NIOSH HEALTH HAZARD EVALUATION REPORT:

HETA #98-0237-2872
Mueller Company
Chattanooga, Tennessee

April 2002

DEPARTMENT OF HEALTH AND HUMAN SERVICES
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health

Preface

The Hazard Evaluations and Technical Assistance Branch (HETAB) of the National Institute for Occupational Safety and Health (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 (OSHA) 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.

HETAB also provides, upon request, technical and consultative assistance to Federal, State, and local agencies; labor; industry; and other groups or individuals to control occupational health hazards and to prevent related trauma and disease. Mention of company names or products does not constitute endorsement by NIOSH.

Acknowledgments and Availability of Report

This report was prepared by Nancy Clark Burton and Joel McCullough of HETAB, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Field assistance was provided by Robert E. McCleery. Analytical support was provided by Ardith E. Grote and Robert P. Streicher of the Division of Applied Research and Technology, and Data Chem Laboratories of Salt Lake City, Utah. Desktop publishing was performed by David Butler. Review and preparation for printing were performed by Penny Arthur.

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Highlights of the NIOSH Health Hazard Evaluation

Evaluation of Molding/Coremaking Operations and Health Issues at Mueller Company

In May 1998, the National Institute for Occupational Safety and Health (NIOSH) received a confidential request for a health hazard evaluation (HHE) at the Mueller Company facility in Chattanooga, Tennessee. The requesters expressed concern over workplace exposures in several areas of the plant. The HHE request listed respiratory symptoms and possibly increased cancer rates as health concerns.

What NIOSH Did

- **We collected air samples for phenol, volatile organic compounds, Stoddard solvent, formaldehyde, toluene, cumene, ammonia, trimethyl benzene, 4,4'-diphenylmethane diisocyanate (MDI), and hexamethylenetetramine (HMTA).**
- **We looked at how employees did their jobs.**
- **We talked to employees about work conditions and asked about their health concerns.**
- **We looked at the medical records of workers with lung conditions.**
- **We examined company records concerning cancer occurring among workers.**

What NIOSH Found

- **Phenol, Stoddard solvent, toluene, cumene, ammonia, trimethyl benzene, and MDI levels were below current exposure limits.**
- **HMTA levels were low.**
- **Formaldehyde levels were below OSHA standards.**
- **The canopy hood in the shell core area drew contaminants into the workers' breathing area.**
- **Some workers reported symptoms of irritation of the upper airways and lungs.**
- **Cancer types were varied and it was not possible to relate cancer types to workplace exposures.**

What Mueller Company Managers Can Do

- **Determine if the exhaust in the shell core area can be improved to decrease worker exposure to fumes**
- **Supply gloves in the molding and coremaking areas to reduce dermal exposure.**

What the Mueller Company Employees Can Do

- **See a health care professional if health problems persist.**
- **Report to management work conditions that cause health concerns.**

What To Do For More Information:
We encourage you to read the full report. If you would like a copy, either ask your health and safety representative to make you a copy or call 1-513-841-4252 and ask for HETA Report #98-0237-2872

CDC Workplace Safety and Health

National Institute for Occupational Safety and Health NIOSH

Health Hazard Evaluation Report 98-0237-2872
Mueller Company
Chattanooga, Tennessee
April 2002

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SUMMARY

In May 1998, the National Institute for Occupational Safety and Health (NIOSH) received a confidential request for a health hazard evaluation (HHE) at the Mueller Company facility in Chattanooga, Tennessee. The HHE requesters expressed concern over exposures to formaldehyde, phenol, xylene, isocyanates, toluene, naphthalene, carbon monoxide, trimethyl benzene, cumene, lead, and silica in the Pepset, No- Bake, shell core, green sand, and iron pouring areas; silica and iron dust in the cleaning room, shell core, green sand, and machining areas; oil mist from hydraulic tanks; and asbestos from the concrete plant floors. The HHE request listed respiratory symptoms and possibly increased cancer rates as health concerns. On March 31-April 1, 1999, NIOSH investigators conducted a walk-through survey, reviewed material safety data sheets and environmental sampling data, and interviewed 22 employees about the work environment and possible work-related health effects. Employer records were examined to determine the number of cancer cases among employees. On August 8-9, 2000, environmental monitoring was conducted for phenol, volatile organic compounds, Stoddard solvent, formaldehyde, toluene, cumene, ammonia, trimethyl benzene isomers, 4,4'-diphenylmethane diisocyanate (MDI), and hexamethylenetetramine (HMTA).

Formaldehyde was detected at low levels in some air samples. MDI and HMTA were detected at low concentrations. Phenol, Stoddard solvent, toluene, cumene, ammonia, and trimethyl benzene isomers were detected at levels below current occupational exposure limits. Smoke released from the shell core ovens was found to move through the employees' breathing zones before being exhausted through the canopy hood.

Twenty-one (4.4% of the 475 production workers) were interviewed. Among those interviewed, most employees who had prolonged exposure to emissions from the Pepset and No-Bake coremaking/molding operations reported transient respiratory irritation. The workers who worked in these areas on a regular basis generally did not report persistent respiratory illnesses that they associated with their workplace exposures. Review of the medical records of six employees who reported work-related respiratory illnesses found that some workers had worsening of pre-existing chronic respiratory conditions, although the cause of this was not determined. Information concerning cancer diagnosed among Mueller Co. employees did not reveal an unusual number or pattern of cancers; however, it is not possible to determine the cause of the cancers that developed among the employees.

All of the substances sampled in the employees' personal breathing zones had concentrations below the occupational exposure limits. The 16 identified cancer cases were of 10 different types, and there was not enough information available to determine if the cancers resulted from workplace exposures. Among the small number of employees interviewed, most who had long term exposures to emissions in the Pepset and No-Bake coremaking/molding areas reported temporary respiratory irritation. Recommendations are provided for additional monitoring for MDI, formaldehyde, and phenol, use of gloves, reporting of health symptoms to medical personnel, and local exhaust ventilation in the shell core area.

Keywords: SIC Code 3321 (Gray and Ductile Iron Foundries), cancer, lung disease, respiratory irritation, coremaking, molding, Stoddard solvent, phenol, ammonia, formaldehyde, cumene, toluene, trimethylbenzene, 4,4'-diphenylmethane diisocyanate, MDI, hexamethylenetetramine, HMTA

Table of Contents

INTRODUCTION

In May 1998, the National Institute for Occupational Safety and Health (NIOSH) received a confidential request for a health hazard evaluation (HHE) at the Mueller Company in Chattanooga, Tennessee. The request listed concerns about exposures to formaldehyde, phenol, xylene, isocyanates, toluene, naphthalene, carbon monoxide, trimethyl benzene, cumene, lead, and silica in the Pepset, No Bake, shell core, green sand, and iron pouring areas; silica and iron dust in the cleaning room, shell core, green sand, and machining areas; oil mist from hydraulic tanks; and asbestos from the concrete plant floors. The HHE request listed respiratory symptoms and possibly increased cancer rates as health concerns. A similar request was submitted to the Tennessee Department of Labor, Division of Occupational Safety and Health, which evaluated concerns related to the silica and asbestos exposure concerns in the summer/fall of 1998 and also conducted a limited evaluation of the chemical exposures in the molding and coremaking areas. In response to the HHE request, NIOSH investigators conducted a walk-through survey on March 31-April 1, 1999, and a follow-up site visit on August 8-9, 2000, which focused on molding and coremaking operations. An interim letter was provided to management and employee representatives in July 2000.

BACKGROUND

The Mueller Co. facility houses a gray iron foundry and machining operation on a 53-acre site. The company produces valves for domestic water supplies. Mueller employs approximately 575 people (475 production workers and 100 management staff) at this site. The company provides annual audiometric testing and pre-employment physicals for its employees. Respiratory protection is optional in the coremaking/mold areas. Hearing protection is required in the foundry and machining areas. Smoking is not allowed in the plant.

Process Description

The shell core line and green sand operation are located on the second floor. Approximately 20 employees were working in these areas which only operated on second shift. The shell core employees load bags of resin-coated sand (phenol-formaldehyde base with hexamethylenetetramine) into a sand hopper which feeds sand into the machine. The unit turns upside down and is heated to 450°F, creating a hard shell. Loose sand is shaken into the hopper. The complete cycle takes about five to seven minutes. The machine opens, and the employee pulls out the core and sets it on a table, checks it for flaws, and applies a water-based graphite core wash. Employees use heavy cloth gloves for protection from the heat. The core wash generates steam when painted on the hot cores. A large supply air unit provides fresh air to the general work area. Exhaust ventilation is provided by a large canopy hood with a dust collector. The green sand operation consists of an automated filling station, a conveyor system on which the molds are assembled, a conveyor pouring line, and a conveyor cooling line that leads to shake-out.

Two employees work in the Pepset area on first shift, using an organic binding system containing an alkyd polyester, Stoddard solvent, polycyclodiene, 1,2,4-trimethylbenzene, dimethylethanolamine, 4,4'-diphenylmethane diisocyanate (MDI), polymethane polyphenyl isocyanate, xylene, a manganese compound, and a zinc compound. A heptane, talc, and mica-based coating is used. The resin is automatically added to the sand in the hopper. Recycled sand is used in this process. A hand-controlled crane is used to move molds to an adjacent open pouring area.

Nine employees were working in the No-Bake coremaking/molding area on first shift. The total operation, from core-making to pouring, is done in that area. A three-part chemical system is used to produce the cores. Part I consists of a phenol-formaldehyde based resin. Part II contains MDI, petroleum naphtha, and trimethylbenzene; and Part III is a drying agent which contains trimethylbenzene, xylene, and cumene. Recycled sand is used in this process. One employee fills the box with pre-heated resin-coated sand at the beginning of the conveyor system. Another employee applies a white Zircon™ wash. The box is turned over and goes through an infrared (IR) heater. Two employees put Pepset cores into the bottom (drag), then add the top (cope) and close. Excess sand is removed using compressed air. Another employee lines up the molds to be poured. The employees use nitrile gloves in the Pepset area. The No-Bake and Pepset areas have a dust collection system.

METHODS

Environmental Monitoring

After reviewing the processes in the areas of concern at Mueller Co., and also reviewing appropriate material safety data sheets (MSDSs), NIOSH industrial hygienists conducted air sampling for the substances noted below. Area air samples were collected in areas where workers were already wearing sampling pumps or when the work activities were such that wearing the sampling equipment (i.e. impingers) was impractical.

Phenol

Ten personal breathing zone (PBZ) air samples were collected in the Pepset, No-Bake, shell core, and green sand areas for phenol. The samples were collected on silica gel sorbent tubes at a flowrate of 0.05 liters per minute (Lpm) and analyzed for phenol according to NIOSH Method 2546[1] using gas chromatography with a flame ionization detector. The samples were desorbed using methanol and sonicated for 0.5 hours. A fused silica capillary column coated with DBWAX was used. The analytical limit of detection (LOD) was 1 microgram (µg), which is equivalent to a minimum detectable concentration (MDC) of 0.013 parts per million (ppm), assuming a sample volume of 20.3 liters (L). The limit of quantitation (LOQ) was 3 µg, which is equivalent to a minimum quantifiable concentration (MQC) of 0.038 ppm, assuming a sample volume of 20.3 L.

Ammonia

Five PBZ air samples for ammonia were collected in the green sand and shell core areas using sulfuric acid-treated silica gel tubes at a flow rate of 0.05 Lpm. Sampling and analysis was conducted according to NIOSH Method 6015 using automated visible spectrophotometry.[2] The LOD was 2 µg per sample which is equivalent to a MDC of 0.13 ppm, assuming a sample volume of 21.2 L. The LOQ was 7 µg, which is equivalent to a MQC of 0.47 ppm, assuming a sample volume of 21.2 L.

Stoddard Solvent

Four PBZ air samples were collected for Stoddard solvent (three in the Pepset and No-Bake molding areas and one in the shell core area) on charcoal tubes at a flowrate of 0.05 Lpm. The analysis was done by gas chromatography (GC) with a flame ionization detector based on NIOSH Method 1550.[3] The samples were desorbed for 30 minutes in 1.0 milliliters (ml) of carbon disulfide. The LOD for Stoddard solvent was 0.007 milligrams per sample (mg/sample) and the LOQ was 0.02 mg/sample. Based on sample volume of 20.2 L, this yielded a MDC of 0.347 milligrams per cubic meter (mg/m^3) and a MQC of 0.99 mg/m^3.

Qualitative Volatile Organic Compounds

PBZ air samples were collected for cumene (three samples in the Pepset and No-Bake molding areas and one in the shell core area), toluene (three samples in the Pepset and No-Bake molding areas and two in the green sand and shell core areas), and trimethylbenzene (two in the No-Bake molding areas). The samples were collected on charcoal tubes using air sampling pumps calibrated to a flow rate of 0.05 Lpm. The analysis was done by GC with a flame ionization detector based on NIOSH Method 1501, with modifications for these particular analytes.[4] The samples were desorbed for 30 minutes in 1.0 ml of carbon disulfide containing 0.5 microliters (µl) per ml of n-hexane as an internal standard. The LOD for cumene was 0.0009 mg/sample and the LOQ was 0.003 mg/sample. Based on sample volumes of 19.45 L, this yielded a MDC of 0.009 ppm and a MQC of 0.031 ppm. The LOD for toluene was 0.0004 mg/sample and the LOQ was 0.001 mg/sample. Based on sample volumes of 17.05 L, this yielded a MDC of 0.006 ppm and a MQC of 0.016 ppm. The LOD for trimethylbenzene was 0.002 mg/sample and the LOQ was 0.007 mg/sample. Based on sample volumes of 20.55 L, this yielded a MDC of 0.02 ppm and a MQC of 0.069 ppm.

Formaldehyde

Ten area air samples were collected for formaldehyde (five in the Pepset and No-Bake molding areas and five in the green sand and shell core areas). Samples were collected on cartridges coated with 2,4-dinitrophenylhydrazine (DNPH) at a calibrated flow rate of 0.05 Lpm for the Pepset and No-Bake molding areas and 1 Lpm for the green sand and shell core areas. The tubes were analyzed by high pressure liquid chromatography (HPLC) with an ultraviolet (UV) detector according to NIOSH Method 2016.[5] The LOD was 0.06 μg/sample for formaldehyde, which is equivalent to a MDC of 0.003 ppm, assuming a sample volume of 18.9 L. The LOQ was 0.2 μg/sample, which is equivalent to a MQC of 0.009 ppm, assuming a sample volume of 18.9 L. Three of the samples collected during the second shift were diluted 10-fold which increases the resulting LOD and LOQ by a factor of ten.

Hexamethylenetetramine (HMTA)

Five area air samples for HMTA and formaldehyde were collected in tandem on Occupational Safety and Health Administration (OSHA) versatile sampler (OVS) tubes (13-mm quartz filters followed by XAD-2 sorbent beds) and DNPH-treated silica gel cartridges, respectively. The samples were collected at a flow rate of 1 Lpm. The formaldehyde analysis was described earlier in this report. The OVS samples for HMTA were fortified with 100 μl of acetone and allowed to equilibrate for 10–30 minutes. This reduces the electrostatic charges in the XAD-2 sorbent. The front sections of sorbent, quartz filters, and plastic rings were desorbed with 2 ml of acetone. The back sections of sorbents with both polyurethane foam plugs were desorbed with 4 ml of acetone. All extracts were tumbled for 1 hour prior to analysis. Portions of the extracts were analyzed for HMTA using gas chromatography with a mass selective detector (GC-MSD). Media standards were used to calculate standard curves. The LOD for HMTA was 0.3 μg/sample and the LOQ was 1.2 μg/sample. Based on sample volumes of 60 L, this yielded a MDC of 0.001 ppm and a MQC of 0.003 ppm. Since the sampling method and analytical techniques used in this HMTA analysis have not been fully evaluated, the results should be considered estimates.

MDI

Five area air samples were collected in the Pepset and No-Bake areas for MDI. The samples were collected at a flow rate of 1 Lpm using midget impingers containing 15 ml of a solution of 1-(9-anthracenylmethyl) piperazine (MAP) in butyl benzoate, followed by a 37-mm diameter quartz fiber filter (QFF) impregnated with MAP.[6] The filters were removed from the cassette immediately after sampling and placed in a jar containing 5 ml of a solution of MAP in acetonitrile. Impinger samples were transferred to glass vials. All samples were shipped to the analytical laboratory in a cooler with ice packs.

Filter samples were analyzed by pH-gradient high pressure liquid chromatography (HPLC) with ultraviolet and fluorescence detection for both the monomer and polyisocyanate species of MDI. The impinger samples were subjected to solid-phase extraction, followed by the same analysis used for the filter samples. Upon receipt, 5μl of acetic anhydride was added to each filter sample. Monomers were quantified based on comparison of their fluorescence peak heights to those of monomer standards. No polymer isocyanate species were detected in the samples. The analytical LODs for the MDI monomer filter and impinger samples were 4 and 18 nanograms per samples, respectively. Assuming a sample volume of 254 L, the resultant MDCs were 0.016 and 0.07 μg/m^3 for filter and impinger samples, respectively. The LOQs for the MDI monomer filter and impinger samples were 14 and 60 nanograms per samples, respectively. Assuming a sample volume of 254 L, the resultant MQCs were 0.055 and 0.24 $\mu g/m^3$ for filter and impinger samples, respectively.

Qualitative Volatile Organic Compounds

Eight area air samples (four in the Pepset and No-Bake molding areas and four in the green sand and shell core areas) were collected on thermal desorption tubes containing three beds of sorbent material for volatile organic compounds (VOCs). Prior to analysis, the samples were dry purged with helium to remove water. The samples were analyzed using a Perkin-Elmer automatic thermal desorption (TD) system interfaced directly to a GC-MSD in accordance with NIOSH Method 2549.[7] Stock solutions in carbon disulfide, containing known amounts of phenol and HMTA, were used to prepare standard spikes for comparison.

Medical

Employees were informed of the NIOSH site visits by union and management representatives. During the initial site visit, those employees who wanted to discuss their health concerns were encouraged by the union to come forward and discuss these concerns in private with the NIOSH medical officer. In addition, other employees who were present that day and worked in the Pepset and No-Bake coremaking/molding areas were invited for an interview because most of the exposures of concern were from these areas.

Medical records from private physicians were reviewed for workers with respiratory concerns. We reviewed the Mueller Co.'s 1989–1998 Accident and Sickness Claims, which reports the medical illnesses or injuries that resulted in lost work days, to identify employees diagnosed with cancer. No other sources of information about cancer among the employees were avialable.

EVALUATION CRITERIA

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

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs),[8] (2) the American Conference of Governmental Industrial Hygienists' (ACGIH®) Threshold Limit Values (TLVs®),[9] and (3) the U.S. Department of Labor, OSHA Permissible Exposure Limits (PELs).[10] Employers are encouraged to follow the OSHA limits, the NIOSH RELs, the ACGIH TLVs, or whichever are the more protective criterion.

OSHA requires an employer to furnish employees a place of employment that is free from recognized hazards that are causing or are likely to cause death or serious physical harm [Occupational Safety and Health Act of 1970, Public Law 91-596, sec. 5(a)(1)]. Thus, employers should understand that not all hazardous chemicals have specific OSHA exposure limits such as PELs and short-term exposure limits (STELs). An employer is still required by OSHA to protect their employees from hazards, even in the absence of a specific OSHA PEL.

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

Phenol

Phenol is an irritant of the eyes, mucous membranes, and skin. The skin is a route of entry for the vapor and liquid phases. Excessive systemic absorption of phenol can cause convulsions, and liver and kidney damage.[11] The NIOSH REL, ACGIH TLV, and OSHA PEL for phenol are 5 ppm as a TWA over the workshift. NIOSH also has a 15 ppm ceiling limit. The REL and TLV include a skin notation, which indicates that skin absorption may be a significant route of exposure.

Ammonia

Ammonia is a severe irritant of the eyes, respiratory tract, and skin.[11] Exposure of the skin to high concentrations of the gas may cause burning and blistering. The NIOSH REL for ammonia is 25 ppm for up to a 10-hour TWA; NIOSH has also established a 15-minute STEL for ammonia of 35 ppm.[8] The ACGIH TLV is 25 ppm as an 8-hour TWA, 35 ppm as a STEL.[9] The OSHA PEL for ammonia is 50 ppm as an 8-hour TWA.[10]

Stoddard Solvent

Stoddard solvent is a mixture of predominantly C_9-C_{11} hydrocarbons, which include paraffins, naphthenes, and aromatic hydrocarbons.[11] It can be used as a paint thinner, is in dry cleaning, degreasing, and cleaning chemicals, and is a component of coatings, inks, and waxes.[12] Stoddard solvent is a central nervous system depressant which can cause symptoms such as dizziness, lightheadedness, and fatigue. Exposure to Stoddard solvent can also cause skin, eye, nose, and throat irritation.[11,12] The NIOSH REL for Stoddard solvent is 350 mg/m^3 for up to a 10-hour workday and 1800 mg/m^3 as a ceiling limit.[8] The OSHA PEL for Stoddard solvent is 2900 mg/m^3 as an 8-hour TWA.[10] The ACGIH has established an 8-hour TLV-TWA of 572 mg/m^3 (100 ppm) for Stoddard solvent.[9]

Cumene

Cumene is used as a paint, enamel, and lacquer thinner, and is an additive in aviation fuel.[11,13] Cumene is an eye, skin, and mucous membrane irritant, and can cause central nervous system depression.[11] NIOSH, OSHA, and ACGIH have established occupational exposure limits of 50 ppm as a TWA over the workshift.[8,9,10]

Toluene

Toluene is a highly flammable, volatile liquid. Approximately 7–10% of the total amount of toluene produced in the U.S. each year is used in paints, oils, adhesives, resins, inks, and detergents, and the other 90% is used to formulate gasoline.[11,14,15] It is a component of cigarette smoke, and has been intentionally inhaled to produce euphoria.

Inhalation and skin absorption are the major occupational routes of entry. Toluene can cause acute irritation of the eyes, respiratory tract, and skin.[16,17] The main effects reported with excessive inhalation exposure to toluene are central nervous system depression and neurotoxicity.[17] Chronic CNS effects may include ataxia, tremors, visual impairment, deafness, and neurobehavioral abnormalities.[15]

The NIOSH REL for toluene is 100 ppm for up to a 10-hour TWA.[8] NIOSH has also set a recommended STEL of 150 ppm for a 15-minute sampling period. The OSHA PEL for toluene is 200 ppm for an 8-hour TWA and 300 ppm as a ceiling limit.[10] The ACGIH TLV for toluene is 50 ppm for an 8-hour TWA.[9] The TLV carries a skin notation, indicating that cutaneous exposure contributes to the overall dose and may cause systemic effects.

Trimethylbenzene

Trimethylbenzene is used during chemical production, as a component of solvents and gasoline, and as an ultraviolet stabilizer in plastics.[11] There are three isomers of trimethylbenzene (1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, and 1,2,3-trimethylbenzene). It is considered an eye, nose, and respiratory irritant, and, at high concentrations, exposure to trimethylbenzene can cause central nervous system depression.[11,18] Skin exposure can result in drying and cracking of the skin. Chronic exposure to 1,3,5-trimethylbenzene can cause liver damage and anemia.[18] NIOSH and ACGIH have established occupational exposure limits for trimethylbenzene isomers of 25 ppm as TWAs over the workshift.[8,9] OSHA does not have an occupational exposure limit for trimethylbenzene isomers.[10]

Formaldehyde

Formaldehyde is a colorless gas with a strong odor. Exposure can occur through inhalation and skin absorption. The acute effects associated with formaldehyde are irritation of the eyes and respiratory tract. It is also a skin irritant and sensitizer.[19]

In two separate studies, formaldehyde has induced a rare form of nasal cancer in rodents.[20] Formaldehyde exposure has been identified as a possible causative factor in cancer of the upper respiratory tract in a proportionate mortality study of workers in the garment industry.[21]

The OSHA PEL is 0.75 ppm as an 8-hour TWA and 2 ppm as a STEL.[22] ACGIH has designated formaldehyde to be a suspected human carcinogen and therefore, recommends that worker exposure by all routes should be carefully controlled to levels "as low as reasonably achievable" below the TLV.[9] ACGIH has set a ceiling limit of 0.3 ppm. NIOSH has identified formaldehyde as a suspected human carcinogen and recommends that exposures be reduced to the lowest feasible concentration (0.016 ppm).

Hexamethylenetetramine (HMTA)

Hexamethylenetetramine (HMTA) is used in the rubber industry as an accelerator, as a curing agent for thermosetting resins, in foundry mold castings as part of binder resins, and in manufacturing of adhesives, coatings, and flame retardants.[23] Primary routes of exposure are direct skin contact and inhalation. Toxicological studies in humans show that HMTA is a respiratory and skin sensitizer.[23] Currently, no occupational exposure criteria for HMTA have been established by NIOSH, OSHA, or ACGIH.

MDI

Methylene diisocyanate is used in the production of polyurethane foams and plastics. Exposure to isocyanates is irritating to the skin, mucous membranes, eyes, and respiratory tract.[24,25] The most common adverse health outcome associated with isocyanate exposure is asthma; less prevalent are contact dermatitis (both irritant and allergic forms) and hypersensitivity pneumonitis (HP).[25,26,27] A worker suspected of having isocyanate-induced asthma will exhibit the traditional symptoms of acute airway obstruction, *e.g.*, coughing, wheezing, shortness of breath, tightness in the chest, and nocturnal awakening.[24,26,27] After sensitization, any exposure, even to levels below an occupational exposure limit or standard, can produce an asthmatic response which may be life threatening. Studies have shown that workers with persistent asthma have a significantly longer duration of symptoms prior to diagnosis, larger decrements in pulmonary function, and a severe degree of nonspecific bronchial hyperreactivity at diagnosis.[28] These data suggest that prognosis is improved with early diagnosis of diisocyanate-induced respiratory sensitization and early removal from diisocyanate exposure. This emphasizes the need to minimize workplace exposure concentrations, and for active medical surveillance of all workers potentially exposed to diisocyanates.

HP, a restrictive respiratory disease, also has been described in workers exposed to isocyanates.[29,30,31,32] The initial symptoms associated with acute isocyanate-induced HP are flu-like, including shortness of breath, non-productive cough, fever, chills, sweats, malaise, and nausea.[26,27] The symptoms resolve but repeated episodes may lead to an irreversible decline in pulmonary function and lung compliance, and to the development of diffuse interstitial fibrosis.[26,27]

NIOSH has established an REL of 50 µg/m^3 for MDI for up to a 10-hour TWA AND 200 µg/m^3 as a ceiling limit.[8] ACGIH has established an 8-hour TWA of 50 µg/m^3 (0.005 ppm) for MDI.[9] The OSHA PEL is a ceiling concentration of 200 µg/m^3.[10]

RESULTS

Industrial Hygiene

Phenol

The ten PBZ air sample concentrations for phenol are shown in Table 1. On the first shift, phenol concentrations ranged from none detected to 0.06 ppm for workers in the Pepset and No-Bake areas. On the second shift, phenol concentrations ranged from none detected to 0.08 ppm in the green sand, pouring, and shell core areas. All the detected concentrations were well below current occupational exposure limits.

Ammonia

The five PBZ air sample concentrations for ammonia are presented in Table 2. Ammonia concentrations ranged from a trace level to 3.7 ppm. These concentrations are well below current occupational exposure limits.

Stoddard Solvent

The four PBZ air sample concentrations for Stoddard solvent are given in Table 3. On the first shift, Stoddard solvent concentrations ranged from 10.5 to 33.2 mg/m^3 for workers in the Pepset and No-Bake areas. On the second shift, the one PBZ sample concentration was 1.9 mg/m^3 in the shell core area. All the detected concentrations were below current occupational exposure limits.

Cumene

The four PBZ air sample concentrations for cumene are shown in Table 4. On the first shift, cumene concentrations ranged from none detected to 0.09 ppm for workers in the Pepset and No-Bake areas. On the second shift, the one PBZ sample concentration did not contain a detectable concentration of cumene. All the detected concentrations were below current occupational exposure limits.

Toluene

The five PBZ air sample concentrations for toluene are presented in Table 5. On the first shift, toluene concentrations were 0.02 ppm collected on the No-Bake paint operator and 0.13 ppm collected on the supervisor. On the second shift, the three PBZ toluene sample concentrations ranged from 0.04 ppm to 0.08 ppm in the green sand area. All the detected concentrations were well below current occupational exposure limits.

Trimethylbenzene Isomers

The two PBZ air sample concentrations from first shift sampling for trimethylbenzene isomers are given in Table 6. Trimethylbenzene concentrations were 0.12 ppm and 2.20 ppm in the No-Bake area. All the detected concentrations were below current occupational exposure limits.

Formaldehyde

Area air sample concentrations for formaldehyde are presented in Table 7. The five formaldehyde sample concentrations collected in the Pepset and No-Bake areas ranged from 0.02 to 0.08 ppm. The three formaldehyde sample concentrations collected in the green sand and shell core areas ranged from 0.03 to 0.17 ppm. Two samples were not analyzed due to pump failure, which was likely due to a high pressure drop (the pump could not pull air through the filter media easily).

Hexamethylenetetramine (HMTA)

The five area air sample concentrations collected for HMTA in the green sand and shell core areas are shown in Table 8. The area HMTA concentrations ranged from none detected to 0.02 ppm, with the higher concentrations found in the green sand area. No exposure criterion is currently established for HMTA.

MDI

The results for the five area air samples for MDI collected in the Pepset and No-Bake areas are presented in Table 9. MDI concentrations ranged from none detected to 0.25 $\mu g/m^3$. None of these concentrations exceeded the current occupational exposure criteria.

Thermal Desorption Tubes

The area samples collected in the morning in the Pepset and No-Bake areas and in the shell core areas on second shift contained methylene chloride, isopropanol, acetone, an aromatic naptha (C_3-C_6 alkyl benzenes), phenol, propane, isobutane, butane, benzene, hexane, ethyl acetate, triethylamine, toluene, xylene, diacetone alcohol, benazaldehyde, benzyl alcohol, naphthalene, hexamethylenetetramine, and various C_9-C_{12} aliphatic hydrocarbons. The samples collected in the Pepset and No-Bake areas in the afternoon contained only methylene chloride, isopropanol, and acetone as the primary components.

Observations

In the shell core area, the local exhaust ventilation consisted of a very large canopy hood over the entire work area. The system was operating during the site visit. NIOSH investigators observed that the emissions from the shell core ovens were drawn directly through the workers' breathing zone when the door was opened. The employees indicated that they held their breath during this activity to avoid breathing in the emissions.

Medical

Interviews

Twenty-one workers were interviewed. The job titles of those interviewed included 7 maintenance mechanics, 4 machine operators, 3 coremaking employees, 2 Pepset employees, 2 No-Bake employees, 1 mechanic, 1 maintenance welder, and 1 cleaning room clerk. The average tenure at Mueller Co. among these employees was 16.5 years (range: 2 to 40 years).

Eight workers reported lower respiratory health problems that they believe were related to workplace exposures. Four workers reported asthma, two emphysema, one asbestosis, and one bronchitis. The worker with bronchitis worked in the coremaking area, the other persons with lower respiratory symptoms were maintenance mechanics.

Among the other employees interviewed, there were concerns about upper respiratory tract irritation. Complaints of upper respiratory tract irritation occurred in most workers who passed through or worked in the Pepset and No-Bake coremaking/molding areas. Employees in these areas reported upper airway irritation during specific phases of the work, such as when fumes from mold spray, pattern spray, or core wash would be produced. The workers reported that they developed work habits to avoid these exposures, such as turning their heads and holding their breaths. Most of these workers reported that the irritation was temporary.

Employees expressed concern about a possible increased risk of cancer because of cadmium exposure among workers in the tool room. The exposure in question was to a welding product known as "preforms" used in brazing and soldering, which contains a cadmium alloy. The product was purchased by Mueller Co. from 1992 to 1995, and is no longer in use at the facility. However, the number of individuals in the tool room who developed cancer or the types of cancer could not be determined.

Medical Record Review

Medical records were obtained from six of the above persons who reported lower respiratory problems. Four medical records revealed chronic obstructive pulmonary disease (COPD) as the underlying lung disease with smoking as primary cause of the COPD in three cases, and in one case, the cause was not reported. In the record of one person with COPD, there was mention of workplace exacerbation from chemical exposure. In addition to the four persons with COPD, the medical records revealed that one person had been diagnosed with asthma and one with restrictive airways disease. The person with restrictive airways disease was considered to have mild disease and was reported to follow an "industrial exposure." The person with asthma was reported to have an exacerbation of pre-existing asthma; specific chemical(s) or work duties potentially related to this exacerbation were not mentioned.

Review of Company Records

The Accident and Sickness Claims data revealed 16 persons with cancer among Mueller Co. employees from 1989 to 1998. Mueller employs approximately 575 employees at one time. The cancer types reported included lung cancer (5), cancer of the larynx (2), cancer of the esophagus (2), cancer of the colon (1), cancer of the prostate (1), bladder cancer (1), cancer of the small intestines (1), multiple myeloma (1), skin cancer (1), and leukemia (1). The claim report did not reveal the smoking status, the work area, or job title of these workers who developed cancer.

DISCUSSION

Most workers who had prolonged exposure to emissions in the Pepset and No-Bake coremaking/molding areas reported temporary respiratory irritation from the fumes produced during the processes, but those who worked in these areas on a regular basis did not report persistent respiratory illnesses, other than one person with bronchitis. Review of the medical records of those who reported work-related respiratory illnesses found that some workers had worsening of pre-existing chronic respiratory conditions. The substances or conditions responsible for the worsening were not identified in the medical records. However, several substances in use at Mueller Co. are potential respiratory irritants. The exposure data collected by NIOSH investigators showed that workers were exposed to concentrations of potential irritants, including Stoddard solvent, ammonia, cumene, trimethylbenzene, phenol, and toluene, at levels below current occupational exposure limits. Worker exposures to formaldehyde were within occupational exposure limits established by OSHA and ACGIH. However, NIOSH recommends that formaldehyde exposure be kept at the lowest feasible concentration because of its potential as a carcinogen. MDI was detected in low concentrations, below the OSHA and ACGIH occupational exposure limits. Although previously sensitized individuals can have adverse health effects related to exposure to low concentrations, we found only one worker with a history of asthma, and there was no indication that exposure to MDI was involved in that worker's illness.

Another concern among some workers was a possible cancer cluster at Mueller Co. Cancers often appear to occur in clusters, which scientists define as an unusual concentration of cancer cases in a defined area or time. A cluster also occurs when the cancers are found more often among workers of a different age or sex group than is usual. Cancer clusters thought to be related to a workplace exposure usually consist of the same types of cancer. When several cases of the same type of cancer occur and that type is not common in the general population, it is more likely that an occupational exposure is involved. However, when the cluster consists of multiple types of cancer, without one type predominating, then an occupational cause of the c1uster is unlikely. Among the sixteen individuals with cancer identified by review of company records, there were ten different types of cancer. Overall, the number and distribution of cancer types do not appear to be unusual. NIOSH investigators believe it is important for employees to raise concerns about cancer in the workplace. Although a cancer cluster at work may not mean there is a workplace problem, this possibility deserves attention. Given the information we have, an occupational cause of the cancers identified among the Mueller Co. employees is unlikely. Although it is possible that the Accident and Sickness Claims report did not include all cancers developed by Mueller Co. employees, we have identified no other Mueller Co. employees with cancer.

There was also concern about the cancer risk associated with breathing fumes from a cadmium-containing alloy among workers in the tool room. The relationship between occupational exposure to cadmium and increased risk of cancer, particularly lung and prostate cancer, has been explored in several studies. Overall, the results provide little evidence of an increased risk of lung cancer in humans following prolonged inhalation exposure to cadmium. Initial studies indicated an elevation in prostate cancer among men occupationally exposed to cadmium, but subsequent investigations found either no increases in prostate cancer or increases that were not statistically significant. The International Agency for Research on Cancer (IARC) has determined that cadmium is carcinogenic to humans (cancer of the prostate).[33] However, among the employees at Mueller Co., only one person with cancer of the prostate was reported in the Accident and Sickness Claims report, and there is no evidence that this case was linked to cadmium exposure.

CONCLUSIONS

Industrial hygiene sampling for substances at Mueller Co. identified as possible occupational hazards revealed air concentrations well below relevant occupational criteria. Interviews with employees revealed that some employees are experiencing respiratory irritation in the Pepset and No-Bake coremaking/molding areas. Among the small number of medical records reviewed, two persons were found to have been evaluated for potentially work-related exacerbations of respiratory illness, although specific substances or conditions responsible for the exacerbations were not identified. MDI was detected at low concentrations that could cause adverse health effects in sensitized individuals, although MDI-related health problems were not identified by NIOSH investigators. An occupational source for the reported cancers among Mueller Co. employees was not identified. Recommendations are provided below to help improve the working environment in the Mueller Co. molding and coremaking operations.

RECOMMENDATIONS

(1) MDI exposure monitoring should be conducted subsequent to any process change or annually to assure that exposures remain below exposure criteria. Sampling should be conducted in a manner which captures full-shift (averaged over 8-hours) and peak (averaged over 15-minutes) exposures.

(2) Formaldehyde and phenol should also be monitored after any process change or on a periodic basis to assure that engineering controls are adequate. Additional monitoring for formaldehyde in the workplace should include a comparison with the outdoor ambient concentration to help determine the background levels and whether concentrations in the workplace can be lowered. Trace concentrations of formaldehyde are common in ambient outdoor air, especially in urbanized areas, and reducing workplace exposure concentrations that are not substantially elevated above the ambient outdoor concentration may not always be feasible.

(3) Since the majority of VOCs used in the Pepset, No-Bake, and Shell core areas can be absorbed through the skin, nitrile or other suitable material gloves should be used by workers in these areas.

(4) Potential work-related symptoms should be reported to health care personnel. Health care personnel should work with Mueller management to identify work areas and processes associated with specific health effects.

(5) To prevent emissions being drawn through workers' personal breathing zones in the shell core area, the canopy hood local exhaust design should be further evaluated by a qualified industrial ventilation engineer. Local exhaust ventilation would be more effective.

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Table 1
Phenol Personal Breathing Zone Air Sampling Results
Mueller Company, Chattanooga, Tennessee
August 8-9, 2000

Sample Location	Sampling Time	Sample Volume (Liters)	Concentration (ppm)*
First Shift			
Pepset Coremaker	7:40 a.m. - 2:40 p.m.	21	0.06
No-Bake Paint Operator	7:48 a.m. - 2:35 p.m.	20.3	ND**
No-Bake Mixer Operator	7:46 a.m. - 2:36 p.m.	20.6	ND
Pepset Coremaker	7:44 a.m. - 2:37 p.m.	20.8	ND
No-Bake Technician	7:52 a.m. - 2:44 p.m.	20.6	0.05
Second Shift			
Coremaker Operator	3:21 p.m. - 10:34 p.m.	21.65	0.08
Iron Pourer	3:32 p.m. - 10:55 p.m.	22.15	ND
Supervisor	3:44 p.m. - 10:35 p.m.	20.55	ND
Green Sand Operator	3:45 p.m. - 10:59 p.m.	21.7	Trace^
Shell Core Machine Operator	3:19 p.m. - 10:57 p.m.	22.9	0.04
Minimum Detectable Concentration (MDC)		20.3	0.013
Minimum Quantifiable Concentration (MQC)		20.3	0.038
NIOSH REL			5
OSHA PEL			5
ACGIH TLV			5

* ppm = parts per million
** ND = not detected at MDC
^Trace = between MDC and MQC

Table 2
Ammonia Personal Breathing Zone Air Sampling Results
Mueller Company, Chattanooga, Tennessee
August 9, 2000

Sample Location	Sampling Time	Sample Volume (Liters)	Concentration (ppm)*
Second Shift			
Green Sand Operator	3:30 p.m. - 10:54 p.m.	22.2	3.7
Green Sand Operator	3:40 p.m. - 10:56 p.m.	21.95	Trace^
Shell Core Supervisor	3:29 p.m. - 10:32 p.m.	21.2	1.01
Green Sand Operator	3:31 p.m. - 10:52 p.m.	22.1	Trace
Green Sand Operator	3:40 p.m. - 10:56 p.m.	21.85	Trace
Minimum Detectable Concentration (MDC)		21.2	0.13
Minimum Quantifiable Concentration (MQC)		21.2	0.47
NIOSH REL			25
OSHA PEL			50
ACGIH TLV			25

* ppm = parts per million
^Trace = between MDC and MQC

Table 3
Stoddard Solvent Personal Breathing Zone Air Sampling Results
Mueller Company, Chattanooga, Tennessee
August 8-9, 2000

Sample Location	Sampling Time	Sample Volume (Liters)	Concentration (mg/m^3)*
First Shift			
Pepset Coremaker	7:40 a.m. - 2:41 p.m.	21.05	10.5
No-Bake Technician	7:54 a.m. - 2:35 p.m.	20.2	33.2
No-Bake Technician	7:52 a.m. - 2:44 p.m.	20.65	17.4
Second Shift			
Shell Core Machine Operator	3:16 p.m. - 10:33 p.m.	21.85	1.9
Minimum Detectable Concentration (MDC)		20.2	0.35
Minimum Quantifiable Concentration (MQC)		20.2	0.99
NIOSH REL			350
OSHA PEL			2900
ACGIH TLV			570

* mg/m^3 = milligrams per cubic meter

Table 4
Cumene Personal Breathing Zone Air Sampling Results
Mueller Company, Chattanooga, Tennessee
August 8-9, 2000

Sample Location	Sampling Time	Sample Volume (Liters)	Concentration (ppm)*
First Shift			
Pepset Coremaker	7:44 a.m. - 2:37 p.m.	20.75	0.09
No-Bake Truck Driver	8:10 a.m. - 2:36 p.m.	19.45	ND**
Labor Pool	8:07 a.m. - 2:59 p.m.	20.2	ND
Second Shift			
Shell Core Machine Operator	3:12 p.m. - 10:34 p.m.	22.1	ND
Minimum Detectable Concentration (MDC)		19.45	0.01
Minimum Quantifiable Concentration (MQC)		19.45	0.03
NIOSH REL			50
ACGIH TLV			50

* ppm = parts per million
** ND = not detected at MDC

Table 5
Toluene Personal Breathing Zone Air Sampling Results
Mueller Company, Chattanooga, Tennessee
August 8-9, 2000

Sample Location	Sampling Time	Sample Volume (Liters)	Concentration (ppm)*
First Shift			
No-Bake Paint Operator	7:48 a.m. - 2:35 p.m.	20.4	0.02
Supervisor	8:02 a.m. - 2:35 p.m.	19.45	0.13
Second Shift			
Green Sand Operator	3:42 p.m. - 11:00 p.m.	21.9	0.04
Green Sand Operator	3:49 p.m. - 10:46 p.m.	20.85	0.06
Green Sand Iron Pourer	3:34 p.m. - 9:15 p.m.	17.05	0.08
Minimum Detectable Concentration (MDC)		17.05	0.006
Minimum Quantifiable Concentration (MQC)		17.05	0.016
NIOSH REL			100
OSHA PEL			200
ACGIH TLV			50

* ppm = parts per million

Table 6
Trimethylbenzene Isomers Personal Breathing Zone Air Sampling Results
Mueller Company, Chattanooga, Tennessee
August 8, 2000

Sample Location	Sampling Time	Sample Volume (Liters)	Concentration (ppm)*
First Shift			
No-Bake Close-up	7:58 a.m. - 2:48 p.m.	20.55	0.12
No-Bake Mold Mixer Operator	7:46 a.m. - 2:36 p.m.	20.6	2.20
Minimum Detectable Concentration (MDC)		20.55	0.02
Minimum Quantifiable Concentration (MQC)		20.55	0.07
NIOSH REL			25
ACGIH TLV			25

* ppm = parts per million

Table 7
Formaldehyde Area Air Sampling Results
Mueller Company, Chattanooga, Tennessee
August 8-9, 2000

Sample Location	Sampling Time	Sample Volume (Liters)	Concentration (ppm)*
First Shift			
Pepset- Coremaking Table	8:12 a.m. - 2:46 p.m.	19.7	0.02
Pepset - Table by Spraying Stations	8:26 a.m. - 2:45 p.m.	18.9	0.08
No-Bake Platform Before Oven	8:16 a.m. - 2:47 p.m.	19.55	0.03
No-Bake Shelves Near Mold Closing	8:24 a.m. - 2:52 p.m.	19.5	0.03
No-Bake Filling Station Platform	8:21 a.m. - 2:50 p.m.	19.55	0.02
Second Shift			
Pouring Line Pole	4:00 p.m. - 5:00 p.m.	60	PF^
Coremaking Table (1142)	4:05 p.m. - 10:45 p.m.	400	0.17
Top of Shelf by Radio (1370)	3:52 p.m. - 10:43 p.m.	411	0.03
Core Machine (1241)	3:50 p.m. - 5:20 p.m.	90	PF
Green Sand Molding Line	3:55 p.m. - 10:50 p.m.	415	0.04
Minimum Detectable Concentration (MDC)		18.9	0.003
Minimum Quantifiable Concentration (MQC)		18.9	0.009
NIOSH REL			LFC (0.016)#
OSHA PEL			0.75
ACGIH TLV			0.3 (ceiling)

* ppm = parts per million
^PF = pump failed
#LFC = lowest feasible concentration

Table 8
Hexamethylenetetramine Area Air Sampling Results
Mueller Company, Chattanooga, Tennessee
August 9, 2000

Sample Location	Sampling Time	Sample Volume (Liters)	Concentration (ppm)*
Second Shift			
Green Sand Pouring Line Pole	4:00 p.m. - 5:00 p.m.	60	PF**
Coremaking Table (1142)	4:05 p.m. - 10:45 p.m.	400	0.005
Shell core - Top of Shelf by Radio (1370)	3:52 p.m. - 10:43 p.m.	411	Trace^
Core Machine (1241)	3:50 p.m. - 5:20 p.m.	90	PF
Green Sand Molding Line	3:55 p.m. - 10:50 p.m.	415	0.02
Minimum Detectable Concentration (MDC)		60	0.0009
Minimum Quantifiable Concentration (MQC)		60	0.003
NIOSH REL			NA^^
OSHA PEL			NA
ACGIH TLV			NA

* ppm = parts per million
** PF = pump failed
^Trace = between MDC and MQC
^^ NA = none available or established

Table 9
MDI Area Air Sampling Results
Mueller Company, Chattanooga, Tennessee
August 9, 2000

Sample Location	Sampling Time	Sample Volume (Liters)	Concentration (μg/m^3)*
First Shift			
No-Bake Filling Station	9:44 a.m. - 2:04 p.m.	260	0.073
Pepset Oven Table	9:45 a.m. - 2:05 p.m.	260	0.25
Mold Closing/Finishing	9:55 a.m. - 2:09 p.m.	254	ND**
Pepset Mold Filling Station	9:50 a.m. - 2:07 p.m.	257	Trace^
No-Bake Table by Spraying Station	9:41 a.m. - 2:03 p.m.	262	ND
Minimum Detectable Concentration (MDC)		254	0.016 (filter) 0.07 (impinger)
Minimum Quantifiable Concentration (MQC)		254	0.055 (filter) 0.24 (impinger)
NIOSH REL			50
OSHA PEL			200 (ceiling)
ACGIH TLV			50

* μg/m^3 = micrograms per cubic meter
** ND = not detected at MDC
^Trace = between MDC and MQC

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