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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 (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 Christopher M. Reh, PhD, CIH of HETAB, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Field assistance was provided by Kevin C. Roegner, MPH of HETAB, DSHEFS. Analytical support was provided by Robert Streicher, PhD with the Analytical Research and Development Branch, Division of Physical Sciences and Engineering. Desktop publishing was performed by Denise Ratliff. Review and preparation for printing were performed by Penny Arthur.

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Highlights of the NIOSH Health Hazard Evaluation

Evaluation of Isocyanate Exposures During Spray Painting Operations

NIOSH was asked by Lockheed Martin Aeronautical Systems (LMAS) management to evaluate exposures to isocyanates during polyurethane spray painting operations. A site visit was conducted in February 1999, and this handout summarizes the findings from this evaluation.

What NIOSH Did

We conducted walk-through surveys of spray painting areas and booths.

We collected personal breathing zone and area air samples for isocyanate-containing compounds in booths 219 and L-64.

We collected information on the use of personal protective equipment during spray painting operations.

What NIOSH Found

Employees spray painting in booths L-64 and 219 were potentially over-exposed to isocyanate-containing compounds.

Area air sampling within these spray painting booths found high levels of isocyanate-containing compounds.

The current use of personal protective equipment offers some protection from painting-related isocyanate exposures.

What LMAS Managers Can Do

Provide spray painting employees with positive-pressure, supplied air respiratory protection.

Provide employees with protective gloves and clothing that are impervious to isocyanates.

Continue to provide industrial hygiene and medical surveillance programs.

Continue to train and educate employees on the hazards and protective equipment associated with isocyanates and spray painting.

What LMAS Employees Can Do

Learn how to properly use the protective equipment needed during spray painting.

Report all possible work-related health problems to the plant doctor.

Attend every safety and health training session that is offered.

Do not eat, drink, or smoke in work areas.

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 # 99-0122-2798

NIOSH National Institute for Occupational Safety and Health

Health Hazard Evaluation Report 99-0122-2798
Lockheed Martin Aeronautical Systems
Marietta, Georgia
June 2000

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SUMMARY

On November 30, 1998, the National Institute for Occupational Safety and Health (NIOSH) received a management request for a health hazard evaluation (HHE) at Lockheed Martin Aeronautical Systems (LMAS) in Marietta, Georgia. The request centered on workers' exposures to isocyanate-containing compounds during spray painting operations. On February 17-18, 1999, investigators from NIOSH conducted a site visit and exposure assessment for these compounds.

At this facility, LMAS manufactures the C-130J *Hercules* military transport aircraft; and conducts research, development, and limited production of the F-22 *Raptor* advanced tactical fighter aircraft. Polyurethane paints are used to coat the surfaces of the aircraft and various parts. Air sampling was conducted during polyurethane spray painting operations in paint booths 219 and L-64. Two different isocyanate-containing polyurethane paints were used in these spray painting operations. Both paints were two-component formulations, and were identified by the in-house designations of code 36 and code 46. The code 36 paint contains 40% by weight 1,6-hexamethylene diisocyanate (HDI)-based polyisocyanate, and less than 0.15% HDI. The code 46 paint contains 40% by weight of 4,4'-diphenylmethane diisocyanate (MDI), and 50% MDI-based polyisocyanate. During spray painting, the painters wore a full-face air-purifying respirator with combined particulate and organic vapor cartridges, and a Tyvek™ suit.

The exposure assessment protocol consisted of personal breathing zone (PBZ) air sampling on the painters, and area air sampling around the perimeter of the spray paint booths. The samples were collected to determine short-term, task-based exposures and airborne concentrations to the isocyanate-containing compounds found in the paints. All area air samples were collected using midget impingers containing 15 milliliters of a solution of 1-(9-anthracenylmethyl) piperazine (MAP) in butyl benzoate, followed by a 37 millimeter diameter quartz fiber filter (QFF) impregnated with MAP. PBZ air samples were collected using the MAP-impregnated QFFs. Filter samples were analyzed by high pressure liquid chromatography (HPLC) with ultraviolet and fluorescence detection for both the monomer and polyisocyanate components of the paints. The impinger samples underwent solid-phase extraction, followed by the same analysis used for the filter samples. Monomers were quantified based on comparison of their fluorescence peak heights to those of monomer standards. If detected, poly-isocyanates/oligomers were quantified based on the comparison of their ultraviolet peak areas to those of monomer standards.

At the time of the NIOSH survey, two painters were painting parts in booth 219. The painter on the right side of the booth used the code 46 paint, the painter on the left side used the code 36 paint. The MDI and MDI-based polyisocyanate exposure concentrations were 300 and 304 micrograms per cubic meter of air ($\mu g/m^3$) for the right side (code 46) painter. For the left side (code 36) painter, the HDI and HDI-based polyisocyanate exposures were 1.9 and 164 $\mu g/m^3$, respectively. Only one painter worked in the L-64 booth. This painter used the code 46 paint, and the MDI exposure was 1364 $\mu g/m^3$ and the MDI-based polyisocyanate exposure was 1080 $\mu g/m^3$. In addition, the total reactive isocyanate group (TRIG) exposures

for painters in booth 219 were 206 and 83 μg-NCO/m^3, and the TRIG exposure for the L-64 painter was 831 μg-NCO/m^3. Finally, significant airborne concentrations of the various isocyanate-containing compounds were found by the area air sampling conducted in both spray painting booths.

Considering the MDI, MDI-based polyisocyanate, HDI-based polyisocyanate, and TRIG exposure concentrations, the NIOSH investigators conclude that a health hazard exists in the LMAS spray painting booths/operations evaluated during this study. Recommendations are provided to increase the level of protection for workers in the spray painting operations. This includes respiratory protection, protective clothing, medical surveillance, and industrial hygiene surveillance.

Keywords: SIC 3721 (Aircraft), spray painting, polyurethane surface coating, isocyanates, 1,6-hexamethylene diisocyanate, 4,4'-diphenylmethane diisocyanate, HDI, MDI, polyisocyanates.

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INTRODUCTION

On November 30, 1998, the National Institute for Occupational Safety and Health (NIOSH) received a management request for a health hazard evaluation (HHE) at Lockheed Martin Aeronautical Systems (LMAS) in Marietta, Georgia. The request centered on workers' exposures to isocyanate-containing compounds during spray painting operations. Pursuant to this request, NIOSH investigators conducted air sampling for these compounds on February 17-18, 1999. This report contains the results from the air sampling, and recommendations for protecting workers potentially exposed to isocyanate-containing compounds during spray painting operations.

BACKGROUND

At this facility, LMAS manufactures the C-130J *Hercules* military transport aircraft, and conducts research, development, and limited production of the F-22 *Raptor* advanced tactical fighter aircraft. As part of the manufacturing processes, polyurethane paints are used to coat the surfaces and various other parts of the aircraft. Hence, LMAS has several spray painting booths and areas within the facility.

The NIOSH air sampling was conducted during polyurethane spray painting operations in paint booths 219 and L-64. Booth 219 is a side-draft booth capable of accommodating 2 painters, and is open on the side opposite the scrubber plenum. L-64 is a smaller side-draft booth that only accommodates 1 painter. High-volume, low-pressure spray guns were used in the painting operations. During spray painting, the painters wore a full-face, negative pressure, air-purifying respirator with combined particulate and organic vapor cartridges, and a Tyvek™ suit. In addition, the facility had a full-time, on-site occupational medicine physician and clinic that conducted periodic medical surveillance for the LMAS employees.

Two isocyanate-containing polyurethane paints were used during the operations surveyed by the NIOSH investigators. Both paints were two-component formulations, and were identified by the in-house designations of code 36 and code 46. The code 36 paint is a 1,6-hexamethylene diisocyanate (HDI) based system, containing 40% by weight HDI-based polyisocyanate (*CAS No. 3779-63-3*) and less than 0.15% HDI (*CAS No. 822-06-0*). The code 46 paint contains 40% by weight of 4,4'-diphenylmethane diisocyanate (MDI, *CAS No. 101-68-8*), and 50% MDI-based polyisocyanate (*CAS No. 9016-87-9*, also known as polymethylenepolyphenol isocyanate).

METHODS

The isocyanate exposure assessment protocol consisted of personal breathing zone (PBZ) air sampling on the painters, and area air sampling around the perimeter of the spray paint booths. The samples were collected to determine short-term, task-based exposures and airborne concentrations to the isocyanate-containing compounds found in the polyurethane paints. All area air samples were collected using midget impingers containing 15 milliliters (mL) of a solution of 1-(9-anthracenylmethyl) piperazine (MAP) in butyl benzoate, followed by a 37 millimeter diameter quartz fiber filter (QFF) impregnated with MAP.[1] PBZ air samples were collected using the MAP-impregnated QFFs.[1] Battery operated sampling pumps calibrated to a nominal flow rate of one liter per minute were connected to the collection media with Tygon® tubing. 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 into glass vials. All samples were shipped and stored in a cold environment prior to analysis.

Filter samples were analyzed by pH-gradient high pressure liquid chromatography (HPLC) with ultraviolet and fluorescence detection for both the monomer and polyisocyanate components of the paints. The impinger samples were subjected to solid-phase extraction, followed by the same analysis used for the filter samples. Upon receipt, 10 microliters of acetic anhydride was added to each filter sample. The acetic anhydride was allowed to react with the excess MAP overnight. The filter-sample solutions were filtered and concentrated to 1 mL. Impinger solutions were

subjected to solid-phase extraction to exchange the butyl benzoate for a more HPLC-compatible solvent. The HPLC analysis used a 150 x 4.6 millimeter (mm) C8 Inertsil column containing 5 micron particles. The mobile phase flow rate was 1.5 milliliter per minute (mL/min). The mobile phase consisted of 65% acetonitrile/35% buffer. The gradient involved beginning the analysis at pH 6.0, holding there for 4 minutes, changing the buffer gradually to pH 1.6 over the next 13 minutes, and holding at pH 1.6 for 13 minutes. Thirty microliters of each sample were injected into the instrument. Analysis of MAP-derivatized monomer standards in the appropriate concentration range were interspersed with the sample analyses. The impinger samples were quantified using standards that passed through the solid-phase extraction procedure. Monomers were quantified based on comparison of their fluorescence peak heights to those of monomer standards. If detected, oligomers were quantified based on the comparison of their ultraviolet peak areas to those of monomer standards.

The limits of detection (LOD) are values determined by the analytical procedure used to analyze the samples, and are not dependent on sample volume. Minimum detectable concentrations (MDCs) are determined by dividing the LODs by air sample volumes appropriate for the given set of samples. In determining the MDC for this study, the NIOSH industrial hygienists used the highest sample volumes from the area air sampling data (impinger and filter in series) and from the PBZ air sampling data (filter only). These sample volumes were 30 and 23 liters, respectively. The LODs and MDCs for this study are shown in Table 1.

EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assess-ment 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 increases the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs),[2] (2) the American Conference of Governmental Industrial Hygienists' (ACGIH®) Threshold Limit Values (TLVs®),[3] and (3) the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs).[4] 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 95–596, 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.

Background Information for Diisocyanates and other Isocyanate-containing Compounds

The unique feature common to all diisocyanates is that they consist of two -N=C=O (isocyanate) functional groups attached to an aromatic or aliphatic parent compound. Because of the highly unsaturated nature of the isocyanate functional group, the diisocyanates readily react with compounds containing active hydrogen atoms (nucleophiles). Thus, the diisocyanates readily react with water (humidity), alcohols, amines, *etc*.; the diisocyanates also react with themselves to form either dimers or trimers. When a diisocyanate species reacts with a primary, secondary, or tertiary alcohol, a carbamate (-NHCOO-) group is formed which is commonly referred to as a urethane. Reactions involving a diisocyanate species and a polyol result in the formation of cross-linked polymers; *i.e*. polyurethanes. Hence, they are used in surface coatings, polyurethane foams, adhesives, resins, elastomers, binders, and sealants. Many material safety data sheets (MSDS) use isocyanate-related terms inter-changeably. 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 HDI, 2,4- and/or 2,6-toluene diisocyanate (TDI), MDI, methylene bis(4-cyclohexylisocyanate (HMDI), isophorone diisocyanate (IPDI), and 1,5-naphthalene diisocyanate (NDI).

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

Prepolymers: Species possessing free isocyanate groups, prepared from the reaction of a polyol with an excess of di- or polyisocyanate.[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. An example is the biuret of HDI, which consists of three molecules of HDI monomer joined together to form a higher molecular weight oligomer having similar characteristics to those found in the monomer. Also, many MDI product formulations consist of a combination of MDI monomer and a MDI-based polyisocyanate (such as polymethylenepolyphenyl isocyanate). Many prepolymer and polyisocyanate formulations contain a small fraction (usually less than 0.5%) of unreacted monomer. This is con-sistent with most polyurethane paint formulations, which predominantly contain HDI-based polyisocyanates and a minute amount of HDI monomer (<0.2%).

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 produc-tion. 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 Isocyanate-containing Compounds

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 symp-toms 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 asthma 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 seatcover operations.[33] The scientific literature contains a limited amount of animal data suggesting that dermal exposure to diisocyanates may produce respiratory sensiti-zation.[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 exposure concentrations, and for active medical surveillance of all workers potentially exposed to diisocyanates.

HP also has 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.

Exposure Evaluation Criteria for Isocyanate-containing Compounds

Since the painting operations lasted 20 minutes or less, the workers' PBZ exposures were compared to ceiling limit criteria for the different isocyanate-containing substances. Exposures to HDI and MDI were evaluated using the NIOSH RELs, which are ceiling limits of 200 and 140 micrograms per cubic meter of air ($\mu g/m^3$), respectively.[6] The exposure evaluation criterion for HDI-based polyisocyanate is the Swedish National Board of Occupational Safety and Health's ceiling limit of 200 $\mu g/m^3$.[42] No specific exposure evaluation criteria exists for MDI-based polyisocyanates.

The United Kingdom's Health and Safety Executive (UK-HSE) has taken a different approach in developing PBZ exposure evaluation criteria for isocyanate-containing compounds. Instead of isocyanate specific criteria, they have developed a non-specific standard based on the concentration of total reactive isocyanate groups (TRIGs) in a volume of air.[43] Airborne TRIG concentration can be determined using data from the NIOSH MAP Method. First, the monomer and oligomer concentrations are summed to obtain the total weight of isocyanate-containing compounds in a given air sample. Next, the molecular weight of the isocyanate functional groups in the parent compound is divided by the molecular weight of the parent compound. This yields a constant that reflects the percentage of a compound's molecular weight that is contributed by the TRIGs. For MDI and MDI-based oligomers, the TRIG constant is 0.34; for HDI and HDI-based oligomers, the TRIG constant is 0.50. Finally, the total weight of isocyanate-containing compounds in a given air sample is multiplied by the TRIG constant, and the product is the concentration of TRIGs in air. The UK-HSE ceiling limit for TRIGs in air is 70 micrograms of isocyanate groups per cubic meter of air ($\mu g\text{-}NCO/m^3$).

RESULTS

The data from the PBZ air sampling of the painters can be found in Table 2. At the time of the NIOSH survey, two painters were painting parts in booth 219. The painter on the right side of the booth used the code 46 paint, the painter on the left side used the code 36 paint. The MDI and MDI-based polyisocyanate exposure concentrations were 300 and 304 $\mu g/m^3$ for the right side (code 46) painter. A low level HDI exposure was also found for this painter, but no HDI-polyisocyanate was detected in the PBZ air sample. For the left side (code 36) painter, no MDI or MDI-based polyisocyanate exposure was detected, and the HDI and HDI-based polyisocyanate exposures were 1.9 and 164 $\mu g/m^3$, respectively. Only one painter worked in the L-64 booth at the time of the NIOSH survey, and this painter used the code 46 paint. This painter's MDI exposure was 1364 $\mu g/m^3$, and the MDI-based polyisocyanate exposure was 1080 $\mu g/m^3$. The TRIG exposures for the booth 219 painters were 206 and 83 $\mu g\text{-}NCO/m^3$, and the TRIG exposure for the L-64 painter was 831 $\mu g\text{-}NCO/m^3$.

The data from the area air sampling are in Table 3. Four area air samples were collected in booth 219. For each spray painting operation in the booth, a sample was taken downstream between the painting table (painter) and water scrubber, and a sample was collected next to the painting table. All area air samples were collected at a height of 3 feet.

Comparatively, the MDI and MDI-based poly-isocyanate concentrations from the right side of booth 219 (code 46 paint) were higher in the air sample collected downstream of the painter when compared to the sample collected near the painting table. Hence, the MDI and MDI-based poly-isocyanate concentrations in the downstream air sample were 1790 and 1650 $\mu g/m^3$, respectively; and the concentrations collected near the painting table were 332 and 277 $\mu g/m^3$, respectively. Low concentrations of HDI were found in these samples, and no HDI-based polyisocyanate was detected.

Similar findings were observed from the air samples collected on the left side (code 36 paint) of booth 219. The HDI and HDI-based poly-isocyanate levels were higher in the air sample downstream of the painter (18.4 and 2350 $\mu g/m^3$, respectively) when compared to the concentrations found in the air sample collected near the painting table (0.9 $\mu g/m^3$ and "none

detected," respectively). No MDI or MDI-based polyisocyanate were collected in these samples.

Three area air samples were collected during the L-64 painting operation (code 46 paint). These samples were located to the left of the painting table, behind the painter, and downstream between the painter and the water scrubber. The MDI concentrations in these samples ranged from 2689 to 4637 $\mu g/m^3$, and the MDI-based polyisocyanate concentrations ranged from 1899 to 4217 $\mu g/m^3$. The highest concentrations were found in the sample to the left of the painting table, and the lowest were found in the sample behind the worker.

DISCUSSION

The exposure data indicate that task-based PBZ MDI exposure concentrations for both workers painting with the code 46 paint exceeded the NIOSH ceiling limit. These exposure concentrations were 1.5 and over 6 times the ceiling limit for the painters in booths 219 and L-64, respectively. The PBZ exposure concentrations for MDI-based polyisocyanate were similar to the measured MDI concentrations. A task-based PBZ HDI exposure concentration for the booth 219 painter (code 36 paint) was well below the NIOSH ceiling limit, and the HDI-based polyisocyanate exposure concentration was 82% of the Swedish ceiling limit. In addition, all three painters had PBZ TRIG exposure concentrations above the UK-HSE ceiling limit for TRIGs. Finally, the area air samples indicate that hazardous concentrations of isocyanate-containing compounds can exist during painting operations

These data indicate a potential for LMAS workers to be over-exposed to isocyanate-containing compounds during spray painting operations. Currently, the LMAS painters are protected from hazardous inhalation exposures by wearing a negative pressure air-purifying respirator with combined particulate and organic vapor cartridges, and from dermal exposures by wearing a Tyvek™ suit. Recent studies have shown that organic vapor cartridges effectively remove isocyanate-containing compounds from inhaled air.[44,45,46] Unfortunately, none of these cartridges have an end-of-service-life-indicator, which would aid in determining when to change cartridges to prevent breakthrough of the isocyanate-containing compounds. Also, the isocyanates have poor odor warning properties; hence, workers wearing an air-purifying respirator will have no indication of when the cartridges have failed, or when the face-to-facepiece seal has been compromised. Considering this, NIOSH recom-mends that all workers with a potential for exposure to isocyanate-containing compounds be provided with and wear supplied-air (positive pressure) respiratory protection. In addition, further efforts should be taken to protect workers from dermal exposures.

CONCLUSIONS

Considering the MDI, MDI-based polyisocyanate, HDI-based polyisocyanate, and the TRIG exposure concentrations, the NIOSH investigators conclude that a potential health hazard exists in the LMAS spray painting operations evaluated during this study. Prior to this study, LMAS had implemented some worker protection measures, which provided the workers with some protection from these exposures. Recommendations are provided below to increase the level of protection for workers in the spray painting operations.

RECOMMENDATIONS

- **Respiratory Protection**: NIOSH recommends that whenever there is a potential for exposure to isocyanate-containing compounds, including concentrations below the NIOSH recommended exposure level, that the employer provide the worker with supplied-air respiratory protection.[6] When using respirators, the employer is required to have a respiratory protection program. This program should be consistent with the NIOSH recommendations and the enforceable requirements set forth in the OSHA Safety and Health Standards.[47,48]

- **Protective Clothing**: All efforts should be taken to prevent dermal exposures to isocyanate-containing substances. The employ-er should provide protective clothing, gloves, and footwear that is impervious to

isocyanate-containing compounds. The gloves should be elbow-length and made of a permeation-resistant material, such as nitrile rubber, butyl rubber, neoprene, PVC, or flexible laminates (*e.g.*, 4H™ [PE/EVAL] and Silver Shield™). Also, the workers should wear long-sleeve coveralls made of laminated or coated, nonwoven materials (*e.g.* Chemrel™, Saranek™, Chemtuff™, Barricade™, Tyvek QC™, CPF III™). Face-shields and aprons should be used whenever there is a possibility of a splash or a spill of liquids containing isocyanate-containing materials. The openings at the interface between different forms of protective clothing should be sealed to prevent exposure through the interface.

- **Medical Surveillance**: NIOSH recommends both preplacement and periodic medical surveil-lance programs for all workers potentially exposed to diisocyanates.[6] The preplacement examinations should consist of detailed medical and work histories with emphasis on pre-existing respiratory and/or allergic conditions, a physical examination that centers on the respiratory tract, a baseline pulmonary function test that measures forced expiratory volume in one second (FEV_1) and forced vital capacity (FVC), and a judgement on the worker's ability to wear a supplied-air respirator. Workers should be provided with annual examinations which update the medical and work histories, and measure the worker's FEV_1 and FVC. The only effective intervention for workers with isocyanate-induced sensitization (asthma) or HP is cessation of all isocyanate exposure.

- **Industrial Hygiene Surveillance**: NIOSH recommends that employers conduct industrial hygiene surveys on all workers potentially exposed to isocyanate-containing compounds.[6] These surveys should be conducted on an annual basis or whenever there are changes in the process or engineering controls. A sufficient number of samples should be collected to characterize each employee's exposure, and to characterize isocyanate emissions from a given process, operation, machine, *etc.* These surveys should encompass both routine (*e.g.* normal operations and scheduled maintenance) and non-routine (*e.g.* repair activities associated with breakdowns or malfunctions) work activities. Task-oriented exposure assessments should be used to determine the isocyanate exposure levels associated with specific tasks within an operation or shift.

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TABLE 1

Limits of Detection and Minimum Detectable Concentrations

HETA 99-0122-2798, Lockheed Martin Aeronautical Systems

Analyte	Sample Type	LOD[1]	MDC[2]
HDI	Impregnated Filter, PBZ Air Sampling	0.016	0.7
MDI	Impregnated Filter, PBZ Air Sampling	0.011	0.5
HDI-based Polyisocyanate	Impregnated Filter, PBZ Air Sampling	2.0	87.0
MDI-based Polyisocyanate	Impregnated Filter, PBZ Air Sampling	2.5	108.7
HDI	Impinger & Filter in Series, Area Air Sampling	0.016	0.5
MDI	Impinger & Filter in Series, Area Air Sampling	0.9	1.4
HDI-based Polyisocyanate	Impinger & Filter in Series, Area Air Sampling	0.6	20.0
MDI-based Polyisocyanate	Impinger & Filter in Series, Area Air Sampling	0.9	30.0

[1] LOD: limit of detection in micrograms per sample.
[2] MDC: minimum detectable concentration in micrograms of analyte per cubic meter of air.

TABLE 2

Exposure to Isocyanate-Containing Compounds During Spray Painting Operations

HETA 99-0122-2798, Lockheed Martin Aeronautical Systems

Job Title/Location	Sample Time[1]	Sample Volume[2]	Isocyanate Specific Exposure Concentrations[3]				TRIGs[4]
			MDI	MDI-based Polyisocyanate	HDI	HDI-based Polyisocyanate	
MDI Painter/Right Side of Booth 219	1235-1255	23	300	304	1.4	ND	206
HDI Painter/Left Side of Booth 219	1232-1245	14	ND	ND	1.9	164	83
Painter/Booth L-64	0944-0951	8.8	1364	1080	NA	NA	831
Exposure Criteria[5]			200	None	140	200	70

[1] Sample time is in military time.

[2] Sample volumes are in liters of air.

[3] The isocyanate-specific concentrations are in micrograms of analyte per cubic meter of air ($\mu g/m^3$).
ND - none detected, analyte not found in the given air sample; NA - not applicable, isocyanate species not used in the given operation.

[4] TRIGs - total reactive isocyanate groups. TRIG concentrations are in micrograms of isocyanate groups per cubic meter of air ($\mu g\text{-}NCO/m^3$).

[5] Criteria for determining if a worker's exposure is a potential health hazard. The sources for these criteria are as follows: MDI - NIOSH REL, HDI - NIOSH REL, HDI-based polyisocyanate - Swedish Standard, TRIGs - UK-HSE Standard.

TABLE 3

Airborne Concentrations of Isocyanate-Containing Compounds During Spray Painting Operations

HETA 99-0122-2798, Lockheed Martin Aeronautical Systems

Sample Location	Sample Time[1] (Volume[2])	Isocyanate Specific Exposure Concentrations[3]			
		MDI	MDI-based Polyisocyanate	HDI	HDI-based Polyisocyanate
Booth 219, MDI side, 3' above floor between water scrubber and parts table	1235-1255 (30)	1790	1650	8.0	ND
Booth 219, MDI side, 3' above floor, right side of booth	1235-1255 (26)	332	277	1.5	ND
Booth 219, HDI side, 3' above floor between water scrubber and parts table	1232-1245 (20)	ND	ND	18.4	2350
Booth 219, HDI side, 3' above floor, left side of booth	1232-1245 (14)	ND	ND	0.9	ND
Booth L-64, 5' to the left of painting table, 3' above floor	0944-0951 (8.3)	4637	4217	NA	NA
Booth L-64, 3' above floor between water scrubber and parts table	0944-0951 (8.1)	4346	3580	NA	NA
Booth L-64, 4' behind painter, 3' above floor	0944-0951 (7.9)	2689	1899	NA	NA

[1] Sample time is in military time.

[2] Sample volumes are in liters of air.

[3] The isocyanate-specific concentrations are in micrograms of analyte per cubic meter of air ($\mu g/m^3$).
ND - none detected, analyte not found in the given air sample; NA - not applicable, isocyanate species not used in the given operation.

[4] TRIGs - total reactive isocyanate groups. TRIG concentrations are in micrograms of isocyanate groups per cubic meter of air ($\mu g\text{-}NCO/m^3$).

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Occupational Safety and Health Concerns

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