

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. 74-130-229

I. F. MANUFACTURING COMPANY, DIVISION OF RIDGE TOOL  
NEW PHILADELPHIA, OHIO

OCTOBER 1975

FILE COPY

I. TOXICITY DETERMINATION

It has been determined that employees in the core room of the I.F. Manufacturing Company, Division of Ridge Tool in New Philadelphia, Ohio are not exposed to toxic concentrations of triethylamine (TEA) because of adopted work practices. However, it should be noted that TEA concentrations are potentially toxic in the immediate vicinity of the one core blow machine used for this cold box process. This is also true of free silica. Potentially toxic concentrations of free silica were found in the immediate vicinity of the bucket elevator, but not in the operator's breathing zone.

This determination is based on environmental evaluations conducted on January 6-7; and May 28, 1975 by NIOSH investigators, lack of medical symptomatology and toxicity information.

Recommendations to correct existing conditions are incorporated within this 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) I.F. Manufacturing Company, Division of Ridge Tool, New Philadelphia, Ohio.
- b) Authorized Representative of Employees
- c) U.S. Department of Labor - Region V
- d) NIOSH - Region V

For the purpose of informing the approximately seven "affected employees" the employer shall promptly "post" the Determination Report in a prominent place(s) near where exposed 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.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 at the I.F. Manufacturing Company regarding core room workers' exposure to triethylamine (TEA). This request was prompted by employees who had reportedly experienced loss of balance, dizziness and headaches.

### IV. HEALTH HAZARD EVALUATION

#### A. Plant Process - Conditions of Use

The I.F. Manufacturing Company in New Philadelphia, Ohio is a ferrous foundry engaged in the manufacture of a variety of tools. As part of the overall process it is necessary that cores be formed in order to cast the various tools.

Core making is conducted in a room 67' 10" x 59' with a relatively low ceiling. These sand cores are produced by either heating a resin coated sand or by a process known as the cold box process.

Cores formed by heating the resin coated sand may be baked in an oven or else heated while in the core box. The major portion of the cores produced at the I.F. Manufacturing Company are produced by the latter method.

There are six core blow machines identified as the 2-automatics, the 2-electrics, and the 2 gas-fired. The core boxes in each of these machines are held at approximately 600°F.

The cold-box process was introduced at the I.F. Manufacturing Company in early 1974 and actual core production started about four months later. This process involves mixing sand with a two part polyurethane binder (phenolic resin and polyisocyanate) and hardening the core by utilizing a catalyst (triethylamine in this case).

The machine used for this cold box process is semi-automatic and requires little attention if operating properly.

One machine operator introduces a silica sand to a hopper and in turn to the mixer (position high above the machine) by utilizing a bucket elevator. The two part binder is piped into the mixer from near by 55-gallon drums as sand is introduced from the hopper. All components of the mixture are automatically regulated by preset controls and

mixing occurs high above the core box.

The damp mixture is then blown into the core box where the (sand) core is hardened in less than 1-1/2 minutes by forcing a catalyst (in gas form) through the core box for a preset amount of time. Excess catalyst is flushed from the box by forcing compressed air through the box immediately after the catalyst has been introduced. The machine is equipped with an aspirator which exhausts into an after-burner.

If all is operating properly, the operator has only to stack the newly formed cores after they drop onto a short conveyor belt and provide needed sand periodically. Also, it is necessary that he periodically blow off any sand build-up from the cores to reduce leakage.

Providing the needed sand to the bucket elevator, and in turn to the hopper and then to the mixer creates a visible dust cloud for a short period of time. The reason for this is that the size of the opening on the bucket elevator is quite small. The operator takes sand from a metal box, with a bucket (2 gal.), and dumps it into the bucket elevator; this results in considerable spillage and dust. Dust is also generated as the sand transfers from the elevator into the hopper.

A metal flask is generally filled with the catalyst (triethylamine) once a day when the machine is being used on a regular basis. This flask is under pressure for about 30 seconds as the amine is being forced through the sand in the core box. During this time an ammonia-like odor is very noticeable adjacent to the machine.

#### B. Evaluation Progress

An initial survey was conducted on January 6-7, 1975 by NIOSH investigators. This consisted of 1) obtaining general company background information during the brief meeting held the 1st day of the investigation; 2) observing work practices during a walk-through survey of the area of concern, also done during the first day; 3) collecting environmental air samples for free silica, isophorone, triethylamine and isocyanates during the second day of the investigation. In conjunction with this investigation, confidential employee interviews were conducted in regard to their work history and any adverse medical symptomatology they may have experienced or were experiencing.

A follow-up survey was conducted on May 28, 1975 and included sampling for free silica and triethylamine. Employees in the immediate work area were again questioned in regard to adverse medical symptomatology.

### C. Evaluation Method

Although free silica was not included in the request for a health hazard evaluation, two area samples were collected during the initial survey and later analyzed colorimetrically. These samples were collected simultaneously at one location with the use of one pump, a glass-T, and two critical orifices. One of the samples was collected open face for total particulate while the other was collected by utilizing a cyclone to obtain the respirable fraction; both were collected at 9 liters per minute.

During the follow-up survey both area and breathing zone samples were collected. The area samples were collected as described above whereas the breathing zone samples were all respirable fraction; these were collected at 1.7 liter per minute while utilizing a 10mm cyclone. All samples collected during the follow-up were analyzed by x-ray diffraction.

Both parts of the organic binder are contained in dissolved form in a solvent which contains isophenone as the major constituent.

Breathing zone and area samples were collected on charcoal tubes. These samples were analyzed by gas chromatograph for isophenone. Also, any major peaks present were to be identified. These samples were collected by utilizing low flow (Sipin) pumps, flow rates were approximately 200 cubic centimeters per minute. These samples were collected for the duration of the operation on the second day of the initial survey only.

During the initial survey triethylamine concentrations were determined by utilizing (Drager) detector tubes and hand pump. In addition to this an attempt to more accurately determine TEA concentration was made by sampling with an impinger containing an acid and then analyzing by gas chromatograph. However, much difficulty was encountered during the analysis of these samples.

During the follow-up survey TEA concentrations were determined by utilizing charcoal tubes, low flow (Sipin) pumps, and analyzing the samples by gas chromatography. These samples were both breathing zone and area samples.

Impinger samples were also collected to determine methylene bisphenyl isocyanate (MDI) concentrations. These area samples were collected at a rate of approximately 1-1/2 liter per minute and were analyzed by a modified version of the Marcali method. This (MDI) sampling was done during the initial survey only.

### D. Evaluation Criteria

#### a. Environmental Criteria

The three primary sources of environmental evaluation criteria considered in this report are (1) NIOSH criteria documents recommending

occupational health standards (2) American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLV) and (3) Federal Occupational Health Standards promulgated by the U.S. Department of Labor (Federal Register, June 27, 1974, Vol. 39, No. 125; Title 29, Chapter XVIII, Part 1910, Subpart G, Tables G1 and G3). Since the determinations made as a result of this evaluation would not be changed by listing all applicable recommended standards, TLVs, or Federal standard, only those considered most applicable are listed along with its source.

8-hour Time Weighted Average

Free silica <sup>a</sup>	50 micrograms/cubic meter*
C Isopherone <sup>b</sup>	5 Parts per Million
Triethylamine <sup>b</sup>	25 Parts per Million
C Methylene bisphenyl isocyanate (MDI) <sup>b</sup>	0.2 milligrams/cubic meter

- a. NIOSH Criteria for a Recommended Standard Occupational Exposure to Crystalline Silica, 1974.
- b. ACGIH Threshold Limit Values for Chemical Substances in Workroom Air Adopted by ACGIH for 1974 and Supporting Documentation.

\* Respirable fraction as determined by a full shift sample for up to a 10-hours workday, 40 hour workweek.

C Ceiling Value

b. Physiological Effects

Free Silica - Exposure to elevated concentrations of free silica for extended periods of time may result in silicosis. Silicosis is anatomically characterized by fibrotic changes and the development of nodulation. Rapidly developing silicosis may develop in a short period of time upon exposure to high concentrations of free silica. Nodulation is generally not detected upon roentgenographic examination of the silicotic lungs which resulted from acute exposure.<sup>3,4</sup>

In the case of chronic silicosis, pulmonary symptomatology usually begins insidiously. Symptoms include presence of cough, dyspnea, wheezes and repeated non-specific chest illnesses. Impairment of pulmonary function may be progressive. In acute silicosis cases severe respiratory symptoms may occur.<sup>3,4</sup>

Isopherone - Isopherone is highly irritating to the eyes, nose and throat. At high concentrations nausea, headache, dizziness, faintness, inebriation and a feeling of suffocation may occur.

Triethylamine - The most significant characteristic of triethylamine is marked irritation to the cornea and lung tissue.

MDI - The most significant toxicologic effect from MDI exposure is the possibility of sensitization upon repeated exposure. Isocyanates in general are irritating to the skin, eyes and respiratory tract.

#### E. Evaluation Results and Discussion

During the initial survey core making by the cold box process was limited to approximately four hours on the day shift only. The sample analyses obtained as a result of that survey are as follows: isopherone concentrations were found to be less than one part per million and TEA concentrations ranged from approximately 4 to 20 parts per million. Free silica concentration determined for that same period of time was  $106 \mu\text{g}/\text{M}^3$  and the MDI concentration determined was  $0.04 \text{ mg}/\text{M}^3$ . Only the MDI concentration and isopherone concentration are considered (by the author) to be representative of a typical exposure. The TEA concentrations turned out to be representative but were questionable because of the sampling method used -- detector tubes. Free silica concentrations were questionable because of the analytical method used -- colormetric method.

For these reasons a follow-up survey was conducted at a later date. Samples collected during this survey are considered to be representative of typical concentrations. However, subsequent to the initial survey the I. F. Manufacturing Company had experienced an inferior core from this machine plus the demand for the cores had decreased. For these reasons this machine (cold box process) was seldom used; it was reportedly used only once in four months.

Based upon isopherone and MDI concentrations measured during the initial survey and the point at which these materials are introduced into the process, it was determined that it would not be necessary to sample for those materials during the follow-up. Area samples for free silica were collected during the follow-up survey and exceeded the NIOSH recommended standard but the breathing zone samples did not (see Table I). The area samples were closer to the source than the core blow machine operator and were expected to yield a higher concentration.

TEA concentrations were found to be higher at one side of the machine (see Table II). However, the operator stands in front of the machine (at the controls) and quite often steps back to avoid the fish-like smell due to the TEA.

TEA leaks from the core box while the TEA is under pressure, due to poor seals or else the aspirator located under the core box is partially ineffective.

Although concentrations at or near the core box exceed the recommended TLV for TEA, employees exposure is limited because of infrequent use plus they avoid the vapor which is detectable by its odor.

In addition to the environmental evaluation, core room employees interviewed in regard to adverse medical symptomatology did not report any symptoms at the time of either survey. All symptoms reported had occurred in the past and were typical of exposure to elevated concentrations of tertiary amines, some of which were burning eyes, nose, and throat, bad tastes, dizziness, light headiness, shortness of breath, nausea, headache, blurred vision.

#### F. Recommendations

1) General housekeeping throughout the core room is poor; a general clean-up program should be instituted immediately and maintained on a periodic basis after that. This would aid in removing accumulated dusts which can easily be stirred up at the present time, plus provide more space through the removal of a number of items which are presently cluttering up the core room.

2) Dust concentration in the core room can also be reduced by modifying the opening of the bucket elevator. A considerable amount of spillage was observed during the transfer of sand into the elevator by bucket.

3) TEA concentration can be reduced by taking steps to assure that the core box is properly sealed and there are no leaks. Also, the efficiency of the aspirator should be determined to assure that it is operating as it should be.

Recommendations 2 and 3 should be instituted if the I. F. Manufacturing Company intends to use this core blow machine (cold box process).

#### V. REFERENCES

1. Patty, F.; Industrial Hygiene and Toxicology, Vol. II, 1963.
2. American Conference of Governmental Industrial Hygienist; Documentations of the Threshold Limit Values for Substances in Workroom Air, 1971.
3. National Institute for Occupational Safety and Health; Criteria for a Recommended Standard...Occupational Exposure to Crystalline Silica, 1974.
4. U.S. Department of Health, Education, and Welfare; Public Health Service; Occupational Diseases, A Guide To Their Recognition, 1964, pp. 45-48.

VI. AUTHORSHIP AND ACKNOWLEDGMENTS

Report prepared by: Raymond O. Rivera  
Industrial Hygienist  
Hazard Evaluation Services Branch  
Cincinnati, Ohio

Acknowledgments

Environmental Evaluation: Beth S. Levy  
Hazard Evaluation Services Branch  
Cincinnati, Ohio

Jack O. Geissert  
Hazard Evaluation Services Branch  
Cincinnati, Ohio

Robert E. Rosensteel  
Hazard Evaluation Services Branch  
Cincinnati, Ohio

Originating Office: Jerome P. Flesch, Chief  
Hazard Evaluation Services Branch  
Cincinnati, Ohio

Table I  
Free Silica Dust Concentrations  
Core Room  
May 28, 1975

Filter #	Type of Sample	Time	Concentration in $\mu\text{g}/\text{M}^3$ *		Comments
			Total Particulate	Free Silica	
MP-71	Area	0748-1427	1064	53	Approximately 5' from "Isocure Machine"; respirable fraction
MP-82	Area	0748-1427	2992	265	Same location as MP-71; total
MP-151	Breathing zone	0735-1420	610	29	Isocure machine operator; respirable fraction
MP-185	Breathing zone	0740-1423	934	29	Operator on adjacent gas fired core bake machine, respirable fraction
MP-74	Area	1526-1825	186	149	Approximately 5' from "Isocure Machine"; total
MP-13	Area	1526-1825	515	56	Same location as sample MP-74; respirable fraction
MP-20	Breathing zone	1523-1820	485	33	Operator on Isocure machine; respirable fraction
MP-75	Breathing zone	1534-1820	497	36	Operator on automatic core making machine; respirable fraction

\*Micrograms per cubic meter

Table II  
Triethylamine Concentrations

Core Room

May 28, 1975

Sample #	Type of Sample	Time	Concentration in PPM*	
1	Breathing zone	0735-1420	4.7	Isocure machine operator
2	Breathing zone	0740-1423	N.D.**	Operator on gas fired core bake machine
3	Area	0830-1430	4.3	About 5' from cold box
4	Area	0830-1147	4.6	About 5' from cold box
5	Area	0922-0932	19.3	About 5' from cold box
6	Area	0936-0946	12.3	About 5' from cold box
7	Area	1151-1430	29.5	About 5' from cold box
8	Area	1351-1401	32.4	About 5' from cold box
9	Area	1613-1630	22.2	About 5' from cold box
11	Area	1526-1825	16.1	About 5' from cold box
12	Area	1526-1707	N.D.	
13	Breathing zone	1529-1820	N.D.	Isocure machine operator
14	Breathing zone	1534-1820	N.D.	Operator on automatic core machine
16	Area	1601-1611	0.2	About 5' from cold box (Isocure machine)
17	Area	1709-1825	18.0	About 5' from cold box (Isocure machine)

January 7, 1975

Detector tube	Area	0938	≈ 20	At side of machine; ≈ 5' away
"	Area	0945	≈ 5	At side of machine; between cycle
"	Area	0950	≈ 5	Back side of machine; during cycle
"	Area	1020	≈ 7	At side of machine; between cycle
"	Area	1034	≈ 4	During lunch break
"	Area	1140	= 5	Operator gen. stands at this location

\*parts per million

\*\*none detected - detection limit 0.01 mg/charcoal tube.