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Shindoni, Inc.
Tesuque, New Mexico

Charles McCammon

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, technical and consultative assistance 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.

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Tesuque, New Mexico
February 1998

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SUMMARY

On March 14, 1997, the National Institute for Occupational Safety and Health received a request for a Health Hazard Evaluation from the Safety Director of Shindoni, Inc., Tesuque, New Mexico. The request asked for help identifying and controlling the chemicals responsible for causing headaches and nausea among workers during pours of bronze castings. The company identified the sand mold resin bonding system as the suspected source of the irritating chemicals.

Shindoni, Inc., is a privately-owned art foundry which produces a wide variety of art products, but primarily bronze castings. The area of interest within the site is the bronze foundry operations. Sand is mixed with an isocyanate-based binder system and then packed around fiberglass patterns, cores, and wax shapes to make a mold. Once the binder has set, the mold is poured. Bronze is the predominant metal used.

Air sampling for phenol, methylene bisphenyl isocyanate (MDI), aldehydes, and volatile organic compounds using thermal desorption tubes was conducted September 23-25, 1997. Only one MDI sample was above the analytical limit of detection (LOD) of 3 micrograms per sample ($\mu\text{g}/\text{sample}$), the airborne concentration measured by that sample was 130 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) over a 32-minute period. One oligomer sample was detectable and equated to an air concentration of $320 \mu\text{g}/\text{m}^3$ for a 19-minute sample. Area and personal air samples for phenol ranged from $<0.15 \text{ mg}/\text{m}^3$ to $3.3 \text{ mg}/\text{m}^3$ [NIOSH Recommended Exposure Limit (REL) is $60 \text{ mg}/\text{m}^3$ as a Ceiling].

Aldehyde area and personal air samples had detectable amounts for four aldehydes: acetaldehyde, formaldehyde, propionaldehyde, and acrolein. Acetaldehyde air concentrations ranged from <0.17 to $2.4 \text{ mg}/\text{m}^3$ [American Conference of Governmental Industrial Hygienists [ACGIH] Threshold Limit Value [TLV®] is $45 \text{ mg}/\text{m}^3$ as a Ceiling). Propionaldehyde air concentrations ranged from <0.17 to $5.1 \text{ mg}/\text{m}^3$. There are no applicable evaluation criteria for this chemical.

Formaldehyde concentrations ranged from <0.1 to $2.9 \text{ mg}/\text{m}^3$. These four detectable samples were all above the various ceiling evaluation criteria from NIOSH, OSHA, and ACGIH. The highest concentrations of formaldehyde (1.7 and $2.9 \text{ mg}/\text{m}^3$ as personal samples) occurred during the mixing of the binder with sand, while the other two occurred during a mold pour.

Acrolein air concentrations ranged from 0.5 to $3.9 \text{ mg}/\text{m}^3$. Four of these air concentrations (2.7 , 2.8 , 3.1 , and $3.9 \text{ mg}/\text{m}^3$) are above the NIOSH REL as a Ceiling ($0.8 \text{ mg}/\text{m}^3$) and the ACGIH TLV as a Ceiling ($0.69 \text{ mg}/\text{m}^3$).

The air concentrations were highest during both the mixing of the binder with sand and during the pouring of bronze into the molds. The area samples collected during the mold pour are not representative of actual worker exposure.

Nearly forty volatile organic compounds or chemical groups were identified using the thermal desorption tubes and gas chromatography/mass spectrometry analysis. However, the amounts of these chemicals are quite low, on the order of 1-10 $\mu\text{g}/\text{sample}$. The highest levels of chemicals of concern were for benzene, which was found in amounts ranging from 0.4-2 $\mu\text{g}/\text{sample}$. The highest sample equates to an air concentration of 0.68 mg/m^3 (the NIOSH REL as a Ceiling is 3.2 mg/m^3 , the OSHA PEL as a Ceiling is 15 mg/m^3). Other chemicals identified relatively in higher amounts, included many alkyl benzenes, but these do not have evaluation criteria due to their low toxicity.

Personal and area air samples indicated an over-exposure to formaldehyde and acrolein in the sand mixing area. Newly installed local exhaust ventilation had helped reduce exposure during mold pours, although area samples directly adjacent to the molds revealed high concentrations of acrolein and formaldehyde. Recommendations are included regarding personal protective equipment to protect against skin and inhalation exposure to aldehydes.

Keywords: SIC 3362 (Brass Foundry), foundry, phenol, methylene bisphenyl isocyanate, MDI, acetaldehyde, formaldehyde, propionaldehyde, acrolein, aldehydes, volatile organic compounds

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INTRODUCTION

On March 14, 1997, the National Institute for Occupational Safety and Health received a request for a Health Hazard Evaluation from the Safety Director of Shindoi, Inc., Tesuque, New Mexico. The requestor asked for assistance in identifying and controlling the process chemicals suspected of causing headaches and nausea among workers during pours of bronze castings. The company identified the sand mold resin bonding system as the suspected source of the irritating chemicals.

BACKGROUND

Shindoni, Inc. is a privately-owned art foundry which produces a wide variety of art products, but primarily bronze castings. The area of interest within the site is the bronze foundry operation. Sand is mixed with an isocyanate-based binder system (Pep Set I & II, Ashland chemical Corporation) and then packed around wax (or fiberglass) shapes to make a mold. Once the binder has set, the mold is poured. The predominant metal used is bronze. The bronze is melted from ingots in a furnace adjacent to the sand mixing/mold preparation area. Once the bronze reaches the appropriate temperature, the ladle is moved via a ceiling crane to the pour area, and the mold is poured. The actual pour takes only a few minutes per mold (usually two molds are poured at once). When the heated bronze contacts the molds, great quantities of irritating smoke are produced. The workers conducting the pours reported that they previously experience coughs, headaches and eye irritation from the smoke, but conditions had greatly improved since the company installed an exhaust ventilation system at the pour area. This system is comprised of a large (roughly 5 feet square) hood which goes to a 2-foot duct that is exhausted through a fan on the roof.

METHODS

Area and personal breathing zone (PBZ) air samples were collected over 3 days for methylene bisphenyl isocyanate (MDI), aldehydes, phenol, and total volatile organic compounds (VOCs).

Area and PBZ air samples for aldehydes were collected on treated XAD resin tubes at 0.05 liters per minute (Lpm) using Gilian LFS 113D C personal sampling pumps. The samples were desorbed with toluene and analyzed by gas chromatography according to NIOSH Analytical Method #2539.¹ This method is capable of analyzing acetaldehyde, formaldehyde, valeraldehyde, hexanal, heptanal, butyraldehyde, propionaldehyde, acrolein, and iso-valeraldehyde.

Area air samples for MDI and MDI-based oligomers (polymeric isocyanate with reactive isocyanate groups attached) were collected using NIOSH method 5522.¹ This method utilizes a midjet impinger containing 20 milliliters of a derivatizing reagent consisting of tryptamine dissolved in dimethyl sulfoxide. Samples were collected by drawing air through the midjet impinger at a nominal flowrate of 1.0 Lpm, using a calibrated sampling pump. Upon completion of the sampling, the impinger solutions were transferred into opaque glass vials, and shipped to the analytical laboratory. The samples were analyzed using high performance liquid chromatography, with both fluorescence and electrochemical detection.

Area and PBZ air samples for phenol were collected on treated XAD-7 sampling tubes at 0.05-0.1 Lpm using Gilian LFS 113D C personal sampling pumps. The samples were desorbed with methanol and analyzed by gas chromatography according to NIOSH Analytical Method 2546.¹

Air samples for VOCs were collected on specially designed thermal desorption tubes. These stainless steel tubes were packed with a front section of Carboxen Y, a middle layer of Carboxen B, and a back section of Carboxen 1003. The samples were

thermally desorbed and analyzed for VOCs using a gas chromatograph coupled to a mass selective detector (TD-GC-MSD).

EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs)², (2) the American Conference of Governmental Industrial Hygienists' (ACGIH®) Threshold Limit Values (TLVs)³ and (3) the U.S. Department of Labor, OSHA Permissible Exposure Limits (PELs)⁴. In July 1992, the 11th Circuit Court of Appeals vacated the 1989 OSHA PEL Air Contaminants Standard. OSHA is currently enforcing the 1971 standards which are listed as transitional values in

the current Code of Federal Regulations; however, some states operating their own OSHA-approved job safety and health programs continue to enforce the 1989 limits. NIOSH encourages employers to follow the 1989 OSHA limits, the NIOSH RELs, the ACGIH TLVs, or whichever are the more protective criterion. The OSHA PELs reflect the feasibility of controlling exposures in various industries where the agents are used, whereas NIOSH RELs are based primarily on concerns relating to the prevention of occupational disease. It should be noted when reviewing this report that employers are legally required to meet those levels specified by an OSHA standard and that the OSHA PELs included in this report reflect the 1971 values.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8-to-10-hour workday. Some substances have recommended short-term exposure limits (STEL) or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short-term.

Aldehydes

Formaldehyde

Formaldehyde is a colorless gas with a strong odor. Exposure can occur through inhalation and skin absorption. The acute effects associated with formaldehyde are irritation of the eyes and respiratory tract, and sensitization of the skin. The first symptoms associated with formaldehyde exposure, at concentrations ranging from 0.1 to 5 parts per million (ppm), are burning of the eyes, tearing, and general irritation of the upper respiratory tract. There is variation among individuals, in terms of their tolerance and susceptibility to acute exposures of the compound.⁵

In two separate studies, formaldehyde has induced a rare form of nasal cancer in rodents. Formaldehyde exposure has been identified as a possible causative factor in cancer of the upper respiratory tract in a

proportionate mortality study of workers in the garment industry.⁶ NIOSH has identified formaldehyde as a suspected human carcinogen and recommends that exposures be reduced to the lowest feasible concentration. The OSHA PEL is 0.75 ppm (0.92 mg/m³) as an 8-hour TWA and 2 ppm (2.4mg/m³) as a STEL.⁷ ACGIH has designated formaldehyde to be a suspected human carcinogen and therefore, recommends that worker exposure by all routes should be carefully controlled to levels "as low as reasonably achievable" below the TLV.³ ACGIH has set a ceiling limit of 0.3 ppm (0.37 mg/m³).

Note: NIOSH testimony to DOL on May 5, 1986, stated the following: "Since NIOSH is not aware of any data that describe a safe exposure concentration to a carcinogen, NIOSH recommends that occupational exposure to formaldehyde be controlled to the lowest feasible concentration; 0.1 ppm (0.123 mg/m³) in air by collection of an air sample for any 15-minute period as described in NIOSH analytical method 3500 which is the lowest reliably quantifiable concentration at the present time." NIOSH also lists a PEL for formaldehyde of 0.016 ppm (0.02 mg/m³) for up to a 10-hour TWA exposure (again using NIOSH analytical method 3500) and indicating that this is the lowest reliably quantifiable concentration at the present time. Investigators should be aware that formaldehyde levels can currently be measured below 0.016 ppm.

Acrolein

Like formaldehyde, acrolein is a severe irritant and is corrosive to the eyes, skin, mucous membranes, and respiratory tract. Eye contact with liquid acrolein can cause pain, intense tearing, swelling of the lids, and corneal damage. Acrolein can be absorbed through the skin in sufficient amounts to cause systemic effects. The NIOSH REL, ACGIH TLV, and OSHA PEL for acrolein are 0.1 ppm (0.23 mg/m³) as a TWA. In addition, NIOSH and ACGIH recommend a ceiling (or STEL) limit of 0.3 ppm (0.8 mg/m³).

Acetaldehyde and Propionaldehyde

Both of these aldehydes, like acrolein, are strong irritants and are corrosive to the skin and mucous membranes. Acetaldehyde is a potential occupational carcinogen, therefore NIOSH recommends that exposure to acetaldehyde be controlled to the lowest feasible concentration. The OSHA PEL for acetaldehyde is 200 ppm (360 mg/m³) as a TWA. The ACGIH recommends a ceiling limit of 25 ppm (45 mg/m³). There are no standards for propionaldehyde.

Phenol

Phenol is an irritant of the eyes, mucous membranes, and skin. Systemic absorption can cause convulsions as well as liver and kidney disease. The skin is a route of entry for the vapor and liquid phases. Phenol has a marked corrosive effect on any tissue. Symptoms of chronic phenol poisoning may include difficulty in swallowing, diarrhea, vomiting, lack of appetite, headache, fainting, dizziness, dark urine, mental disturbances, and possibly a skin rash.⁸ The NIOSH REL, ACGIH TLV, and OSHA PEL for phenol is 5 ppm (19 mg/m³) as a TWA. All criteria include a skin notation, which indicates that skin absorption may be a significant route of exposure. NIOSH also recommends a 15-minute ceiling REL of 60 mg/m³.

Isocyanates

The unique feature common to all diisocyanates is that they consist of two -N=C=O (isocyanate) functional groups attached to an aromatic or aliphatic parent compound. Because of the highly unsaturated nature of the isocyanate functional group, the diisocyanates readily react with compounds containing active hydrogen atoms (nucleophiles). Thus, the diisocyanates readily react with water (humidity), alcohols, amines, etc.; the diisocyanates also react with themselves to form either dimers or trimers. When a diisocyanate species reacts with a primary, secondary, or tertiary

alcohol, a carbamate (-NHCOO-) group is formed which is commonly referred to as a urethane. Reactions involving a diisocyanate species and a polyol result in the formation of cross-linked polymers; i.e., polyurethanes. Hence, they are used in surface coatings, polyurethane foams, adhesives, resins, elastomers, binders, and sealants. Many material safety data sheets (MSDS) use isocyanate-related terms interchangeably. For the purpose of this report, terms are defined as follows.

Diisocyanates (Monomers): The difunctional isocyanate species from which polyisocyanates and polyurethanes are derived. A common example of monomeric isocyanates is 4,4'-diphenylmethane diisocyanate or methylene bisphenyl isocyanate (MDI).

Polyisocyanates: Species possessing free isocyanate groups and derived from monomeric isocyanates either by directly linking these monomeric units (a homopolymer) or by reacting these monomers with di- or polyfunctional alcohols or amines (a copolymer).

Prepolymers: Species possessing free isocyanate groups, prepared from the reaction of a polyol with an excess of di- or polyisocyanate.⁹ Commercially available isocyanate products frequently contain prepolymers in lieu of more volatile isocyanate monomers.

Oligomeric Isocyanates (Oligomers): Relatively low molecular weight polyisocyanates.

Intermediates: Species possessing free isocyanate groups, formed during use of an isocyanate product by partial reaction of the isocyanate species with a polyol.

Isocyanates exist in many different physical forms in the workplace. Not only are workers potentially exposed to the unreacted monomer, prepolymer, polyisocyanate, and/or oligomer species found in a given product formulation, they can also be exposed to partially reacted isocyanate-containing intermediates formed during polyurethane

production. In addition, isocyanate-containing mixtures of vapors and aerosols can be generated during the thermal degradation of polyurethane coatings and plastics. The capability to measure all isocyanate-containing substances in air, whether they are in monomer, prepolymer, polyisocyanate, oligomer, and/or intermediate forms, is important when assessing a worker's total airborne isocyanate exposure.

Review of Health Effects Associated with Isocyanates

Isocyanates are irritating to the skin, mucous membranes, eyes, and respiratory tract.^{10,11} The most common adverse health outcome associated with isocyanate exposure is asthma due to sensitization; less prevalent are contact dermatitis (both irritant and allergic forms) and hypersensitivity pneumonitis (HP).^{12,13} Contact dermatitis can result in symptoms such as rash, itching, hives, and swelling of the extremities. A worker suspected of having isocyanate-induced asthma/sensitization will exhibit the traditional symptoms of acute airway obstruction, e.g., coughing, wheezing, shortness of breath, tightness in the chest, and nocturnal awakening. An isocyanate-exposed worker may first develop an asthmatic condition (i.e., become sensitized) after a single (acute) exposure, but sensitization usually takes a few months to several years of exposure.^{14,15} The asthmatic reaction may occur minutes after exposure (immediate), several hours after exposure (late), or a combination of both immediate and late components after exposure (dual). The late asthmatic reaction is the most common, occurring in approximately 40% of isocyanate sensitized workers.¹⁶ After sensitization, any exposure, even to levels below an occupational exposure limit or standard, can produce an asthmatic response which may be life threatening. Experience with isocyanates has shown that monomeric, prepolymeric and polyisocyanate species are capable of producing respiratory sensitization in exposed workers.^{17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33} Since the intermediates may be chemically similar to these compounds, it is reasonable to assume that they may also produce this condition. Prevalence estimates for

isocyanate-induced asthma in exposed worker populations vary considerably: from 5% to 10% in diisocyanate production facilities³⁴ to 25% in polyurethane production plants,³⁵ and 30% in polyurethane seatcover operations.³⁶ The scientific literature contains a limited amount of animal data suggesting that dermal exposure to diisocyanates may produce respiratory sensitization.^{37,38,39,40} This finding has not been tested in dermally-exposed workers.

Evaluation Criteria for Isocyanate Exposures

The NIOSH REL and ACGIH TLV for MDI are 50 $\mu\text{g}/\text{m}^3$ (for up to a 10-hour TWA exposure concentration) and 51 $\mu\text{g}/\text{m}^3$ (8-hour TWA exposure concentration), respectively.^{2,3} OSHA does not have an 8-hr PEL for MDI.⁴

NIOSH, OSHA, and ACGIH have exposure criteria for the evaluation of short-term or transient exposures to diisocyanates.^{2,4} Both NIOSH and OSHA have ceiling limits for MDI of 200 $\mu\text{g}/\text{m}^3$. The NIOSH ceiling limit (based on a 10-minute TWA) and the ACGIH STEL (based on a 15-minute TWA) are limits that should not be exceeded during the work-day. The OSHA ceiling limit is a concentration that should never be exceeded during a workday.

Currently, there are no U.S. standards for MDI-based oligomers (including prepolymers, polyisocyanates, and intermediates). The United Kingdom's Health and Safety Executive (UK-HSE) has taken a different approach, i.e., developed a non-specific standard based on the Total Reactive Isocyanate Groups (TRIGs) in a volume of air.⁴¹ The UK-HSE standards for TRIGs in air are an 8-hour, TWA exposure of 20 micrograms of isocyanate groups per cubic meter of air ($\mu\text{g-NCO}/\text{m}^3$), and a ceiling limit of 70 $\mu\text{g-NCO}/\text{m}^3$.

RESULTS

The personal and area air sampling results for MDI are summarized in Table 1. Only one air sample was above the analytical limit of detection (LOD) of 3 micrograms per sample ($\mu\text{g}/\text{sample}$). The airborne sample concentration reflected by this sample was 130 $\mu\text{g}/\text{m}^3$ which is below the NIOSH REL as a ceiling of 200 $\mu\text{g}/\text{m}^3$. Only one isocyanate oligomer sample was detectable, and it equated to air concentration of 320 $\mu\text{g}/\text{m}^3$ for a 19-minute sample.

Air sampling results for phenol are summarized in Table 2. The samples ranged from <0.15 to 3.3 mg/m^3 . All phenol samples were well below the NIOSH/OSHA exposure limit of 19 mg/m^3 as a TWA and the NIOSH ceiling REL of 60 mg/m^3 .

The aldehyde air sample results are summarized in Table 3. Air samples for acetaldehyde ranged from <0.17 to 2.4 mg/m^3 . These concentrations are well below the OSHA PEL and ACGIH TLV. Propionaldehyde air concentrations ranged from <0.17 to 5.1 mg/m^3 . There are no applicable evaluation criteria for this chemical.

Formaldehyde concentrations ranged from <0.10 to 2.9 mg/m^3 . The four detectable samples are all above the ceiling evaluation criteria from NIOSH, OSHA, and ACGIH. The highest concentrations of formaldehyde (1.7 and 2.9 mg/m^3) occurred during the mixing of the binder with sand and the other two occurred during a mold pour. The mold pour samples were area samples collected immediately adjacent to the molds and do not reflect actual worker exposures.

Acrolein air concentrations ranged from 0.5 to 3.9 mg/m^3 . Four of these air concentration (2.7, 2.8, 3.1, and 3.9 mg/m^3) are above the NIOSH ceiling REL and the ACGIH TLV. The air concentrations were highest during the mixing of the binder with sand and during the pouring of bronze into the molds.

A list of the major peaks identified during the gas chromatography/mass spectrometry (GC/MS) scan of the thermal desorption tubes is given in Figure 1. A chromatogram from one of the samples collected during a pour is shown in Figure 2. There were about forty different chemicals or chemical groups identified during the GC/MS analysis. However, most of these chemicals were found in low concentrations, approximately 1-10 µg/sample. The highest levels of those chemicals with significant toxicity are for benzene, which was found in amounts ranging from 0.4-2 µg/sample. For the highest sample, this equates to an air concentration of 0.68 mg/m³ (the NIOSH REL as a ceiling is 3.2 mg/m³, the OSHA PEL as a ceiling is 15 mg/m³). Some of the other identified chemicals were found in higher amounts, such as many of the alkyl benzenes, but these chemicals do not have any evaluation criteria, due to their low toxicity.

DISCUSSION

Of all the chemicals measured and identified, only the aldehydes were present in sufficient concentrations to be a potential problem. The two aldehydes of concern are formaldehyde and acrolein. Interestingly, the air concentrations of both of these aldehydes were as high or higher during the mixing of the resin binder with sand as they were in close proximity to the molds during the mold pours. The Pep Set binders are the obvious source of the aldehydes.

The air samples collected in the pour area were all area samples collected as close to the mold as possible without damaging the sampling equipment. The area air samples collected during the mold pours sampled for much longer time periods and in closer proximity to the off-gassing on the molds than would be representative of the exposure potential for the workers conducting the pour. These workers were exposed for only the few minutes it took to conduct the pour.

CONCLUSIONS

The requestor was concerned about the chemical content of the smoke that came off the molds when liquid bronze was poured. Initial worker complaints had decreased since the new exhaust ventilation had been installed, but there was still concern about what chemicals were in the smoke and in what quantities. Sample analyses revealed no detectable MDI during the pour and only trace amount of phenol. A large number of compounds (approximately 40) were identified using gas chromatography/mass spectrometry analysis. However, none of the chemicals were found in sufficient quantity to pose a problem. An aldehyde screen did identify two chemicals, formaldehyde and acrolein, which were present in sufficient quantities (above the respective RELs, PELs, and TLVs) to explain worker irritation. Personal samples collected during the mixing of sand with the Pep Set binders were above the REL, PEL and TLV for the two aldehydes. Although the area air samples collected during the mold pour were above the various evaluation criteria, they did not represent actual worker exposure. The workers conducting the pour were not as near to the molds as the air samples and they were only in the area for about 5 minutes total. Therefore, actual personal exposure to the aldehydes during mold pours cannot be determined from these area samples.

RECOMMENDATIONS

1. Workers in the sand mixing areas are over-exposed to formaldehyde and acrolein. Additional exhaust ventilation is recommended in the sand mix area, particularly at the mixing station, to reduce exposures below the exposure limits. Another possible option is to substitute the binding resin with one that is less toxic. Until either ventilation or substitution is accomplished, workers conducting the sand mixing, packing the sand into the molds, and those conducting mold pours should wear full-face air-purifying respirators. The full-face respirators add protection to the eyes against the irritating effects of the aldehydes (and any isocyanates that

may be present). The air-purifying cartridges should be specific for formaldehyde and acrolein. Since formaldehyde does not have a low enough odor threshold to detect at the REL, and since the approved cartridges for formaldehyde do not have end-of-service-life indicators, the respirator cartridges must be changed out on a regular basis before the end of their service life. This can be estimated by obtaining capacity data for the cartridges and calculating how long they will last at the highest concentrations documented in this evaluation.

2. Long sleeve shirts are recommended for all workers in the sand mixing area to avoid skin contact with the binding chemicals in the sand. Some of the workers reported skin problems in this area which could be due to contact with isocyanates, aldehydes, or other chemicals in the binder.

3. Personal monitoring for aldehydes should be conducted on workers performing the mold pours to determine their actual exposure.

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Table 1

Summary of Air Sample Results for Methylene Bisphenyl Isocyanate (MDI)
 HETA 97-0138
 Shindoi, Inc., Tesuque, New Mexico
 September 23-25, 1997

Sample #	Sample Description/Location	Sample Duration (min)	Sample Flow Rate (L/min)	MDI Concentration ($\mu\text{g}/\text{m}^3$)	
				Monomer	Oligomer
ISO-50	Area, East side of mixer while making batch	19	1.0	<160	320
ISO-51	Area, West side of mixer, with ISO-50	19	1.0	<160	ND
ISO-52	Personal, Spreading sand mix (combination of 2 jobs)	32	1.0	<90	ND
ISO-53	Personal, Mixing sand (combination of 2 jobs)	32	1.0	(130)	ND
ISO-54	Area, During pour, to the right of the mold	61	1.0	<50	ND
ISO-55	Area, During pour, on metal wall to left of mold	60	1.0	<50	ND
ISO-56	Area, During pour, on wall to the left of the mold	30	1.0	<100	ND
ISO-57	Area, During pour, center of exhaust vent face	30	1.0	<100	ND
NIOSH REL (10-hr TWA) for MDI				50	-
NIOSH Ceiling (10-min) for MDI				200	-

¹ min = minutes ; L/min = Liters of air per minute;

² Concentrations are expressed in micrograms of analyte per cubic meter of air ($\mu\text{g}/\text{m}^3$). An "ND" (none detected) or '<' in this column indicates that none of the analyte was detected in the sample, and the airborne concentration was below the minimum detectable concentration (MDC) for the sampling and analytical method. Concentrations in parentheses are between the minimum quantifiable concentration (MQC) and the MDC and are considered to be semi-quantitative.

Table 2
 Summary of Air Sample Results for Phenol
 HETA 97-0138
 Shindoi, Inc., Tesuque, New Mexico
 September 23-25, 1997

Sample #	Sample Description/Location	Sample Duration (min)	Sample Flow Rate (mL/min)	Phenol Concentration (mg/m ³)
PS-10	Area, East side of mixer while making batch of sand	19	50	2.2
PS-11	Personal, Mixing sand (combination of 2 jobs)	30	50	3.3
PS-12	Personal, Spreading sand mix (combination of 2 jobs)	30	100	1.9
PS-13	Area, During pour, on metal wall to the left of the mold	60	100	(0.2)
PS-14	Area, During pour, to the right of the mold	66	100	<0.15
PS-15	Area, During pour, center of exhaust vent face	30	100	(0.7)
PS-16	Area, During pour, on wall to the left of the mold	30	100	1.2
NIOSH REL (10-hr TWA) / OSHA PEL (8-hr TWA) for Phenol				19
NIOSH Ceiling (10-min) for Phenol				60

min = minutes; L/min = Liters of air per minute; mg/m³ = milligrams of phenol per cubic meter of air
 () Analysis is between the Limit of Detection (1 µg/sample) and the Limit of Quantitation (3 µg/sample) and sample result is considered to be semi-quantitative.
 < Denotes sample is below the Limit of Detection

Table 3
 Summary of Air Sample Results for Aldehydes
 HETA 97-0138
 Shindoi, Inc., Tesuque, New Mexico
 September 23-25, 1997

Sample #	Sample Description/Location	Sample Duration (min)	Aldehyde Concentration (mg/m ³)			
			Acetaldehyde	Formaldehyde	Propionaldehyde	Acrolein
AS-01	Area, Mixing Pep Set with sand	19	(2.2)#	1.7	3.0	2.8
AS-02	Personal, Operating sand mixer	34	2.4	2.9	4.8	3.1
AS-03	Area, During pour, on wall left of mold	60	<0.17	<0.10	<0.17	0.5
AS-04	Area, During pour, to right of mold	61	<0.17	<0.10	<0.17	0.5
AS-05	Area, During pour, center of exhaust face	30	(0.4)	(0.5)	(1.3)	2.7
AS-06	Area, During pour, left of mold	30	1.4	1.5	5.1	3.9
Analytical Limit of Detection -micrograms per sample			0.5	0.3	0.5	0.3
NIOSH REL -10-hr TWA (mg/m ³)			LFC+	0.013	None	0.25
Ceiling			-	0.125	None	0.8
OSHA PEL -8-hr TWA (mg/m ³)			360	0.61	None	0.25
ACGIH TLV -Ceiling (mg/m ³)			45	0.37	None	0.69

min = minutes; L/min = Liters of air per minute; mg/m³ = milligrams of aldehyde per cubic meter of air

() Analysis is between the Limit of Detection and the Limit of Quantitation and is considered only semi-quantitative

+ LFC = Lowest Feasible concentration

<Denotes that sample is below the Limit of Detection

Figure 1 -List of GC/MS Peaks

SEQ 8816
THERMAL DESORPTION TUBES
PEAK IDENTIFICATION

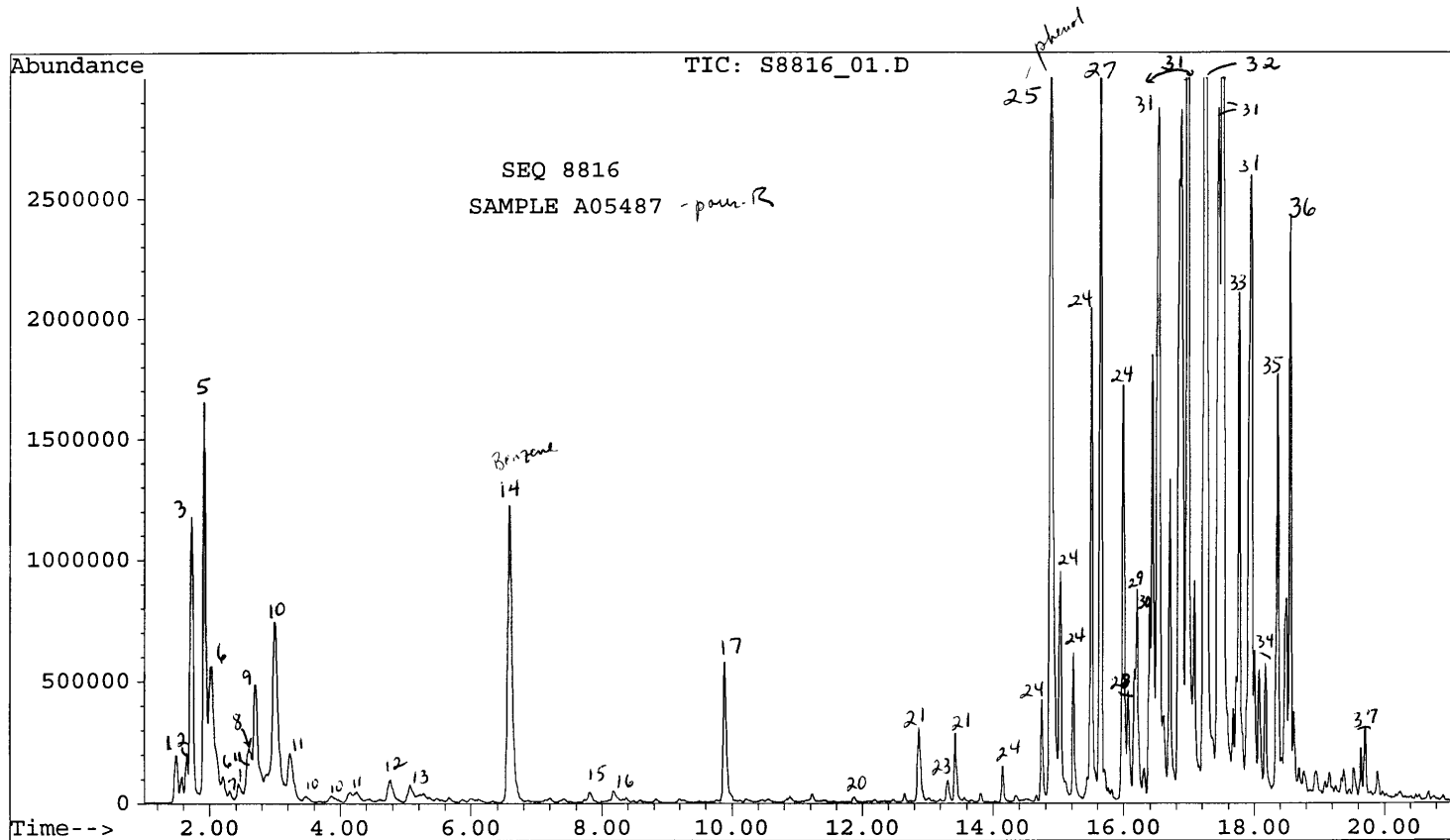
- 1) Air*/CO₂*
- 2) Formaldehyde
- 3) Propene
- 4) Dimethyl ether
- 5) Methanol/isobutane
- 6) C₄H₈ isomer (butene/methyl propene)
- 7) Ethanol
- 8) Acetone
- 9) Isopropanol
- 10) C₅H₈ isomer (pentadiene)
- 11) C₅H₁₀ isomer (pentene, ethyl cyclopropane)
- 12) Hexene
- 13) Hexane
- 14) Benzene
- 15) Heptene
- 16) Heptane
- 17) Toluene
- 18) Hexanal*
- 19) Dimethylsulfoxide (DMSO)**
- 20) Hexamethylcyclotrisiloxane*
- 21) Ethyl benzene/xylene isomers
- 22) Cellosolve acetate*
- 23) Styrene
- 24) C₉H₁₂ alkyl benzenes (trimethyl-, propyl-, methylethyl benzenes, etc.)
- 25) Phenol
- 26) Aliphatic aldehydes*, C₉-C₁₂
- 27) Dimethyl succinate
- 28) Hydroxybenzaldehyde
- 29) Cresol isomer
- 30) Indan
- 31) C₁₀H₁₄ alkyl benzenes (tetramethyl-, ethyl dimethyl-, methyl propyl benzene, etc.)
- 32) Dimethyl glutarate
- 33) Methyl indan
- 34) C₁₁H₁₆ alkyl benzenes (pentamethylbenzene, etc.)
- 35) Naphthalene
- 36) Dimethyl adipate
- 37) Methyl naphthalenes

*Also present on some media and/or field blanks.

**Used in impinger solutions to sample for isocyanates.

Figure 2- GC/MS Scan of Air Sample During Pour

File : C:\HPCHEM\1\DATA\OCT97\S8816_01.D
Operator : AAG
Acquired : 14 Oct 97 10:58 am using AcqMethod ATD
Instrument : 5970 - In
Sample Name: SAMPLE A05487 PURGED
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 1





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Safety and health at work
For all people
Through research and prevention