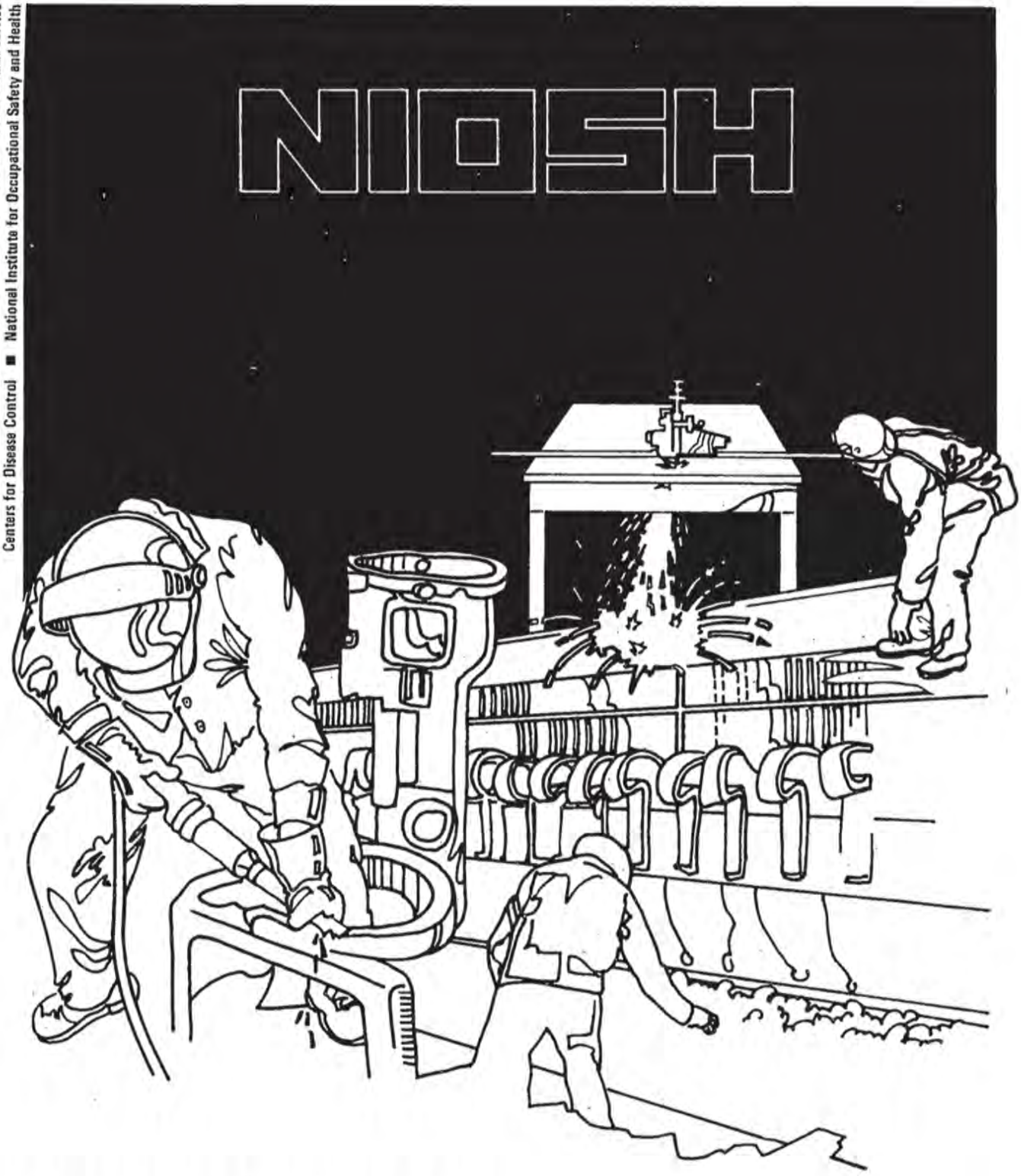
U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ■ Public Health Service
Centers for Disease Control ■ National Institute for Occupational Safety and Health

NIOSH



Health Hazard Evaluation Report

HHE 79-063-817
S.W.S. SILICONES CORPORATION
ADRIAN, MICHIGAN

PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 699(a)(6), which authorizes the Secretary of Health and Human Services, following a written request from 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.

HE 79-063-817
FEBRUARY 1981
S.W.S. SILICONES CORPORATION
ADRIAN, MICHIGAN

NIOSH INVESTIGATORS
SHAWN MCQUILKIN, IH
WILLIAM DANIELS, IH

I. SUMMARY

In March 1979, the National Institute for Occupational Safety and Health (NIOSH) received a request for a Health Hazard Evaluation from the United Steelworkers of America, Local 7237, at S.W.S. Silicones, Adrian Michigan. The requestor was concerned that skin contact with treated filler (amorphous silica) and iron oxide dusts were possibly causing health problems.

S.W.S. Silicones is engaged in the manufacture of silicone fluids, rubber, and grease. The two areas of the plant included in this investigation were the heat curable rubber (HCR) compounding area and the room temperature vulcanizing (RTV) rubber area. Approximately 126 employees work in these areas.

An initial survey was conducted by NIOSH investigators in April 1979. Confidential interviews were conducted with twenty-nine employees. An environmental survey was conducted in August 1979. Personal and area air samples were collected for determination of the following air contaminant levels: amorphous silica (measured as total particulate), iron oxide, cyclohexylamine, sec-butylamine, and organotin compounds.

Analysis of the environmental data indicated no overexposure to iron oxide, cyclohexylamine, sec-butylamine, or organotin. One of the nine personal samples for amorphous silica was in excess of the evaluation criteria used in this report of 6 milligrams per cubic meter of air (mg/M^3). Sample range of silica concentration was 0.15 - 10 mg/M^3, with a mean of 1.7 mg/M^3.

Fourteen (48%) of the twenty-nine employees interviewed indicated the presence of work related health problems, particularly upper respiratory and eye irritation, nausea, and skin rash. Ten workers attributed these adverse effects to exposure to catalysts, while four workers indicated that the dust was the cause.

Although environmental findings indicate levels of the hydrolysis products of the various catalysts to be below environmental criteria, employee interviews indicate a significant number of health problems related to their use.

On the basis of the data obtained in this investigation, NIOSH determined that an overexposure to amorphous silica did exist at the time of this survey. NIOSH has also determined that a potential for ill effects from exposure exists for the hydrolysis products of the various catalysts. Measured concentrations for these substances were below environmental criteria, but were, nonetheless, found to be irritating and offensive to the employees. Recommendations for engineering controls, worker education, and environmental monitoring, designed to alleviate this potential exposure hazard, are incorporated in detail in Section VIII.

KEY WORDS: SIC 2869, silicone, heat curable rubber, room temperature vulcanization, silicone catalysts, amorphous silica, iron oxide, cyclohexylamine, sec-butylamine, organotin compounds, irritants

II. INTRODUCTION

On March 6, 1979, NIOSH received a request from the United Steelworkers of America, Local No. 7237 for a health hazard evaluation at S.W.S. Silicones Corp., (SIC 2869) Adrian, Michigan. The purpose of the request was to evaluate complaints of employee exposure to iron oxide and treated filler (amorphous silica) dust. A NIOSH initial survey was conducted on March 17-18, 1979. An interim report was issued in July 1979, listing the preliminary findings. On August 22-23, 1979, NIOSH conducted an environmental survey to assess employee exposure to iron oxide, amorphous silica, and other chemicals.

III. BACKGROUND

On January 28-29 and April 6-7, 1976, a survey team from NIOSH conducted a health hazard evaluation at S.W.S. Silicones, Adrian, Michigan. Environmental and medical evaluations were conducted to assess employee exposure to amorphous silica and mica dust. Based upon environmental data gathered during the surveys, medical interviews, limited physical examinations of employees, observation of work practices, and available literature regarding the toxicity of substances used in the work area, the NIOSH investigators concluded that employee exposure to fumed amorphous silica powders and mica were not toxic at concentrations measured during the evaluation. Since the substances evaluated were determined to be capable of producing drying and subsequent irritation of the skin and upper respiratory tract, recommendations pertaining to engineering controls and use of protective equipment were included in final report (Health Hazard Evaluation Determination Report #75-183-303). The second health hazard evaluation was requested to evaluate additional substances being used in the work area.

A. Process Description

S.W.S. Silicones is engaged in the manufacture of various silicone products, including silicone fluids, rubber, and grease. These products are sold to other companies for further processing, or as finished marketable products. The two areas of the plant included in this investigation were the HCR compounding area and the RTV rubber area.

1. HCR Compounding area

Heat curable rubber (HCR) base and compound are mixed, milled, extruded and packaged in this area. Various ingredients including silica gum powder, treated filler, pigments, and catalysts are added to a base mixer, then mixed and heated. The end product, referred to as "base" is removed from the mixer and undergoes a further blending of ingredients, and in some instances is extruded. The base may be packaged and sold at this point, or again mixed with small amounts of catalyst and pigments, depending upon customer order. Approximately twenty six persons per shift are employed in the HCR compounding area and are rotated among the various jobs.

2. RTV Rubber Area

The manufacturing process for the RTV (room temperature vulcanizing) rubber is similiar to that for the HCR except that all batches are smaller and charged differently. A potential for exposure occurs when iron oxide and various catalysts are charged into the mixers. Each mixer operator is responsible for

cleaning the mixer tank between batches. The final products include silicone grease, caulking material, the formed-in-place gaskets. Approximately eleven persons per shift are employed in the RTV area.

IV. METHODS AND MATERIALS

Environmental samples for total particulate were collected on 37 mm diameter polyvinyl chloride copolymer filters held in closed-face cassettes and attached via tygon tubing to battery powered air sampling pumps operating at flow rates of approximately 1.75 liter per minute (lpm). The weights of the samples were determined by subtracting the pre-sampling weight from the post-sampling weight of the filter.

Samples for iron oxide and tin were collected on 37mm diameter mixed cellulose ester membrane filters held in closed-face cassettes and attached via tygon tubing to battery powered pumps operating at flow rates of approximately 1.2-2.0 lpm. The samples were analysed for the metals according to the NIOSH Physical and Chemical Analytical Method (P&CAM) #173 (modified)[1].

Samples for aliphatic amines were collected on silica gel tubes attached via tubing to battery powered air sampling pumps operating at flow rates of 50-100 cubic centimeters (cc) per minute. The samples were analysed for the amines according to NIOSH P&CAM #221 (modified)[2].

Twenty-nine confidential employee interviews were conducted by NIOSH industrial hygienists to detect the presence of work related health problems.

V. EVALUATION CRITERIA

The environmental evaluation criteria used for this study are presented in the following table. Listed for each substance is the recommended environmental limit and its source, the primary health effects, and the current OSHA standard. All air concentrations are 8-10 hour time weighted average (TWA) exposures.

Substance	Recommended Limit*	Primary Health Effects	OSHA Standard(4)
Amorphous silica (as total particulate)	6 mg/M^3 ACGIH(3)	Skin and mucous membrane irritant	20 million particles per cubic foot of air (mppcf)
Iron Oxide fume (as iron)	5 mg/M^3 ACGIH(3)	Benign pneumoconiosis	10 mg/M^3
Cyclohexylamine	10 ppm ACGIH(3)	Skin irritant, systemic effects	no standard
Organotin compounds (as tin)	0.1 mg/M^3 NIOSH(8)	Eye, skin, liver, nervous system, and heart effects	0.1 mg/m^3

*These values have been selected as the evaluation criteria for this report. The source and reference are listed below each recommended limit.

A number of sources recommend airborne levels of substances under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect. Such airborne levels are referred to as standards or threshold limit values (TLV's). It is believed that concentrations below these limits represent conditions under which nearly all workers may be repeatedly exposed 8-10 hours per day, 40 hours per week, without suffering adverse health effects. Due to variations in individual susceptability, a small percentage of workers may experience effects at levels at or below the threshold limit; a smaller percentage may be more seriously affected by aggravation of a pre-existing condition or by a hypersensitivity reaction[3].

A. Amorphous Silica

There is only limited information available relating to the specific toxicities of amorphous silica. As it contains no free silica, it would not be expected to cause silicosis [5]. The most important properties with respect to handling difficulties are the ease of dispersal (due to the low density) and the potent dessicant effects of the powders. These characteristics lead to mucous membrane drying and irritation while possibly increasing the incidence of respiratory infection. Contact with the skin removes moisture and irritates the skin.

B. Iron Oxide

Long term occupational exposure (on the order of 6-10 years) to iron oxide fume may cause a condition known as siderosis, a condition noted by the literature to be a non-disabling lung disease. There is a lack of information in the literature on the relationship between iron dust deposits in the lungs and other industrial dusts, and their combined effect on the worker. Although benign, it cannot be stated that iron dust deposits in the lungs are totally harmless[6].

C. Cyclohexylamine

Modern compendiums rate cyclohexylamine as moderately toxic to very toxic, and note that the amine is intensely irritating to the skin and is regarded as having moderate sensitizing potential [5,7].

D. Organotin

In general, the organotin compounds are irritating locally both to mucous membranes and the skin. The major concern in occupational exposure to organotins is the potential for liver, kidney, pulmonary, and central nervous system damage at low concentrations[8].

E. Sec-butylamine

Presently there is no environmental standard for occupational exposure to sec-butylamine. Little data is available regarding the toxicity of this substance. One source indicates a moderate irritation hazard to the skin and mucous membranes[7].

VI. RESULTS

A. Evaluation of Employee Interviews

Twenty-nine individual employee interviews were conducted. Of these, 15 worked in the RTV Department representing 33% of the approximately 46 workers in this department. About half were from the day shift with the rest from other shifts. Only 4 of the 15 workers had no medical complaints they felt might relate to their work in the department, although one of these had some problems with eye irritation and nose bleeds from exposure to cleaning solvents several years earlier. Ten of the 15 complained of irritation of eyes, nose, and/or throat, or problems with excessive sinus discharge and possibly some difficulty breathing. Most identified the catalysts as the offending substances although 3 indicated the amorphous silica as being the problem. Two of the 15 indicated they had trouble with skin rashes from exposures, one to catalysts, one to mineral spirits. Besides the single case of irritation several years ago, one other worker reported a chemical burn in the eye in the past.

In the HCR Department, 14 of the approximately 80 workers (18%) were interviewed with 8 being from the first shift and 6 from the second shift. Only one worker complained of nausea and eye irritation due to the catalysts and one other worker complained of headaches from extruded compounds. Two other workers complained of rashes or dermatitis from exposure to substances in the workplace, and one worker had received a chemical burn in the past.

For the workers in the RTV department the mean age was 29.6 with a mean of 1.6 years in the department and 2.6 years in the company. In the HCR department the mean age was 25.5 years with a mean time in the department of 2.8 years and a mean time with the company of 3.3 years. Most of the HCR workers interviewed were males, whereas in the RTV Department the workers were equally divided between men and women.

B. Environmental Results

Results of environmental sampling for amorphous silica (measured as total particulate) are shown in Table 1. Nine personal air samples for total particulate were collected. The 8-hour TWA values ranged from 0.15 to 10 mg/M^3, whereas the average exposure was 1.7 mg/M^3. One of the nine samples (10 mg/M^3) was in excess of the 6 mg/M^3 evaluation criterion.

Results of the environmental sampling for iron oxide dust are shown in Table 2. The values for the personal exposure to iron oxide dust were well below the current environmental criterion. The values ranged from 0.0032-0.21 mg/M^3, whereas the average exposure was 0.053 mg/M^3. The OSHA standard for iron oxide fume is 10 mg/m^3. The ACGIH TLV is 5 mg/M^3.

The 8-hour TWA values for exposure to cyclohexylamine (Table 3) ranged from below the limit of detection to 1.8 ppm, while the average exposure was 0.59 ppm. These values are within the 10 ppm TLV recommended by the ACGIH. No sec-butylamine was detected in any of the samples collected. The origin of cyclohexylamine is the Vernetzer CA 40 catalyst.

No tin was detected in any of the samples collected. Tin serves as an indicator for the presence of organotin compounds, which are hydrolysis products of the various Cotin catalysts.

VII. DISCUSSION AND CONCLUSIONS

In response to the recommendations presented in the June, 1976, NIOSH Determination Report, management installed a local exhaust ventilation system. The system includes slotted hoods which service the mixers and are designed to capture air contaminants released during the mixing process. These slotted hoods are not designed for capturing dust as the mixer is charged with the treated fillers.

Based upon the environmental data, it has been determined that overexposure to amorphous silica is a potential problem. The greatest potential for exposure to the treated filler occurs when the filler is charged into the mixer. It should be noted that the company has a comprehensive respiratory protection program and that the employees wore respiratory protective equipment during the charging operations.

Concentrations of iron oxide dust in the breathing zone of workers were well below the established environmental criterion and are not expected to cause any serious health effects.

Concentrations of the hydrolysis products of the various catalysts (cyclohexylamine, sec-butylamine, organotin) were either not detected or below the established criteria. Yet, the results of the employee interviews revealed a significant number of employee complaints related to the use of the various catalysts. Significant exposure to the hydrolysis products of the catalysts could potentially occur during charging of the mixer or when the employee hand cleans the change cans. Therefore, short term exposures to high concentrations of these substances could be responsible for the adverse health effects that are being experienced.

VIII. RECOMMENDATIONS

1. Install an enclosed catalyst delivery system to minimize employee exposure to the hydrolysis products of the catalysts.

2. Apply local exhaust ventilation to capture excess treated filler when the mixer is being charged.

3. Open surface change cans that require hand cleaning and that are likely to emit hydrolysis products of the catalysts should receive slotted local exhaust ventilation.

4. An improved education program should be instituted so that employees are made aware of the toxicity and hazards associated with the materials handled during operations covered by this evaluation. Good work practices and good personal hygiene should be stressed with the goal of preventing or minimizing inhalation and skin and eye contact with chemicals and dusts.

5. Periodically evaluate employee exposure to potential environmental contaminants including amorphous silica, iron oxide, and hydrolysis products of the catalysts.

IX. REFERENCES

1. P&CAM No. 173: NIOSH Manual of Analytical Methods, Volume 5, DHEW (NIOSH) Publication 79-141, August 1979.

2. P&CAM No. 221: NIOSH Manual of Analytical Methods, Volume 1, DHEW (NIOSH) Publication 77-157A, April, 1977.

3. American Conference of Governmental Industrial Hygienists, Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1980.

4. General Industry Standards: Occupational Safety and Health Administration Safety and Health Standards (29 CFR 1910) revised January 1976.

5. American Conference of Governmental Industrial Hygienist: Documentation of Threshold Limit Values, 3rd Edition, 4th Printing - 1977.

6. Occupational Diseases, A Guide to Their Recognition, Revised Edition, DHEW (NIOSH) Publication 77-181, pp. 360-1.

7. Sax, N. Irving, Dangerous Properties of Industrial Materials, Third Edition, Van Nostrand Reinhold Co., New York, 1968, p. 604.

8. Criteria for a Recommended Standard...Occupational exposure to Organotin Compounds, NIOSH Publication No. 77-115, Nov. 1976.

X. AUTHORSHIP AND ACKNOWLEDGEMENTS

Report Prepared By:

Shawn D. McQuilkin
Industrial Hygienist
NIOSH - Region V
Chicago, Illinois

William J. Daniels
Industrial Hygienist
NIOSH - Region V
Chicago, Illinois

Originating Office:

Division of Surveillance Hazard Evaluations & Field Studies
Hazard Evaluation and Technical Assistance Branch
Cincinnati, Ohio

Analytical Laboratory Services:

Measurement Support Branch
Cincinnati, Ohio

XI. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are currently available upon request from NIOSH, Division of Technical Services, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days the report will be available through the National Technical Information Services (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 the following:

A. United Steelworkers of America Local No. 7237

B. United Steelworkers International

C. U. S. Department of Labor, OSHA

D. S.W.S Silicones Corp., Adrian, Michigan

E. NIOSH Regional Offices/Divisions

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

S.W.S. SILICONES (Samples collected August 22-23, 1980)

TABLE 1
RESULTS OF ENVIRONMENTAL SAMPLING FOR AMORPHOUS SILICA

Job/Location	Time of Sample	Type of Sample	Total Particulate mg/M3
mixer operator/HCR	1045-1527	personal	3.9
mixer charger/HCR	0832-1529	personal	1.4
mixer charger/HCR	0829-1515	personal	1.9
mixer charger/HCR	0836-1514	personal	10
extruder/HCR	0842-1524	personal	0.50
compounder/HCR	0840-1526	personal	1.0
unloader/warehouse	1242-1500	personal	void
bag changing/bag house	1028-1043	personal	0.15
bag changing/bag house	1028-1043	personal	0.19
bag house	1047-1545	area	1.1
RTV redroom	1117-1554	area	0.43
RTV	1121-1554	area	0.22

EVALUATION CRITERIA---------- 6 mg/M3

TABLE 2
RESULTS OF BREATHING ZONE SAMPLING FOR IRON OXIDE DUST (as Fe)

Job/Location	Time of Sample	Iron Oxide (mg/M3)
coxmill/RTV	1023-1537	0.013
utility/RTV	1036-1535	0.027
mixing/RTV	1029-1525	0.21
batching/HCR	1041-1528	0.0032
mixing/HCR	0834-1517	0.012

EVALUATION CRITERIA---------- 5 mg/M3

TABLE 3
RESULTS OF ENVIRONMENTAL SAMPLING FOR CYCLOHEXYLAMINE

Job/Location	Time of Sample	Type of Sample	Cyclohexylamine (ppm)
rotofeed operator/RTV	1025-1533	personal	0.38
rotofeed operator/RTV	1025-1533	personal	0.38
kalex operator/RTV	1019-1524	personal	1.1
kalex operator/RTV	1019-1524	personal	0.95
adjacent to kalex	1114-1551	area	0.25
mixer/RTV	0900-1538	personal	0.24
mixer/RTV	0900-1538	personal	0.13
mixer/RTV	0855-1543	personal	ND
clean out change can/RTV	0852-1535	personal	1.8
clean out change can/RTV	0852-1535	personal	0.92
RTV redroom	1014-1554	area	1.5
RTV redroom	1117-1656	area	0.87
compounder/HCR	0906-1526	personal	ND

EVALUATION CRITERIA----------10 ppm

Abbreviations: ppm = parts of contaminant per million parts of air
ND = Not detected