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Health Hazard Evaluation Report

HETA 81-052-896 MARBLE PRODUCTS OF MEMPHIS MEMPHIS, TENNESSEE

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. 669(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.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

HETA 81-052-896 June 1981 Marble Products of Memphis Memphis, Tennessee

NIOSH INVESTIGATOR: Richard W. Gorman, IH

I. SUMMARY

In October, 1980, the National Institute for Occupational Safety and Health (NIOSH) received a request for a health hazard evaluation from Marble Products of Memphis, Memphis, Tennessee. The two co-owners, who were also the primary operators of the company, were concerned that exposure to the vapors and dust generated during manufacture of synthetic marble products might be a health hazard.

The company employs two to three workers and manufactures 25 vanity tops, 2 bathtubs and 100 square feet of wall sections each week using a styrenated polyester resin system. Workers experienced occasional mild headaches and slight stomach discomfort which they felt may be work related. However, the major complaint was a strong disagreeable odor noted particularly during the gelcoat and pouring phase of production.

Personal breathing zone and area air sampling was conducted to determine exposure to vapors and dust. The primary contaminant was determined to be styrene. The highest exposures found for long-term (up to 5 hours), 15-minute and 5-minute personal breathing zone samples were 18, 60 and 82 parts per million (ppm) respectively. These exposures were well below the OSHA standard for styrene - 100 ppm (8 hour, TWA), 200 ppm (15-minute ceiling) and 600 ppm (5-minute peak). These standards may be too high in light of the growing body of evidence (6,7,8,9) that suggest that styrene may be a carcinogen. Acetone, toluene and methyl-ethyl-ketone were all detected in air samples but in concentrations less than 3 percent of applicable exposure criteria. In a two hour sanding operation, an operator was found to be exposed to 7.8 milligrams per cubic meter (mg/M³) of marble dust of which 0.5 mg/M³ was determined to be respirable. The 8 hour - TWA total dust exposure was calculated to be 2.0 mg/M³, a level well below the OSHA standard of 15.0 mg/M³ for total nuisance dusts. The mass median diameter of the marble dust was 15.3 microns, with a standard geometric deviation of 2. Only 5% of the marble dust was respirable.

On the basis of the data obtained in this investigation, occupational exposures at Marble Products of Memphis do not exceed OSHA standards. However, in light of the growing body of evidence suggesting that styrene may be carcinogenic, it would be prudent to further minimize exposures. Accordingly, Section VIII of this report discusses methods of accomplishing this goal.

KEYWORDS: SIC 2821 and 3079. Marble dust, styrene, Acetone, toluene, methyl-ethyl-ketone, MEK.

II. INTRODUCTION

On October 24, 1980, NIOSH received a management request for a Health Hazard Evaluation at Marble Products of Memphis, Memphis, Tennessee. There was concern that exposure to airborne contaminants, generated during the fabrication of synthetic marble products may be a health hazard. Initial attempts to contact the requestor to validate the request were unsuccessful. Confirmation to proceed with the study was received on February 9, 1981. An environmental survey was conducted on February 18-19, 1981 to identify airborne contaminants and estimate the extent of exposure.

III. BACKGROUND

Marble Products of Memphis is a small, family-owned operation that, on the average, manufactures 25 synthetic marble vanity tops and 2 bathtubs per week. Two brothers own and operate the business with the occassional help of one part-time employee. The company was started approximately 6 years ago by the father. A new facility was constructed 3 years ago and is described as a one-story, wooden structure that measures 100'X100'X10' (interior ceiling height). Approximately 20% of the space is leased and used as a retail sales business. The various process locations within the facility are shown in Figure 1. Environmental systems include a Sears "15" gas-fired furnace and a ceiling gas-fired heating unit. There are three wall fans that service the production area.

The process begins by applying gelcoat (a modified resin containing styrene) to the surface of the molds. In addition to acting as a mold release agent, the gelcoat provides a thin, smooth plastic film on the surface of the finished product. This operation takes less than one hour. Marble dust (coarse and fine), styrenated-polyester resin and approximately 20 milliliters of methyl-ethyl-ketone-peroxide (MEKP) are mixed in prescribed proportion and poured onto the molds. A teaspoon or less of pigment is usually added prior to the pouring stage to produce swirls of a contrasting color. After curing for several hours, the pieces are removed from the molds, sanded, buffed and either stored or delivered. Equipment is cleaned using recycled acetone either by wiping with a rag wetted with acetone or by dipping the part in a 5 gallon bucket of the acetone while brushing.

IV. EVALUATION DESIGN AND PROCEDURES

An environmental survey was performed on February 18-19, 1981 which included:

- 1. Employee interviews discussing working condition and health effects that may be related to work.
- 2. Environmental sampling using personal breathing zone and area sampling techniques to estimate exposure to organic vapors (styrene, acetone, toluene, methyl-ethyl-ketone) and dust.

- Evaluation of existing ventilation systems using a velometer and smoke tubes.
 - a. Organic vapors

Battery operated sampling pumps were used to pull air through 150 mg charcoal tubes at sampling rates ranging from 100 to 560 cubic centimeters per minute. Samples were analyzed by gas chromatography in accordance with NIOSH standard method P&CAM 127 except for one bulk air sample which was analyzed using a gas chromatographic/mass spectrophotometric technique.

b. Dust

Battery operated sampling pumps were used to pull air through preweighed polyvinyl chloride (PVC) filters at a sampling rate of 1.7 liters per minute (lpm). Total dust exposure was determined by weight difference. The respirable fraction in the dust exposure was determined by pulling air through a 10 millimeter cyclone at a rate of 1.7 lpm. The amount of dust passing the cyclone and collected on a preweighed filter represents the concentration of dust that is respirable. Further characterization of the dust was accomplished using a 7-stage, cascade impactor sampler.

V. EVALUATION CRITERIA

Styrene

Styrene is an irritant of the eyes and mucous membranes and a central nervous system depressant. Humans exposed to 376 ppm experienced eye and nasal irritation within 15 minutes; after one hour at 376 ppm, effects were headache, nausea and decreased dexterity and coordination(2). While early reports indicate that styrene monomer is readily absorbed through the skin(3), a recent study suggests that cutaneous absorption of styrene is not a significant exposure in the plastic industry(1 6). The fact that styrene binds to the polyester resin molecules and therefore prevents absorption through the skin was offered as a possible explanation of this phenomena. The odor threshold is 0.1 ppm(4). Prolonged or repeated skin contact may lead to dermatitis due to deffating action.

The current OSHA standard is 100 ppm with a 200 ppm ceiling and a 600 ppm peak limit during any 5 minutes of a 3 hour exposure period. There is a growing concern that styrene may be carcinogenic (6,7,8,9). NIOSH is preparing a styrene criteria document (5).

Acetone

Acetone, a mucous membrane irritant, is generally considered to be relatively non-toxic. Concentrations as high as 1000 ppm can be tolerated without adverse health effects (10). Repeated or prolonged contact with the skin can cause dryness and redness. An OSHA standard of 1000 ppm is currently in effect.

Toluene

Toluene is a central nervousness system depressant. Symptoms of over-exposure include fatigue, weakness, confusjon, euphoria, dizziness, headache, nervousness and muscular fatigue⁽¹⁰⁾. Mild symptoms have been experienced at controlled exposure to 200 ppm for 8 hours⁽¹¹⁾. The OSHA standard is 200 ppm. NIOSH recommends that exposure be limited to 100 ppm.

Methy-ethyl-ketone (MEK)

MEK is an irritant of the eyes, mucous membranes, and skin. Short-term exposure to 300 ppm is "objectionable", causing headache and throat irritation; 200 ppm can cause mild irritation of the eyes; 100 ppm can cause slight nose and throat irritation(12). High concentration can cause central nervous system depression. The current OSHA standard is 200 ppm.

Marble Dust

Marble (calcium carbonate) dust is considered a nuisance dust and has been found to be essentially free of silica. Even mild fibrosis of the lung is unusual in marble workers. This has been attributed to the fact that marble dust is highly soluble and therefore rapidly eliminated from the body (13). The OSHA standard for nuisance dust is $15~\text{mg/M}^3$ total dust and $5~\text{mg/M}^3$ respirable dust (14).

VI. RESULTS/DISCUSSION

1. Interviews

Other than occasional symptoms of a mild headache and/or mild stomach discomfort there were no other complaints. However, due to the strong disagreeable odor present during the gelcoating and pouring phase of the operation and the recent death of the previous owner, there was a growing feeling of apprehension in the two current owners, who were also the primary operators.

The hands of one operator, who frequently washed them with recycled acetone, were dry and slightly scaly, but not fissured.

2. Environmental Sampling

a. Organic Vapors

A bulk air sample, analyzed by a gas chromatographic/mass spectrophotometric technique, identified styrene as the primary contaminant. Acetone, toluene and MEK were also detected. Air sampling results are presented in Table 1. Four long-term area, 4 long-term personal breathing zone, 9 short-term (15 minute) personal breathing zone and 1 short-term (5 minute) personal breathing zone samples were obtained. Results represent time-weighted-average for the period sampled (5 minutes to 5 hours).

(1) Styrene

Styrene area samples ranged from 0.5 ppm (lunchroom) to 83 ppm (pouring table). Long-term exposure representing all phases of production ranged from 15.0 to 18.1 ppm. Short-term (15 minute) exposure ranged from 1.6 ppm (mixing operation) to 60.0 ppm (gelcoat application). One 5-minute sample taken during gelcoat application was 81.6 ppm. Exposures were well within the current OSHA standard of 100 ppm (8 hour, TWA), 200 ppm (15 minute ceiling) and 600 ppm (5 minute peak).

A closer look at the 15 minute samples taken during each production operated, Figure 2, indicates that styrene exposure is highest during the gelcoat application, followed in decreasing order by pouring a wall section, pouring vanity tops and mixing.

(2) Acetone, Toluene, MEK, Other Organics

Samples were less than 3% of applicable exposure criteria. The acetone and toluene vapors were from the recycled acetone used for cleanup. Traces of isopropanol, methyl-isobutyl-ketone (MIBK), xylene, pinene and benzaldehyde were detected in the bulk air sample but were not present in high enough concentrations to be detected in exposure samples.

(3) Dust

Sanding the edges of the product usually takes from 1-2 hours per day. Total dust and respirable dust exposure were determined to be 7.8 and 0.5 $\rm mg/M^3$ respectively (Table 2). Assuming a log-normal particle size distribution, a log-probability plot, Figure 3, allows for a graphical determination of a mass median diameter (dm) and a standard geometric deviation ($\rm CG$). The mass median diameter is 15.3 microns with a standard geometric deviation of 2.0. Results indicate that approximately 5% or less of the marble dust is respirable.

Ventilation

Three 15 inch wall fans exhaust a total of 22,000 ft 3 /min which results in approximately 30 air changes per hour. Make-up air is passively brought into the building through attic vents and into the production area by an open door leading to the attic. With all three fans operating, the production area was cleared of objectionable styrene odors in 30-60 minutes.

A paint spray booth was purchased, but not received, prior to the survey. The intention is to accomplish at least the gelcoat operation in this booth. A conveyor system will be used to move pieces in an out of the booth and the exhaust will be turned on only when needed.

VII. CONCLUSIONS

Although the styrene odor was objectionable, concentrations of this organic vapor and other contaminants evaluated, were all below current occupational health standards and would not be expected to cause headaches or stomach discomfort in most people.

The new spray-booth type exhaust system should significantly reduce exposures from gelcoat application, except for the wall section process which is too large for the booth.

VIII. RECOMMENDATIONS

Although current exposure standards were not exceeded during this study, the disagreeable odor of the styrene vapor and its implication as a possible carcinogenic justify taking measures to further reduce exposures. A combination of material substitution, engineering controls, and the use of personal protective equipment can be used.

Material Substitution

A new "styrene-suppressed" resin reportedly reduces the volatilization of styrene and is especially suited for casting operations (14,15). A film-former-like wax is added to the resin. The wax floats to the surface within 2 minutes after the casting is poured, forming a thin film that inhibits styrene release. Also, ways of reducing the heat generated because of exothermic curing reactions are being evaluated. A reduction in the heat generated will result in a lower styrene vapor pressure, thereby decreasing vapor emissions.

The current resin distributor should be contacted to see if a "styrene-suppressed" resin is available.

Engineering Controls

The local exhaust system, such as the one purchased, will significantly reduce exposures during gelcoat operations. This system can be activated for short periods after pouring two exhaust contaminants in a shorter time period. It will be necessary to partially open one of the overhead garage doors during the operation of the exhaust booth to provide adequate makeup air.

The acetone cleanup area should be relocated under one of the wall exhaust fans so that solvent vapors can be removed more efficiently.

Personal Protective Equipment

The current practice of using a disposable dust respirator should be continued during the sanding operation.

NIOSH-approved half-mask respirators equipped with organic vapor cartridges should be on hand for each worker and used as needed.

Although recent data suggests that skin absorption in plastics workers do not contribute significantly to styrene levels in the body, there is a risk of dermatitis. Skin contact with the resin or solvents should be avoided to the extent possible. Protective gloves should be worn when handling the resin or solvent.

IX. REFERENCES

- 1. Operating Manual for Anderson Samplers Inc., TR# 76-900016, January, 1979.
- 2. Stewart, R.D. Dodd, H.C., Baretta, E.D., and Schaffer, A.W.: Human Exposure to Styrene Vapor. Ach. Environ. Health, 16:656, 1968.
- 3. Dutkiewicz, T., and Tyras, H.: Skin Absorption of Toluene, Styrene, and Xylene by Man. Br. J. Ind. Med., 25:243, 1968.
- 4. Hellman, T.M., Small, F.H.: Characterization of the Odor Properties of 101 Petrochemicals Using Sensory Methods, Jr. Air Pol. Control Ass. 24:10, October, 1974.
- 5. Personal Communication with Dr. F. Mitchell, NIOSH, April 21, 1981.
- 6. Hotz, P., Guillemin, M.P. Lob, M.: Study of Some Hepatic Effects (induction and toxicity) Caused by Occupational Exposure to Styrene in the Polyester Industry, Scand. J. Work Environ. Health, 6:206-215, 1980.
- 7. Ponomarkov, V., Tomatis, L.: Effects of Long Term Oral Administration of Styrene to Mice and Rats: Scand. J. Work Environ. Health (Suppl. 2), 4:127-135, 1978.
- 8. Vainio, H., et al: A Study on the Mutagenic Activity of Styrene and Styrene Oxide, Scand. J. Work Environ. Health, 2:147-151, 1976.
- Loprieno, N., et al: Mutagenicity of Industrial Compounds Styrene and Its Possible Metabolite Styrene Oxide, Mutat. Res., 40:317-324, 1976.
- 10. Proctor, N.H., Hughes, J.P.: Chemical Hazards of the Workplace, J.B. Lippincott Company, Philadelphia, 1978.
- 11. NIOSH, US Department of Health Education and Welfare: Criteria for a Recommended Standard ... Occupational Exposure to Toluene (HSM) 73-11023, pp. 14-45. Washington, D.C.: U.S. Government Printing Office, 1973.
- 12. Nelson, K.W. et al: Sensory Response to Certain Industrial Solvent Vapors. J. Ind. Hyg. Toxicol., 25:282, 1943.
- 13. Drinker, P., Hatch, T.: Industrial Dust, McGraw Hill Book Co., 2nd Edition, New York, pp 56-75, 1954.
- 14. Schumacher, R.L. et al: Syrene Exposure in the Fiberglass Fabrication Industry in Washington State, AIHA, 42:2, February, 1981.
- 15. Joe Studenburg, USS Chemical, New Jersey, Personal Communication, April 22, 1981.
- 16. Brooks, S.M.: The Effects of Protective Equipment on Styrene Exposure in the Workers in the Reinforced Plastic Industry, Archives of Environmental Health, 35:5, September, 1980.

X. AUTHORSHIP/ACKNOWLEDGEMENTS

Evaluation Conducted and Report Prepared by:

Richard W. Gorman, M.S., C.I.H. Industrial Hygienist

Industrial Hygiene Section

Originating Office:

Hazard Evaluations and Technical Assistance Branch Division of Surveillance, Hazard Evaluations and Field Studies

Cincinnati, Ohio

Report Typed by:

Jackie Woodruff Clerk/Typist Industrial Hygiene Section

XI. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

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 ninety (90) days, the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia 22161. Information regarding its availability through NTIS can be obtained from NIOSH, Publications Office, at the Cincinnati, Ohio, address.

Copies of this report have been sent to:

- a) Marble Products of Memphis
- b) OSHA, Region IVc) NIOSH, Region IV

For the purposes of informing the affected employees, a copy of this report shall be posted in a prominent place, accessible to the employees, for a period of thirty (30) calendar days.

FIGURE 1
MARBLE PRODUCTS OF MEMPHIS
HHE 81-052
February 18-19, 1981

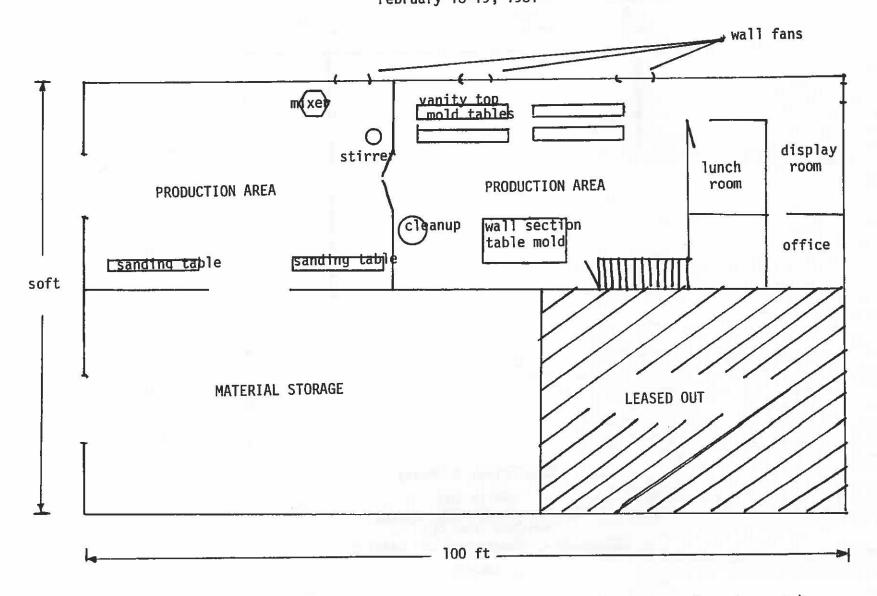


FIGURE 2
STYRENE CONCENTRATIONS BY OPERATION
(15 min. samples)
MARBLE PRODUCTS OF MEMPHIS
HHE 81-052

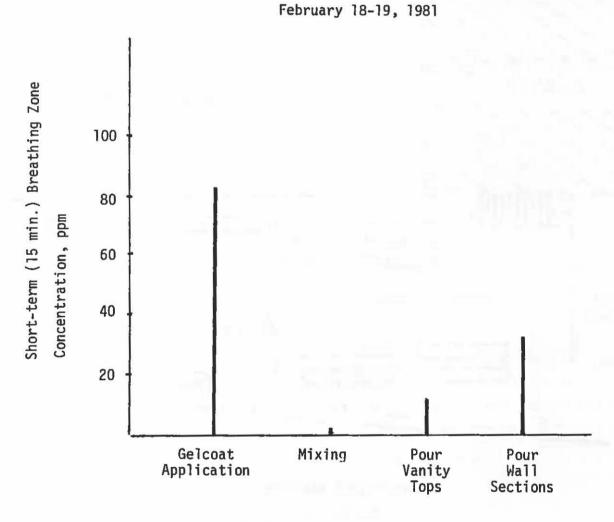


FIGURE 3 AERODYNAMIC PARTICLE SIZE DISTRIBUTION MARBLE PRODUCTS OF MEMPHIS HHE 81-052 February 18-19, 1981 20.0 10.0 9 8 7 d m = 15.3 μ m 6 Particle size, um 5 4 3 2 1.0 50 60 70 30 10 20 30 0.010.05 0.10.2 0.5 Cumulative Mass % less than stated size

Table 1

ORGANIC VAPOR RESULTS
MARBLE PRODUCTS OF MEMPHIS
HHE 81-052

February 18-19, 1981

Date	Job/Location		ample ype*	Sampling Time	Sample Vol (1)	Styrene	Acetone ppm	Toluene ppm	Mek ppm
2/18	Lunchroom		А	10:45am-12:30pm	9.1	0.5	<0.9	<0.3	<0.4
2/18	NIOSH Representa	tive -	Р	10:45am-12:30pm	10.2	1.2	1.2	0.3	1.0
2/18	Mixing Area on S		A	10:45am-12:30pm	52.5	5.0	3.5	0.7	1.0
2/10	Openator #1	Minima Datah #1	0/15)	10.45 11.00		1		11	
2/18	Operator #1	Mixing Batch #1	P(15)	10:45am-11:00am	1.5	1.6	<5.6	<1.8	4.5
2/18 2/18	Operator #1	Pour Batch #1	P(15)	11:00am-11:15am	1.5	36.8	<5.6	<1.8	<2.3
2/10	Operator #1	Acetone Cleanup - Mix Batch #2	P(15)	11:15am-11:30am	1 5	10.0	25.0		
2/18	Operator #1	Pour Batch #2 -	F(15)	11:15am=11:50am	1.5	12.8	25.2	3.6	13.6
2710	operator #1	Acetone Cleanup	P(15)	11:30am-11:45am	1.5	20.8	16.8	1.0	
2/18	Operator #1	Pour Bowl Shells	P(15)	11:45am-12:00pm	1.5	19.2	11.2	1.8 3.6	6.8 6.8
	Spo. 333		. (10)	111.13 din 12.00pm	113	13.2	11.2	3.0	0.0
2/19	Operator #2	Complete Process for 6 Top	S						
		& 50 ft of wall section	Р	7:13am-12:10pm	22.5	15.0	17.0	1.1	3.3
2/19	Operator #2	Gelcoat Application Only	Р	7:13am-8:05am	9.4	18.9	8.1	0.6	2.7
2/19	Operator #1	Complete Process,							
	APRIL 1999 STANDARD IN 18 19 19	Except Gelcoat	Р	9:00am-12:10pm	18.2	0.1	<0.5	<0.2	0.2
2/19	Lunchroom	₩	Α	9:07am-12:10pm	14.2	3.1	0.9	0.2	0.7
2/19	Operator #2	Gelcoat Application	P(15)	7:34am-7:46am	1.2	60.0	10 5	<0.0	0.0
2/19	Operator #2	Gelcoat Application	P(5)	7:46am-7:51am	0.5	81.6	10.5	<2.2	2.3
2/19	Pouring Table	Gelcoat Operation	A A	7:45am-7:50am	2.8	83.0	<16.8 16.5	<5.4 1.9	6.8
2/19	Operator #2	Pouring Operation	P(15)	9:25am-9:44am	1.9	10.1	11.1	<1.4	3.7
2/19	Operator #1	Pouring Phase	P(15)	9:45am-10:00am	1.5	12.8	<5.6	<1.8	5.4 2.3
2/19	Operator #2	Pour Wall Section on Table		9:12am-9:27am	1.5	33.6	5.6	<1.7	4.5
				- J the artir of the 2 Mills		00.0	3.0	1 4 7	7.5

^{*} Sample Type Code: P - personal breathing zone sample, A - Area Sample. Number in parenthesis is sampling time, i.e., P(15) is 15 minute short-term breathing zone sample

Table 2

DUST SAMPLE RESULTS MARBLE PRODUCTS OF MEMPHIS HHE 81-052

February 18-19, 1981

Job/Location	Sample Type*	Sampling Time	Sample Vol. (1)	Dust Concentration** (mg/M ³)
Sanding Tops	P(R)	9:00am-11:05am	212	0.48
Sanding Tops	Р	9:00am-11:05am	212	7.80
Sanding Area	A(R)	9:00am-11:05am	212	0.48
Sanding Area	A	9:00am-11:05am	212	6.60
Mixing Area	R	9:00am-11L05am	212	0.39

* Sample Type Code: P(R) is personal breathing zone sample (respirable fraction) P is personal breathing zone sample (total dust)

A(R) is area sample (respirable fraction)
A is area sample (total dust)

** Dust Concentration is the time-weighted-average concentration for sampling

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