

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. 76-101-376

FMC CORPORATION
BROOMFIELD, COLORADO

MARCH 1977

I. TOXICITY DETERMINATION

A health hazard evaluation was conducted by the National Institute for Occupational Safety and Health (NIOSH) on August 27 and September 8, 1976, at the FMC Corporation in Broomfield, Colorado. At the time of this evaluation, breathing zone samples were taken for methanol, ethyl acetate, isopropyl alcohol, copper, nickel, tin, trichloroethylene, acetone, Freon-11^R, chloroform, hydrochloric acid, nitric acid, aluminum oxide, and hydrofluoric acid. Concentrations of chloroform and Freon-11^R exceeded the most recent evaluation criteria. A health hazard existed at the time of this evaluation to both chloroform and Freon-11^R.

II. DISTRIBUTION AND AVAILABILITY

Copies of this determination report are currently available upon request from NIOSH, Division of Technical Services, Information and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia. Information regarding its availability through NTIS can be obtained from NIOSH, Publications Office, at the Cincinnati address.

Copies of this report have been sent to:

FMC Corporation
U.S. Department of Labor - Region VIII
NIOSH - Region VIII

For the purpose of informing the 40 affected employees, copies of the report shall be posted in a prominent place accessible to the employees for a period of 30 calendar days.

II. 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 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.

NIOSH received such a request from plant management at FMC Corporation, Broomfield, Colorado, to evaluate the potential hazards associated with exposures to methanol, ethyl acetate, isopropyl alcohol, copper, nickel, tin, trichloroethylene, acetone, Freon-11^R, chloroform, hydrochloric acid, nitric acid, aluminum oxide, and hydrofluoric acid during the manufacture of semi-conductors.

IV. HEALTH HAZARD EVALUATION

A. Process Evaluated

The FMC Corporation, Broomfield, Colorado, produces semi-conductors. There are several processes involved in the preparation of the conductors. These processes include:

Metal Electroplating--during the process of copper plating small metal parts, there is a potential for exposure to copper, nickel, tin, and hydrochloric acid. This is a new electroplating shop and was operating very efficiently during the time of this evaluation. Slot ventilation was provided with a face velocity of approximately 150 linear feet per minute.

Etching and Diffusion Areas--in this area small parts are etched with hydrochloric acid and nitric acid and are cleaned with either chloroform, methanol, or acetone. All employees were well informed regarding the proper use of these acids and solvents. All were being used with the proper precautions and under well-ventilated hoods.

Polishing, Mounting, and Assembling Areas--trichloroethylene, chloroform, Freon-11^R, ethyl acetate, and nitric acid were used throughout this area during the assembly of semi-conductors. Proper protective clothing and proper use of all these substances was being practiced at the time of this evaluation, with the exception of two workers who were cleaning a degreaser filled with Freon-11^R. One worker was grossly overexposing herself by either placing her head into the degreaser or very close to the Freon-11^R that was being removed from the degreaser.

B. Evaluation Design and Methods

Breathing zone samples were taken on almost all of the workers in this facility. Isopropyl alcohol, trichloroethylene, ethyl acetate, acetone, Freon-11^R, and chloroform were collected on organic vapor charcoal sampling tubes using Sipin pumps at approximately 50 cubic centimeters (cc) per minute. Methanol samples were collected on silica gel sampling tubes using Sipin pumps at approximately 50 cc per minute. Hydrofluoric acid and

nitric acid samples were collected in sodium hydroxide. Hydrochloric acid was collected in sodium acetate. All acid samples were collected with impingers using MSA Model G pumps at 1.5 liters per minute. Copper, nickel, tin, and aluminum oxide samples were collected on AA filters using MSA Model G pumps at 1.5 liters per minute.

Copper, nickel, tin, and aluminum oxide samples were analyzed by atomic absorption spectroscopy. Methanol, ethyl acetate, isopropyl alcohol, trichloroethylene, acetone, Freon-11^R, and chloroform were analyzed by gas chromatography. Hydrofluoric acid was analyzed by ion specific electrode. Nitric acid was analyzed colorimetrically. Hydrochloric acid was analyzed turbidimetrically.

Approximately 20 workers were interviewed. Two of these workers complained about previous exposures to hydrofluoric acid. One of the workers suggested that the hydrofluoric acid exposure caused some nerve damage in her fingers. The other worker had only minor irritation from exposure to hydrochloric acid. Both workers were briefed on proper procedures when using these acids.

C. Criteria for Assessing Workroom Concentrations of Air Contaminants

The two sources of criteria used to assess workroom concentrations of air contaminants in this evaluation are: (1) NIOSH recommended criteria for occupational exposures and (2) recommended threshold limit values (TLV's) and their supporting documentation as set forth by the American Conference of Governmental Industrial Hygienists (ACGIH)(1976).

<u>Substance</u>	<u>Permissible Exposures 8-Hour Time-Weighted Exposure Basis (mg/M³)</u>	
	<u>1976 TLV's</u>	<u>NIOSH Criteria</u>
Methanol	260	260
Ethyl Acetate	1400	---
Isopropyl Alcohol	980	980
Copper	1	---
Nickel	0.1	---
Tin	0.1	---
Trichloroethylene	535	535
Acetone	2400	---
Freon-11 ^R	7600 <u>1/</u>	---
Chloroform	120	9.78 <u>2/</u>
Hydrochloric Acid	"C" 7	---
Nitric Acid	5	5
Aluminum Oxide	10 <u>3/</u>	---
Hydrofluoric Acid	2	5

mg/M³ = approximate milligrams of substance per cubic meter of air.

"C" = ceiling concentration which should never be exceeded.

1/ = this is not a specific TLV for Freon-11^R but is an average TLV for several of the freons whose toxicities are similar.

2/ = NIOSH recommended standard (July 6, 1976).

3/ = no standard exists; therefore, nuisance dust standard was used.

Occupational health standards are established at levels designed to protect individuals occupationally exposed to individual toxic substances on an 8-hour per day, 40-hour per week basis over a normal working lifetime.

D. Toxicology

Methanol--is slowly eliminated from the body. Therefore, repeated exposures will result in an increased concentration in blood and tissue. Chronic exposures to methanol cause headaches, giddiness, insomnia, gastric disturbances, and failure of vision. Concentrations ranging from 200 to 1000 mg/M³ showed no evidence of injury to exposed workers. The evaluation criteria of 260 mg/M³ probably incorporates a fairly large margin of safety against serious toxic effects.¹

Ethyl Acetate--produces a mild narcotic action among unacclimated workers. Workers exposed regularly to 1400 mg/M³ for several months showed no unusual signs or symptoms. Therefore, the evaluation criteria of 1400 mg/M³ should provide a margin of safety.²

Isopropyl Alcohol--is relatively non-toxic and is used widely for medicinal purposes such as massages and disinfecting. Concentrations in excess of 400 parts per million (ppm) may produce mild irritation of the mucous membranes. The evaluation criteria of 980 mg/M³ will prevent narcosis. However, some workers may experience slight irritation to the mucous membranes.³

Copper--inhalation of copper either as a dust, fume, or mist may result in congestion of the nasal mucous membrane which can lead to ulceration and perforation of the nasal septum. In chronic exposures, the liver, kidneys, and spleen may be injured and can cause anemia. Acute exposures to copper cause gastrointestinal irritation, mainly to the nerve endings in the stomach, and immediately cause vomiting. The evaluation criteria of 1 mg/M³ has a large safety factor, and worker exposures maintained at or below this level should eliminate any physiological damage.⁴

Nickel--there is strong evidence that nickel is a respiratory tract carcinogen. It is also responsible for cancer of the nasal sinuses and lungs. The risk of cancer is not confined to nickel carbonyl but is caused by both solid and gaseous forms of nickel. Maintaining worker exposures below the evaluation criteria of 0.1 mg/M³ should protect the worker from physiological damage.⁵

Tin--when tin is inhaled as a dust or a fume, it may cause a benign pneumoconiosis without changes in pulmonary function. Dermal lesions may result from exposures. This may be acute localized burns or subacute irritation. Maintaining worker exposure at or below 0.1 mg/M^3 should offer adequate protection.⁶

Trichloroethylene--high exposures produce an acute narcotic effect which may cause death from respiratory failure. There is no evidence that it is a chronic or cumulative type toxin. High concentrations to trichloroethylene, as well as any other chlorinated solvent, will cause liver damage. Maintaining worker exposure at or below 535 mg/M^3 should protect the worker from the narcotic effect and should also protect him from liver damage. From animal tests, there is a strong possibility that trichloroethylene may be a carcinogen.⁷

Acetone--maintaining worker exposure below 2400 mg/M^3 will prevent the narcotic action and eliminate any organic injury. The major problem when using acetone is its volatility. It should be considered as one of the least toxic of the common solvents but presents an extremely high fire risk.⁸

Freon-11^R--the freons produce a narcotic effect and also cause a shallow, rapid pulse. These both subside when the worker is removed from the exposure with no apparent side effects. The evaluation criteria of 7600 mg/M^3 should protect the worker from any physiological damage.

Chloroform--the most recent criteria indicate that chloroform concentrations in the workplace should be controlled to levels not exceeding 9.78 mg/M^3 in the workers' breathing zone. Recent information indicates that chloroform causes cancer in experimental test animals.⁹ This concentration should protect the worker from the possible carcinogenic properties of chloroform and would eliminate any deleterious effects on the liver, kidneys, and central nervous system.

Hydrochloric Acid--is very irritating to the throat on short exposures. The evaluation criteria of 7 mg/M^3 will prevent toxic injury but is a borderline as far as irritation is concerned.¹⁰

Nitric Acid--chronic exposure to nitric acid may result in bronchitis, and high exposures may result in a chemical pneumonitis. Vapors from nitric acid also erode the teeth. The irritating effect of nitric acid is similar to all strong acids. It irritates the body upon contact. Exposures of 5 mg/M^3 should protect the body from any physiological damage.¹¹

Aluminum Oxide--exposure to aluminum oxide produces Shaver's disease. The role of aluminum oxide in producing this disease is still not completely understood. Maintaining worker exposure below the nuisance dust standard of 10 mg/M^3 should protect the worker from physiological damage.¹²

Hydrofluoric Acid--causes intolerable sensations to the nose, throat, eyes, and mouth. It has a marked effect on the skin and underlying tissue. On the skin it causes chemical burns, while subcutaneously its destructive action causes necrosis of tissue and blood vessels and may even penetrate to the bone. It is a potent protoplasmic poison. Inhalation of hydrofluoric acid vapors may cause lung edema which can lead to death. Maintaining work exposure below 5 mg/M³ should protect the worker.¹³

E. Evaluation Results

There were two overexposed workers during the time of this evaluation. One of these workers was cleaning a vapor degreaser which contained Freon-11^R. The worker overexposed to chloroform was working in the mounting department. Other workers in these areas were monitored, but all concentrations were within the most recent evaluation criteria. All results may be reviewed in Tables I through IX.

This plant was very clean, had adequate ventilation, and training of employees was sufficient. Chloroform exposures must be kept at a minimum, since recent information indicates that chloroform causes cancer in experimental test animals.⁹

F. Recommendations

1. When cleaning the vapor degreaser, it should be drained from the bottom; the worker should be equipped with a NIOSH-approved respirator throughout the cleaning operation. The cleaning operation should be performed on the night shift, since fewer workers are in the facility; therefore, the potential number of workers exposed would be at a minimum.
2. Since hydrofluoric acid is used in this facility, adequate protection should be provided for workers who accidentally become exposed. Magnesium oxide ointment should be kept in the dispensary to treat the hydrofluoric acid burns, since the magnesium oxide will precipitate the fluoride ion and prevent nerve and blood vessel damage.
3. All hoods should be checked frequently to ensure proper amount of air flow.
4. Periodic sampling for chloroform should be initiated, since recent bioassay data indicates that it is a carcinogen.

V. REFERENCES

1. American Conference of Governmental Industrial Hygienists: Documentation of the Threshold Limit Values for Substances in Workroom Air, third edition, 1971, page 155.
2. Ibid, page 102.
3. Ibid, page 141.

4. Industrial Hygiene and Toxicology, second edition, Frank Patty (editor), Interscience Publishers, 1967, Vol. II, page 1035.
5. Johnstone, R. T., M.D., and Miller, S. E. M.D.: Occupational Diseases and Industrial Medicine, W. B. Saunders Company, 1960, page 333.
6. Industrial Hygiene and Toxicology, second edition, Frank Patty (editor), Interscience Publishers, 1967, Vol. II, pages 1151-53.
7. Carcinogenesis Bioassay of Trichloroethylene, 1976 U.S.G.P.O., Washington, D.C. Publication No. NCI - CG-TR-2.
8. American Conference of Governmental Industrial Hygienists: Documentation of the Threshold Limit Values for Substances in Workroom Air, third edition, 1971, page 3.
9. NIOSH recommended standard for chloroform (July 6, 1976).
10. American Conference of Governmental Industrial Hygienists: Documentation of the Threshold Limit Values for Substances in Workroom Air, third edition, 1971, page 129.
11. Ibid, page 181.
12. Ibid, pages 9-10.
13. Johnstone, R. T., M.D., and Miller, S. E., M.D.: Occupational Diseases and Industrial Medicine, W. B. Saunders Company, 1960, pages 130-3, and NIOSH Criteria for a Recommended Standard...Occupational Exposure to Hydrogen Fluoride, 1976.

VI. AUTHORSHIP

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TABLE I
ATMOSPHERIC CONCENTRATIONS OF METHANOL

FMC Corporation
August 27, 1976

Sample Number	Location	Job Classification	Time of Sample	Methanol mg/M ³	Type of Sample
5	Edge Polishing	Polisher	1:35- 3:30	8	BZ
6	Diffusion	Plater	2:15- 3:30	3	BZ
7	Diffusion	----	7:55-10:45	13	General Room
20	Assembly	Mounter	8:30-10:50	1	BZ
EVALUATION CRITERIA				260	
NIOSH LIMIT OF DETECTION				0.01 mg/sample	

mg/M³ = approximate milligrams of substance per cubic meter of air

BZ = breathing zone

TABLE II

ATMOSPHERIC CONCENTRATIONS OF ETHYL ACETATE AND ISOPROPYL ALCOHOL

FMC Corporation
August 27, 1976

Sample Number	Location	Job Classification	Time of Sample	Ethyl Acetate mg/M ³	Isopropyl Alcohol mg/M ³	Type of Sample
17	Etching	Etcher	8:00 - 11:00	8	3.5	BZ
24	Etching	Etcher	8:30 - 11:00	13	5.2	BZ
EVALUATION CRITERIA				1400	980.0	
NIOSH LIMIT OF DETECTION				0.01 mg/sample	0.01 mg/sample	

mg/M³ = approximate milligrams of substance per cubic meter of air

BZ = breathing zone

TABLE III
 ATMOSPHERIC CONCENTRATIONS OF COPPER, NICKEL, AND TIN

FMC Corporation
 August 27, 1976

Sample Number	Location	Job Classification	Time of Sample	Copper	Nickel mg/M ³	Tin	Type of Sample
14	Metal Electroplating	Electroplater	7:40-1:50	*	*	*	BZ
15	Metal Electroplating	----	7:40-2:00	*	*	*	General Room
16	Metal Electroplating	----	7:40-2:00	*	*	*	General Room
EVALUATION CRITERIA				1	0.1	0.1	
NIOSH LIMIT OF DETECTION				0.002 mg/sample	0.008 mg/sample	0.035 mg/sample	

mg/M³ = approximate milligrams of substance per cubic meter of air

BZ = breathing zone

* = below the NIOSH limit of detection

TABLE IV
 ATMOSPHERIC CONCENTRATIONS OF
 TRICHLOROETHYLENE, ACETONE, AND FREON-11

FMC Corporation
 August 27, 1976

Sample Number	Location	Job Classification	Time of Sample	Trichloroethylene mg/M ³	Acetone mg/M ³	Freon-11	Type of Sample
1	Diffusion	Degreaser	1:25- 3:30	2	*	35,000	BZ
2	Diffusion	Screen Painter	1:26- 3:30	2	8	6,088	BZ
3	Edge Polishing	Engraver	1:26- 3:30	40	*	1,486	BZ
4	Edge Polishing	Polisher	1:35- 3:30	9	5	858	BZ
8	Edge Polishing	Engraver	7:50-10:45	10	3	73	BZ
9	Diffusion	Degreaser	7:50-10:45	5	1	198	BZ
10	Mounting	Mounter	2:15- 3:30	28	*	655	BZ
21	Diffusion	Degreaser	8:30-10:50	57	*	60	BZ
25	Diffusion	Screen Painter	8:30-11:00	5	*	231	BZ
26	Diffusion	----	8:30-11:00	3	*	116	General Room
EVALUATION CRITERIA				535	2400	7600	
NIOSH LIMIT OF DETECTION				0.01 mg/sample	0.01 mg/sample	0.01 mg/sample	

mg/M³ = approximate milligrams of substance per cubic meter of air

BZ = breathing zone

* = below the NIOSH limit of detection

TABLE V
 ATMOSPHERIC CONCENTRATIONS OF
 ACETONE, CHLOROFORM, AND FREON-11

FMC Corporation
 August 27, 1976

Sample Number	Location	Job Classification	Time of Sample	Acetone	Chloroform mg/M ³	Freon-11	Type of Sample
18	Mounting	Mounter	8:00- 2:00	*	23	1272	BZ
19	Mounting	Mounter	8:20- 2:00	1	*	5896	BZ
22	Mounting	Mounter	8:30-10:50	2	2	8	BZ
23	Mounting	Mounter	8:30-10:55	*	*	36	BZ
EVALUATION CRITERIA				2400	9.78	7600	
NIOSH LIMIT OF DETECTION				0.01 mg/sample	0.01 mg/sample	0.01 mg/sample	

mg/M³ = approximate milligrams of substance per cubic meter of air

BZ = breathing zone

* = below the NIOSH limit of detection

TABLE VI
ATMOSPHERIC CONCENTRATIONS OF
HYDROCHLORIC ACID

FMC Corporation
September 8, 1976

Sample Number	Location	Job Classification	Time of Sample	Hydrochloric Acid mg/M ³	Time of Sample
3	Nickel Plating Area	----	9:16-9:59	*	General Room
4	Nickel Plating Area	Plater	9:13-9:58	*	BZ
EVALUATION CRITERIA				7	
NIOSH LIMIT OF DETECTION				0.01 mg/sample	

mg/M³ = approximate milligrams of substance per cubic meter of air

BZ = breathing zone

* = below the NIOSH limit of detection

TABLE VII
 ATMOSPHERIC CONCENTRATIONS OF
 NITRIC ACID

FMC Corporation
 September 8, 1976

Sample Number	Location	Job Classification	Time of Sample	Nitric Acid mg/M ³	Type of Sample
7	Etching	Etcher	8:17-9:25	*	BZ
8	Etching	Etcher	8:20-9:26	*	BZ
EVALUATION CRITERIA				5	
NIOSH LIMIT OF DETECTION				0.0004 mg/sample	

mg/M³ = approximate milligrams of substance per cubic meter of air

BZ = breathing zone

* = below the NIOSH limit of detection

TABLE VIII
 ATMOSPHERIC CONCENTRATIONS OF
 HYDROCHLORIC ACID

FMC Corporation
 September 8, 1976

Sample Number	Location	Job Classification	Time of Sample	Hydrofluoric Acid mg/M ³	Type of Sample
1	Diffusion	Spinner	7:40-8:22	*	BZ
2	Diffusion	Spinner	7:45-8:25	*	BZ
5	Diffusion	Spinner	8:24-9:02	*	BZ
6	Diffusion	Spinner	8:26-9:04	*	BZ
EVALUATION CRITERIA				2	
NIOSH LIMIT OF DETECTION				0.001 mg/sample	

mg/M³ = approximate milligrams of substance per cubic meter of air

BZ = breathing zone

* = below the NIOSH limit of detection

TABLE IX
ATMOSPHERIC CONCENTRATIONS OF
ALUMINUM OXIDE

FMC Corporation
September 8, 1976

Sample Number	Location	Time of Sample	Aluminum Oxide mg/M ³	Type of Sample
417	Aluminum Oxide Blasting Room	7:59-2:40	*	BZ
427	Aluminum Oxide Blasting Room	7:59-2:41	0.00002	BZ
EVALUATION CRITERIA			10	
NIOSH LIMIT OF DETECTION			0.011 mg/sample	

mg/M³ = approximate milligrams of substance per cubic meter of air

BZ = breathing zone

* = below the NIOSH limit of detection