Determination 73-160

During the last NIOSH visit, medical questionnaire interviews took place with two workers (drum filler and reactor operator) before and after the work shift. The drum filler noted the development of no symptoms over the shift, while the reactor operator (who was a non-smoker) complained of coughing and chest pains developing over the shift. These symptoms were related to an accidental spill of about 125 pounds of DCDMH. The symptoms subsided rapidly after exposure terminated.

(2) Review of blood test results

Blood counts (hemoglobin, white blood count, and differential) were reviewed in the seven production employees who were interviewed and examined. Blood test results dated from June, 1967, until January, 1974. All men had two or more blood count determinations during this period. The results are shown in Table I.

> (3) Review of health status of men who had worked with DCDMH in past years.

Thirteen men were interviewed who had worked in the manufacturing of DCDMH for periods of time ranging from 2 to 19 years (average 9 years) and were currently employed in other areas of the plant. All were generally in good health. The problems noted in this group of men were: individual #2 related a history of red, scaly, itching rash of the hands in the past after handling DCDMH. #3 had a history of gout; #6 described sinus problems aggrevated when working with DCDMH. #7 had a history of hypertension.

- F. Discussion and Conclusion
  - 1. Environmental

During the visit of May 6-7, 1974, there was a malfunction in the fluid bed drier. It was noted that maintenance personnel entered the drier without testing the atmosphere or being supplied protective clothing. Entry into the drier can be considered entry into a confined space. There was a possibility of lack of oxygen and also chlorine gas being present. Additionally, it is felt that DCDMH only releases chlorine when it is wet. Doing work in the drier causes men to perspire and the contact of powder with the skin can cause dermatologic problems and possibly release some chlorine gas.

It was also noted during the accidental malfunction that personnel did not properly utilize the provided respiratory protective equipment. This was discussed with management at the time of the visit and appropriate use of the equipment was to be included in the training program.

# Page 7 - Health Hazard Evaluation Determination 73-160

## 2. Medical

The results from the medical interviews and physical examinations indicate that DCDMH acts as a mucous membrane and skin irritant at times but appears not to cause systemic toxicity at the concentrations to which workers are presently exposed or have previously been exposed. There is also suggestive evidence that, with sufficient acute levels of exposure, it may cause bronchoconstriction and lead to chest discomfort or tightness. This latter effect appears to be irritant, rather than allergic, in nature. Furthermore, these effects seem to be brought on by short-term high level exposure to DCDMH. A good example of this was noted during the last NIOSH visit when a reactor operator noted cough and chest discomfort shortly after an accidental spill of DCDMH.

Review of the blood test results over a several year period in seven long-term employees showed no evidence of deleterious effects in the hemoglobin, white blood cell, or differential counts. Also, review of the health status of thirteen other men who had worked for considerable periods in DCDMH production showed no systemic problems of particular note. All of the above information suggests that long-term exposure to DCDMH poses no systemic toxicity for workers.

The following recommendations are made as a result of this evaluation:

- Institution of engineering and/or education controls to prevent over-reactions. The following engineering controls, were discussed previously: complete enclosure, pH controls, heat controls and alarms.
- (2) Periodic education of all employees in the proper utilization and maintenance of personal respiratory protective equipment.
- (3) Prior to entry into confined spaces, one should:
  - a) test the atmosphere for contaminant and oxygen content or
  - b) in lieu of the above, utilize air line respirators;
- c) supply employees entering confined spaces impervious clothing
  (4) Maintenance of all local exhaust ventilation systems at maximum capacity. A minimum air velocity of 150 cubic feet of air per minute per square foot of open face area is recommended at the packaging station.
  - (5) Installation of local exhaust ventilation at the reactor opening.

Medical: An appropriate medical program should include:

Complete occupational history.

- (2) Medical history focusing on the respiratory and dermatologic systems.
- (3) A physical examination focusing on the respiratory system.

## Page 8 - Health Hazard Evaluation Determination 73-160

It should be recognized that individuals with past or present respiratory or dermatologic problems are particularly susceptible to ill effects when exposed to even low levels of chlorine gas. For this reason, the above recommendations are made. Furthermore, consideration should be given to periodic evaluation of respiratory function (e.g. pulmonary function testing). A suitable program should include the above as preplacement and periodic examinations.

# V. REFERENCES

- 1. Federal Register, Vol. 39, No. 125, Part II, Subpart G, June 27, 1974.
- Pennsylvania Department of Environmental Resources, Title 25, Rules and Regulations, Subpart D, Environmental Health and Safety, Article IV, Occupational Health and Safety, Chapter 201, Places of Employment, Subchapter A, Threshold Limits, Table III, November, 1971.
- 3. Encyclopedia of Chemical Technology, 4:920 (1964).
- 4. "Dichlorodimethyl Hydantoin Properties and Uses," DuPont Biochemical Bulletin, May, 1941.
- 5. Unpublished correspondence from Toxicologist, R.A. Taft, S.E.C. (1963).
- 6. Stokinger, H.E., Woodward, R.L. J. Amer. Water Works Assoc. 50:515 (1958).
- 7. Communication to TLV Committee (February, 1964).
- 8. Grob, P.J. & Herold, G.E., Brit. Med. J. June 3, 1972, 557-563.
- 9. Gams, et al, Annals of Int. Med. V. 69, No. 3, Sept. 1968, 557-568.
- 10. Moore, M.T., J. of AMA, V. 171, No. 10, Nov. 7, 1959, 1328-1333.
- 11. Marques-Monter, et al, The Lancet, Aug. 22, 1970. 426-427.

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		1/74			9/72			5/70			4/68			5/67	
	Н	WBC	Diff.   SLME*	НБ	WBC	Diff.	Hb	WBC	Diff.	Hb	WBC	Diff.	Hb Hb	WBC	Diff.
#1	14.6	9.6	63 25 8 3	16.5	10.6	63 29 7 0							16	15000	67 27 5 1
#2	16.7	8.0	62 25 10 2					-					15.8	8300	68 24 7 1
#3	14.8	6.9	63 30 6 1	14.2	5.3	53 39 6 2	15.2	7.2	66 29 3 2	15.0	6.0	49 44 5 1	14.8	6.1	61 '32 4 1
#4	16.0	6.1	59 29 8 2	14.6	6.6	55 32 9 2	16.2	6.4	48 43 5 4				17.1	7.3	59 28 9 4
#5	15.5	5.8	57 36 2 3	15.9	6.6	66 27 6 1									
#6	15.1	9.4	54 36 3 7	16.0	9.6	57 25 9. 8	15.0	7.9	45 41 6 8				14.8	9500	50 41 5 4
#7	15.7	7.3					16.1	6.9	52 39 9 1				15.6	5.7	54 38 8 0

\*The numbers refer, from top to bottom, to: segmented forms(S), lymphocytes(L), monocytes(M), eosinophils(E). For example, in 1/74 individual #1 had a differential of: 63(S), 25(L), 8(M), 3(E).

7

LOCATION	SAMPLE NUMBER	AIR VOL LITERS	CONCENTRATION mg/M <sup>3</sup> *	TIME DURATION MINUTES	CALCULATED 8-HR. T.W.A.**
Reactor operator's exposure respirator worn for 48 minutes	307	83.4	.804	202	A.
52	310	21.0	6.619	48	2.229
	344	61.3	.189	140	
Drum packaging operator's exposure	298	90.2	.211	192	
	139	88.4	.208	188	0.166
General air fluid bed drier	207	133	.178	350	0.130

1,3-Dichloro-5,5-dimethylhydantoin Air Concentration Data

 $*mg/M^3$  - denotes - milligrams of substance per meter of air samples \*\*T.W.A. - denotes - Time Weighted Average

15

TABLE II

# SUPPLEMENT #1 TO SHORT TERM LIMITS FOR EXPOSURE TO AIRBORNE CONTAMINANTS A Documentation 1967-1969



Pennsylvania Department of Health Division of Occupational Health P. O. Box 90 Harrisburg, Pennsylvania 17120

## 1, 3 – DICHLORO – 5, 5 – DIMETHYLHYDANTOIN

## Short-term limit: 0.5 mg/m<sup>3</sup> for 15 minutes

ACGIH (Documentation, P 60, 1966) threshold limit value is based on pharmocology of hydantoins and conversion of aqueous dosage to an air TLV, using a safety factor of 2.5. The compound releases hydrochlorous acid and, at PH 9, it decomposes.

Unpublished data from Pennsylvania Department of Health files indicate that extreme irritation was experienced by industrial hygienists from an average concentration of about  $2 \text{ mg/m}^3$ . The lowest concentration giving rise to symptoms was about 0.7 mg/m<sup>3</sup>.

Pennsylvania Department of Health, Division of Occupational Health, P. O. Box 90, Harrisburg, Pa. 17120