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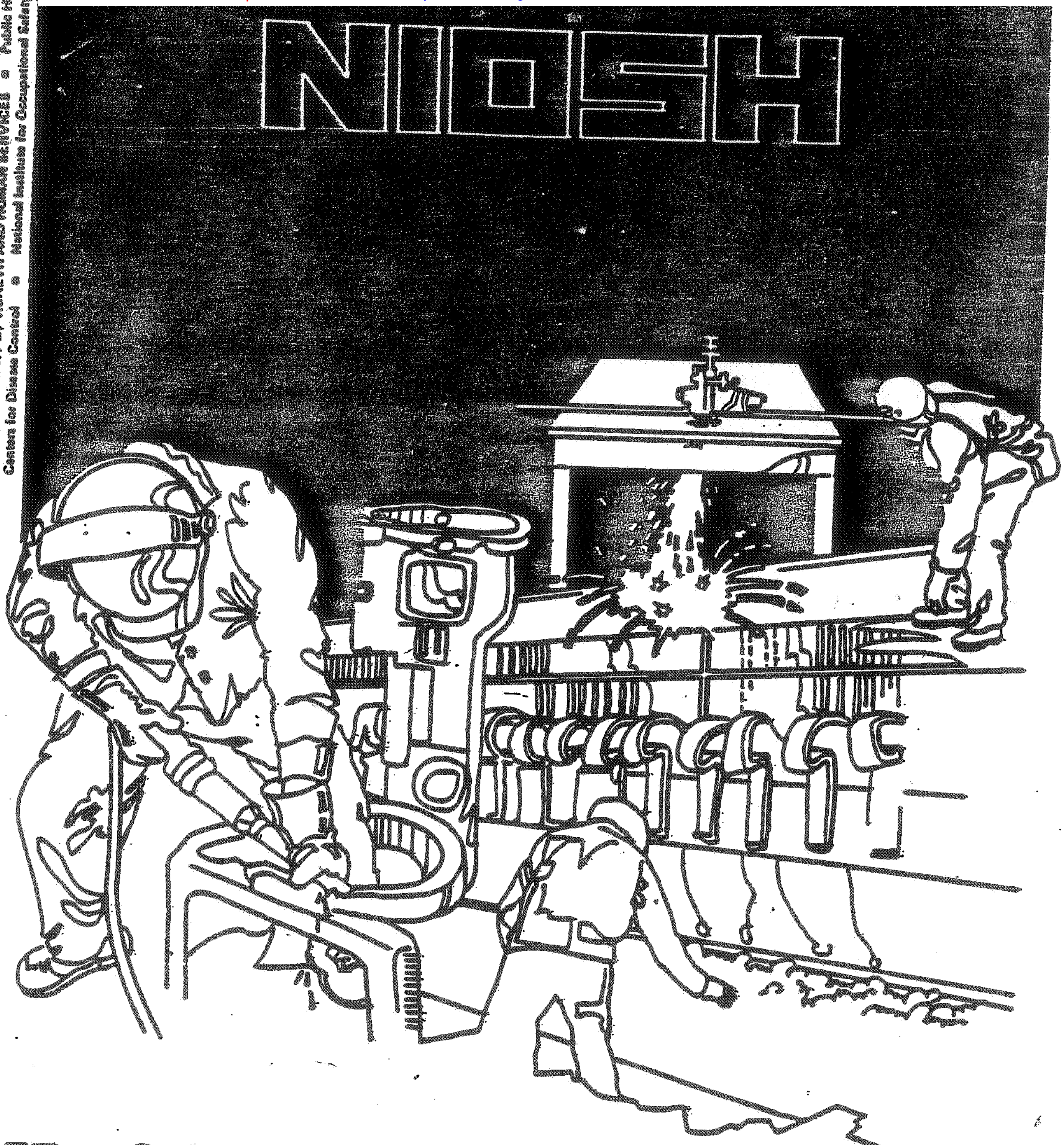

Health Hazard Evaluation Report

HETA 85-482-1730
86-116-1730
WINTERS INDUSTRY FOUNDRY
CANTON, OHIO

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.

HETA 85-482-1730
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WINTERS INDUSTRY FOUNDRY
CANTON, OHIO

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I. SUMMARY

On August 8, 1985, the National Institute for Occupational Safety and Health (NIOSH) was requested to evaluate coreroom employee exposures at the Winters Industry Foundry, a subsidiary of the Whittaker Corporation in Canton, Ohio. The request was prompted by the employees' reported symptoms of vision disturbances (blurred, foggy, or halovision), headaches and stomach pain during the core production operations. Their primary concern was the assessment of exposure to dimethylethylamine (DMEA) gas used as a catalyst in the coreroom sand binder system.

On September 19-20, 1985, December 18-19, 1985, and on January 21-22, 1986, NIOSH investigators conducted surveys at the plant. Long-term personal breathing-zone air sampling was performed during core manufacturing processes to characterize exposures to DMEA, respirable free silica, and several organic solvents including methylene chloride, perchlorethylene, 1,1,1-trichloroethane and trichloroethylene. Stationary long-term air samples were taken at selected locations in the coreroom to assess exposures to ammonia, DMEA, isocyanates (MDI monomer and total reactive isocyanate groups (TRIG)), nitrosamines and silica. These samples revealed the following airborne concentration ranges which are compared to their respective environmental criteria (EC): DMEA, nondetectable (ND)-29 mg/m^3 (EC-there is no OSHA standard, ACGIH TLV® or NIOSH recommended standard in the United States for DMEA); respirable free silica, ND-1,144 ug/m^3 (EC-50 ug/m^3-NIOSH); methylene chloride, ND-4.7 mg/m^3 (EC-lowest feasible level -NIOSH); perchloroethylene, 2.2 mg/m^3 and 6.4 mg/m^3 (EC-lowest feasible level -NIOSH); 1,1,1-trichloroethane, 451 mg/m^3 and 764 mg/m^3 (EC-lowest feasible level-NIOSH); monomeric MDI, ND-23.1 ug/m^3 (EC-50 ug/m^3-NIOSH); TRIG, ND-144 ug/m^3 (EC-there is no standard in the United States for TRIG). No detectable airborne concentrations of ammonia or nitrosamines were found.

Over 90% of coreroom employees reported experiencing at least one symptom or health effect consistent with exposure to DMEA. Most graphic among these reported symptoms was the halovision phenomena, but other vision disturbances as well as systemic effects consistent with absorption of DMEA were also prominently reported by the employees.

On the basis of the data obtained during this investigation, it has been determined that a health hazard existed at the Winters Foundry due to overexposure to respirable free silica. In addition, vision disturbances reported by the employees were compatible with present and previous exposures to levels of DMEA which potentially jeopardize the workers' safety and health. Although no OSHA standard or other environmental criteria exists for DMEA in the work place, common sense judgment dictates that DMEA concentrations should be maintained below the threshold for the occurrence of the vision disturbances reported. For the purpose of providing an adequate margin of safety for the vision-related problems, it is recommended that DMEA concentrations be kept to a minimum through engineering controls and work practices. Furthermore, sampling data indicated worker exposure to 1,1,1-trichloroethane, methylene chloride, perchloroethylene and potential exposure to dioxane and formaldehyde. Based on NIOSH's recommendation that perchloroethylene and methylene chloride be considered as potential human carcinogens, and because of 1,1,1-trichloroethane's chemical similarity to four chloroethane compounds designated as potential carcinogens, attempts should be made to reduce the concentrations of these solvents to the lowest feasible level. Measures to further evaluate silica, reduce exposures to DMEA and organic solvents and to improve engineering controls and working conditions are recommended in Section VIII of this report.

KEYWORDS: SIC 3321 (Aluminum Foundries), 3565 (Industrial Patterns: Foundry Cores), coremakers, core machines, dimethylethylamine (DMEA), Isocure®, phenolic urethanes, no-bake binders, silica, organic solvents, 1,1,1-trichloroethane, methylene bisphenyl isocyanate (MDI), histamine, halovision.

II. INTRODUCTION

On August 8, 1985, the National Institute For Occupational Safety and Health (NIOSH) received a request from the Molders and Allied Workers Union, Local 154, to evaluate employee exposures to chemicals used in the coremaking operation at the Winters Industry Foundry, a subsidiary of the Whittaker Corporation, in Canton, Ohio. The request was prompted by the employees' reported symptoms of vision disturbances (blurred, foggy, or halovision), headaches, and stomach pain during core manufacturing processes. Their primary concern was the assessment of exposure to the dimethylethylamine gas used as a catalyst in the core sand binder system.

NIOSH investigators conducted an initial survey on September 19-20, 1985. A letter summarizing the environmental/medical activities conducted during the survey was distributed to plant management and union representatives in October 1985.

On December 16, 1985, NIOSH investigators obtained a warrant to conduct the follow-up environmental and medical survey. However, access to the plant was denied by Winters management representatives. On December 18, 1985 an agreement reached between NIOSH and Winters and approved by a federal magistrate allowed NIOSH to proceed with the environmental sampling and medical questionnaires on December 18, 1985, and during January 21-22, 1986.

The International Molders and Allied Workers Union, in the interest of identifying other potential employee exposures in the foundry coreroom submitted a health hazard evaluation request on January 6, 1986. In addition to DMEA, ammonia, formaldehyde, isocyanates, nitrosamines, and silica exposures were evaluated during the follow-up environmental/medical survey on January 21-22, 1986.

III. BACKGROUND

The Winters aluminum foundry, with nearly 240,000 square feet of production area, has been operational since 1946. Originally, it was a "jobbing shop" type ferrous foundry prior to its purchase by the Whittaker Corporation in 1970. In 1975, production processes were changed from casting nonferrous metals to producing aluminum castings exclusively. Presently, a variety of sizes and styles of aluminum automotive intake manifolds and engine heads are manufactured at the foundry. Marine engine manifolds and some custom prototype manifolds are also made but they comprise only 5% or less of all the manifolds produced. The plant workforce fluctuates with production demands. During the initial NIOSH survey in September, 1985, it totaled about 615 (approximately 350 production employees) and increased to nearly 700 (410 hourly workers) at the time of the NIOSH follow-up evaluation in January 1986.

A. Coreroom

Coremaking operations run on three shifts, five to seven days per week depending upon production schedules. During the NIOSH follow-up environmental/medical survey, the numbers and types of job classifications in the coreroom included 2 core floor makers, 22 (A) core machine operators, 91 core finishers or assemblers, 3 core sand mixers, 4 core haul laborers, 3 forklift operators and 3 utility personnel. These 128 coreroom production workers employed by Winters in January 1986 represented a 40% increase from the number of coreroom staff from September 1985.

Eighty five percent of the cores are made using the Isocure® sand binder system (phenolic urethane gas-cured no-bake) and the remaining cores are produced either by the Pep-Set® (phenolic urethane liquid cured no-bake) or the more traditional Shell Core binder systems. The Ashland Isocure® binder process used in the coreroom consists of three parts:

Part I, a liquid phenolic resin (phenol-formaldehyde resin with organic solvents), designated Isocure® 308, 306 or 340;

Part II, a liquid diisocyanate (methylene bisphenyl isocyanate (MDI) with solvents), designated Isocure® 610, 606, 608 or 612; and

Part III, an amine gas catalyst (dimethylethylamine (DMEA)) designated Isocure® 702 or 712. Triethylamine has been used as a catalyst in the past at Winters.

In the mezzanine area the phenolic resin and isocyanate components are added to, and mixed in approximately equal amounts (1-1.5% each by weight of the total sand mix) with silica sand in a screw muller that has a 250 lb/minute capacity. Resin and isocyanate are stored in 300 gallon tanks located in the mezzanine area and adjacent to the coreroom floor. The core sand is pneumatically fed to the muller from one of three storage silos. Thirty to thirty-five tons of core sand are used per day to make about 6000 core manifolds. Mixed sand from the muller is transported to hoppers above the eight automated vertical press-type core machines (excluding the two smaller prototypes) and is pneumatically forced into the corebox. One core machine was installed in October 1985 following the preliminary September 1985 survey.

Once in the metallic corebox mold, the sand mixture is gassed with varying amounts of the DMEA gas for about 0.5-3.0 seconds under 50-60 lbs psi. This varies with the size of the core and somewhat upon the ambient temperature and humidity. DMEA gas pressure was nearly halved by plant management (upon recommendation from Ashland Company representatives) about the time of the January follow-up survey. When the amine gas contacts the binder coated sand it produces an instantaneous curing or hardening at room temperature, thus eliminating the need for the cores to be "baked". Liquid DMEA is stored in an enclosed spark proof area adjacent to the coreroom in a 200 gallon tank. Except for the prototype core machines, the amine liquid is converted to a gas (using nitrogen as a carrier) in 5 gallon generators attached to the core machines. Nearly 200 gallons of the catalyst are used per week.

After the solidified cores are manually removed from the corebox they are either temporarily placed on storage racks or they are assembled directly. After every 20-25 cores, a solvent based release agent is dispersed into the core machine coreboxes to prevent the sand from sticking to the corebox mold. Core finishers work adjacent to several of the core machines and perform various intricate manual tasks to assemble the cores including filing, securing two core halves together with wire and a beeswax-like material, inserting small wooden or styrofoam chips as spacers, and filling minor cracks or crevices in the cores with a core mud paste.

Ten to fifteen percent of all cores are either partially or fully painted via brushing or dipping with a silver pigmented organic solvent based paint. The paint is used to "chill" the metal and help prevent shrinkage of the molten aluminum as it cools in the mold. Cores are painted on first shift only.

A core sand tensile test (for compactability and strength) is performed occasionally throughout each shift for quality control purposes. From the coreroom, the finished cores, which are solid reproductions of the hollow spaces desired within the finished casting, are sent to the mold floor where they are placed in the molds prior to the pouring of the molten aluminum.

B. Personal Protective Equipment

Although the core sand mixers (one per shift) in the mezzanine area are provided with disposable half-face 3M® brand #8710 respirators for nuisance dusts/particulates, these workers are not required by plant management to wear them. During the follow-up survey in January 1986, the third shift core sand mixer did wear the respirator described above. However, the first and second shift sand mixers did not. The core painter and some of the core machine operators wear gloves while performing their jobs.

On or around January 13, 1986, Winters Foundry, in the interest of reducing employee exposures to DMEA, instituted a policy requiring all workers to wear chemical splash goggles in the coreroom.

C. Engineering Controls

All the Isocure® core machines are equipped with local exhaust ventilation systems that were designed to aid in purging excess amine gas from the cores. The exhausted air from the core machine is treated in a two stage tower (sulfuric acid and sodium hydroxide) prior to its release to the inside of the plant. At the periphery of the corebox cavities between the two corebox halves, are rubber compression seals that serve to prevent DMEA gas leaks, especially during the gassing phase of the core machine cycle.

D. Medical

One-hundred twenty-nine symptom questionnaires were individually administered on two occasions. On September 19-20, 1985, NIOSH personnel performed a walk-through survey of the facility. They also conducted informal medical interviews with all core machine operators on first and second shifts, and a representative number of core finishers in order to ascertain the type and extent of symptoms which were being experienced. This was done in order to compose a questionnaire which specifically addressed the concerns of the requester and the affected workers.

Initial employee concerns centered about exposure to the catalyst used in the coremaking process. During the informal interviews, employees mostly remarked that after sufficient exposure to this gas, their vision became impaired to the point that they felt it was unsafe to work around machinery. More importantly, they reported severe exposures altered their vision to the point whereby it became hazardous to drive home at night.

During the third shift on November 25, 1985, four coreroom employees reported to the emergency room of Timkin-Mercy Hospital, Canton, Ohio. While working in the coreroom, they were overcome by a suspected large release of DMEA. Their symptoms apparently became so severe that they opted for medical attention. Because the company nurse works only during the first shift, emergency room treatment was the only source of attention.

On December 27, 1985, 12 more third shift employees sought medical attention at the local emergency room after an incident described as identical to the one on November 25.

IV. EVALUATION DESIGN AND METHODS

The initial health hazard evaluation request filed by the Molders Union, Local #154, concerned employee exposures to the DMEA gas catalyst used in the coreroom and expressed a specific interest in the potential acute and chronic health effects due to exposure to this tertiary amine. Of major interest were the reported vision disturbances due to the DMEA exposures and what effects the workers' impaired vision could have on their safety at work as well as driving home following work. The subsequent survey request from the International Molders Union focused on coreroom employees' exposures to isocyanates, formaldehyde, nitrosamines, ammonia and silica. Since the primary concern for our survey was the evaluation of employee exposures during the manufacturing of cores made by the Isocure® process, the industrial hygiene and medical protocols placed special emphasis on that process and no air monitoring or medical interviews were conducted to characterize exposures from the Shell Core or PepSet® coremaking operations.

A. Environmental

On September 19-20, 1985, an initial environmental/medical survey was conducted at the plant. Activities accomplished during the initial survey included opening conferences with management and union representatives present, a walkthrough of the coreroom to observe work practices and conditions of exposure, and collection of pertinent Material Safety Data Sheets from plant management to aid in the development of future air sampling protocols and medical assessments. In addition, bulk samples of the aluminum pigmented paint and thinner used on some of the cores were collected. The company's OSHA 200 forms concerning worker injuries and illnesses (annual summary for 1981-1984 and year to date data for 1985) were briefly reviewed and historical environmental data regarding DMEA exposures in the coreroom were obtained from management officials.

During the January 1986 follow-up survey an in-depth environmental evaluation was performed to characterize coreroom workers' exposures to various contaminants. Both long-term and short-term personal breathing-zone air samples were collected on January 21-22, 1986 to determine employee exposures to DMEA [long-term for overall exposure and short-term for peak exposures], respirable free silica and several organic solvents including methylene chloride, perchloroethylene, 1,1,1-trichloroethane, and trichloroethylene. Stationary area long-term air samples were taken on these dates at selected locations in the coreroom to assess exposures to ammonia, DMEA, isocyanates (MDI monomer and total reactive isocyanate groups (TRIG)), nitrosamines and silica. The sampling and analytical methodologies for these substances, including collection device, flow rate, and referenced analytical procedures, are presented in Table V.[1,2,3]

1. Isocyanates

A brief synopsis of the NIOSH air sampling/analytical method for total reactive isocyanate groups is as follows:

A known volume of air is bubbled through a midget impinger containing a known quantity of 1-(2-methoxyphenyl)-piperazine in toluene. A portion of the toluene solution is acetylated and then evaporated to dryness. This residue is redissolved in methanol and analyzed by high-pressure liquid chromatography (ultraviolet detector at 254 nm). The change in concentration of 1-(2-methoxyphenyl)-piperazine is quantitated and the number of moles of reactive isocyanate groups present determined. The isocyanate groups are quantitated regardless of the size of the molecule to which they are attached.

2. Paint

A bulk sample of the aluminum pigmented paint used on some of the cores was collected and analyzed by gas chromatography/mass spectrometry (GC/MS) for specific chemical compound identification prior to the analysis of the charcoal tubes for organic solvents. A description of the bulk paint analytical method is provided below:

The paint was filtered and screened directly by GC using an HP 5790 GC equipped with a 30 meter DB-1 fused silica capillary column (split mode) and a flame ionization detector. It was then analyzed by GC/MS for chemical compound identification of detected peaks. Because many solvents were identified, the major components were distinguished from the minor components based on relative peak heights.

3. Formaldehyde

The NIOSH project officer had intended to collect short-term, direct reading, colorimetric detector tube air samples for formaldehyde in the coreroom during the January 21-22, 1986 survey. However, due to the industrial hygiene's sampling protocol emphasis on other contaminants and exposures and collection of long-term samples, an oversight was made and inadvertently the formaldehyde measurements were not performed. A brief discussion concerning the need for formaldehyde samples to be obtained in the foundry coreroom is included later in this report.

B. Medical

On December 18, 1985, NIOSH personnel administered medical questionnaires to 80 coreroom employees as per the court agreement. On January 21-22, 1986, the NIOSH medical officer administered questionnaires to 49 other coreroom employees.

Of the 129 workers, 55% were male and 45% were female. The coreroom workforce was employed over three shifts with 40% on 1st shift, 32% on 2nd, and 28% on 3rd shift. At the time of the survey, the total core-room workforce was comprised of:

91 core-finisher/assemblers
4 core-haul laborers
3 core-sand mixers
2 floor-coremakers
22 core-machine "A" operators
3 fork-lift operators
3 utility men

One coremachine "B" operator was also included in the study. "A" operators are responsible for the Isocure® process which uses DMEA. "B" operators use the Shell-Core process which does not use DMEA.

Since earlier work (Akesson, et al., 1985)[43] had failed under field conditions to observe corneal injury during symptoms of the vision disturbance, no evaluation of the corneal integrity or visual acuity was attempted. Under experimental conditions however, exposure to a tertiary amine produced corneal edema as evaluated by pachymetry (measurement of corneal thickness). This edema subsided shortly after the cessation of exposure.[4]

The questionnaire sought to ascertain the nature of the vision disturbance, the frequency of its occurrence, factors in the coreroom that may contribute to its occurrence, and other symptoms caused by exposure to the catalyst. Additional symptomatology was made available to NIOSH through the medical records of sixteen employees who required emergency room treatment in November and December 1985 after being exposed to suspected large releases of DMEA.

V. EVALUATION CRITERIA

A. Environmental Criteria

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for 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 if 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 evaluation 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 Criteria Documents and recommendations, 2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLV's), and 3) the U.S. Department of Labor (OSHA) occupational health standards. Often, the NIOSH recommendations and ACGIH TLV's are lower than the corresponding OSHA standards. Both NIOSH recommendations and ACGIH TLV's usually are based on more recent information than are the OSHA standards. The OSHA standards also may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH-recommended standards, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that industry is legally required to meet those levels specified by an OSHA standard.

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 or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures.

The TWA's and ceiling values used as exposure criteria for assessing potential health hazard are discussed in the following paragraphs.

B. <u>Toxic Effects</u>

1. <u>Methylene Bisphenyl Isocyanate</u>

Methylene bisphenyl diisocyanate (MDI), chemical formula $C_{15} H_{10} N_2 O_2$, normally a solid material at room temperature, is white to pale yellow in color. This odorless substance, with a molecular weight of 250.3, has a low but significant vapor pressure of 0.05 mm/Hg at 20°C (69°F). High molecular weight diisocyanates like MDI present significant vapor hazards when heated or used in exothermic production processes.[5,6]

In general, the potential respiratory hazards encountered during the use of diisocyanates in the workplace are related to their vapor pressures. The lower-molecular-weight diisocyanates tend to be more readily volatilized into the work place atmosphere than the higher-molecular-weight diisocyanates. Although the vapor pressures of the higher-molecular-weight diisocyanates are relatively low, they may generate vapor concentrations sufficient to cause respiratory and mucous membrane irritation if they are handled in poorly ventilated areas. Also, the potential for skin irritation is generally higher for the lower-molecular-weight diisocyanates, and the serverity of these irritant responses is reduced with increasing molecular weight.[5]

MDI vapor is a potent respiratory sensitizer. It is also a strong irritant to the eyes, mucous membranes, and skin, and may cause pulmonary edema. Excess exposure causes cough, dyspnea, increased pulmonary secretions, and chest pain. Isocyanates cause pulmonary sensitization in susceptible individuals. Should this occur, further exposure should be avoided, since even extremely low concentrations can produce asthma-like symptoms in sensitized people.[7]

Asthmatic attacks may occur immediately after exposure or at an interval of hours after cessation of exposure, presenting as nocturnal cough and breathlessness. Exposure to isocyanates may also result in chronic impairment of pulmonary function.[5] Isocyanate exposure during accidental spills is a major cause of sensitization, and there is evidence that massive exposures may produce effects on the central nervous system.[5] One recently completed animal study found dose related statistically significant cancer excesses in mice and rats administered toluene diisocyanate (TDI) by gavage (not the usual route of human exposure) in very high concentrations. The tumors were distant from the site of administration.[8]

The current OSHA Permissible Exposure Limit (PEL)[9] and ACGIH TLV®[10] for MDI is a ceiling limit of 0.02 parts of MDI per million parts of air (ppm) (0.2 milligrams per cubic meter of air, mg/m^3). The current NIOSH Recommended Exposure Limit (REL)[5] for occupational exposure to MDI is 0.005 ppm (0.05 mg/m^3) for up to a 10-hour workshift, 40-hour workweek, and a ceiling limit of 0.02 ppm (0.2 mg/m^3) for any 10-minute sampling period. The NIOSH REL was based on three types of effects of exposure: direct irritation, sensitization, and chronic decrease in pulmonary function. This standard applies to diisocyanate monomers only, and not to higher polymers of these compounds.[5] Little is known about the toxicological effects of polymeric isocyanates. No long-term studies have been conducted on polymeric isocyanates, and furthermore, their potential for inducing pulmonary hypersensitivity, as shown for monomeric isocyanates, has not been investigated.[11] However, results of a recent NIOSH study revealed that work in an industrial setting where polymeric isocyanate exposures were documented was associated with small mean decreases in FEV_1 and FVC which were not observed in an unexposed group. Also, the change in FEV_1 over the shift correlated with personal airborne exposure to polymeric but not monomeric MDI.[12]

Recently, in February, 1983, the United Kingdom Health and Safety Commission set a "common control limit" for workplace exposure to all isocyanates. This new control limit is an 8-hour TWA of 20 ug of isocyanate group per cubic meter of air, and a 10-minute TWA of 70 ug of isocyanate group per cubic meter of air. This new control limit, in units of ug $(NCO)/m^3$, requires that the analytical methods be applicable to "total isocyanate", i.e., the sum of all isocyanate species, including monomers and prepolymers.[13]

2. Methylene Chloride

Methylene chloride CH_2Cl_2, is a colorless volatile liquid that is widely used as a degreasing agent, as a blowing agent in foams and as a solvent for paints, lacquers, varnishes, enamels and adhesives.[7,6] It has a relatively high vapor pressure (350 mm Hg @20°C (68°F) and substantial concentrations of vapor are readily achieved whenever methylene chloride is spilled or spread out over a large surface, even in a space that is not closely confined.[7,6] Various authors have reported odor thresholds for methylene chloride ranging fom 25-320 ppm (87-111 mg/m^3). Since adaptation to the odor of methylene chloride can occur, the odor is not a good indicator of exposure and thus it cannot be considered an adequate warning property.[7]

Methylene chloride is readily absorbed through the lungs and across the skin.[14,15] Repeated skin contact with methylene chloride may cause a dry, scaly, and fissured dermatitis. It is an eye, skin and respiratory tract irritant and causes depression of the central nervous system.[16] Symptoms of methylene chloride intoxication may include headache, giddiness, stupor, irritability, numbness, tingling in the arms and legs, nausea and vomiting.[7,17] A metal degreaser briefly exposed to an undetermined but high concentration of methylene chloride vapor suffered from latent pulmonary edema.[18]

The toxicities of carbon monoxide and methylene chloride are additive.[19] The body has the capacity to metabolize methylene chloride to carbon monoxide and significant quantities of carbon monoxide and carboxyhemoglobin have been found in persons receiving single exposures to methylene chloride.[6] Carboxyhemoglobin, which is formed when carbon monoxide combines with hemoglobin, interferes with the oxygen carrying capacity of blood resulting in a state of tissue hypoxia. This may be significant in smokers or workers with anemia or heart disease, and those exposed to both carbon monoxide and methylene chloride.[17]

In its 1976 criteria document for methylene chloride[19] NIOSH recommended a 10-hour TWA occupational exposure limit of 261 mg/m^3 (75 ppm) in order to prevent interference by methylene chloride with delivery of oxygen to tissues, and impairment in central nervous system functions.

However, since 1976, several studies of chronic effects in animals have been reported documenting the carcinogenicity of methylene chloride.[20] Recently, the National Toxicology Program released a technical report[21] on the toxicology and carcinogenesis of methylene chloride. Under the conditions of this methylene chloride inhalation study mice developed cancers (alveolar/ bronchiolar carcinomas) and tumors (alveolar/bronchiolar adenomas) of the lung, plus cancers (hepatocellular carcinomas) of the liver. Furthermore, rats exposed to methylene chloride in air developed tumors (fibromas and fibroadenomas) of the mammary glands and cancers (sarcomas) of the salivary glands. Although the potential for methylene chloride to induce cancer in humans has not been determined, the observation of cancers and tumors in both rats and mice treated with methylene chloride meets the criteria established in the OSHA Cancer Policy (29 CFR 1990) for considering methylene chloride a "potential occupational carcinogen."[20,22] Therefore, NIOSH now (1986) recommends that occupational exposure to methylene chloride be controlled to the lowest feasible level.[20]

The current OSHA PEL for methylene chloride (29 CFR 1910.1000 Table Z-2)[9] was adopted in 1971 without rulemaking under the authority of section 6 (a) of the Occupational Safety and Health Act of 1970. The OSHA PEL was derived from a standard recommended by the American National Standards Institute (ANSI). The current OSHA[9] PEL is an 8-hour TWA concentration of 1,740 mg/m^3.

The 8-hour TWA, TLV® for methylene chloride recommended by ACGIH[10] is 350 mg/m^3 (100 ppm) with a 15-minute 1,740 mg/m^3 (500 ppm) Short Term Exposure Level (STEL). The documentation on the TLV® cautioned that: "concurrent exposures to other sources of carbon monoxide or physical activity will require assessment of the overall exposure and adjustment for the combined effect".[10,6]

3. Perchloroethylene

Perchloroethylene (also known as tetrachloroethylene) is a clear, colorless, non-flammable liquid with an ether odor detectable around 50 ppm. Repeated contact may cause a dry, scaly, and fissured dermatitis with high concentrations producing eye and nose irritation. Acute exposure has caused effects on the central nervous system, mucous membranes, eyes, kidneys, liver, heart, lungs, and skin. Symptoms of overexposure include headache, dizziness, vertigo, and unconsciousness.[16] While perchloroethylene can be metabolized and eliminated from the body, the process is relatively slow. The substance is deposited in body fat and the biologic half-life in man is estimated at six days.[23]

The National Cancer Institute (NCI), in a long term animal study, has demonstrated that perchloroethylene, administered by gavage, causes hepatocellular carcinoma (liver cancer) in laboratory mice of both sexes.[24] The 50 ppm (339 mg/m^3) exposure criteria recommended by NIOSH in 1976[26] and the current 100 ppm (678 mg/m^3) OSHA PEL[9] were both based on information known before the NCI study and without knowledge of its carcinogenic potential.

NIOSH's current recommendation that it is prudent to handle perchloroethylene in the workplace as if it were a human carcinogen, and therefore exposure be minimized, was issued in a Current Intelligence Bulletin in 1978.[23]

4. Silica

Crystalline silica, usually referred to as free silica, is defined as silicon dioxide (SiO_2) molecules arranged in a fixed pattern, as opposed to a nonperiodic, random molecular arrangement referred to as amorphous silica. The three most common crystalline forms of free silica encountered in industry are quartz, tridymite, and cristobalite, with quartz being by far the most common of these. The principle adverse health effect of crystalline silica is the dust related respiratory disease, silicosis. Silicosis is a form of diffuse interstitial pulmonary fibrosis resulting from the deposition of respirable crystalline silica in the lung. Conditions of exposure may affect both the occurrence and severity of silicosis. Although it usually occurs after 15 or more years of exposure, latent periods of only a few years are well recognized and are associated with intense exposures to respirable dust high in free silica. Early, simple silicosis usually produces no symptoms. However, both acute and complicated silicosis (progressive massive fibrosis, PMF) are associated with shortness of breath, intolerance for exercise, and a marked reduction in measured pulmonary function. Diagnosis is most often based on a history of occupational exposure to free silica and the characteristic appearance of a chest radiograph. Respiratory failure and premature death may occur in advanced forms of the disease. Individuals with silicosis are also at increased risk of contracting tuberculosis. No specific treatment is available, and the disease may progress even after a worker is no longer exposed to silica.[27]

NIOSH, in its recommendations for a free silica standard, has proposed that exposures to all forms of free silica be controlled so that no worker is exposed to respirable airborne concentrations greater than 0.05 mg/m^3 (50 ug/m^3), as averaged over a 10-hour working day, 40-hour work week. This recommendation was designed to protect workers from silicosis. Exposures to free silica greater than one-half the recommended standard, or "action level", should initiate adherence to the environmental, medical, labeling, recordkeeping, and worker protection guidelines contained in the NIOSH criteria document, "Occupational Exposure to Crystalline Silica".[28]

The current federal OSHA PEL[9] for respirable free silica exposure is an 8-hour time-weighted average based upon the 1968 ACGIH TLV® formula of 10 mg/m^3 divided by the sum of the percent SiO_2 and 2 [10 $mg/m^3 \div \%SiO_2 + 2$] for respirable quartz. One-half this amount was established as the limit for cristobalite and tridymite. As can be seen from the calculation, the OSHA regulation is based on the percentage of free silica contained in the respirable particulate exposure, whereas the NIOSH REL applies directly to the airborne concentrations of respirable free silica. In its 1983-84, 84-85, and 85-86 notice of intended changes, ACGIH[10] lists a 100 ug/m^3 TLV® for respirable quartz and a 50 ug/m^3 TLV for respirable cristobalite and tridymite.

5. 1,1,1-Trichloroethane

The primary adverse health effects associated with exposure to 1,1,1-trichloroethane by inhalation, skin absorption or ingestion may include central nervous system depression, headache, dizziness, incoordination, lightheadedness, drowsiness, generalized weakness, fatigue, nausea, vomiting, diarrhea, hypotension, bradycardia, cardiac arrhythmias, skin dryness and irritation, and mucous membrane irritation and liver function abnormalities.[29]

In 1976, NIOSH published a Criteria Document for a Recommended standard for Occupational Exposure to 1,1,1-trichloroethane, recommending that exposure be controlled below a ceiling concentration of 350 ppm.[30] This level was designed to prevent acute respiratory, eye, nose and throat irritation, and chronic effects on the central nervous system. In 1978, NIOSH published a Current Intelligence Bulletin (CIB) (#27) which reviewed the toxicity of nine chloroethane compounds, four of which NIOSH recommended should be handled in the workplace as if they were human carcinogens. The CIB[29] recommended caution in the use of 1,1,1-TCE because of its chemical similarity to the four chloroethane compounds designated as potential carcinogens. The National Toxicology Program under its Carcinognensis Testing Program is currently studying the carcinogenic potential of 1,1,1-TCE in laboratory animals. Results of this research should be available in 1986. In the interim, NIOSH recommends prudence in the use of this substance, including control of workplace exposures to the fullest possible extent.

ACGIH[10] has adopted an 8-hour TLV® of 350 ppm (1,900 mg/m^3) for 1,1,1-trichloroethane with a 15-minute STEL of 450 ppm (2,450 mg/m^3). The OSHA[9] 8-hour PEL is also 350 ppm.

6. Dimethylethylamine

a. Chemistry/acute effects

Dimethylethylamine is a clear, colorless, volatile liquid with a high vapor pressure of 414 mm Hg at 68^oF (20^oC), and a suffocating ammonia-like odor.[31,32] This tertiary aliphatic amine is an extremely flammable liquid that has a flashpoint of -36^oC. It is soluble in water and many organic solvents. It is also used in the polymerization of polyamides as well as the production of mold cores in foundries.[31]

Exposure to vapors of volatile aliphatic amines may produce irritation of the mucous membranes of the nose and throat, and lung irritation with cough and respiratory distress.[33] Many studies have shown that exposure to amines may induce bronchial asthma.[4,35,36] Some aliphatic amines may cause the liberation of histamine, and histamine can bring about a decrease in blood pressure, tachycardia (rapid heartrate), itching, erythema (reddening of the skin), urticaria (hives), and facial edema (swelling).[33] Specifically, exposure to DMEA vapor can cause dizziness, weakness, fatigue, headache and nausea.[37] These systemic symptoms (those affecting the body generally, due to exposure via the lungs or skin, or from ingestion, followed by absorption and a toxic effect of the chemical) may be related to the pharmacologic action of the amines. Skin contact with DMEA can result in irritation, burns, and dermatitis.[37] The ethyleneamines have been shown to cause cutaneous sensitization.[33]

b. <u>Dimethylethylamine Toxicity Toward the Eye</u>

The cornea is the clear window through which light rays pass on their way to the retina. The tear-air interface at the cornea accounts for about 80% of the eye's total refractive power. Thus, the corneal surface must remain smooth and the eyelids must spread the tears uniformly over the epithelium since the slightest distortion degrades the optical image received by the retina. Any opacity (cloudiness) in the cornea will scatter light, degrading the optical image.[39] The halo-perception phenomenon is hypothesized to occur as light is broken up into the spectral colors by droplets of fluid in the corneal epithelium. This happens in the same way that light passing through droplets of rain is broken up to form a rainbow.[38]

Amines being alkaline compounds, are irritating to the eyes and cause lacrimation and conjunctivitis.[40,33] Exposure to the vapor of a few amines results in glaucopsia (hazy or blurry vision), similar to looking through cigarette smoke.[41] The amine vapors have a direct irritating effect on the cornea and the haziness in vision may result from the swelling of the cells (edema) that make up the corneal epithelium. Edema of the epithelium may cause light scattering or a diffraction (Tyndall effect) of the denatured proteins.[42] Amines tend to be fat soluble, which favor their absorption by the cornea.[40]

Edema of the corneal epithelium has caused colored halos to be seen around lights, usually in the evening, after exposure to tertiary amines. Typically, vision becomes misty and halos have appeared several hours after workmen have been exposed to the vapors of the amines at concentrations sometimes too low to cause discomfort during the working day. Generally, the corneal edema clears up spontaneously by the next day.[40] People exposed to the amine vapors and opthamologically examined a few hours after the onset of glaucopsia did not show any striking changes in the eye.[42] However, after very intense exposures, the edema and blurring have taken several days to clear and have been accompanied by photophobia and discomfort from roughness of the corneal surface.[40]

c. <u>Dimethylethylamine Exposure Criteria</u>

There are no proposed or existing NIOSH, OSHA, ACGIH or other criteria or standards for occupational exposure to DMEA in the United States. The lack of any recognized exposure standards for DMEA is due largely to the small amount of health hazard research conducted on this compound.

Triethylamine (TEA), also a tertiary aliphatic amine, has an ACGIH[10] TLV® of 40 mg/m^3 (10ppm) for an eight-hour TWA. [The appropriateness of this level in regards to preventing occupationally related health effects has been questionned].[43] Symptoms of vision disturbances (foggy vision, blue haze and occasional halo-phenomena) were recently reported among workers exposed to triethylamine at TWA levels of 12 to 13 mg/m^3, well below the recommended TLV®.[43] DMEA, being more volatile (vapor pressure 414 mm Hg at 20^{o}C vs. 54 mm Hg for TEA) presents a greater potential hazard.

d. <u>Medical Evaluation Criteria For DMEA</u>

As stated previously, no accepted standards exist for an allowable concentration of DMEA in workplace air. Not surprisingly, there are no particular medical criteria for evaluating exposures either. Because of the ephemeral nature of the vision disturbance, and because other investigators had attempted to evaluate the condition under field conditions, but failed to quantitate any corneal damage, NIOSH investigators had to rely solely on historical data provided by Winters Foundry, emergency room medical records, and symptom questionnaire information provided by affected workers.

At this time, it is thought that the effect of dimethylethylamine on the cornea is transient. Likewise, it seems that the systemic effects experienced by exposed workers remain only for four hours or less. Nevertheless, an "adverse health effect" cannot be ascribed solely on the basis of chronic symptomatology. It is clear that any exposure which directly endangers employee health by reducing work vigilence (especially around dangerous machinery), or impairing driving ability, relates to an "adverse health effect". A level which is generally considered safe for employees working a regular week has not been determined. Until one is formally established, exposures should be reduced to a level below which symptoms do not occur. Vision disturbances were reported during the NIOSH survey at levels of DMEA as low as 6 mg/m^3 (full-shift TWA).

Ashland Chemical Corporation, until NIOSH began its health hazard evaluation at Winters Foundry, recommended 10 ppm (29.9 mg/m^3) as their TLV for DMEA. No published documentation supporting this figure could be found.

While a detailed explanation of possible mechanisms of histamine release is outside the purview of this report, a summary of histaminic action and plausible symptoms of intoxication in humans is as follows:

Table I

SUMMARY OF SOME HISTAMINIC ACTIONS ON HUMAN PHYSIOLOGY

Action of histamine	Possible symptom
1. Constriction of bronchiolar smooth muscle	Tight feeling in chest Difficulty breathing
2. Constriction of gut smooth muscle	Nausea / vomiting Cramps / diarrhea
3. Vasodilatation	Flushed face Headache Dizziness or faintness Increased heartrate
4. Release in dermal tissue	Itching
5. Unexplained but unique action	Metallic taste

Ammonia, as well as structurally simple monoamines can liberate endogenous histamine from mast cells. Substitution on the nitrogen atom may increase activity. DMEA fits this description, as does triethylamine. Lecomte has studied in detail the reaction of two histamine liberators in man (1953; 1955).[45,46] The substituted butylamine (RTECS[47] #GO6839000, 2-hydroxy-4-dimethylaminobenzyl- dimethylamine), L-1935, at low dose (0.1 mg/kg) caused itching, flushing, and tachycardia. At an intermediate dose (0.3 mg/kg) more intense itching, flushing of the face, tachycardia, a 20-40 mm drop in blood pressure, and some headache was seen. His high dose (0.5 mg/kg) caused immediate itching and a generalized feeling of warmth. Blood pressure fell 40-60 mm with a firm but accelerated pulse, and severe headache. Five minutes later, blood pressure rose above normal, there was colic (intestinal cramping), nausea, acid vomit, and swelling of the face and eyes.

VI. RESULTS

A. Environmental

1. Dimethylethylamine

Results of the personal and area air samples obtained on the NIOSH January 21-22, 1986, survey for assessment of employees' exposures to DMEA during coreroom operations are presented in Tables VIa through VIe. Long-term personal breathing-zone DMEA samples revealed concentrations among the core machine operators ranging from 3.1 - 24 mg/m^3, number of samples (N) of 34, a mean (x) of 8.3 mg/m^3, and standard deviation (s) of 4.6 mg/m^3. Airborne DMEA samples collected on the core finishers ranged from 1.6 - 19 mg/m^3, N of 22, x of 6.8 mg/m^3, and s of 4.2 mg/m^3. For these full shift personal samples, the highest DMEA exposed job was the prototype core machine operator with a mean of 14 mg/m^3, whereas, the lowest job exposure was the core sand mixer with a mean of 1.2 mg/m^3.

Thirty one short-term (15 minute) personal samples taken only on core machine operators showed DMEA levels from nondetectable (ND) to 29 mg/m^3. Even though the prototype core machines were only run on first shift, as is typical, the prototype operators had the highest mean DMEA exposure of the short-term samples collected, 17.8 mg/m^3.

During the time three of the thirty one short-term samples were collected, a recognizable DMEA gas leak from the core machines occurred and the machines were temporarily shut down by plant management until maintenance operations could be completed. The three DMEA leak samples (collected on the core machine operators) are included in Tables VI-a (25 mg/m^3), VI-d (15 mg/m^3) and VI-b (Trace). The range of DMEA concentrations on these personal air samples possibly reflects how much time the operators actually spent around the gas-leaking machines, the distance from the core machine, as well as how long the machine leaked the gas prior to it being shut down for repair. Due to the strongly offensive and suffocating DMEA odor that was emitted during one of these easily detectable catalyst leaks, the NIOSH investigators did have to temporarily leave the work area nearest the malfunctioning core machine.

All coreroom personnel who had their DMEA exposures characterized by collection of air samples were questioned after the shift whether they had any vision disturbances (specifically halovision). Three core machine operators reported experiencing acute episodes of halovision during their shift: Table VI-a prototype operator with a long-term DMEA sample (10.0 mg/m^3) and short-term DMEA sample (29.0 mg/m^3); Table VI-a CB-18 operator with a long-term DMEA sample (6.4 mg/m^3) and a short-term DMEA sample (25.0 mg/m^3) and, Table VI-b Isocure #1 operator with a long-term DMEA sample (5.5 mg/m^3). It is interesting to note that of these three positive halovision responses, the prototype operator had the highest measured DMEA concentration of the short-term samples, a DMEA leak occurred during the shift at the CB-18 core machine, and all three core machine operators wore chemical splash goggles.

2. Organic Solvents

The environmental air sample values for the two personal solvent samples collected during the core painting operations on two consecutive days (January 21-22, 1986) in the coreroom are shown in Table VII. Analysis of these full-shift air samples revealed concentrations of 1,1,1-trichloroethane at 764 mg/m^3 and 451 mg/m^3, perchloroethylene at 6.4 mg/m^3 and 2.2 mg/m^3, and methylene chloride at 4.7 mg/m^3. The two personal samples obtained for trichloroethylene were nondetectable as was one of the air samples collected for methylene chloride. All three detectable solvents were below their respective OSHA and ACGIH criterion:

1,1,1-trichloroethane with an 8-hour OSHA PEL[9] and ACGIH[10] TLV® of 1,900 mg/m^3; perchloroethylene with an 8-hour OSHA PEL[9] of 678 mg/m^3 and an ACGIH[10] TLV® of 335 mg/m^3, and; methylene chloride with an 8-hour OSHA PEL[9] of 1,740 mg/m^3 and an ACGIH[10] TLV® of 350 mg/m^3. Based on more recent data (See Evaluation Criteria, Section V of this report), some of which were unknown at the time OSHA and ACGIH set their standards for these three solvents, NIOSH recommends prudence in the use of these solvents and that occupational exposures to methylene chloride, perchloroethylene and 1,1,1-trichloroethane be reduced and controlled to the lowest feasible level.

As mentioned previously in this report, a bulk sample of the silver pigmented paint used in the core painting process in the coreroom was obtained and analyzed via GC/MS for chemical compound identification. One of the additionally detected major peaks besides those identified and sampled for was dioxane. No air samples were collected for dioxane. It is the NIOSH investigators understanding that dioxane is not used in the manufacturing processes and it is not thought to be in any of the production materials. However, dioxane is known to be used as a stablilizer in 1,1,1-trichloroethane, and may be in the paint and possibly found in detectable airborne concentrations in the coreroom, at the painting processes, due to the trichloroethane content of the paint. NIOSH's recommended exposure limit for dioxane is the lowest concentration of dioxane reliably measureable by the sampling and analytical methods selected since animal studies have shown dioxane to be carcinogenic, and hence, dioxane is judged to be a potential carcinogen in man.[16]

3. <u>Silica</u>

Two personal air samples and two stationary area air samples were collected for respirable free silica in the coreroom on third shift on January 21, 1986 (See Table VIII). In the mezzanine area, the two silica samples included one breathing-zone sample on the sand mixer operator and one general area sample on top of a drum. The personal sample data documented that the core sand mixer (4.8 mg/m^3) was overexposed to the calculated OSHA PEL[9] and ACGIH[10] TLV® for respirable quartz (4.6 mg/m^3) and the NIOSH REL of 50 ug/m^3 for any form of respirable free silica,[28] was exceeded (940 ug/m^3) by a factor of nearly 19. Analytical results of the area air sample collected in the mezzanine area also indicated an excessive silica level of 5.1 mg/m^3 which was above the OSHA and ACGIH calculated criterion of 4.5 mg/m^3, and the NIOSH silica REL (50 ug/m^3) was exceeded by almost 23 times (1,144 ug/m^3). If the quartz content of this area respirable quartz sample was disregarded, then the concentration of particulates found on this sample (5.1 mg/m^3) was greater than the OSHA PEL[9] and ACGIH[10] TLV® for respirable dusts (5.0 mg/m^3). Of the other two silica air samples taken, one personal sample on the third shift clean-up operator and one stationary air sample placed near the Isocure® #5 core machine, an overexposure to the NIOSH silica REL was found on the personal sample at 66 ug/m^3.

4. Isocyanates

Concentrations of isocyanates found on the area air samples taken in the coreroom were as follows: monomeric MDI, N of 23, range of ND - 23.1 ug/m^3. None of the full-shift area air samples collected for MDI exceeded the NIOSH REL of 50 ug/m^3 for up to a 10-hour workshift (See Tables IXa-IXe).

The analytical results for the total reactive isocyanate groups (TRIG) are originally reported in micromoles of NCO per sample. These values are converted to micrograms per cubic meter using the molecular weight of 42 (N+C+O) for the NCO radical. These calculations were performed so that the resulting values could be compared with the United Kingdom's standard for total isocyanate groups 20 ug/m^3 for an 8-hour TWA.[13]

Of the 23 long-term area air samples collected for TRIG, 15 had detectable quantities (43.4 - 144 ug/m^3) which were in excess of the United Kingdom's 20 ug/m^3 standard.

5. Ammonia & Nitrosamines

Area air samples for ammonia and nitrosamines were taken on January 21-22, 1986, on five consecutive shifts, to determine exposures during coremaking operations. Analysis of five ammonia and nitrosamine air samples collected at various locations throughout the coreroom revealed no detectable levels (limit of detection: ammonia, 2 ug/sample; nitrosamine, 15 ng/sample for N-nitrosodimethylamine).

B. Medical

The summarized symptom information can be found in TABLES II-IV.

TABLE II

SUMMARY OF VISION DISTURBANCE SYMPTOMS REPORTED BY COREROOM PERSONNEL

SYMPTOM	Percent YES
Hazy (looking through smoke) vision	91
Blurry (out of focus) vision	79
Watery eyes	72
Itchy eyes	48
Halos or rings around lights	67
Colored halos around lights	64
Difficulty doing your job	66
Difficulty driving after work	64
Vision disturbances while experiencing other symptoms	85

More than 90% of coreroom personnel reportedly experienced some degree of vision disturbance over the past year. From the questionnaire data it may be concluded that there is a gradient of vision disturbance progressing from hazy and blurry vision to halo-perception and colored halo-perception (Figure II). Presumably the more graphic halo-perception occurs at higher doses or longer exposures or both. It is difficult to speculate as to whether duration or degree of exposure is the more important factor in determining the extent of the vision disturbance experienced by an individual. Watery eyes occur more often than itchy (dry) eyes, and systemic symptoms are very frequently experienced at the same time the vision disturbance is occurring.

Most employees reported that the vision disturbance developed gradually or slowly, such that prodromal symptoms were not observed. It appears that once the vision disturbance affects an employee, it can last anywhere from ten minutes to more than four hours. One employee reported that it lasted overnight until late the next morning. Overall, leaving the exposure seems to lessen the duration of the effect, and almost everyone remarked that vision was restored to normal by the next morning. Except for a few cases, apparently no eye rinses easily available to those affected could lessen or abate the vision disturbance. Apparently time away from exposure was the only relief from symptoms. Even though many workers had been recently hired, 56% reported having vision disturbance within the past year. 33% said they had had it more than 12 times during the past year. "Gas", presumed to mean the DMEA catalyst, was mentioned most often (44%) as the cause of the vision disturbance. Core machines were mentioned almost as often (41%). Specifically indicated as the "cause" of the vision disturbance were the Redford machines I (10%) and II (8%). Cores and the scrubber (5% each) were also cited as causes.

Besides the alteration of vision, many systemic symptoms were reported by workers in the coreroom (Table III). Systemic symptoms refer to all direct or indirect actions of DMEA on an individual caused by it being inhaled or ingested, and absorbed.

TABLE III

SUMMARY OF SYSTEMIC SYMPTOMS REPORTED BY COREROOM PERSONNEL

SYMPTOM	Percent YES
Felt nauseous or vomited	59
Diarrhea	16
Headache	81
Dizzy or faint	62
Increased heartrate	53
Flushed face	46
Difficulty breathing	71
Tight feeling in the chest	61
Itchy skin	62
Rash	35
Difficulty driving after work	64
Difficulty doing your job	62
Metallic taste	64
Vision disturbances while experiencing other symptoms	85

TABLE IV

SUMMARY OF SYMPTOMS REPORTED ON EMERGENCY ROOM RECORDS AFTER TWO SUSPECTED RELEASES OF DMEA INTO THE COREROOM

SYMPTOM	Number w/symptom	% (n=16)
metallic taste	2/16	13%
eye/nose/throat irritation	4/16	25%
dizziness or faintness	5/16	31%
tight feeling or pain in the chest	7/16	44%
abdominal cramps	8/16	50%
blurred vision	8/16	50%
heartrate >95 beats/minute	10/16	63%
headache	12/16	75%
nausea	13/16	81%

Data from both the questionnaire survey (TABLE III), the emergency room records (TABLE IV), and OSHA documentation (APPENDIX I) indicates a high prevalence of systemic effects as well as vision effects were present among the coreroom personnel. Although involvement of endogenous histamine release has not been demonstrated directly, the myriad pharmacologic actions of amine definitely include the release of preformed histamine (and other neuroeffector compounds such as heparin and serotonin) from granules contained in mast cells and basophils. Referring again to Lecomte (1953; 1955)[45,46] the effects of a histamine liberator on human subjects, are fully in accord with the symptoms reported during the health hazard evaluation and during the two incidents of emergency room visits. It is extremely unlikely that such a symptom profile could result from other systemic actions of DMEA.

Vasodilatory effects and constriction of bronchiolar smooth muscle are most prominent among the systemic symptoms noted. Not unsurprisingly, these are also the main pharmacologic actions of histamine. Vasodilation in the periphery would account for flushed face and dizziness/faintness (venous pooling). In the same manner, increased heartrate (reflex tachycardia) would result as a compensatory mechanism. Histamine, as well as vasodilatation, is associated with headache. Because histamine is a locally-acting hormone (autocoid) it is quickly metabolized. The systemic effects experienced by exposed workers were of a brief (usually less than four hours) duration, also consistent with effects of histamine intoxication.

Bronchoconstrictor action can be ascribed to histamine also. Symptoms of "tight feeling in the chest" and "difficulty breathing" reflect the sensitivity the human lung has toward histamine. Interestingly, Schmitter (1977)[54] has shown that tertiary amine can be deposited on respirable dust in foundries. While not evaluated in this study, respirable dust, along with vapor phase exposure, may contribute to bronchial reactivity and overall exposure to amine catalysts.

Most importantly, high proportions of workers reported that they had difficulty doing their job (62%) and driving home after work (64%). These symptoms may relate more directly to safety aspects of employment at this foundry than "health effects".

VII. DISCUSSION

A. Environmental

1. DMEA

The lack of any established standard or other evaluation criteria (e.g. NIOSH or ACGIH) for occupational exposure to DMEA is mostly due to the scarcity of information available concerning actual exposure levels and thresholds at which acute or chronic toxic effects develop. Because no recognized occupational exposure standards or other evaluation criteria exists for DMEA does not mean that health effects from DMEA exposures are any less relevant and do not or cannot occur. Several reports in the occupational health literature have previously described the visual disturbances phenomena (blue foggy haze and halos around lights) that are often characteristic of industrial amine exposure.[43]

Under the conditions of our study, the environmental air samples revealed coreroom workers were exposed to airborne DMEA and in three cases (core machine operators) at levels sufficient to cause, according to the employees sampled, acute episodes of halovision during the workshift. These reported vision effects from DMEA exposures in this foundry are compatible with the long and repetitious history of high DMEA levels, and symptoms of vision disturbance reportedly occurred despite the curtailed coreroom production operations during the January 21-22 survey. (letter from Gaswirth stated that 1000 fewer cores were made during the NIOSH survey).[44]

A review of historical data on DMEA exposures (see Appendix I.), including NIOSH medical interviews and questionnaires in the Winters Foundry coreroom, indicates that workers have previously been exposed to higher DMEA concentrations than measured during January 21-22, 1986, and reportedly suffered from more frequent and graphic episodes of vision disturbance symptoms than were measured and reported during the NIOSH surveys. Fortunately, more recent reports (February - August 1986) from worker representatives at the plant indicate that improved maintenance on the core machines, including replacing gasket/seals when necessary has helped reduce the number of employees experiencing visual health effects. In the future, however, it is important to remember that acute vision disturbances, commonly experienced by the coreroom personnel due to overexposure to DMEA, have the potential to be contributing factors to accidents and may jeopardize the employees' safety at work and/or driving home after work.

2. DMEA & Goggles

Just prior to our January 1986 survey, Winters Foundry administration, in the interest of reducing DMEA exposures and subsequent visual health effects, implemented a mandatory policy for all workers that chemical splash goggles be worn in the coreroom. During the survey, however, some employees reported that the goggles 1) were more uncomfortable than the safety glasses previously required, 2) restricted their peripheral and vertical vision more than the glasses, and 3) frequently fogged up which further restricted their vision. If the current and future modifications to work practices and engineering controls attempted are successful in reducing workers exposures to DMEA, the need for coreroom personnel to don protective goggles in order to mitigate visual effects (from DMEA exposures) may be unnecessary.

3. Organic Solvents

The results of the environmental air samples obtained by NIOSH personnel revealed that the core painter in the coreroom was exposed to 1,1,1-trichloroethane, perchloroethylene, methylene chloride and may be potentially exposed to dioxane. NIOSH recommends caution in the use of 1,1,1-TCE because of its chemical similarity to four chloroethane compounds which NIOSH designated as potential carcinogens.[29] A long-term animal study conducted by NCI showed that perchloroethylene administered by gavage caused liver cancer in laboratory mice of both sexes.[24] Methylene chloride has been shown to induce cancer in rats and mice.[21] Animal studies have shown dose response relationships between dioxane applied to skin or inhaled and hepatic and nasal neoplasms.[48] Although humans and animals may differ in their susceptibility to specifiic chemical compounds, any substance that produces cancer in experimental animals should be considered a cancer risk to humans. NIOSH recommends prudence in the use of these solvents in the workplace and suggests that effective engineering controls and stringent work practices be employed to reduce and control occupational exposures to methylene chloride, perchloroethylene, 1,1,1-trichloroethane and dioxane, to the lowest feasible level.

4. Silica

Overexposure to silica was confirmed as evidenced by the personal and area air sample results. Improved respiratory protection is necessary to control the employee overexposures while engineering controls are designed and installed. The respirator currently in use by only one of the core sand mixers in the mezzanine area (half-face piece disposable dust respirator) is not appropriate for silica levels of the magnitude measured. Since both the personal and area silica air samples in the mezzanine area were well in excess of the 50 ug/m^3 NIOSH standard and also exceeded the OSHA PEL[9] and ACGIH[10] TLV®, the use of a full facepiece respirator with a replaceable high efficiency dust filter or a type C, supplied air respirator, demand type (negative pressure), with full facepiece is recommended.[28] The silica levels documented by the personal sample taken on the clean up operator would justify the use of any dust respirator (valveless type) approved for use with silica.

5. <u>Formaldehyde</u>

As mentioned previously in this report NIOSH was requested by the International Molders Union to evaluate the coremaking workers exposures to formaldehyde. At the time of the NIOSH January 1986 survey, a greater emphasis was placed on characterizing the employees' exposures to other contaminants besides formaldehyde that would most likely be in higher detectable concentrations in the air, and inadvertently collection of formaldehyde samples was overlooked.

Exposures to low levels of formaldehyde (0.3 - 0.9 mg/m^3) have been documented previously at Shell Core and Isocure® coremaking processes.[49,50] These concentrations of formaldehyde are within the ACGIH eight hour TLV-TWA of 1.5 mg/m^3 and the OSHA eight hour PEL of 3.7 mg/m^3. Bourne and Seferian[51] found formaldehyde levels between 0.16 mg/m^3 and 0.55 mg/m^3 to promote eye irritation and lachrymation. NIOSH however, considers formaldehyde as an occupational carcinogen and as such concludes that an absolute safe level cannot be established.[52] Because the chance for exposure to a potential occupational carcinogen exists, it is appropriate for industrial hygiene consultants to assess the Winters coreroom workers' current exposures to formaldehyde by collecting air monitoring data and taking corrective action if detectable concentrations are found.

B. <u>Medical</u>

According to industrial hygiene monitoring data provided by Winters Foundry and its advisors (letter from Gaswirth, 1985),[44] ambient levels of DMEA up to 32 ppm (94 mg/m^3) have been recorded in the facility. Similarly, exposures which necessitated sixteen coreroom personnel to seek emergency treatment must have been excessive. The lower DMEA exposures measured during the survey of January 21-22, 1986, appear to have reduced the number of coreroom employees experiencing visual health effects. However, during the NIOSH survey vision disturbances were reported at levels of DMEA of 6 mg/m^3 (full-shift TWA). Short-term excursions to levels as high as 29 mg/m^3 may be directly responsible for the vision effects reported by these workers.

It is the opinion of the NIOSH investigators that the standard for exposure to DMEA should be based on the threshold for the occurence of the vision disturbance. Important (and obviously distressing) systemic symptoms appear to occur at higher DMEA exposures. It appears that an appropriate evaluation criteria based on obviating a vision disturbance will preclude the need to address concerns over systemic symptoms, whatever their nature.

VIII. RECOMMENDATIONS

In view of the findings of this investigation, the following recommendations are made to ameliorate existing or potential hazards and to provide a better work environment for the employees covered by this determination.

1. Ideally, the reduction of employee overexposures should be accomplished by the implementation of improved engineering control of workplace contaminants such as substitution of less hazardous process materials, automation, redesign or replacement of existing mechanical ventilation systems and/or process equipment, better work practices or a combination of these measures. Industrial hygiene and engineering consultants should be retained by the plant management to provide additional silica, DMEA and organic solvent monitoring data to determine points of generation of these contaminants within the coreroom and advice as to what specific modifications to the ventilation systems would be effective in controlling and reducing exposures to these contaminants.

2. (a) Increased maintenance efforts on the core machine corebox gaskets to ensure a good pressure-tight seal is formed and cleaning of the joints of the coreboxes to remove excess core sand should be routinely conducted to help reduce existing or potential exposures to DMEA.

   (b) An immersion test should be made with the seal in all of the liquid materials used in the process: Part I resin, Part II isocyanate, the amine catalyst, the release agents, and the metal cleaner. If immersion testing in these materials reveals excess softening or swelling, a more resistant gasket/seal should be chosen (from Tooling Design Ashland Booklet).

(c) Periodic core machine operational checks (with specific attention towards limiting and controlling the release of DMEA into the workplace) by representatives of Winters Foundry, Ashland Chemical Company, and the core machine manufacturer should be employed to ascertain that the core machine and its rigging, is functioning properly.

(d) The modifications to work practices, process controls and recommendations to reduce DMEA exposures outlined in OSHA's May 23, 1986 letter to Winters management representatives (See Appendix I: February 1986) should be carried out.

3. The local exhaust ventilation systems for the core machines, including the scrubber, should have regular thorough evaluations to assure that the capture velocities are adequate, that there are no leaks in the system, and that DMEA concentrations are controlled and reduced.

4. Employees should be encouraged to report every case of amine induced visual disturbance, no matter how minor, so that prompt medical attention may be received and the potential occupational causes can be identified, controlled and rectified.

5. A monitoring system should be instituted and maintained by the plant nurse (on all three shifts) to keep concise updated records on the type and number of health complaints (specific attention to potential DMEA effects reported by workers). This monitoring system should help indicate if the modifications to work practices and new engineering controls implemented are effective in controlling DMEA exposures and its potential symptoms.

6. Due to the greater potential for higher DMEA exposures and for resulting visual disturbance symptoms to develop, in the event of gas catalyst leaks from the core machines, the immediate area should be evacuated until the leaks are located and repaired.

Recommendations Regarding Silica

7. An effective medical and environmental monitoring process to detect cases of pneumoconiosis (silicosis) should be instituted at Winters Foundry. The components of this program are described in the NIOSH criteria document, a Recommended Standard for Occupational Exposure to Crystalline Silica[28] and should include the following:

(a) Exposure to crystalline silica should be controlled so that no worker is exposed to a time-weighted average (TWA) concentration of respirable free silica greater than 50 ug/m^3 of air as determined by a full-shift sample of up to a 10-hour workday, 40-hour workweek. Exposure should be determined by a personal (breathing zone) sample. Procedures for sampling, calibration and analyses of environmental samples are specified in Appendices in the NIOSH criteria document for occupational exposure to crystalline silica.

(b) Engineering controls should be used to maintain free silica dust exposure within the NIOSH recommended standard. Periodic air sampling for silica is necessary in order to determine the extent of the potential silica problem and the effectiveness of engineering controls and work practices, and to identify particularly hazardous work areas where more frequent monitoring or examination of workers is necessary. Preferably, this should be done at least once every six months. Proper respiratory equipment should be available, evaluated and maintained when its use becomes necessary.

(c) A medical examination should be made available to all workers subject to "exposure to free silica" at preplacement. The examination should include (1) a medical and occupational history to elicit data on worker exposure to silica and other fibrogenic dusts, other significant occupational exposures, significant past medical illness, smoking history, and symptoms and signs of respiratory disease; (2) a baseline chest roentgenogram (14" x 17" posteroanterior x-ray), interpreted according to the ILO/UC International Classification of Radiographs of pneumoconiosis; and (3) pulmonary function testing including FVC, FEV_1 and FEV_1/FVC ratio to provide a baseline for evaluation of pulmonary function and to help determine the advisability of workers using negative- or positive-pressure respirators. Standardized procedures for calibrating the spirometer, performing the tests, calculating the results, interpreting the observed spirograms, and using accepted normal values are available and should be utilized.

(d) A periodic medical examination should be performed at least once every three years and should include the three elements described above. Results of pulmonary function should be compared to the previous best test. A 10% reduction in FEV_1 or FVC over a 2-3 year period should be considered a significant change.

8. Chest x-rays performed should be of adequate quality. Chest x-rays should be compared to baseline x-rays and should be interpreted by trained "B readers", or radiologists or chest physicians who are familiar with the use of the ILO/UC classification. Independent reading by three "B readers", or by two "B readers" followed by a consensus interpretation may be a reasonable approach.

9. Medical records should be of such a form that information is easily accessible and retrievable, so that comparisons can be made from one examination to the next and should be maintained for at least 30 years following the employee's termination of employment.

10. Medical management of any employee with or without x-ray evidence of silicosis who has significant respiratory symptoms or signs or significant abnormalities on pulmonary function testing should be fully evaluated by a physician (preferably by a chest physician) qualified to advise the employee whether he should continue working in a dusty trade. Employees with definite or suspected silicosis should be promptly evaluated by a chest physician.

11. Any workers with simple or complicated silicosis should be notified of this finding and warned of the hazards of further exposure. They should be removed from further "exposure" to silica dust. If no pulmonary function impairment is noted, this may be accomplished by combination of environmental dust control, reduced exposure time, and adequate respiratory protective equipment (if the silica dust level meets the NIOSH recommended standard).

<u>Silica and Respirators</u>

12. Plant management should implement a respirator program consistent with the guidelines found in DHEW (NIOSH) Publication No. 76-189, "A Guide to Industrial Respiratory Protection," and the requirements of the General Industry Occupational Safety and Health Standards (29CFR 1910.134). (Copies have been provided to both management and union representatives). Any respirators used, including the approved components and replacement parts should have NIOSH/MSHA approval.

    If non-certified or substituted respirator components are used, the NIOSH/MSHA approval of the entire respirator assembly is voided, and the protection offered by the respirator may be compromised. It must be realized that providing respiratory protection for individuals wearing glasses is a problem. A proper seal cannot be established if the temple bars of eye glasses extend through the sealing edge of the full facepiece. Systems have been developed for mounting corrective lenses inside full facepieces. When a worker must wear corrective lenses as part of the facepiece, the facepiece and lenses should be fitted by qualified individuals to provide good vision, comfort, and a good tight seal.

    Beards should be prohibited on employees who are required to use respirators. Similar to the glasses problem respirators cannot provide sufficient protection if facial hair interferes with a proper facepiece to face seal.

To ensure that workers wearing respirators are afforded an adequate fit and a reasonable protection factor, fit testing procedures (preferably quantitative, however,qualitative as a minimum) should be conducted.

Silica and Work Practices/Engineering Controls

13. It is common practice for the coremakers to disperse excess particulates off the work surfaces using compressed air. With the knowledge that the clean-up operator (and possible other employees) is exposed to silica levels in excess of the NIOSH REL, attempts should be made to collect particulate debris from work surfaces by an alternative method, such as a vacuum cleaning system equipped with high efficiency particulate (HEPA) filters.

14. In the mezzanine area, when the sand muller contains excess mixed sand which isn't used or needed in the batch made, the sand is purged from the mezzanine deck through chutes or hoses to an open transfer box positioned on the coreroom floor below. When this dumping process occurs particulates become airborne and contribute to a dust problem in the coreroom area. Also, during the routine cycling of mixed sand from the mezzanine area to the core machines, leaks of particulates from joints or gaps in the ductwork is occasionally observed. In an attempt to control fugitive dust emissions (silica) and exposures in the coreroom, plant management should enclose the transfer box and tighten any leaks in the sand chutes/ductwork above the core machines.

Organic Solvents

15. The installation and utilization of effective engineering controls, similar in principal to these described in Appendix II (DIP TANK)[53] for the core painting/dipping operations and Appendix III (BARREL FILLING)[53] for the core paint mixing operations should be attempted to help decrease the potential cancer risks, symptoms of irritation, and spread of organic solvent levels from the core painting processes.

General

16. Training of all employees in the potential health problems associated with exposure to the materials used at the plant and the methods of protection utilized should be offered on a regular basis. This continuing education program, conducted by persons qualified by experience and special training, should be instituted to ensure that all have current knowledge and understanding of proper work practices and maintenance procedures, and that they know how to use respirators correctly.

17. Periodic environmental evaluations of employee exposures to DMEA, silica and organic solvents should be conducted to assure that the above recommendations are adequate to protect the affected employees.

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1. Winters Industry Foundry, Canton, Ohio
2. Molders and Allied Workers Union, Local 154
3. International Molders and Allied Workers Union
4. Whittaker Corporation
5. NIOSH, Region V
6. OSHA, Region V

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

Air Sampling and Analysis Methodology
Winters Foundry
Canton, Ohio
HETA 85-482 & 86-116

Substance	Collection Device	Flow Rate (liters per minute)	Analysis	References*
Ammonia	Silica Gel Tube (treated with H_2SO_4)	0.05	Ion Chromatography	NIOSH 6701[1]/S-3472[2] (Ammonia) with modifications**
Dimethylethylamine	Silica Gel Tube	0.05 & 0.2	Gas Chromatography	NIOSH P&CAM 221[3] (Aliphatic Amines with modifications
Isocyanates				
Monomeric Methylene Bisphenyl Isocyanate (MDI)	Midget Impinger with 15 ml of 1-(2-methoxyphenyl)-piperazine in toluene	1.0	High Performance Liquid Chromatography	NIOSH METHOD 5505[1] (Total Isocyanates
Total Reactive Isocyanate Groups (TRIG) (monomer & polymer)		1.0	High Performance Liquid Chromatography	NIOSH METHOD 5505[1] (Total Isocyanates
Nitrosamines	Thermosorb/N tube	0.2	Gas Chromatograph Equipped With A Thermal Energy Analyzer	NIOSH METHOD 2522[1] (Nitrosamines)
Organic Solvents				
Methylene Chloride	2 Charcoal Tubes in series	0.03	Gas Chromatograph Equipped With A Flame Ionization Detector	NIOSH METHOD 1005[1] (Methylene Chloride with modifications
Perchloroethylene	Charcoal Tube	0.05	Gas Chromatograph Equipped With A Flame Ionization Detector	NIOSH METHOD 1003[1] (Halogenated Hydrocarbons) with modifications

*The numerical references are listed in Section IX of this report.
**The modifications included sample preparation, instrument condition settings, and/or column selection.

(continued)

Table V
(continued)

Substance	Collection Device	Flow Rate (liters per minute)	Analysis	References*
1,1,1-Trichloroethane	Charcoal Tube	0.05	Gas Chromatograph Equipped With A Flame Ionization Detector	NIOSH METHOD 1003[1] (Halogenated Hydr carbons) with modifications**
Trichloroethylene	Charcoal Tube	0.05	Gas Chromatograph Equipped With A Flame Ionization Detector	NIOSH METHOD 1003[1] (Halogenated Hydr carbons) with modifications**
Silica	Tared PVC/FWSB Filter	1.7	X-Ray Diffraction	NIOSH METHOD 7500[1] (Respirable Crystalline Silic with modifications**

*The numerical references are listed in Section IX of this report.
**The modifications included sample preparation, instrument condition settings, and/or column selection.

Results of Environmental Air Samples For Dimethylethylamine
Winters Foundry
Canton, Ohio
HETA 85-482 & 86-116
January 21, 1986
First Shift

SAMPLE LOCATION	TIME	DIMETHYLETHYLAMINE CONCENTRATIONS[a] mg/m3[b] Long-Term Silica Gel Tubes	Short-Term Silica Gel
Redford #1/#2 Core Machine Operator	Long-Term 704-1437 Short-Term 1132-1148	7.2 (22.3)[c]	Trace[d] (2.9)
Isocure #4 Core Machine Operator	Long-Term 710-1439 Short-Term 1132-1147	6.2 (22.5)	ND[f] (3.0)
Isocure #3 Core Machine Operator	Long-Term 712-1448 Short-Term 1240-1256	4.2 (21.4)	Trace (3.1)
Isocure #5 Core Machine Operator	Long-Term 716-1442 Short-Term 1223-1238	3.9 (23.3)	Trace (3.1)
Core Finisher Adjacent to Isocure Core Machine #5	Long-Term 719-1442	5.9 (22.1)	
Core Finisher Adjacent to Isocure Core Machine #3	Long-Term 727-1443	5.5 (22.0)	
Isocure #2 Core Machine Operator	Long-Term 739-1448 Short-Term 1222-1237	10.6 (20.7)	22.6 (3.1)

(continued)

TABLE VIa
(continued)

SAMPLE LOCATION	TIME	DIMETHYLETHYLAMINE CONCENTRATIONS[a] mg/m[3b] Long-Term Silica Gel Tubes	Short-Term Silica Gel
Core Finisher Working On Cores From Isocure Core Machine #2	Long Term 722-1445	6.1 (23.0)	
Core Finisher Adjacent to Core Machine CB-18	Long-Term 732-1444	3.8 (21.1)[c]	
Core Finisher Near Isocure Machine #5	Long-Term 735-1446	5.3 (22.4)	
Utility Person	Long-Term 855-1446	4.6 (17.2)	
Prototype Operator Closest to Isocure Core Machine #4	Long-Term 706-1438 Short-Term 1115-1130	10.0 (22.0)[c]	29.0 (3.1)
Prototype Operator Closest to Corner	Long-Term 712-1438 Short-Term 1114-1129	8.5 (23.4)	Trace[d] (3.1)
CB-18 Core Machine Operator	Long-Term 715-1446 Short-Term 1241-1256	6.4 (22.0)	25[e] (2.8)
Core Finisher Between CB-18 and Isocure Core Machine #2	Long-Term 719-1449	7.1 (22.6)	

(continued)

TABLE VIa
(continued)

SAMPLE LOCATION	TIME	DIMETHYLETHYLAMINE CONCENTRATIONS[a] mg/m^3[b] Long-Term Silica Gel Tubes	Short-Term Silica Gel
Core Finisher Adjacent to Isocure Core Machine #3	Long-Term 722-1445	Trace (22.2)	
Laboratory analytical limit of detection (LOD) in mg/sample=		0.02	0.02
Laboratory analytical limit of quantitation (LOQ) in mg/sample=		0.05	0.05

a. All concentrations are time-weighted averages for the period sampled.
b. mg/m^3=milligrams per cubic meter of air.
c. Air sample volumes in liters are indicated in brackets ().
d. Trace quantities are: LOD $\leq$ Trace $\leq$ LOQ. (Detectable concentration but too low for reliable quantitation)
e. Core machine DMEA leak occurred while this sample was collected.
f. ND = nondetectable concentration. (less than the LOD)
g. The concentration should be considered as a minimum due to break through (greater than 30% of the total concentration) occurring on the B section of the silica gel tube.

TABLE VID

Results of Environmental Air Samples For Dimethylethylamine

Winters Foundry

Canton, Ohio

HETA 85-482 & 86-116

January 21, 1986

Second Shift

SAMPLE LOCATION	TIME	DIMETHYLETHYLAMINE CONCENTRATIONS[a] mg/m3[b] Long-Term Silica Gel Tubes	Short-Term Silica Gel
Redford #2 Core Machine Operator	Long-Term 1646-2248 Short-Term 1654-1711	11.6 (19.0)[c]	Trace[d] (3.7)
CB-18 Core Machine Operator	Long-Term 1506-2231 Short-Term 2022-2037	7.5 (21.3)	Trace (3.1)
Isocure #1 Core Machine Operator	Long-Term 1501-2238	5.5 (23.6)	
Isocure #4 Core Machine Operator	Long-Term 1458-2239	4.5 (24.7)	
Core Sand Mixer Mezzanine Area	Long-Term 1533-2249	Trace (20.8)	
Redford #2 Core Machine Operator	Short-Term 1824-1839		Trace[e] (3.1)
Core Finisher Isocure #5	Long-Term 1518-2245	5.1 (23.7)	

(continued)

TABLE VIb
(continued)

SAMPLE LOCATION	TIME	DIMETHYLETHYLAMINE CONCENTRATIONS[a] mg/m^{3}[b] Long-Term Silica Gel Tubes	Short-Term Silica Gel
Utility Person	Long-Term 1342-2230	3.1 (28.6)	
Core Finisher Between CB-18 & Isocure #5	Long-Term 1514-2242	8.8 (22.7)	
Core Finisher Isocure #4	Long Term 1513-2241	9.9 (22.2)	
Core Finisher CB-18	Long-Term 1515-2243	4.7 (23.2)	
Isocure #3 Core Machine Operator	Long-Term 1522-2231 Short-Term 2025-2040	3.8 (21.2)	Trace (3.1)
Isocure #2 Core Machine Operator	Long-Term 1502-2231 Short-Term 2120-2140	12.1 (22.3)	Trace (3.8)
Isocure #5 Core Machine Operator	Long-Term 1504-2235	3.1 (22.6)	

(continued)

TABLE VIb
(continued)

SAMPLE LOCATION	TIME	DIMETHYLETHYLAMINE CONCENTRATIONS[a] mg/m^3[b] Long-Term Silica Gel Tubes	Short-Term Silica Gel
Core Finisher Isocure #5	Long-Term 1518-2245	3.9 (20.6)	
Laboratory analytical limit of detection (LOD) in mg/sample=		0.02	0.02
Laboratory analytical limit of quantitation (LOQ) in mg/sample=		0.05	0.05

a. All concentrations are time-weighted averages for the period sampled.
b. mg/m^3-milligrams per cubic meter of air.
c. Air sample volumes in liters are indicated in brackets ().
d. Trace quantities are: LOD $\leq$ Trace $\leq$ LOQ. (Detectable concentration but too low for reliable quantitation)
e. Core machine DMEA leak occurred while this sample was collected.
f. ND = nondetectable concentration. (less than the LOD)
g. The concentration should be considered as a minimum due to break through (greater than 30% of the total concentration) occurring on the B section of the silica gel tube.

TABLE VIc
Results of Environmental Air Samples For Dimethylethylamine
Winters Foundry
Canton, Ohio
HETA 85-482 & 86-116
January 21-22, 1986
Third Shift

SAMPLE LOCATION	TIME	DIMETHYLETHYLAMINE CONCENTRATIONS[a] mg/m^3[b] Long-Term Silica Gel Tubes	Short-Term Silica Gel
Isocure #3 Core Machine Operator	Long-Term 2308-0638 Short-Term 0246-0301	5.6 (23.1)[c]	Trace[d] (3.4)
Core Sand Mixer Mezzanine Area	Long-Term 2314-0638 Short-Term 0254-0310	1.9 (21.1)	ND[f] (3.3)
Isocure #5 Core Machine Operator	Long-Term 2322-0635 Short-Term 0604-0623	5.3 (24.4)	ND (3.7)
Isocure #4 Core Machine Operator	Short-Term 0615-0631		Trace (3.2)
Isocure #1 Core Machine Operator	Long-Term 2303-0633	7.5 (22.8)	
Work Table Near Isocure #5 Core Machine	Long-Term 2326-0700	2.4 (25.1)	
Attached To A Beam Near Isocure #3	Long-Term 2328-0700	3.5 (25.5)	

(continued)

TABLE VIc
(continued)

SAMPLE LOCATION	TIME	DIMETHYLETHYLAMINE CONCENTRATIONS[a] mg/m³[b] Long-Term Silica Gel Tubes	Short-Term Silica Gel
Mezzainine Area On Top Of 55 Gal. Barrel	Long-Term 2348-0705	2.4 (20.9)	
Laboratory analytical limit of detection (LOD) in mg/sample=		0.02	0.02
Laboratory analytical limit of quantitation (LOQ) in mg/sample=		0.05	0.05

a. All concentrations are time-weighted averages for the period sampled.
b. mg/m^3=milligrams per cubic meter of air.
c. Air sample volumes in liters are indicated in brackets ().
d. Trace quantities are: LOD $\leq$ Trace $\leq$ LOQ. (Detectable concentration but too low for reliable quantitation)
e. Core machine DMEA leak occurred while this sample was collected.
f. ND = nondetectable concentration. (less than the LOD)
g. The concentration should be considered as a minimum due to break through (greater than 30% of the total concentration) occurring on the B section of the silica gel tube.

Table VIa

Results of Environmental Air Samples For Dimethylethylamine
Winters Foundry
Canton, Ohio
HETA 85-482 & 86-116
January 22, 1986
First Shift

SAMPLE LOCATION	TIME	DIMETHYLETHYLAMINE CONCENTRATIONS[a] mg/m[3b]	
		Long-Term Silica Gel Tubes	Short-Term Silica Gel
Isocure #1 Core Machine Operator	Long-Term 0706-1446 Short-Term 1208-1223	13.8 (23.9)[c]	ND[f] (2.8)
Core Finisher Isocure #4	Long-Term 0709-1441	15.5 (23.2)	
Core Finisher Farthest Worker From Core Machine on	Long-Term 0713-1443	3.5 (23.2)	

Table VId
(continued)

SAMPLE LOCATION	TIME	DIMETHYLETHYLAMINE CONCENTRATIONS[a] mg/m^{3}[b] Long-Term Silica Gel Tubes	Short-Term Silica Gel
Redford #1/#2 Core Machine Operator	Long-Term 0654-1438 Short-Term 1002-1017	6.8 (22.0)	15.4[e] (3.3)
Prototype (Closest to Corner) Core Machine Operator	Long-Term 0628-1437 Short-Term 1152-1207	12.8 (24.3)	17.5 (2.9)
Prototype Core Machine Operator Nearest Isocure #4	Long-Term 0626-1438 Short-Term 1153-1207	24.0 (25.0)	24.5 (2.9)
Isocure #4 Core Machine Operator	Long-Term 0655-1440 Short-Term 1209-1224	19.4 (23.2)	Trace (3.1)
Isocure #2 Core Machine Operator	Long-Term 0701-1446 Short-Term 1227-1242	12.7 (22.8)	Trace (3.1)
Core Finisher Isocure #5	Long-Term 0706-1444	8.6 (23.2)	
Core Finisher Isocure #5	Long-Term 0708-1445	10 (24.1)	
Core Finisher Isocure #3	Long-Term 0711-1441	4.8 (23.1)	

(continued)

Table VId
(continued)

SAMPLE LOCATION	TIME	DIMETHYLETHYLAMINE CONCENTRATIONS[a] mg/m[3b] Long-Term Silica Gel Tubes	Short-Term Silica Gel
Core Finisher Isocure #3	Long-Term 0738-1443	3.6 (22.2)	
Laboratory analytical limit of detection (LOD) in mg/sample=		0.02	0.02
Laboratory analytical limit of quantitation (LOQ) in mg/sample=		0.05	0.05

a. All concentrations are time-weighted averages for the period sampled.
b. mg/m^3=milligrams per cubic meter of air.
c. Air sample volumes in liters are indicated in brackets ().
d. Trace quantities are: LOD $\leq$ Trace $\leq$ LOQ. (Detectable concentration but too low for reliable quantitation)
e. *Core machine DMEA leak occurred while this sample was collected.
f. ND = nondetectable concentration. (less than the LOD)
g. The concentration should be considered as a minimum due to break through (greater than 30% of the total concentration) occurring on the B section of the silica gel tube.

Results of Environmental Air Samples For Dimethylethylamine
Winters Foundry
Canton, Ohio
HETA 85-482 & 86-116
January 22, 1986
Second Shift

SAMPLE LOCATION	TIME	DIMETHYLETHYLAMINE CONCENTRATIONS[a] mg/m³[b] Long-Term Silica Gel Tubes	Short-Term Silica Gel
Utility Person	Long-Term 1512-2237	4.3 (23.2)[c]	
Isocure #5 Core Macnine Operator	Long-Term 1504-2229 Short-Term 0850-0905	5.3 (20.8)	ND[f] (3.0)
Core Finisher Isocure #5	Long-Term 1506-2245	18.5 (23.2)	
CB-18 Core Machine Operator	Long-Term 1501-2240	9.3 (23.7)	
Isocure #3 Core Machine Operator	Long-Term 1459-2234 Short-Term 0815-0830	4.8 (25.0)	Trace[d] (3.0)
Core Sand Mixer Mezzanine Area	Long-Term 1611-2247	1.6 (19.3)	
Mezzanine Area Attached to Core Sand Chute	Long-Term 1622-2233	1.6 (18.8)	
Redford #1/#2 Core Machine Operator	Long-Term 1452-2232 Short-Term 0846-0905	7.0 (22.9)	ND (2.9)

(continued)

(continued)

SAMPLE LOCATION	TIME	DIMETHYLETHYLAMINE CONCENTRATIONS[a] mg/m³[b] Long-Term Silica Gel Tubes	Short-Term Silica Gel
Isocure #4 Core Machine Operator	Long-Term 1454-2243	3.3 (24.5)	
Isocure #1 Core Machine Operator	Long-Term 1456-2226	9.2 (25.1)	
	Short-Term 0814-0829		Trace (2.9)
Core Finisher Isocure #3	Long-Term 1511-2238	2.1 (24.3)	
Core Finisher Isocure #4	Long-Term 1509-2243	1.6 (24.2)	
Isocure #2 Core Machine Operator	Long-Term 1503-2227	11.7 (23.0)	
	Short-Term 0825-0840		Trace (2.9)
Core Finisher Isocure #2	Long-Term 1519-2244	8.2 (22.0)	
Laboratory analytical limit of detection (LOD) in mg/sample=		0.02	0.02
Laboratory analytical limit of quantitation (LOQ) in mg/sample=		0.05	0.05

a. All concentrations are time-weighted averages for the period sampled.
b. mg/m^3=milligrams per cubic meter of air.
c. Air sample volumes in liters are indicated in brackets ().
d. Trace quantities are: LOD $\leq$ Trace $\leq$ LOQ. (Detectable concentration but too low for reliable quantitation)
e. Core machine DMEA leak occurred while this sample was collected.
f. ND = nondetectable concentration. (less than the LOD)
g. The concentration should be considered as a minimum due to break through (greater than 30% of the total concentration) occurring on the B section of the silica gel tube.

Results of Environmental Air Samples For Organic Solvents[a]
Core Painting Operations
Winters Foundry
Canton, Ohio
HETA 85-482 & 86-116
January 21-22, 1986

SAMPLE LOCATION	DATE	TIME	SAMPLE VOLUME (liters)	(mg/m³)[b] 1,1,1-Trichloroethane	Trichloroethylene	Perchloroethylene	Methylene Chloride
Isocure #4 Core Finisher Painting Cores	1/21/86	1754-2245	15.7	764	ND[c]	6.4	4.7 (8.5)[d]
Isocure #4 Core Finisher Painting Cores	1/22/86	0742-1440	23.1	451	ND	2.2	ND (12.1)
EVALUATION CRITERIA							
Normal Workday, 40 hr/wk, time-weighted average:				Lowest Feasible Level[e]	134	Lowest Feasible Level	Lowest Feasible Level
Laboratory analytical limit of detection in milligrams/sample				0.01	0.02	0.01	0.02
Laboratory analytical limit of quantitation in milligrams/sample				0.02	0.05	0.02	0.02

a. All samples are personal breathing zone air samples. All concentrations are time-weighted averages for the period sampled.
b. mg/m^3 = milligrams per cubic meter of air.
c. ND = nondetectable concentration.
d. Air sample volumes for the Methylene Chloride samples are indicated in brackets ().
e. NIOSH recommends that occupational exposure to 1,1,1-Trichloroethane, Perchloroethylene, and Methylene Chloride be controlled to the lowest feasbile level.

Results of Environmental Air Samples[a] For Silica
Winters Foundry
Canton, Ohio
HETA 85-482 & 86-116
January 21-22, 1986
Third Shift

Sample Location	Sample Time	Sample Volume (liters)	Respirable Dust (mg/m³)[b]	Respirable Free Silica (ug/m³)[c]	%Respirable Free Silica	Calculated OSHA-PEL & ACGIH - TLV™ For Respirable Free Silica	Ratio Sample Concentration To PEL or TLV
Personal Sample Sand Mixer Mezzanine Area	2314-0638	755	4.8	940	19.7	4.6	4.8/4.6 = 1.
Personal Sample Clean-up Operation	2315-0636	750	0.9	66	7.3	4.8	0.9/4.8 = 0.
Area Sample Mezzanine Area On Top of 55-Gallon Drum	2348-0705	743	5.1	1,144	22.5	4.5	5.1/4.5 = 1.
Area Sample On Table Near Isocure #5	2327-0700	770	0.6	ND	ND	5.0	0.6/5.0 = 0.
EVALUATION CRITERIA (TWA, normal workday, 40 hour/week)			5.0[d]	50[e]	f	g	h

Laboratory analytical limit of detection (LOD) and limit of quantitation (LOQ) for quartz in micrograms/filter: LOD = 15; LOQ = 30.

a. All concentratons are time-weighted averages for the period sampled. All samples were collected using a 10 mm nylon cyclone.
b. mg/m³=milligrams per cubic meter of air.
c. ug/m³=micrograms per cubic meter of air.
d. The 5.0 mg/m³ PEL/TLV™ is intended solely for respirable dusts containing less than 1% quartz. Since all samples listed under Respirable Dust exceeded the 1% quartz criterion (with the exception of one at 0.6 mg/m³), the 5.0 mg/m³ is only applicable to the 0.6 mg/m³ concentration.
e. The NIOSH REL of 50 ug/m³ applies to any form of respirable free silica. The ACGIH 1983-1986 Notice of Intended Changes lists a 100 ug/m³ TLV-TWA for respirable quartz.
f. The percent respirable free silica was obtained by the fraction of the weight of the respirable quartz sample and the total weight of the respirable sample.
g. These values for the respirable quartz PEL's and TLV™ were calculated using the formula 10mg/m³ / % SiO_2 + 2.
h. Ratios equal to or greater than unity (1.0) indicate overexposures.

Table IXa

Results of Environmental Air Samples For Methylene Bisphenyl Isocyanate[a]

Winters Foundry

Canton, Ohio

HETA 85-482 & 86-116

January 21, 1986

First Shift

Area Sample Location	Time	Sample Volume (liters)	Monomeric MDI[b] (ug/m^3)[c]
Adjacent To Isocure Core Machine #3	832-1501	389	ND[d]
Isocure Core Machine #5 Above Control Panel	819-1506	407	13.0
Above Control Box On Redford #1 or #2 Core Machine	806-1458	412	5.9
Mezzanine Area On Sand Chute	901-1511	370	3.5
Above Control Panel Prototype Core Machine	915-1455	340	3.9
EVALUATION CRITERIA (normal workday, 40 hour week for up to a 10-hour time-weighted average)			50

a. All concentrations are time-weighted averages for the period sampled.
b. It was not possible to statistically determine the analytical limit of quantitation for the MDI samples.
c. ug/m^3 = micrograms per cubic meter of air.
d. ND = nondetectable concentration.

Results of Environmental Air Samples For Methylene Bisphenyl Isocyanate[a]
Winters Foundry
Canton, Ohio
HETA 85-482 & 86-116
January 21, 1986
Second Shift

Area Sample Location	Time	Sample Volume (liters)	Monomeric MDI[b] (ug/m^3)[c]
Adjacent To Isocure Core Machine #4	1622-2258	396	ND[d]
Above Control Panel On Redford #2	1636-2255	379	1.8
Above Control Box On Redford #1	1607-2310	423	0.9
Isocure Core Machine #5	1614-2301	407	0.3
Isocure Core Machine #3	1630-2304	394	ND
EVALUATION CRITERIA (normal workday, 40-hour week for up to a 10-hour time-weighted average)			50

a. All concentrations are time-weighted averages for the period sampled.
b. It was not possible to statistically determine the analytical limit of quantitation for the MDI samples.
c. ug/m^3 = micrograms per cubic meter of air.
d. ND = nondetectable concentration

Results of Environmental Air Samples For Methylene Bisphenyl Isocyanate[a]
Winters Foundry
Canton, Ohio
HETA 85-482 & 86-116
January 21-22, 1986
Third Shift

Area Sample Location	Time	Sample Volume (liters)	Monomeric MDI[b] (ug/m^3)[c]
On Work Table Near Isocure			

Table IXd

Results of Environmental Air Samples For Methylene Bisphenyl Isocyanate[a]
Winters Foundry
Canton, Ohio
HETA 85-482 & 86-116
January 22, 1986
First Shift

Area Sample Location	Time	Sample Volume (liters)	Monomeric MDI[b] (ug/m^3)[c]
Above Control Panel On Prototype Core Machine	754-1452	418	0.4
Adjacent To Isocure Core Machine #3	807-1455	408	0.5
On Top Of Control Panel Isocure Core Machine #5	800-1503	423	16.4
On Redford #2 Core Machine	747-1449	422	2.2
Mezzanine Area On Sand Chute	732-1507	455	1.1
EVALUATION CRITERIA (normal workday, 40-hour week for up to a 10-hour time-weighted average)			50

a. All concentrations are time-weighted averages for the period sampled.
b. It was not possible to statistically determine the analytical limit of quantitation for the MDI samples.
c. ug/m^3 = micrograms per cubic meter of air.

Table IXe
Results of Environmental Air Samples For Methylene Bisphenyl Isocyanate[a]
Winters Foundry
Canton, Ohio
HETA 85-482 & 86-116
January 22, 1986
Second Shift

Area Sample Location	Time	Sample Volume (liters)	Monomeric MDI[b] (ug/m^3)[c]
On Table Adjacent To Isocure Core Machine #5	1531-2222	411	ND[d]
On Top Of Control Panel Of Redford Core Machine #2	1527-2239	432	23.1
Adjacent To Isocure Core Machine #3 On Beam	1537-2217	400	1.0
On Back Side Of Redford Core Machine #1	1550-2224	394	9.3
Mezzanine Area On Sand Chute	1622-2233	371	3.4
EVALUATION CRITERIA (normal workday, 40-hour week for up to a 10-hour time-weighted average)			50

a. All concentrations are time-weighted averages for the period sampled.
b. It was not possible to statistically determine the analytical limit of quantitation for the MDI samples.
c. ug/m^3 = micrograms per cubic meter of air.
d. ND = nondetectable concentration

APPENDIX I.

SUMMARY OF HISTORICAL DATA RELATING TO DMEA EXPOSURES AT WINTERS FOUNDRY

A review of some of the numerous non-NIOSH environmental surveys conducted in the foundry coreroom and data pertaining to airborne DMEA levels are as follows:

March 1980 - Employee complaint filed with OSHA concerning gas catalyst exposures in the coreroom as quoted from the OSHA-7 Complaint Form, "There are nine employees who are exposed to fumes from machines recently installed, also five other machines and many other employees. Fumes are from a gas called catalyst. They cause a smokey film over eyes, very bad chest pains, and upset stomachs. Many employees wonder why nothing has been done since OSHA has been there before. Two weeks ago an OSHA Representative was there and that day, the recently installed machine was not run and that was the only day since installed that it did not run."

June 1980 - Whittaker Corporation representatives collected personal air samples in the coreroom for DMEA. Employees' exposures to DMEA were found to be from 0.3 to 5.4 ppm.

July 1980 - The following statements were extracted from the Consent Decree reached by the State of Ohio and Whittaker Corporation, Winters Industries in the Court of Common Pleas, Stark County Ohio:

"The Defendant is hereby permanently enjoined from operating its Isocure process of core-making at its facility at 4125 Mahoning Road, N.E., Canton, Ohio, in such a manner as to create an odor nuisance to the public in violation of Sections 3704.05 and 3767.13 of the Revised Code.

E. On or before the entry of this (1980) Consent Decree, Defendant shall operate and maintain all core-making machines and scrubbing equipment according to the manufacturer's recommendations, which shall be filed with the Air Pollution Control Division, Department of Health, Canton, Ohio.

F. On or before the entry of this Consent Decreee, Defendant shall employ at least one maintenance employee for each shift during which Isocure cores are being produced whose primary job function will be to inspect, maintain, and repair the Isocure core-making machines and scrubbing equipment, so as to minimize the leaking of catalyst chemicals into the Winters building.

K. Defendant shall report, by telephone, to the Air Pollution Control Division, Department of Health, Canton, Ohio, any malfunction of

(continued)

scrubbing equipment or of Isocure core-making machines or other event which causes substantial leakage of catalyst into the Winters plant, or to the ambient air.

L. Defendant may be required to temporarily cease operations of portions of the Isocure core-making facilities if the Air Pollution Control Division, Department of Health, Canton, Ohio, finds, after adequate inspection, that a malfunction as described in Paragraph K above is causing nuisance conditions off of Defendant's premises."

September 1980 - Industrial hygienists from the Ashland Chemical Company, Ohio Industrial Relations Department, On-Site Consultants and Whittaker Corporation took air samples for DMEA on the same day. Their results addressed individually were as follows:

Ashland's corporate industrial hygienist submitted the DMEA data to Winters management representatives in an October 20, 1980 letter wherein it was stated "during the survey I found several exposure levels to DMEA that exceeded the recommended 10 ppm at the CB-5, prototype core producing area. The DMEA results that were found during the survey, at this area, indicate that corrective measures are in order. We have found that such airborne levels of DMEA that were reported during the survey can cause upper respiratory and eye irritation and edema of the corneal membranes, which results in blurred vision or the "blue haze" effect and these symptoms were indeed occuring. Even though this is not a full scale production operation, additional corrective measures are needed to control DMEA release. I suggest that you use a core machine for prototype core production similar to the types of core machines that you are using for normal core production. These machines, as you know, make it easier to control catalyst emissions than through your current practice of hand-gassing."

Results: CB-5 prototype operator was exposed to 13-24 ppm DMEA (short-term 6-30 minute personal samples). Since the time these samples were collected the prototype core machines have been equipped with local ventilation exhausting to the scrubber.

Core Handler, No. 2 Machine "Although the exposure levels were found to be less than recommended 10 ppm (Ashland's criteria), these levels are higher than we normally find at a core handler's station. You did indicate to me that you do have problems with over-gassing cores, therefore, this might be the reason for the high levels that were found at this core handling station."

"If excess levels of catalyst are introduced into the box and are not adequately removed during the purge cycle, higher than normal catalyst levels could be released into the air, particularly during core handling. I suggest that you test each core box to find the minimum

(continued)

amount of catalyst that would be needed to produce a quality core. You should also determine the correct purge cycle for each core box to adequately remove the amine catalyst."

Results: Core handler for the Isocure #2 machine was exposed to 5.0 ppm DMEA for an 8-hour TWA.

The Ohio On-Site Consultation Service found DMEA exposures in the coreroom ranging from non-detectable to 11 ppm (personal and area air samples). Whittaker's data revealed DMEA levels in the coreroom from 0.8 - 5.7 ppm. The 5.7 ppm concentration was a full-shift TWA personal sample.

October 1980 - Employee complaint filed with OSHA regarding (as quoted from the OSHA-7 Form) "irritating and excessive vapors" from the Isocure® Process.

May 1981 - Worker(s) filed a complaint with OSHA about DMEA exposures in the coreroom. The following statements were excerpted from the OSHA-7 Form:

"Approximately 7 machine operators and 25 core finishers in the coreroom exposed to the hazard of airborne chemical vapors from catalyst material leaking from the core machines into the workplace; of the seven core machines in the department two leak the worst; employees are experiencing blurred vision from exposure to the vapors."

August 1981 - OSHA collected two air samples for DMEA in the coreroom. One personal sample showed 1.3 ppm and one area sample revealed 2.8 ppm. Winters health & safety personnel monitored worker exposures to DMEA in the coreroom and found levels ranging from nondetectable to 4.0 ppm.

November 1981 - Whittaker's industrial hygienst collected six air samples for DMEA in the coreroom area. Results: nondetectable - 2.2 ppm.

February 1984 - Employee complaint filed with OSHA concerning "overexposure to the isocure catalyst on the redford machine" (as stated on the OSHA-7 Complaint Form). OSHA representatives did not collect air samples for DMEA.

March 1984 - Ashland Chemical Company's industrial hygienist collected personal and area air samples for DMEA in the coreroom at or near the core machines. The sampling results were transmitted in a March 28, 1984 letter from Ashland to Winters' management. DMEA concentrations on the long-term personal samples ranged from 2.7 - 32 ppm and short term area samples collected at the core machines ranged from 1.2 - 8.5 ppm. Ashland's letter stated that "no problems were encountered with the sampling or analytical procedures that could alter the results.

(continued)

The airborne concentrations for the most part seem to be below the OSHA Permissible Exposure Limit of 25 ppm 8-Hour Time-Weighted-Average (TWA). Ashland Chemical Company has recommended that exposures to DEMA at the workstation be controlled to less than 10 ppm 8-Hour TWA. The highest sample result was found to be a personal sample. I did not notice, nor did the operator report, any unusual occurrence that could explain this exceptionally high value of 32 ppm. Slight leaks were detected during my visit around the seals and gaskets of the coreboxes. It must be understood that the condition of the corebox and gasket have more of an effect on quantity of catalyst released than most any other parameter. Other conditions, such as excessive gassing pressures, short purge time and inadequate clamp pressure can affect the rate and quantity of DMEA released."

A Winters management representative wrote to NIOSH in September 1985[44] concerning the Ashland Chemicals DMEA sampling results of March 1984, and stated that "you will note that all of the tests for DMEA were within the acceptable permissable limits with the exception of one test which was conducted on one worker who had an exposure of 32 parts per million (ppm). Winter's does not feel that this single test is indicative of the exposure in that area. It is so out-of-line compared to the other tests conducted on the same day that Winter's believes that the employee affected the test results by exposing the silica gel tube to direct DMEA."

September 1984 - As a result of a complaint concerning exposures to "fumes of the isocure catalyst used in the coreroom" OSHA representatives began an investigation at Winters Industries. Following the survey OSHA sent a letter in December 1984 to Winters Foundry management officials and stated

"The main constituent of the catalyst, dimethylethylamine (DMEA) is reported by the supplier to be capable of causing eye and respiratory distress resulting in severe eye irritation, blurred vision, an appearance of halo rings around lights and respiratory irritation.

During the inspection it was learned that employees in the coreroom were experiencing eye distress including impaired vision on the drive at the end of the work day. The worst symptoms seem to occur on days when there was excessive leakage of DMEA from the core boxes into the workroom air.

At the present time, OSHA does not have a standard regulating exposure to DMEA. If the plants' change over to triethylanine is not successful and, in light of employees symptoms and possible safety hazards due to impaired vision, it is recommended that all leaks of DMEA be reported and fixed in a timely manner to reduce any time employees may be exposed. Additional local ventilation on any machines that consistently leak DMEA (ie. the "older" Redford machine and the "CBS" area) may be another way of reducing employee symptoms.

(continued)

Representatives of the Ashland Chemical Co. (DMEA supplier) report that they believe that leakage problems can be substantially reduced and offer the continued services of the Technical Services Group."

February 1986 - Based on an OSHA industrial hygiene inspection conducted at Winters Foundry in February 1986 two alleged violations were issued: 29 CFR 1904.2(a): The log and summary of occupational injuries and illnesses (OSHA Form No. 200 or equivalent) was not completed in the detail provided in the form and the instructions contained therein:

(a) The log did not include entries for three employees sent to the hospital on 11/25/85, with symptoms including blurred vision due to exposures to chemicals in the coreroom.

(b) The log did not include entries for twelve employees who went to the hospital on 12/27/85, with symptoms including dizzines, nausea, headaches and blurry vision due to exposures to chemicals in the coreroom.

The Whittaker Corporation, Winters Foundry, as of the printing of this NIOSH report is contesting these citations.

As a follow up to their February 1986 inspection, OSHA administrative authorities wrote a letter to Winters management representatives in May 1986 summarizing their survey results. The following paragraphs were excerpted from this letter,

"Our inspection revealed that symptoms of dizziness, nausea, headaches and blurred vision had been experienced by employees prior to 12/27/85, date; in fact, this situation, namely, the leakage of dimethylethyl-amine (DMEA) from the core box system, had been brought to your attention in a letter from this agency dated 12/19/84, as a result of our inspection on 12/12/84.

During our last visit, it was learned that modifications of the system by Ashland Chemical Co., had improved the air quality in the coreroom, thereby reducing the number of complaints of illness from employees working in the area. The nature of these modifications include:

1) An increase in damping pressure to insure seals of the core box.

2) A reduction in pressure used to deliver DMEA to boxes to 40 PSI.

3) An adjustment in the system which converts DMEA liquid to a gas, resulting in less liquid DMEA being present in the finished cores.

4) Setting scrubber times so as to allow sufficient time for excess vapors to be removed from the box before removing core.

(continued)

5) Revision of the Redford machines.

6) Improved response on the part of plant personel in initiating repairs due to such problems as worn gaskets.

Since the above listed modifications have proven that leakage problems can be substantially reduced, they should be continued in the same vigilant manner. The following additional steps should be implemented:

1) Locking out controls for adjusting scrubber time.

2) Exploring means of venting scrubber out of the plant rather than back into the shop.

3) Insuring that sand is thoroughly blown off seals before closing box by affixing a step so that operators can view the area that is being cleaned.

4) Exploring means of local exhaust ventilation over core finisher tables.

5) Continued training of operators to reduce potential exposure to other employees in the vicinity from DMEA releases.

6) Continued supervisory concern for employees experiencing discomfort resulting from exposure to DMEA."

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