HETA 98-0347-2758
Lockheed Martin Aeronautical Systems
Marietta, Georgia

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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 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 Angela Weber and Helga Daftarian of HETAB, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Field assistance was provided by Christopher Reh and Max Kiefer. Desktop publishing was performed by Patricia Lovell. Review and preparation for printing was performed by Penny Arthur.

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Health Hazard Evaluation Report 98-0347-2758
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Marietta, Georgia
November 1999

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SUMMARY

In September 1998, the National Institute for Occupational Safety and Health (NIOSH) received a health hazard evaluation (HHE) request from Lockheed Martin Aeronautical Systems (LMAS) in Marietta, Georgia. The joint management and employee request concerned potential office employee exposures to diisocyanate-containing paints, primers, solvents, and cured and uncured composite materials used during the manufacturing of the F-22 fighter jet (office area is located directly above the production area). The request stated that office workers in Area K of Building 11 had experienced breathing difficulties, asthma, burning eyes, and neurological and memory impairment. In response to the request, NIOSH investigators conducted an initial site visit at LMAS on October 30, 1998, and returned to conduct medical interviews and a tracer gas ventilation study on February 17-18, 1999.

Employee interviews revealed that approximately 88% of the employees (14 of 16) who had worked in Area K during May 1998 reported that they had experienced a variety of symptoms. Symptoms included eye, nose and throat irritation, cough, wheezing, shortness of breath, chest pain, headache, nausea, dizziness, fatigue, numbness/tingling of the extremities, and skin rashes. All but one of the symptomatic employees reported that their symptoms were most pronounced when they were at work and tended to diminish away from work. Medical records were reviewed for 13 of the 14 symptomatic employees. Nine of these employees were eventually referred to a pulmonary specialist and diagnosed with a variety of respiratory conditions attributable to chemical exposure in the workplace (these included seven cases of mild asthma/reactive airway disease, one case of acute exacerbation of asthma/status asthmaticus, one case of chemical pharyngitis, and two cases of chemical conjunctivitis).

The tracer gas ventilation study consisted of evaluating the potential for contaminant migration from the first floor production area to Area K on the second floor. Specifically, a one-percent concentration of sulfur hexafluoride (SF_6) was released in two chemical use areas (paint spray booth and core-clean room), where it was suspected that contaminant dissemination to other areas may occur. Additionally, tracer gas was released around one of the air handling units (AHU), located on the first floor mezzanine level which served Area K to evaluate the potential for contaminant migration from the autoclave area into the AHU. At the time of the initial site visit, LMAS was implementing several engineering controls; therefore, the tracer gas study was used to evaluate these changes. Results indicated that corrective actions to control emissions and migration of chemicals from the paint spray booth and the core-clean room had prevented substances generated in these areas from reaching Area K employees. Tracer gas release around the AHU served two purposes. First, it was determined that Area K is undergoing approximately four air changes per hour (ACH) which is consistent with a recent test and balancing report describing the ventilation system serving this area. Second, tracer gas entrained into the AHU and supplied to Area

K indicates that any chemicals, contaminants, or odors generated in this area could potentially expose individuals in Area K.

The results of the medical evaluation appear to indicate that the respiratory symptoms which were being experienced by the affected employees who were working in Area K during May 1998 are most consistent with known exposure to isocyanates at the time the employees' symptoms became manifest. Possible concomitant exposure to solvents such as MEK or isopropyl alcohol may also explain some of the irritant mucous membrane and respiratory symptoms experienced by Area K employees. However, no specific cause can be identified which would explain why some of the employees continued to experience symptoms after being relocated to another building. Results from the tracer gas ventilation study indicate that corrective actions to control emissions and migration of chemicals from the paint spray booth and the core-clean room were successful, while chemicals, contaminants, or odors generated in the near vicinity of the AHU located in the production area could potentially expose individuals in Area K. Recommendations to help prevent and address future indoor environmental quality concerns among Area K employees are provided in this report.

Keywords: SIC 381 (Search, Detection, Navigation, Guidance, Aeronautical, and Nautical Systems, Instruments, and Equipment) Indoor Environmental Quality, Indoor Air Quality, IEQ, IAQ, Ventilation, Tracer Gas, Sulfur Hexafluoride, Composites, Diisocyanate-Containing Paints, Methyl Ethyl Ketone, MEK, Methyl Ethyl Isobutyl Ketone, MIBK, Isoproponal, Occupational Asthma, Chemical Sensitization, Mucous Membrane Irritation.

Highlights of the NIOSH Health Hazard Evaluation

Airborne Exposures to Isocyanates and Organic Solvents

The NIOSH Health Hazard Evaluation (HHE) was jointly requested by management and employees from Lockheed Martin Aeronautical Systems (LMAS). NIOSH was asked to see if office workers in Area K were becoming ill from isocyanate-based paints and organic solvents used in making the F-22 fighter jet. Jets are made in the same building on the first floor directly below the offices.

What NIOSH Did

We talked to employees who were working in Area K when problems started.
We looked at medical records and injury and illness records for Area K employees.
We checked material safety data sheets for chemicals used on the first floor.
We looked for ways that chemicals on the first floor could get into Area K through the air.
We reviewed changes LMAS made to the building and the ventilation to stop air from moving from the first floor into Area K.
We released tracer gas in selected areas of the first floor to see if corrections had stopped air from moving into Area K.

What NIOSH Found

Health complaints were most likely caused by exposures to isocyanate paints.
Most of the sick employees in Area K worked near the paint spray booth exhaust fan room found on the second floor.
Further exposure to organic solvents could have caused breathing problems and eye irritation among Area K employees.
Air most likely moved from the paint spray booth exhaust system into Area K before changes were made to the building and the ventilation system.
After changes were made, tracer gas released in the paint spray booth did not reach Area K.
Chemicals and odors found in the air around the ventilation unit for Area K could pass through the ventilation system to Area K.

What LMAS Managers Can Do

Don't use isocyanate paints in the building.
Require the production area to notify LMAS safety and health representatives of all activities and changes made to the process.
Start an indoor air quality management plan to quickly identify future problems.
Tell workers about the dangers associated with the chemicals used in the production area.
Encourage Area K employees to quickly report odors and/or symptoms to LMAS management.
Look into all complaints and explain findings to employees.
Keep Area K under positive pressure.
Move or enclose the ventilation unit on the first floor to stop chemicals and odors from passing on into Area K.

What LMAS Employees Can Do

Continue to check with your own doctor if health problems continue.
Get permission from your doctor before moving back into Area K.
Don't close off supply vents in Area K since this changes the ventilation system.
Report all odor complaints and/or continuing symptoms to LMAS management.

CDC
CENTERS FOR DISEASE CONTROL AND PREVENTION

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 # 98-0347-2758

NIOSH

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INTRODUCTION

In September 1998, the National Institute for Occupational Safety and Health (NIOSH) received a health hazard evaluation (HHE) request from Lockheed Martin Aeronautical Systems (LMAS) in Marietta, Georgia. The joint management and employee request concerned potential office employee exposures to diisocyanate-containing paints, primers, solvents, and cured and uncured composite materials used during the manufacturing of the F-22 fighter jet. The request stated that office workers in Area K of Building 11 had experienced breathing difficulties, asthma, burning eyes, and neurological and memory impairment. In response to the request, NIOSH investigators conducted an initial site visit at LMAS on October 30, 1998, and returned to conduct medical interviews and a tracer gas ventilation study on February 17-18, 1999.

BACKGROUND

Indoor Environmental Quality (IEQ) in Area K

An initial IEQ complaint from an employee in Area K occurred on May 22, 1998. Historical documentation provided by the company physician indicated that a bottle of cleaning solution (containing limonene) had spilled onto the carpeting in Area K (limonene is a terpene and essential oil that is a major constituent in oils of orange, lemon, caraway, dill, bergamot, and pine needle. It is used in flavoring, fragrance and perfume materials, as well as in solvents and wetting agents). In response to this complaint, LMAS had the carpeting removed a week later. Shortly after this, in what appeared to be unrelated to the spill, other Area K workers began reporting symptoms including respiratory and mucous membrane irritation. Based on the number of growing odor complaints and symptoms among Area K workers, LMAS personnel took a number of actions to better characterize the scope of the problem, identify possible environmental explanations for the intermittent odors, and improve the workplace environment. In addition, a consulting firm was hired to evaluate chemical exposures in Building L-11. Based upon the company physician's recommendation, employees in Area K were relocated to Building L-22 on June 25, 1998, due to the continuing presence of unexplained odors and the persistent symptoms on the part of several employees.

Based on the types of symptoms experienced by employees and the clustering of affected employees in the vicinity of the mechanical room housing the exhaust fan for the paint spray booth, continuous low-level exposures to isocyanate-containing paints was viewed as a potential cause. The mechanical room adjacent to Area K was found to be under positive pressure (air moved from the mechanical room into Area K) because the exhaust fans for the paint spray booth were located within the room instead of on the roof. Air sampling performed in the spray paint booth and Area K sections of L-11 by the consulting firm detected trace amounts of isocyanates contained in the paints. However, NIOSH investigators reviewed the sampling techniques and analytical procedures used by the consulting firm, and concluded that the reported concentrations were most likely underestimated. Specifically, the methods employed during the consultant's survey (Occupational Safety and Health Administration [OSHA] Methods 42 and 47) did not have the capability to measure the two major isocyanate compounds (HDI- and MDI-based polyisocyanates) present in the 624 and 648 polyurethane paints used in Building 11. In addition, the OSHA methods are not recommended when sampling for aerosolized isocyanates in spray painting operations. This review was reported in a letter sent to LMAS by NIOSH on February 10, 1999. It should be noted that LMAS had discontinued the use of isocyanate-containing paints before the initial NIOSH site visit. In addition to the paint spray booth exhaust, there was an open catwalk leading from the first floor production area into the mechanical room above. Therefore, any chemicals used in this area, could potentially migrate into Area K by being drawn into the air handling unit (AHU) serving Area K.

Building Description

The L-11 Building, located on the LMAS campus in Marietta, Georgia, was originally built in the 1970s for the assembly of jets. In the early 1990s, more office space was added to accommodate the additional personnel needed for the production of the F-22 fighter jet. Since space on the LMAS campus was limited based on building security requirements, all personnel (including production, engineering, and administrative employees) involved with the F-22

composite fabrication process were housed in the L-11 Building.

The 71,000 square feet (ft^2) composite area is located on the first floor of the L-11 Building. Office space in L-11 is divided into Areas A through L. All of the offices (except for Area A) are located on the second floor of the building above the manufacturing areas. The 12,000 ft^2 office space evaluated by NIOSH (Area K) is located directly above the paint spray booth. Two separate air handling units (AHU), which share a common outdoor air intake plenum, serve Area K. While one of the AHUs is located on the roof of the building, the other AHU is located on the mezzanine level in the manufacturing area. Approximately 70 employees, who were originally assigned to area K, had been either relocated to other areas of Building L-11, or to other buildings on the Lockheed-Martin campus at the time of the NIOSH site visit.

Process Description

The composite fabrication in Building L-11 is comprised of the following steps:

1. Pre-impregnated Composite Material (Prepregs) Preparation. The prepreg composite material consists of either unidirectional fibers or woven fabric that has been impregnated with a resin system. Prepregs used in L-11 contain either 977-3 Epoxyn or 5250-4 BMI resins. All prepregs in L-11 are stored below freezing to retard potential chemical reactions. In preparation to construct a composite part, the prepreg is cut with a Gerber Cutter to a desired shape.

2. Lay-up. Once the prepreg has been cut to shape, the lay-up process begins. Lay-up is performed in a temperature and humidity controlled clean room area. The precut prepreg plies are manually placed on a tool (frame) in layers, and in a specified orientation to obtain the desired shape and properties. Before the prepreg is placed on the tool, the tool is hand-wiped with a solvent soaked rag, and a mold release agent is applied from an aerosol can to the tool to assist in removal of the part following the curing cycle.

3. Bagging the Part. After the lay-up is complete, an airtight bagging material is placed over the prepreg and sealed to the tool. A vacuum is drawn on the bag to maintain the integrity of the part.

4. Autoclave Cure. The autoclave is used to support and control the chemical reaction through the application of heat and pressure. The part, while under vacuum, is placed in the autoclave and heated to initiate cross-linking (polymerization) and give the composite its characteristic properties. The part remains under a vacuum during the curing process. Volatiles generated during the process are drawn off, run through a cold trap, and exhausted to the outdoors by a vacuum system. The autoclave is pressurized during processing to further consolidate the laminate and support the chemical reaction. The autoclave and the vacuum system have independent exhaust systems, and both are exhausted to the outside. The autoclave is sealed during the curing process and is under a nitrogen purge. Once the curing cycle is complete, the autoclave is exhausted and the nitrogen is replaced with normal air. Once a normal atmosphere is achieved, the autoclave door is opened and the part is removed.

5. De-bag/Tool Clean-up. Once the initial curing cycle is complete, the part is removed from the bag. The part may undergo further processing in ovens to complete the curing cycle. Like the autoclaves, the ovens are ventilated directly to the outdoors. Once the cure is complete, no further chemical reactions occur. After the part is separated from the tool, the tool is cleaned with a solvent-soaked rag to prepare it for its next use.

6. Part Trim/Machining. Composite machining consists of mechanical processes (trimming, drilling, sanding, etc.) that may liberate particulate matter. The composite parts are cut into shape with tools equipped with local exhaust to control the release of dust. The exhaust system from each machine is tied into a central exhaust that is vented to a dust collector located outside the building.

7. Part Priming/Painting. Once the machining is complete, the part is cleaned with a solvent then primed and painted. All painting occurs in a dedicated paint booth that is directly vented to the outdoors. The exhaust fan for the paint booth is located in a mechanical room on the second floor adjacent to Area K.

The employees who worked in the Area K offices were engaged in strictly administrative duties (which included aerospace procurement contract administration, cost analysis, logistics analysis, engineering technology management, and secretarial/clerical duties). The equipment in Area

K was limited to standard office furniture and office supplies. No smoking was permitted in the Area K offices.

METHODS

On October 30, 1998, NIOSH held an opening meeting with management and employee representatives. During this meeting, information about NIOSH was provided, and the HHE request was discussed. Various operational parameters regarding the use of isocyanate-based paints and organic solvents, as well as the health problems being reported, were discussed. Following the opening conference, a walk-through evaluation was conducted in several areas of Building L-11, including three office areas on the second floor and the composite manufacturing area on the first floor.

The follow-up site visit was made on February 17-18, 1999, and consisted of medical interviews and evaluating the potential for contaminant migration from the first floor to Area K on the second floor with a tracer gas. At the time of the initial site visit, LMAS was in the process of implementing several engineering controls; therefore, the tracer gas study was used to evaluate these changes. Because the tracer gas study was conducted after engineering modifications were implemented to improve the isolation of Area K, this study only provides information on conditions at the time of the site visit. The potential for contaminant migration prior to implementing the control measures was not determined.

Medical Evaluation

NIOSH staff conducted individual, confidential medical interviews with 28 plant employees during the follow-up visit. Employees were selected at random from an employee roster provided by the company. Employees who were interviewed included 15 employees who had worked in Area K during May 1998, one L-11 paint spray booth employee, and 12 additional administrative support and engineering personnel who worked in other areas of Building L-11 (including areas A, B, C, D, E, F, and G), as well as Building L-12. The 12 additional employees were interviewed in order to determine whether any similar health effects were occurring in any of the other L-11 work areas. Information from the structured interviews addressed occupational work history, chemical exposures, the use of personal protective equipment (PPE), history of health problems/symptoms, medication history, alcohol/tobacco use, and history of chemical exposures outside of the workplace. Medical records for 15 interviewed employees were obtained from the plant medical department and private medical providers. Medical records were reviewed for all employees who reported health problems. Employee Injury/Illness Records were also reviewed for an additional 12 employees who had worked in Area K during May 1998, but were unavailable at the time of the site visit. A comprehensive list of L-11 employee names and each individual's symptoms was provided by the LMAS occupational medicine physician, and upon the NIOSH medical investigator's request, copies of the injury and illness records for these individuals were provided. The OSHA Log and Summary of Occupational Injuries and Illnesses (Form 200) for the years 1995-1998 were also reviewed.

Environmental Evaluation

A one percent (10,000 parts per million [ppm]) concentration of sulfur hexafluoride (SF_6) in nitrogen was released as the source tracer from a compressed gas cylinder equipped with a regulator and a flow meter. SF_6 was released in two chemical use areas (paint spray booth and core-clean room) where we suspected that contaminant dissemination to other areas could occur. Additionally, tracer gas was released around one of the air handling units (AHU), located on the first floor mezzanine level, which served Area K. This test was conducted to evaluate the potential for contaminant migration from the autoclave area into the AHU. Prior to the release of the gas, a Brüel and Kjaer (B&K) model 1302 multi-gas continuous monitor was placed approximately 20 feet from the door of the mechanical room in the southwest corner of Area K. Continuous background sampling prior to the release of tracer gas was initiated to establish a baseline.

SF_6 is a colorless, odorless, and essentially chemically inert gas that has ideal properties for use as a tracer. SF_6 is not metabolized and is considered to be toxicologically inert.[2] The NIOSH Recommended exposure limit (REL) for SF_6 is 1,000 ppm as a 10-hour time-weighted average (TWA).[1] In addition to low toxicity and reactivity, SF_6 is easily detectable at low concentrations. Although SF_6 is a heavy gas, at dilute concentrations the overall air

density is not much different from pure air, and thus the tracer gas will follow room air currents.

The principle of detection by the B & K is infrared absorption at a specific wavelength with subsequent analysis via a photoacoustic effect. With this technique, sample gas, collected via a teflon sample hose, is pumped into a sample chamber where SF_6 gas absorbs infrared energy proportional to the concentration of the gas. The absorbed infrared energy is released as heat, resulting in a pressure increase which is measured with a microphone. The monitor records SF_6 concentrations in ppm approximately every minute. The monitor has a detection limit of approximately 0.05 ppm for SF_6. Data collected was logged in the instrument's internal memory and subsequently uploaded into a personal computer. In addition to monitoring in the continuous sampling mode, an air sampling bag was used to collect samples in the core-clean room to verify the calculated concentration. The bag was filled using a portable air sampling pump and subsequently analyzed with the B&K monitor.

The dimensions of the paint booth room and the core-clean room were determined, and the room volume calculated. This information was used to determine the amount of tracer gas which needed to be released to generate a concentration of SF_6 between 10 and 20 ppm. Given a detection limit of 0.05 ppm, potential migration to Area K up to a maximum dilution factor of 400 could be determined. Prior to each trial, the ventilation in each area was turned off and the doors closed. Gas was released at a flow rate of four cubic feet per minute (cfm) until the calculated concentration was reached. At that time, the gas was shut off and the ventilation turned back on. Communication between the point of tracer release and the monitor in Area K was established so the specific timing of each sequence (gas on, gas off, ventilation on) could be recorded. This would allow for the determination of contaminant migration, migration time, and the dilution effect.

EVALUATION CRITERIA

General

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 important, however, 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 which can 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 RELs,[1] (2) the American Conference of Governmental Industrial Hygienists' (ACGIH®) Threshold Limit Values (TLVs®) and Biological Exposure Indices (BEIs®),[2] and (3) the U.S. Department of Labor OSHA Permissible Exposure Limits (PELs).[3] 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.[4] Thus, employers should understand that not all hazardous chemicals have specific OSHA exposure limits such as PELs's and STEL's. An employer is still required by OSHA to protect their employees from hazards, even in the absence of a specific OSHA PELs.

TWA exposure refers to the average airborne concentration of a substance during a normal 8 to 10 hour workday. Some substances have recommended short-term exposure limits (STEL) or ceiling values which are intended to supplement the

TWA where there are recognized toxic effects from higher exposures over the short-term.

Agents Used in the Composite Area

Isocyanate-Containing Paints

Review

The unique feature common to all diisocyanates is that they consist of two -N=C=O (isocyanate) functional groups attached to an aromatic or aliphatic parent compound. Because of the highly unsaturated nature of the isocyanate functional group, the diisocyanates readily react with compounds containing active hydrogen atoms (nucleophiles). Thus, the diisocyanates readily react with water (humidity), alcohols, amines, etc.; diisocyanates also react with themselves to form either dimers or trimers. When a diisocyanate species reacts with a primary, secondary, or tertiary alcohol, a carbamate (-NHCOO-) group is formed which is commonly referred to as a urethane. Reactions involving a diisocyanate species and a polyol result in the formation of cross-linked polymers; *i.e.* polyurethanes. Hence, they are used in surface coatings, polyurethane foams, adhesives, resins, elastomers, binders, and sealants. Many material safety data sheets (MSDS) use isocyanate-related terms interchangeably. For the purpose of this report, terms are defined as follows.

Diisocyanates (Monomers): The difunctional isocyanate species from which polyisocyanates and polyurethanes are derived. Common examples of monomeric isocyanates include 1,6-hexamethylene diisocyanate (HDI), 2,4- and/or 2,6-toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), methylene bis(4-yclohexylisocyanate)(HMDI), isophorone diisocyanate (IPDI), and 1,5-naphthalene diisocyanate (NDI). Commercial-grade TDI is an 80:20 or 65:35 mixture of the 2,4- and 2,6- isomers of TDI, respectively.

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

Prepolymers: Species possessing free isocyanate groups, prepared from the reaction of a polyol with an excess of di- or polyisocyanate.[5] Commercially available isocyanate products frequently contain prepolymers in lieu of more volatile isocyanate monomers.

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

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

In general, the types of exposures encountered during the use of isocyanates (*i.e.*, monomers, prepolymers, polyisocyanates, and oligomers) in the workplace are related to the vapor pressures of the individual compounds. The lower molecular weight isocyanates tend to volatilize at room temperature, creating a vapor inhalation hazard. Conversely, the higher molecular weight isocyanates do not readily volatilize at ambient temperatures, but are still an inhalation hazard if aerosolized or heated in the work environment. The latter is important since many reactions involving isocyanates are exothermic in nature, thus providing the heat for volatilization. To reduce the vapor hazards associated with the lower molecular weight diisocyanates, prepolymer and polyisocyanate forms of these diisocyanates were developed and have replaced the monomers in many product formulations.

Isocyanates exist in many different physical forms in the workplace. Not only are workers potentially exposed to the unreacted monomer, prepolymer, polyisocyanate, and/or oligomer species found in a given product formulation, they can also be exposed to partially reacted isocyanate-containing intermediates formed during polyurethane production. In addition, isocyanate-containing mixtures of vapors and aerosols can be generated during the thermal degradation of polyurethane coatings and plastics. The capability to measure all isocyanate-containing substances in air, whether they are in monomer, prepolymer, polyisocyanate, oligomer, and/or intermediate forms, is important when assessing a worker's total airborne isocyanate exposure.

Health Effects Associated With Isocyanates

Exposure to isocyanates is irritating to the skin, mucous membranes, eyes, and respiratory tract.[6,7] 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).[7,8,9] Contact dermatitis can result in symptoms such as rash, itching, hives, and swelling of the extremities.[6,7,9] 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).[6,8,9] An isocyanate-exposed worker may first develop asthma-like symptoms or an asthmatic condition after a single (acute) exposure, but sensitization usually takes a few months to several years of exposure.[6,8,10,11,12] The asthmatic reaction may occur minutes after exposure (immediate), several hours after exposure (late), or a combination of both immediate and late components after exposure (dual).[8,11] The late asthmatic reaction is the most common, occurring in approximately 40% of isocyanate sensitized workers.[13] An improvement in symptoms may be observed during periods away from the work environment (weekends, vacations).[6,8,11] After sensitization, any exposure, even to levels below an occupational exposure limit or standard, can produce an asthmatic response which may be life threatening. Experience with isocyanates has shown that monomeric, prepolymeric and polyisocyanate species are capable of producing respiratory sensitization in exposed workers.[14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30] Since the intermediates may be chemically similar to these compounds, it is reasonable to assume that they may also produce this condition. Prevalence estimates for isocyanate-induced asthma in exposed worker populations vary considerably: from 5% to 10% in diisocyanate production facilities[10,31] to 25% in polyurethane production plants[31,32] and 30% in polyurethane seat cover operations.[33] The scientific literature contains a limited amount of animal data suggesting that dermal exposure to diisocyanates may produce respiratory sensitization.[34,35,36,37] This finding has not been tested in dermally-exposed workers.

The percentage of sensitized workers with persistent symptoms of asthma after years of no exposure may be 50% or higher. 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.[11] 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 exposures, and for active medical surveillance of all workers potentially exposed to diisocyanates.

HP has also been described in workers exposed to isocyanates.[38,39,40,41] Currently, the prevalence of isocyanate-induced HP in the worker population is unknown, and is considered to be rare when compared to the prevalence rates for isocyanate-induced asthma.[9] Whereas asthma is an obstructive respiratory disease usually affecting the bronchi, HP is a restrictive respiratory disease affecting the lung parenchyma (bronchioles and alveoli). The initial symptoms associated with isocyanate-induced HP are flu-like, including shortness of breath, non-productive cough, fever, chills, sweats, malaise, and nausea.[8,9] After the onset of HP, prolonged and/or repeated exposures may lead to an irreversible decline in pulmonary function and lung compliance, and to the development of diffuse interstitial fibrosis.[8,9] Early diagnosis is difficult since many aspects of HP, *i.e.*, the flu-like symptoms and the changes in pulmonary function are manifestations common to many other respiratory diseases and conditions.

A limited number of animal studies have demonstrated that commercial-grade TDI is carcinogenic in both rats and mice.[42] Statistically significant excesses of liver and pancreatic tumors were observed in male and female rats and female mice that received TDI by gavage (route of exposure via the digestive tract). In addition, a statistically non-significant excess in rare brain tumors were observed in male rats also treated with TDI by gavage. Also, commercial-grade TDI was found to have a dose-dependent mutagenic effect on two strains of *Salmonella typhimurium* in the presence of a metabolic activator (S-9 liver fractions from rats or hamsters treated with Aroclor 254).[43] Based on these animal and *in vitro* studies, the National Institute for Occupational Safety and Health (NIOSH) concluded that sufficient evidence exists to classify TDI as a potential occupational carcinogen.[44] It is important to note that no epidemiologic data exists linking TDI exposure to elevated cancer rates in exposed workers.

In regards to the two types of paints used in Building 11, there are currently no recommended exposure limits for HDI (including HDI-based trimer). The OSHA and NIOSH ceiling limit for MDI (including polymethylenepolyphenyl isocyanate) is set at 200 micrograms per cubic meter ($\mu g/m^3$). The NIOSH REL and the ACGIH TLV (up to an 8-hour TWA) are set at 50 $\mu g/m^3$ and 51 $\mu g/m^3$, respectively.

Methyl Ethyl Ketone (MEK)

Methyl ethyl ketone (MEK) is a colorless, flammable organic solvent with a characteristic odor similar to acetone and is typically used as a solvent in surface coating and synthetic resin industries.[2]

MEK is absorbed primarily through inhalation and causes irritation of the eyes, mucous membranes, and skin. At high concentrations, MEK may cause central nervous system depression. Short-duration inhalation exposure to 100 (ppm) of MEK was reported to cause slight nose and throat irritation, 200 ppm caused mild eye irritation, and 300 ppm was associated with headaches, and throat irritation, as well as an objectional odor.[45] Additional studies indicate that MEK by itself does not cause neurologic toxicity of the extremities (peripheral neuropathy), but it may potentiate the toxic effects of substances known to cause peripheral neuropathy, such as n-hexane.[46,47,48] Continued or prolonged skin contact with MEK liquid can cause dermatitis.[45]

The National Toxicology Program, an interagency research program, has not found evidence supporting an association between MEK exposure and the development of cancer in humans or experimental animals.[49]

NIOSH, OSHA, and ACGIH have the same exposure limit for MEK: a full-shift TWA of 200 ppm and a 15-minute STEL of 300 ppm.

Methyl Isobutyl Ketone (MIBK)

Used in paints, glues, and as a cleaning agent, MIBK can irritate the eyes, skin, and mucous membranes.[45] Exposures to concentrations between 50 and 500 ppm in humans have caused eye irritation, headache, loss of appetite, and weakness.[46] This compound has a distinctive camphor-like odor which is detectable at a level of 100 ppm.[45] The NIOSH REL and ACGIH TLV for MIBK are both 50 ppm for a full-shift TWA and 75 ppm for a 15-minute STEL. The OSHA PELS for this chemical is 100 ppm for an 8-hour TWA.

Isopropanol (Isopropoyl Alcohol)

Isopropanol is a colorless, volatile, flammable liquid of low toxicity that is used as a chemical intermediate, a general purpose solvent, and an ingredient in skin lotions, cosmetics, and pharmaceuticals.[2,45] The vapor of isopropanol is irritating to the eyes and mucous membranes; inhalation of high concentrations can cause depression of the central nervous system.[45,50] The potential effects from occupational skin contact with the liquid are insignificant; cutaneous absorption should not contribute to systemic toxicity and generally does not produce skin irritation, except with allergic individuals.[2,45,50] The inhalation exposure limits established for isopropanol by NIOSH, OSHA, and ACGIH are equivalent. All are set at a full-shift TWA of 400 ppm, and a 15-minute STEL of 500 ppm.

RESULTS

Medical Evaluation

The average age of the 28 interviewed employees was 49 years (range: 26-65 years). Most had worked at LMAS in various administrative positions (such as engineers, engineering technologists, data management, procurement supervisors, secretarial/clerical duties, subcontractors, materiel and management specialists, materiel representatives, and cost analysts) for three years or more and were working in their current positions for at least six months. All stated that they worked an 8 ½-hour shift. Most stated that their jobs did not require the use of PPE. Employees' use of workplace chemicals was confined to standard office supplies, such as white-out, copier solutions, and general office cleaning supplies.

Of the 28 employees interviewed, 16 stated that they had been working in Area K or in the paint booth area at the time when employee complaints and symptoms were first reported (May 1998). Three of

the employees who had cubicles closest to the mechanical room stated that they were among the first to become ill. One of these three employees was seen at the LMAS clinic on May 26, 1998, with a chief complaint of acute onset of wheezing while at work. This individual was diagnosed with an acute exacerbation of asthma, and was referred to a pulmonary specialist three days later. At the time of the pulmonary evaluation, a diagnosis of status asthmaticus was made, and the employee was admitted to the hospital the same day. The second of the three employees experienced a sore throat and the acute onset of chest tightness while traveling on a business trip on the afternoon of May 27, 1998. These symptoms began approximately five hours after the individual was evaluated in the LMAS clinic with a chief complaint of cough and pain upon swallowing which had started the previous day while at work. The employee presented to the emergency room the same evening, and was treated and released.

Fourteen of the 16 employees who were working in Area K during May 1998 reported one or more of the following symptoms: eye, nose, and throat irritation, cough, wheezing, shortness of breath, chest pain, headache, nausea, dizziness, fatigue, numbness/and or tingling of the extremities, and skin rash. Of the 14 symptomatic employees, 13 stated that the symptoms they experienced improved with time away from work and worsened after returning to the workplace. Seven of the 14 stated that they had experienced acute symptoms (including shortness of breath, wheezing, chest tightness, cough, and hoarse voice) upon briefly reentering their previous work area in Building L-11. Two of the 14 employees, who have since been relocated to Building L-22, stated that they experienced respiratory symptoms shortly after receiving paperwork which was originally stored in Area K. Six of the 14 employees stated that they had become "increasingly sensitive" to household chemicals (such as home cleaning solutions, nail polish remover, indoor-use pesticides, and fertilizers/lawn chemicals); these employees related experiencing an acute onset of mucous membrane and respiratory irritation symptoms shortly after exposure to these chemicals, with symptom improvement occurring after cessation of exposure. None of the symptomatic employees interviewed related any participation in hobbies or other non-occupational activities involving significant exposures to chemicals.

Medical records were obtained for 15 of the employees interviewed. Medical records from the plant medical clinic as well as private medical provider records were reviewed. Plant medical records indicated that 12 of the symptomatic employees had been evaluated for mucous membrane and upper respiratory irritation secondary to chemical exposure (characterized as exposure to either D-limonene, TDI, or MEK between May and June 1998). Nine of the 12 employees were referred to a pulmonary specialist for further evaluation of their respiratory symptoms. Each of the nine employees underwent a comprehensive pulmonary evaluation (including history and physical examination, pre-and post-bronchodilator pulmonary function testing, diffusion capacity for carbon monoxide [DLCO] testing, and chest X-ray studies). Of the nine employees evaluated, seven were diagnosed with "reactive airway disease" (plus either "mild obstructive airway disease" or "mild asthma") secondary to inhalation of chemical sensitizers. One employee with a previous history of asthma was diagnosed with an "acute exacerbation of asthma"/status asthmaticus as a result of presumed workplace exposure to MEK. Another employee was diagnosed with a "chemical pharyngitis/laryngitis" and "vocal cord dysfunction" consistent with exposure to isocyanate-type irritants. According to plant medical records, 8 of the 15 symptomatic employees had been placed on class VI permanent work restrictions (i.e., these employees were not to reenter Building L-11 without prior medical clearance), as a result of exposure to unspecified chemicals in this building. Injury and illness record forms were also reviewed for 12 Area K employees which NIOSH did not interview. These employees had experienced a variety of symptoms suggestive of chemical exposure (including mucous membrane irritation, cough, shortness of breath, headaches, nausea, dizziness, fatigue, skin rash, and numbness of the hands and legs). All were evaluated in the occupational medicine clinic for possible chemical fume exposure. Four individuals underwent chest X-ray and pulmonary function testing as part of their symptom work-up. The remainder were evaluated by physical exam, released, and instructed to follow-up as needed should further symptoms develop.

OSHA 200 log entries for 1995, 1996, 1997, and 1998 were reviewed. In 1998, there were 1,519 total entries noted. Thirty entries (2%) involved fume exposure (not otherwise specified) involving the eyes, head, chest, lungs, and stomach which were

directly related to exposures in Area K. The majority of the other injuries and illnesses recorded for all years involved sprains/strains, lacerations, abrasions, contusions, foreign body injuries, burns, and dermatitis.

Environmental Evaluation

To establish baseline concentrations of SF_6 in Area K, continuous background sampling was conducted over a 25-minute period prior to the release of tracer gas in any of the evaluated areas. As seen in Figure 1, background concentrations of SF_6 in Area K ranged from approximately 7.3×10^{-3} ppm to 22.7×10^{-3} ppm, with an average concentration of 15.5×10^{-3} ppm.

Tracer gas was released in the two chemical use areas of concern: the paint spray booth, and the core room where parts are cleaned with MEK. After determining that the volume of the paint spray booth was approximately 15,775 cubic feet (ft^3), tracer gas was released for five minutes at four cfm in the booth, resulting in a calculated concentration of approximately 12 ppm prior to turning on the exhaust fan in the booth. Continuous sampling was conducted over a 22-minute period after turning on the exhaust fan (see Figure 2). Concentrations of SF_6 in Area K remained similar to previous baseline measurements, ranging from 6.94×10^{-3} ppm to 17.8×10^{-3} ppm, with an average concentration of 13.0×10^{-3} ppm. These results indicate that tracer gas did not migrate into the office space of Area K from the paint spray booth under the environmental conditions present at the time of the NIOSH evaluation.

SF_6 was released for a total of five minutes at 4 cfm in the core room, resulting in a calculated concentration of 15.6 ppm (based on an approximate room volume of 12,840 ft^3) prior to activating the local exhaust ventilation. As shown in Figure 3, concentrations of SF_6 in Area K were also unchanged during the release of tracer gas in the core room. An average concentration of 13.7×10^{-3} ppm was measured in Area K, with a range from 9.7×10^{-3} ppm to 18.1×10^{-3} ppm. To ensure that the appropriate concentration of SF_6 was being released, a bag sample was collected in the core room prior to turning on the local exhaust ventilation. The bag sample was found to contain 16 ppm SF_6, thereby confirming the calculated concentrations (see Figure 4).

In addition to the chemical use areas, tracer gas was released around one of the two AHUs serving Area K. Since the AHU was situated in an open space on the mezzanine level of the production area, tracer gas was released in the proximity of the negative pressure components of the AHU. Unlike the enclosed chemical use areas, for which an initial SF_6 concentration could be determined, the results from this trial only provided information on the potential for entrainment and dissemination to Area K. The degree of dilution during migration (concentration at sample point versus concentration at the release point) could thus not be determined. Approximately one minute after releasing tracer gas around the AHU, concentrations of SF_6 in Area K increased to 45.7×10^{-3} ppm, in comparison to background concentrations averaging around 15.0×10^{-3} ppm. After four minutes, the concentration of SF_6 in Area K peaked at 74.7×10^{-3} ppm as shown in Figure 5. Monitoring was continued for approximately one hour after the tracer gas was no longer being released to estimate the decay or clearance of SF_6 from Area K. By estimating the curve-fit line of the natural log concentrations over time, the slope or number of ACH, was calculated to be approximately 4.6 ACH (see Figure 6).

DISCUSSION AND CONCLUSIONS

Chemicals, including solvents such as MEK, MIBK, isopropyl alcohol, and tolytriazole (a corrosion inhibitor with corrosive and irritant properties) were being used on a regular basis in the first floor production area located directly below Area K during the time period workers first began to experience symptoms. In addition, paints containing HDI- and MDI-based polyisocyanate compounds were being used in the paint spray booth. The constellation of symptoms (particularly mucous membrane and respiratory symptoms) reported by Area K employees during interviews, as well as the medical record findings, appear to be consistent with workplace exposure to either isocyanates or organic solvents, such as MEK and MIBK.

The predominant symptoms reported by employees who were working in Area K during mid-1998 were mucous membrane irritation, respiratory symptoms (including cough, wheezing, shortness of breath, chest discomfort), headache, dizziness, nausea and fatigue. Other symptoms reported included skin

rashes and numbness/tingling of the extremities. A number of employees who experienced respiratory problems and were referred to a pulmonary specialist for further evaluation (which included spirometric testing) were diagnosed with a variety of respiratory conditions, including reactive airway disease secondary to inhalation of respiratory irritants at work, obstructive airway disease, and presumptive occupational asthma. According to the medical records reviewed, one employee was diagnosed with chemical pharyngitis and two employees developed chemical conjunctivitis related to chemical fume exposure in the workplace.

In summary, the results of the medical evaluation appear to indicate that the respiratory symptoms which were being experienced by the affected employees who were working in Area K during May 1998 are most consistent with known exposure to isocyanates at the time the employees' symptoms became manifest. Possible concomitant exposure to solvents such as MEK and isopropyl alcohol may also explain some of the irritant mucous membrane and respiratory symptoms experienced by Area K employees. However, there were employees whose respiratory symptoms clearly continued even after they were removed from Area K, and this pattern of symptom persistence cannot be explained by the time-limited isocyanate/solvent exposure scenario described above. It is unclear as to why Area K employees would continue to experience symptoms in the absence of any verifiable continuous chemical exposure. Therefore, the available medical evidence does suggest, but cannot verify with certainty, the possibility of workplace isocyanate and/or solvent exposure as a cause of the health problems being reported by Area K employees.

Prior to the implementation of engineering controls and changes in work practices, the following three migration pathways potentially existed from the production area on the first floor to Area K on the second floor. The first, and most likely route of entrainment was from the paint spray booth mechanical room into Area K. Entrainment of isocyanate-containing paints into Area K would have been a feasible mechanism allowing for low-level airborne exposure to the paints over a specified time period. This theory is strengthened by the fact that a significant number of Area K employees, whose cubicles resided closest to the mechanical room, experienced more numerous and severe symptoms which occurred very early in the course of the chemical exposure time frame. Secondly, there was an open catwalk leading from the first floor production area into the mechanical room above. Therefore, any chemicals used for cleaning parts, etc. in this area, could have migrated into Area K. A third potential route of entrainment was from the AHU located on the mezzanine level of the production area. Because the AHU is under negative pressure, it draws in air from the surrounding areas. Any chemical being used in this area could then be supplied to Area K through the supply ductwork. A LMAS management representative reported that parts had been cleaned in this area in the past before the core-clean room was designated for this use.

In response to the health complaints in Area K, LMAS initiated a number of actions to control emissions and migration from the production area to Area K. These general improvements to the workplace environment included modifications to the existing ventilation system, such as increasing the amount of supply air received by Area K, as well as limiting the use of chemicals in the production area to the core-clean room. Other improvements focused on preventing the migration of contaminants from the first floor to Area K. The mechanical room was renovated, including moving the exhaust fans for the paint spray booth to the roof, removing the doors of the mechanical room leading into Area K and replacing them with sheetrock, and closing off access from the catwalk to the mechanical room. The release of tracer gas in the paint spray booth suggests that these measures have successfully addressed the concerns of migration from the mechanical room into Area K. It should be noted that isocyanate paints are no longer being used in Building L-11. In addition to the paint spray booth, LMAS has limited the use of MEK to the core-clean room. As shown from tracer gas released in the core-clean room, migration from this room or its exhausts into Area K does not appear likely. Air sampling for MEK and MIBK immediately outside of this room has indicated no detectable amounts of these agents. Tracer gas release around the AHU served two purposes. First, it was determined that Area K is undergoing approximately four ACH, which is consistent with a recent test and balancing report describing the ventilation system serving this area. The fact that tracer gas was entrained into the AHU and supplied to Area K indicates that any chemicals, contaminants, or odors generated in this area could potentially expose individuals in Area K.
Additionally, LMAS hired an outside contractor (who specializes in asbestos abatement) to clean all surfaces in Area K in preparation for moving

employees back into this office space. According to a representative from the LMAS industrial hygiene group, the contractors wet-wiped the walls, ceilings, and office furniture, and vacuumed the carpeting with a high-efficiancy particulate air filtered vacuum. LMAS has also continued to monitor for airborne solvents in the production area on the first floor.

RECOMMENDATIONS

1. Employees who are currently experiencing respiratory or other symptoms should continue to follow up with the occupational physician and/or specialty physician provider.

2. Employees' treating physicians should be informed of both LMAS's and NIOSH's environmental findings, to assist them in evaluating the work-related nature of their symptoms.

3. The AHU serving Area K should be isolated from the production area. This can be accomplished by either moving it to the roof of the building or enclosing it.

4. Area K should be maintained under positive pressure at all times to prevent contaminant migration from chemical use areas into the office area.

5. An IEQ Management Plan should be implemented for Building L-11. An IEQ manager or administrator with clearly defined responsibilities, authority, and resources should be selected. This individual should have a good understanding of the building's structure and function, and should be able to effectively communicate with occupants. The elements of a good plan include the following:

- Proper operation and maintenance of HVAC equipment.

- Overseeing the activities of occupants and contractors that affect IEQ (e.g., housekeeping, pest control, maintenance).

- Maintaining and ensuring effective and timely communication with occupants regarding IEQ.

- Educating building occupants and contractors about their responsibilities in relation to IEQ.

- Pro-active identification and management of projects that may affect IEQ (e.g., redecoration, renovation, relocation of personnel, etc.).

The NIOSH/Environmental Protection Agency (EPA) Building Air Quality Guidance Document should be consulted for details on developing and implementing IEQ management plans.[51]

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Figure 1. Background Concentrations of Sulfur Hexafluoride in Area K.

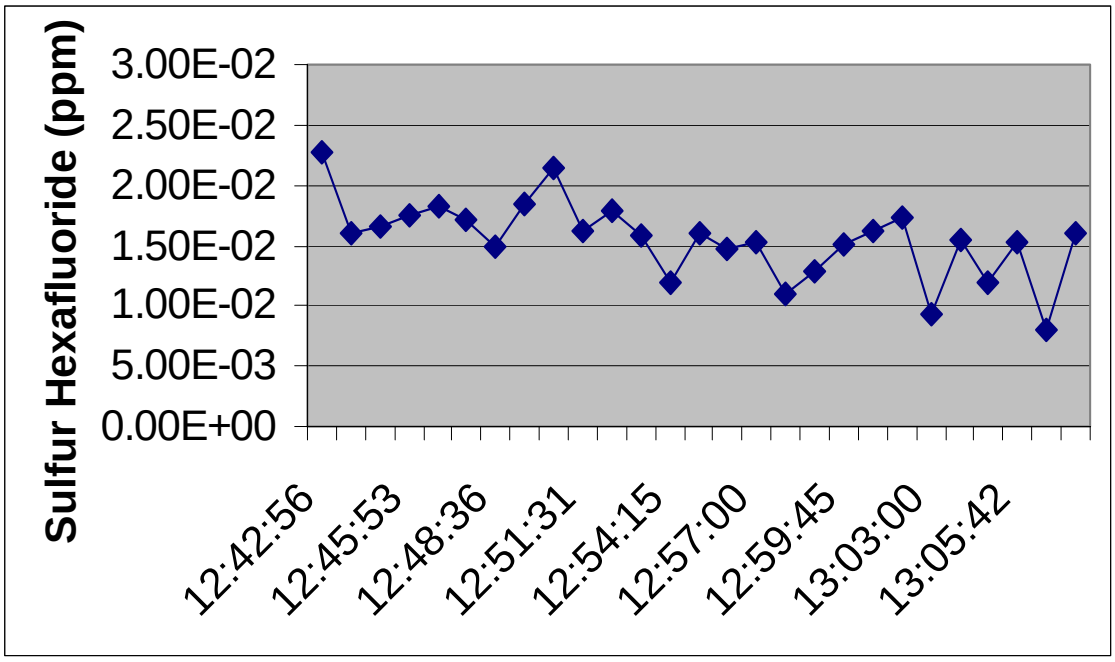


Figure 2. Concentrations of Sulfur Hexafluoride in Area K During Release in Paint Booth.

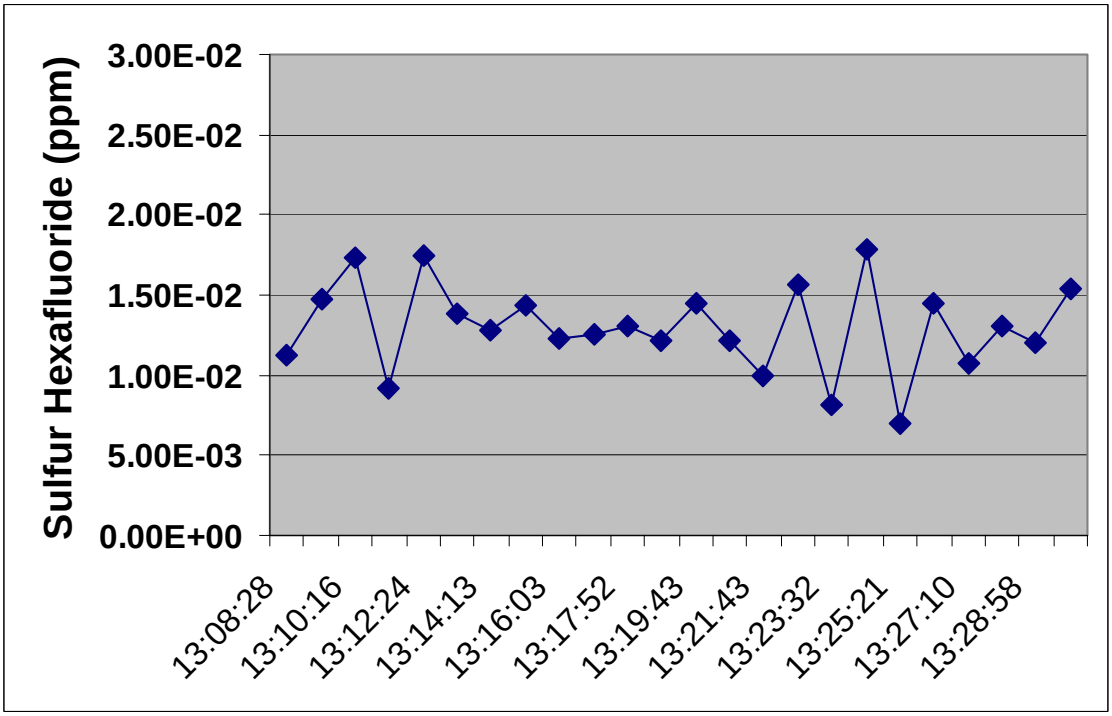


Figure 3. Concentrations of Sulfur Hexafluoride in Area K During Release in Core Room.

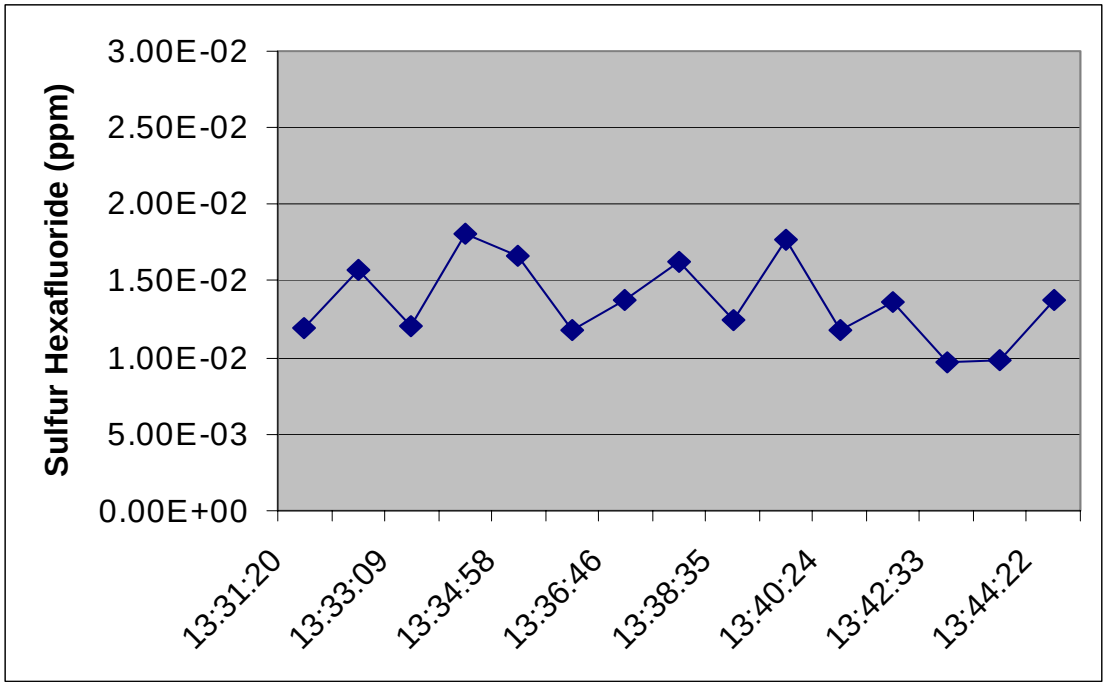


Figure 4. Concentrations of Sulfur Hexafluoride in Bag Sample From Core Room.

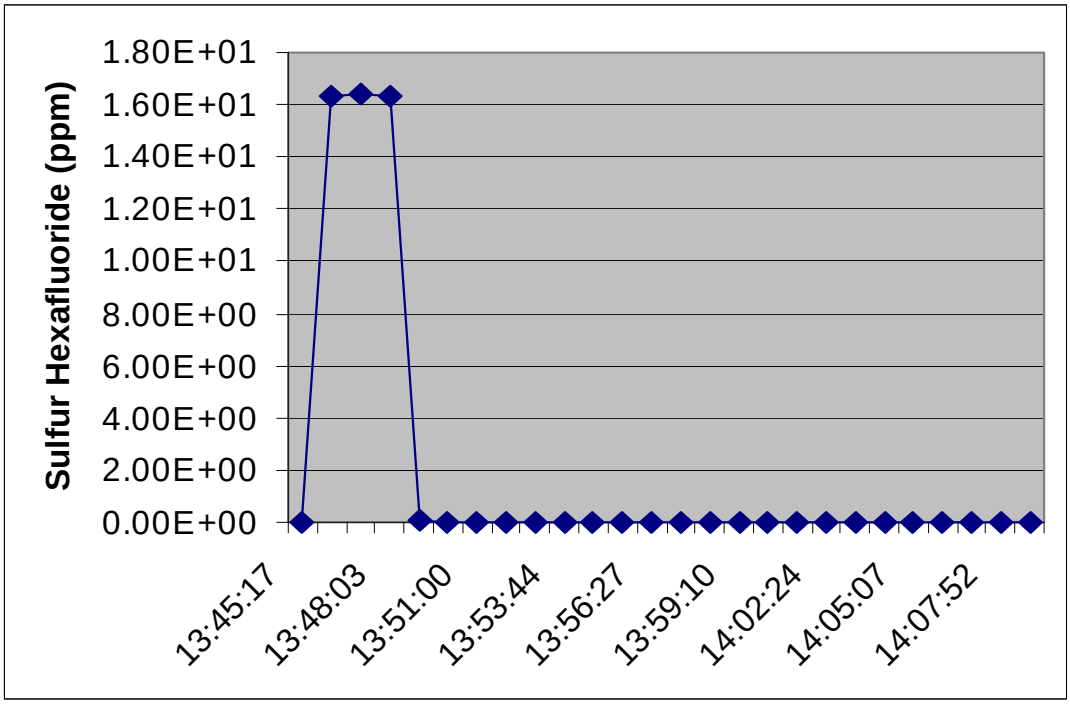


Figure 5. Concentrations of Sulfur Hexafluoride in Area K During Release by AHU.

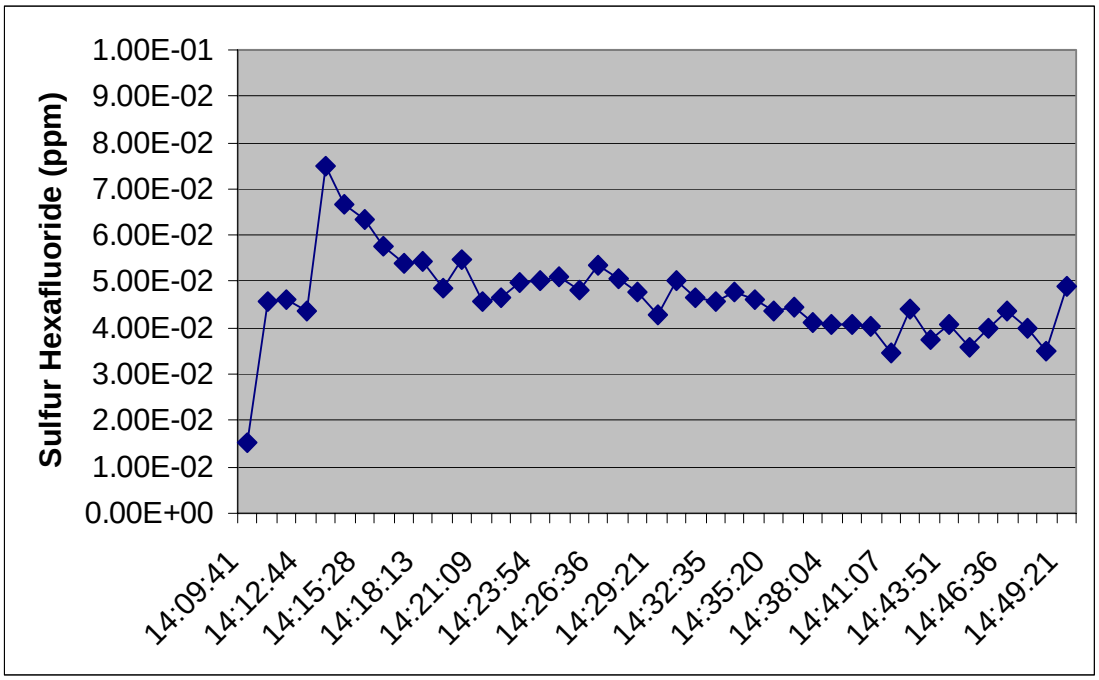
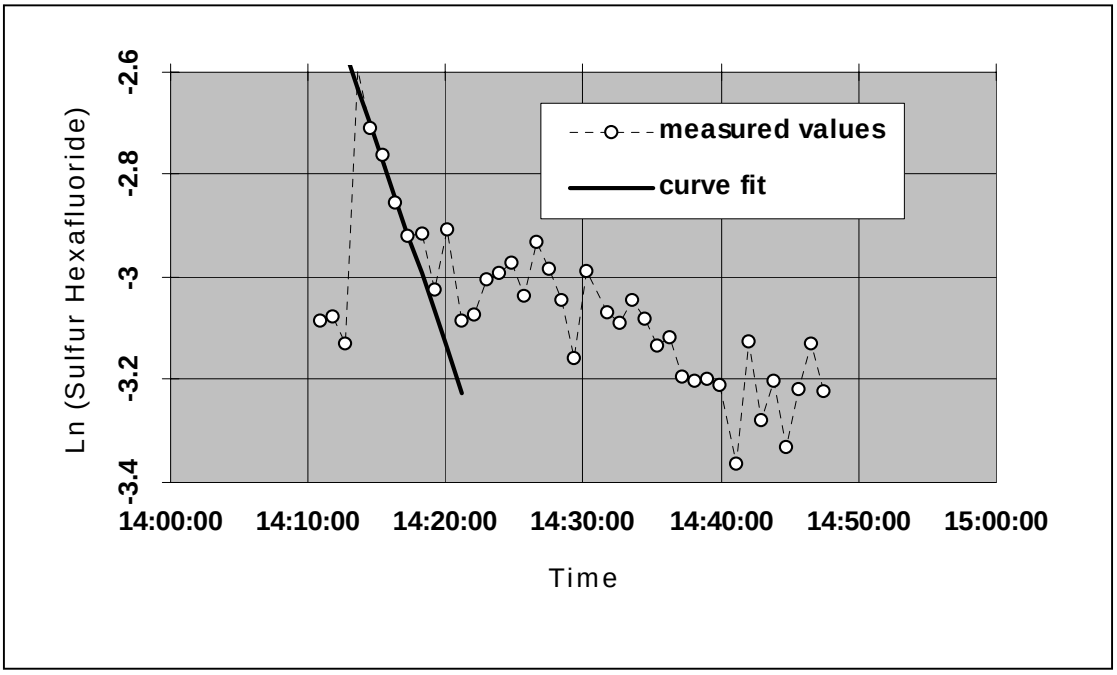


Figure 6. Curve Fit Concentration of Sulfur Hexafluoride During Release by AHU.



For Information on Other

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HHE #: 98-0347-2758

SIC Code: 381 (Search, Detection, Navigation, Guidance, Aeronautical, and Nautical Sytems, Instruments, and Equipment

Keywords: Indoor Environmental Quality, Indoor Air Quality, IEQ, IAQ, Ventilation, Tracer Gas, Sulfur Hexafluoride, Composites, Diisocyanate-Containing Paints, Methyl Ethyl Ketone, MEK, Methyl Ethyl Isobutyl Ketone, MIBK, Isoproponal.

Toxicity Determination: Negative
Positive Medical
Positive IH
Positive Both
Undetermined