U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
CINCINNATI, OHIO 45226

HEALTH HAZARD EVALUATION DETERMINATION
REPORT NO. 74-93-296

CALHIO CHEMICALS, INC.
PERRY, OHIO

JUNE 1976

I. TOXICITY DETERMINATION

It has been determined based upon environmental and medical evaluations conducted at Calhio Chemicals, Inc., Perry, Ohio on September 10, 1974 and March 9, 1976 that no evidence of an excessive incidence of chronic disease in workers was found which could be associated with any of the substances in use including perchloromethyl mercaptan. However, subjective evidence of transient irritation associated with perchloromethyl mercaptan during the first plant visit and with Captan® dust, chlorine gas, and imide dust during the follow-up visit was found. This determination is based upon an evaluation of workers and the environment including: medical questionnaires, physical examinations, review of the causes of death of employees, and personal and area samples for air concontaminants.

II. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are available upon request from NIOSH, Division of Technical Services, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. Copies have been sent to:

a) Calhio Chemicals, Inc., Perry, Ohio
b) United Steelworkers of America
c) U. S. Department of Labor - Region V
d) NIOSH - Region V

This report shall be posted in a prominent place(s) accessible to the workers 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.C. 669(a)(6), authorizes the Secretary of Health, Education, and Welfare, following a written request by an 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 an authorized representative of employees, United Steelworkers of America, regarding exposure of workers to perchloromethyl mercaptan and the sudden death of a 35 year old employee.

IV. HEALTH HAZARD EVALUATION

A. Process Description - Conditions of Use

The process at Calhio Chemicals, Inc. produces two fungicides: Folpet® and Captan®. At the time of the initial survey in September, 1974, the plant was manufacturing Folpet® which is prepared by reacting perchloromethyl mercaptan (PMM) with the sodium salt of phthalimide. Captan®, which is the major product produced at this plant, is prepared by reacting the sodium salt of tetrahydrophthalimide (imide) with PMM. The Captan® is filtered and dried and the product is packed in 50 pound bags for shipment and was being manufactured at the time of the follow-up visit in March 1976.

The PMM for manufacture of either fungicide is prepared in batch reactors by chlorinating carbon disulfide in the presence of an iodine catalyst. In addition to the raw materials, waste sulfur chloride consisting of sulfur monochloride and carbon tetrachloride are produced as by-products in the reactors. The PMM is separated from the waste sulfur chlorides by distillation.

The manufacturing process is a closed system with few exceptions, and exposure occurs primarily as the result of process leaks, accidental spills, or maintenance work. Three sample points are available for obtaining process samples for quality control purposes, but at the time of the follow-up visit only one was being used. Each sample point is equipped with local exhaust ventilation. There is also a bagging station for the final products which is also equipped with local exhaust ventilation. Maintenance work was being performed on a batch reactor at the time of the initial visit; this type of work may result in non-routine exposure to some workers, especially mechanics and their helpers.

B. Evaluation Design

The manufacturing areas were inspected by the NIOSH investigators while accompanied by representatives of the employer and employees. Process operators and maintenance workers judged to have the greatest potential for exposure were selected for assessment of their time-weighted exposure to PMM, carbon disulfide, and carbon tetrachloride. Area sample locations also were selected for measurement of sulfur monochloride and carbon tetrachloride levels. Peak exposures to carbon disulfide, chlorine, and carbon tetrachloride were evaluated with detector tubes. A cross-section of the plant work force was selected for detailed medical evaluation by obtaining medical histories, performing physical examinations, and reviewing available death certificates.

C. Evaluation Methods

Time weighted average measurements of PMM and carbon tetrachloride were obtained by trapping their vapors on charcoal tubes and analyzing by the method of White, et.al.[1]. Time-weighted average measurements of carbon disulfide were evaluated by the charcoal tube sampling and analytical

methods of McCammon, et.al.[2] Sulfur monochloride was measured by collecting samples in midget impingers containing 0.1 N sodium hydroxide and analyzing the liberated chloride ion[3]. Peak exposures to carbon disulfide, carbon tetrachloride, and chlorine were measured with length of stain detector tubes.

D. Criteria for Assessing Workroom Concentrations of Air Contaminants

1. Standards for Air Contaminants

The two sources of criteria used to assess workroom concentrations of air contaminants in this evaluation were: (1) the recommended environmental standard for exposure to carbon tetrachloride contained in the NIOSH Criteria Document and (2) recommended threshold limit values (TLV's) established by the American Conference of Governmental Industrial Hygienists (1975) for carbon disulfide, chlorine, PMM, and sulfur monochloride. The 8 hour time-weighted average health standards of the U.S. Department of Labor (Federal Register, June 27, 1974, Title 29, Chapter XVII, Subpart G) are identical to the TLV's for these four substances. A summary of the environmental evaluation criteria is:

Substance	Permissible 8-hour time-weighed average exposure (ppm)*
Carbon disulfide	20 (60 mg/M^3)(a)
Carbon tetrachloride	2 (b)
Chlorine	1.0 (3 mg/M^3)
Perchloromethyl mercaptan	0.1 (0.8 mg/M^3)
Sulfurmonochloride	1.0

* ppm - Parts of vapor or gas per million parts of air.

(a) For the Federal Standard a ceiling concentration of 30 ppm with a maximum duration of 30 minutes with an acceptable maximum peak of 100 ppm also applies.

(b) A time-weighted average exposure for up to a 10 hour workday, 40 hour workweek.

There currently is no occupational health standard of TLV for imide dusts.

2. Industrial Experience with Perchloromethyl Mercaptan

An environmental-medical study has been reported by Blagodatin, et.al.[4] which was performed at a Russian plant manufacturing perchloromethyl mercaptan. The environmental data from this study are contained in Table I. The process was not entirely enclosed which probably accounts for the environmental concentrations of PMM many times in excess of those measured at Calhio. The health of 62 workers (39 males and 23 females) mainly in the age group 21-30, was evaluated; the work force had 1 1/2 to 2 1/2 years of work experience in the plant. Eye irritation was associated at least in part with perchloromethyl mercaptan vapors. Objective observation of respiratory organs, gastro-intestinal tract, liver, and nervous system did not reveal significant deviations from normal. However, emergency situations resulted in six cases of acute intoxication, five of these cases were as a result of perchloromethyl mercaptan exposure.

E. Discussion of Results

1. Environmental

The results of time-weighted average measurements made on September 10, 1974 are presented in Table 1. The results for PMM, the primary substance of the evaluation, were less than the detection limit of the analytical method which was 9 micrograms per charcoal tube for all measurements. The results of time-weighted average personal samples for PMM ranged from less than 0.04 to less than 0.15 ppm, the differences in concentration are due to differences in collected air volumes. These results of time-weighted average concentrations for PMM cannot be interpreted since the detection limit of the analytical method is too high and it was not known if the environmental criteria had been exceeded or if an analytical procedure with a lower detection limit would bring all results within the environmental criteria. Carbon disulfide levels ranged from 0.008 to 0.07 ppm for personal samples with area samples ranging form 0.003 to 0.08 ppm. Detector tubes used to determine peak levels of chlorine, carbon disulfide, and carbon tetrachloride were all less than the detection limit of the tubes with the exception of a slight color change which could not be quantitated for carbon disulfide noted near a sampling station. Measurements were made to evaluate peak levels with six carbon disulfide, four chlorine, and three carbon tetrachloride detection tubes.

Two area samples were obtained in the reactor area to measure levels of sulfur monochloride. At the sample location near the PMM Control Room a concentration of 0.11 ppm was measured while a sample located near the C-2 Reactor resulted in a measurement of 11.4 ppm. The C-2 Reactor was not operating, its cover was removed and maintenance work was being performed; this result did not represent actual exposure since workers were in and out of the immediate area.

During the evaluation, smoke tubes were used to observe the effect of the local exhaust ventilation at the three sampling stations. The exhaust ventilation was observed to be effective in removing the smoke from the area where vapors would be generated during quality control sample collection. However, the damper between the local exhaust hood and the main header was closed in one local exhaust duct, rendering the local exhaust at that station ineffective.

Development work was accomplished through a NIOSH contract to determine if a sampling and analytical method could be developed with an improved detection limit for measurement of PMM exposure levels. A follow-up evaluation was conducted on March 9, 1976 at which time a sampling and analytical method for PMM with a detection limit of 0.5 µg per charcoal tube was utilized. The time-weighted average exposures for two workshifts of production and maintenance workers were evaluated; samples also were obtained to evaluate time-weighted average exposures to carbon tetrachloride. Results for sampling conducted on March 9, 1976 are presented in Table 2. All results for PMM were less than the detection limit; however, the lower detection limit of 0.5 µg per charcoal tube results in a concentration range of <0.0007 ppm to <0.005 ppm depending upon air sample volumes which is considerably lower than the environmental criteria cited in this

evaluation. The results of carbon tetrachloride sampling were also less than the detection limit of the sampling and analytical method, resulting in levels of <0.41 ppm and <0.51 ppm which are also well below the NIOSH recommended environmental level.

The effectiveness of the local exhaust at the Captan® bagging station was observed by using a smoke tube. A "mancooler" fan was located so as to blow air onto the operator at the bagging station and was noted to interfere with the local exhaust effectiveness at this station by noting that the smoke was dispersed before it could be completely trapped by the exhaust hood. During the second shift, a chlorine leak near the bagging station resulted in respiratory irritation to some workers. Two detector tube measurements for chlorine gas in this area shortly thereafter did not detect the presence of chlorine.

2. Medical

Twenty-three (23) individuals were interviewed and examined on September 10, 1974. History and/or physical examination revealed evidence of the following medical problems:

Age Group	No. in Group	Medical Problem
20-29	3	None - 3
30-39	2	Anxiety - 1 None - 1
40-49	6	Chronic Obstructive Pulmonary disease - 1 Peptic ulcer disease - 1 Hypertension - 2 Ruptured disc - 1 Myocardial infarct - 1 None - 1
50-59	12	Hypertension - 4 Chronic obstructive pulmonary disease - 1 Peptic ulcer disease - 1 None - 6

The medical problems that are noted above are all very common and do not appear to be excessive in number for the age group in which they are found. In the literature, there is no reported relationship between PMM and any of the above diagnoses.

In reviewing the eight death certificates of men who died over the past 15 years while in the employ of Calhio, the following causes of mortality were identified: 4 men (average age 50 years) died from diagnosed or presumed myocardial infarction; 4 men (average age 52 years) died from

other causes which include cerebrovascular disease, chronic alcoholism and pneumonia, cardiac arrest during induction of anesthesia, and pulmonary edema resulting from chlorine gas inhalation. Comparing these data with U.S. Vital Statistics Tables, it was found that these death certificates do not reveal an inordinate number of deaths from myocardial infarction over the 15-year time period.

A survey of the literature reveals no known relationship between PMM and sudden death or heart disease. Indeed, the literature of PMM is quite scanty. It is known from experimental studies that mice and rats exposed for 15 minutes at 45 ppm of PMM died within one or two days from pulmonary edema. At lower concentrations men who were exposed developed strong eye, throat and chest irritation; nausea also resulted.[5]

The risk factors for sudden death are the same as those for atherosclerotic coronary artery disease, namely, elevated blood pressure, elevated blood cholesterol, obesity, diabetes mellitus, cigarette smoking, and physical inactivity. In the United States and Western Europe, the leading cause of death is cardiovascular disease; atherosclerotic coronary artery disease is the cause of two-thirds of all the cardiovascular deaths in men.[6]

In the unfortunate case of the worker who died suddenly in June 1974, the outstanding finding at autopsy was severe occlusive atherosclerotic coronary artery disease that involved all three major coronary vessels. This finding was associated with a normal-sized heart and interstitial fibrosis and focal myocarditis. It is most likely that his sudden death resulted from myocardial infarction and superimposed arrhythmia rather than chronic interstitial myocarditis.

> "....Myocarditis is no longer considered a proper diagnosis in cases of myocardial infarction due to coronary artery occlusion, even though an inflammatory reaction is elicited by injury of the muscle fibers. Diffuse and focal fibrosis of the myocardium associated with hypertension and coronary artery disease should <u>not</u> (emphasis - mine) be classified as chronic myocarditis or fibroid myocarditis since fibrous scars are due to the healing of the inflammatory lesion."[7]

Seven men (30%) noted symptoms that they related to PMM during times when exposure to PMM might be higher than that on an average working day, namely, during spills, breaking into PMM lines for repair, or when taking PMM samples. These men related the following symptoms: headache, burning watery eyes, sore throat, burning nose, chest discomfort, and nausea and vomiting. On the day of the visit, which was a usual working day, none of the men noted any of the above symptoms. Physical exams revealed inflamed mucous membranes of the eyes, nose, and throat. The incidence of these symptoms in smokers and non-smokers was not statistically different.

From the above worker interviews it would appear that PMM may produce irritation under circumstances when the exposures to PMM are greater than usual--spills, maintenance operations and sampling.

On March 9, 1976, a non-directed questionnaire was administered to employees of Calhio Chemicals who worked in the areas where perchloromethyl mercaptan (PMM) is found. Twenty-four (24) persons on the first and second shifts were interviewed. Seventeen persons worked on the first shift and seven on the second shift. The group interviewed included three women and 21 men, whose mean age was 42 years (range: 18-60 years). Mean duration of employment was 10.3 years (range: 3 months - 22 years) and mean duration of employment at present job was 5.5 years (range: 6 weeks - 22 years). The following numbers and types of personnel were interviewed.

Machine Operator:	6
Maintenance (including mechanics and electrical trainees):	11
Packer:	5
Laborer:	1
Welder:	1
Total	24

The questionnaire was specifically directed toward finding out whether or not during the shift the employee developed any of the following symptoms and to what they could be related by the interviewee: irritation of the mucous membranes of the eyes, nose, throat; chest discomfort; coughing; wheezing, difficulty breathing, shortness of breath; nausea and/or vomiting; and headache. Each person was specifically asked what job he or she performed as well as whether or not anything unusual (such as broken lines, chemical spills, etc.) occurred during the course of the shift.

Twelve persons (50%) out of the 24 persons interviewed did not report the development of symptoms over the course of the shift. The remaining 12 persons reported the development of symptoms over the course of the shift. Table 3 summarizes the symptoms that were reported on the day of the NIOSH study. On the day of this study, a chlorine gas line broke resulting in reported, acute symptoms, in four persons. The remaining symptoms were related to dusts of Captan® or imide encountered during packing, mechanical difficulties or while working in the areas where dusts are present. It should be noted that none of the symptoms were related to PMM.

It is concluded that employees have experienced symptoms of mucous membrane irritation related to dusts of Captan® and less frequently to vapors of perchloromethyl mercaptan, resulting from process leaks or accidental spills, exposures which did not occur during this evaluation. Workers reported similar symptoms due to imide dust less frequently.

V. RECOMMENDATIONS

1. Local exhaust systems should be inspected at the beginning of each shift to insure proper operation.

2. A respirator with a full facepiece approved by NIOSH should be worn when short-term exposures which might cause irritation are likely to occur to Captan®, imide, and PMM. Such occurrences may include but not necessarily limited to quality control sampling, cleaning up spills, and maintenance work near reactors.

3. The "mancooler" fan at the Captan® bagging station should be moved so it won't cause any disruption to dust capture to the exhaust hood at this station.

4. In addition to pre-employment and periodic examinations, termination physical examinations are recommended.

VI. REFERENCES

1. White, W.D., Taylor, D.B., Mauer, P.A. and Kupel, R.E. A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere. Am. Ind. Hyg. Assoc. J., Vol. 31, Mar-Apr, 1970.

2. McCammon, C.S., Quinn, P., and Kupel, R.E., A Charcoal Sampling Method and a Gas Chromatographic Analytical Procedure for Carbon Disulfide, Am. Ind. Hyg. Assoc. J., ppgs. 618-624, August, 1975.

3. Book of ASTM Standards, Mercuric Thiocyanate Method, part 23, ppgs. 21-28.

4. Blagodatin, V.M., et.al., Some Problems of Labor Hygiene and the Status of Workers Occupied in the Manufacture of Phthalan, Gig. Truda 12(12), 35-37, 1968.

5. Documentation of TLV's for Substances in Workroom Air, ACGIH, 1971, p. 202.

6. J. Anders Vedin, Sudden Death: Identification of High Risk Groups, Am. Heart Journal 86: 124-132, 1973.

7. Charles K. Friedberg, Diseases of the Heart, Philadelphia, W. B. Saunders, p. 984.

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TABLE 1

RESULTS OF PERSONAL AND AREA ENVIRONMENTAL SAMPLING

September 10, 1974

CALHIO CHEMICALS, INC.
PERRY, OHIO

Job Description	Time of Sample (min.)	Concentration (ppm) Perchloromethyl Mercaptan	Concentration (ppm) Carbon Disulfide	Comments
PMM Operator	243	<0.06	0.02	
Packer Operator	250	<0.07	0.07	
Folpet Operator	235	<0.06	0.04	
Laborer	200	<0.05	0.01	
Mechanic	204	<0.05	0.009	
Maintenance Helper	201	<0.04	0.01	
Maintenance Helper	193	<0.05	0.008	
PMM Operator	151	<0.09	0.07	
Packer Operator	155	<0.12	0.06	
Folpet Operator	155	<0.08	0.02	
Laborer	155	<0.07	0.02	
Mechanic	144	<0.06	0.01	
Maintenance Helper	149	<0.07	0.01	
Maintenance Helper	144	<0.06	0.03	
PMM Operator	7.5	<0.15	0.07	Drawing QC Sample
Area	70	<0.006	0.01	Inspection Platform Near PMM Control Room
Area	70	<0.006	0.003	Inside PMM Control Room
Area	60	<0.006	0.007	Near C-2 Reactor
Area	85	<0.01	0.08	Folpet® Dop Desk

(1) Area sample for sulfur monochloride - 71 min. sample - 0.11 ppm at Inspection Platform near PMM Control Room

(2) Area sample for sulfur monochloride - 61 min. sample - 11.4 ppm near C-2 Reactor.

TABLE 2

RESULTS OF PERSONAL AND AREA ENVIRONMENTAL SAMPLING

March 9, 1976

CALHIO CHEMICALS, INC.
PERRY, OHIO

Job Description	Time of Sample (min.)	Concentration (ppm) Perchloromethyl Mercaptan	Comments
PMM Operator	417	<0.004	1st Shift
Captan Operator	410	<0.004	1st Shift
Imide Operator	412	<0.003	1st Shift
Shift Maintenance Worker	388	<0.004	1st Shift
Captan Packer	351	<0.004	1st Shift
Captan Packer-Helper	335	<0.004	1st Shift
Laborer	298	<0.005	1st Shift - working at Captan® dump station
Laborer	316	<0.005	1st Shift - working at Captan® dump station
Captan Operator	492	<0.0007	2nd Shift
Maintenance Trainee	418	<0.0009	2nd Shift
Captan Packer	461	<0.001	2nd Shift
Captan Packer-Helper	395	<0.0009	2nd Shift
Imide Operator	384	<0.0009	2nd Shift
		Carbon Tetrachloride	
Captan Operator	402	<0.41	2nd Shift
Area Sample	414	<0.51	2nd Shift - 10 feet from PMM Control Room

TABLE 3

SUMMARY OF POSSIBLE WORK-RELATED SYMPTOMS

CALHIO CHEMICALS, INC.

PERRY, OHIO

9 MARCH, 1976

JOB DESCRIPTION	SYMPTOMS REPORTED ON DAY OF NIOSH STUDY	RELATED TO WHAT
1. PACKER	Nasal irritation, cough, and wheezing	Chlorine Gas
2. MECHANIC	Eye irritation	CAPTAN dust
	shortness of breath	Chlorine Gas
3. MAINTENANCE	Eye irritation	CAPTAN dust
4. IMIDE MACHINE OPERATOR	Eyes, nose, and throat irritation; shortness of breath, coughing	IMIDE dust
5. PMM OPERATOR	Eyes, nose, and throat irritattion, wheezing, shortness of breath, and neadache	Chlorine Gas
6. PACKER	Headache, coughing	Chlorine Gas
	Eyes, nose, and throat irritation	CAPTAN dust
7. PACKER	Eye irritation	CAPTAN dust
8. CAPTAN PACKER	Sore throat, nasal irritation and discharge, chest discomfort and coughing	CAPTAN dust
9. MAINTENANCE	Nasal irritation and discharge	CAPTAN dust
10. OPERATOR	Eye, nose and throat irritation, chest discomfort, and coughing	CAPTAN DUST
11. PACKER	Eyes, nose, and throat irritation, chest discomfort, and coughing	Captan dust
12. TRAINEE	Dry throat	CAPTAN DUST

TABLE I*

CONCENTRATION OF TOXIC SUBSTANCES IN THE AIR

Substance	Max. PC	Total # of tests	Content samples, toxic (mg/cu.m)					
			none	0.1-1	1.1-5	5.1-10	10.1-20	>20
PCMM	--	91	19	8	36	7	4	5
Bisulfide of C	10	23	3	12	2	1	3	2
Ammonia	20	26	2	8	7	8	1	--
Phthalic Anh.	1	26	--	16	4	--	--	6
Phthalan	--	10	2	--	3	1	1	3
Chlorine	1	12	12	--	--	--	--	--

*From Blagodatin, et.al.[4]