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**NIOSH HEALTH HAZARD EVALUATION REPORT:**

**HETA #99-0196-2860  
Future Aviation, Inc.  
Naples, Florida**

## 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 Christine Kasting, Kevin Roegner, and Christopher Reh of HETAB, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Field assistance was provided by Max Kiefer. Analytical support was provided by Ardie Grote, NIOSH Division of Applied Research and Technology, and Data Chem Laboratory, Salt Lake City, Utah. Desktop publishing was performed by Pat Lovell. Review and preparation for printing were performed by Penny Arthur.

Copies of this report have been sent to employee and management representatives at Future Aviation and the OSHA Regional Office. This report is not copyrighted and may be freely reproduced. Single copies of this report will be available for a period of three years from the date of this report. To expedite your request, include a self-addressed mailing label along with your written request to:

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

# Highlights of the NIOSH Health Hazard Evaluation

## Evaluation of Health Complaints at Future Aviation, Inc.

In June and October 1999, NIOSH conducted a health hazard evaluation at Future Aviation, Inc. in Naples, Florida. We talked to workers and assessed exposures to isocyanate paints and packaging foam, and to cleaning solvents during cleaning, repairing, and reassembling aircraft parts.

### What NIOSH Did

- We reviewed the health complaints with employees and management.
- We inspected the work area and observed work practices.
- We talked with workers about their concerns.
- We measured airborne concentrations of some chemicals.

### What NIOSH Found

- All measured air concentrations were below applicable limits.
- Gloves were not cleaned or maintained properly.
- Air purifying respirators were being worn although a respirator program had not been established.

### What Future Aviation Managers Can Do

- Implement a comprehensive personal protection program.
- Reduce the pressure in the Varsol spray gun to less than 30 psi to minimize over spray.
- Provide employees using the isocyanate paints and foam with protective gloves.

### What the Future Aviation Employees Can Do

- Promptly report any suspected work-related health problems.
- Use gloves when foam packaging or painting parts.
- Do not eat, drink, or smoke in the workplace.



**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 #99-0196-2860



**Health Hazard Evaluation Report 99-0196-2860**  
**Future Aviation, Inc.**  
**Naples, Florida**  
**September 2001**

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## SUMMARY

On April 30, 1999, the National Institute for Occupational Safety and Health (NIOSH) received a management request for a health hazard evaluation (HHE) at Future Aviation, Inc., in Naples, Florida. The request asked NIOSH to determine if workplace exposures are related to health problems reportedly experienced by some employees. Health problems identified in the request included headaches and eye irritation. Potential exposures included emissions from isocyanate containing paints and polyurethane packing foam, and cleaning solvents during cleaning, repairing, and reassembling aircraft parts.

On June 16-17, 1999, NIOSH investigators conducted an initial site visit at Future Aviation, Inc. The purpose of this site visit was to inspect the facility, observe work practices and chemical handling activities, and monitor exposures to selected workplace compounds. On June 17, 1999, full-shift personal breathing zone (PBZ) samples for petroleum solvents were collected on five workers. A 1.5 hour activity-specific PBZ sample was also collected on one worker while he cleaned a wheel hub with solvent in a wash tank. Bulk samples were collected from both wash tanks in the Test Area, and work practices, including the use of personal protective equipment, were observed. Safety procedures, policies, and employee training programs were also reviewed. Local exhaust ventilation systems at various workstations were evaluated.

All exposures were below the applicable NIOSH Recommended Exposure Limit (REL) on the day of the monitoring. The highest full-shift total hydrocarbon concentration (57.1 milligrams per cubic meter [ $\text{mg}/\text{m}^3$ ]) was from the worker cleaning generators in the Test Area. The highest total hydrocarbon concentration (211.5  $\text{mg}/\text{m}^3$ ) was measured on the worker cleaning the wheel hub. The NIOSH REL for total hydrocarbon is 350  $\text{mg}/\text{m}^3$  as a full-shift time-weighted average.

On October 19, 1999, a follow-up site visit was conducted to measure exposure to isocyanate-containing compounds during the spray painting and foam packaging operations. Two PBZ exposure measurements were collected from the painter. No 1,6-hexamethylene diisocyanate (HDI) monomer was detected, and the HDI-based polyisocyanate exposures were 10.7 and 5.1 micrograms per cubic meter of air ( $\mu\text{g}/\text{m}^3$ ). HDI monomer was detected in only one of the seven area air samples collected during spray painting; a concentration of 0.4  $\mu\text{g}/\text{m}^3$  was found at the curing oven doors. Also, HDI-based polyisocyanate concentrations were below the minimum detectable concentration (MDC) of 1.6  $\mu\text{g}/\text{m}^3$  in the area air samples.

Foam packaging occurred three times during the October sampling. A 10-minute PBZ exposure measurement was collected each time the foam system was used. The foamer's 4,4'-diphenylmethane diisocyanate (MDI) exposures were 3.5  $\mu\text{g}/\text{m}^3$ , 5.2  $\mu\text{g}/\text{m}^3$ , and "none detected" (<2.6  $\mu\text{g}/\text{m}^3$ ). MDI-based polyisocyanate was not detected in any

sample. In an attempt to determine the worst-case exposure, a single (serial) sample was collected in the foamer's breathing zone only when MDI was being dispensed. These sampling times included short samples during each of the three packaging jobs, and a one-minute period that began when the gun malfunctioned and a small volume of MDI spilled into a box. The results of this sampling indicate an average peak exposure of 7.5  $\mu\text{g}/\text{m}^3$ . All these exposure concentrations are well below the NIOSH REL of 200  $\mu\text{g}/\text{m}^3$  as a 10-minute ceiling limit. Neither MDI nor MDI-based polyisocyanates were detected at any of four area-sample locations near the foam packaging station.

Personal protection programs were found to be deficient in certain areas. Gloves were not cleaned properly or maintained in an appropriate manner. Air purifying respirators were worn by a number of employees although a respirator program had not been established and exposure information had not been obtained. Recommendations in this report include implementing a comprehensive personal protection equipment program.

Local exhaust ventilation was found to be sufficient; however, work practices at the Varsol hood negated the efficiency of the hood. Recommendations include reducing the pressure in the Varsol spray gun to less than 30 pounds per square inch to minimize over spray.

All measured exposures were below applicable NIOSH limits. Minimizing skin contact with the polyurethane foam used in the shipping and receiving department is encouraged. Recommendations regarding the use of personal protective equipment (glove use, eye protection, respiratory protection, hearing conservation) are in the Recommendations section of this report. Engineering controls (e.g., containment, ventilation) or work practice changes (eliminating use of compressed air, depressurization, etc.) should be a first consideration to reduce the potential for exposure.

Keywords: SIC 3721 (Aircraft and Parts), solvents, naphtha, isocyanates, headache, irritation, polyurethane packing foam, ventilation

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## INTRODUCTION

On April 30, 1999, the National Institute for Occupational Safety and Health (NIOSH) received a management request for a health hazard evaluation (HHE) at Future Aviation, Inc., in Naples, Florida. The request indicated some employees at this location experienced health problems possibly associated with their workplace, including headaches and eye irritation. Potential exposures included isocyanate emissions from isocyanate-containing paints and polyurethane packing foam, and cleaning solvent exposures from cleaning, repairing, and reassembling aircraft parts.

On June 16-17, 1999, NIOSH investigators conducted an initial site visit to inspect the facility, observe work practices and chemical handling activities, and monitor exposures to selected workplace compounds. A walk-through inspection was conducted to review various operational parameters. Bulk samples of solvent were collected from both wash tanks in the Test Area. Work practices and the use of personal protective equipment were observed, and safety procedures, policies, and employee training programs were reviewed. Environmental monitoring was conducted to assess worker exposures to petroleum solvents. An interim report was issued on August 25, 1999, and an analytical results report was issued September 2, 1999. A follow-up site visit was conducted on October 19, 1999, to assess workers' exposures to different isocyanate-containing compounds during polyurethane spray painting and polyurethane foam packaging operations. The findings from this site visit were reported in a letter dated May 19, 2000.

## BACKGROUND

Future Aviation, Inc., was established in 1984 to service the airline industry, and was relocated to the facility on Industrial Boulevard in 1994. The 16,000 square foot plant is comprised of shops specializing in electrical parts, starter/generators, generator control units, fans, hydraulics, wheels, and brakes. The plant contains an Assembly area which also

houses the Shipping and Receiving Department, Nickel Plating Shop, Non-Destructive Testing Shop, Test and Clean Area, Mica Saw Area, Break room, and Office Area. Parts are serviced and then tested to meet Federal Aviation Administration standards. Nineteen technicians (eighteen males, one female) and office support staff are currently employed. The plant hours are 8:30 a.m. to 6:30 p.m., Monday thru Friday, 7:30 a.m. to 4:00 p.m. on Saturday, and closed Sunday. There is no union representing employees.

Aircraft parts are spray painted in a large side-draft hood that is vented outside of the building. Spray painting is accomplished using a compressed air, siphon-cup feed gun. The polyurethane paint contains 1,6-hexamethylene diisocyanate (HDI)-based polyisocyanate, with a small residual amount of the HDI monomer. During this operation, the operator dons an air-purifying half-mask respirator with combined particulate and organic vapor cartridges, and wears elbow-length rubber gloves. In addition, the painter is the only worker in the room during painting operations, and the door connecting adjacent areas remains shut during the application. After painting, the parts are placed in a curing oven for 30-60 minutes.

After repair or servicing, the parts are packaged and returned to the owner. An Insta-Foam polyurethane foam system is used to package aircraft parts (typically 10 parts per day). The polyurethane foam is produced from a two-part/component system. Part A contains 45 percent (% by weight) 4,4'-diphenylmethane diisocyanate (MDI) and 55% MDI-based polyisocyanate; part B is a polyurethane resin containing a mixture of polyols, urethane catalysts, and silicone surfactant. The components are preheated to 130-150°F and are mixed at the injection nozzle just before injection into the packaging box. After injection, the exothermic polymerization reaction results in formation of a rigid polyurethane foam. The company has used the Insta-Foam equipment for approximately 10 years.

During packaging, a cardboard box is assembled and a sheet of plastic is placed in the box. Foam is then applied and covered by plastic prior to placing the

part in the box. Finally, a sheet of plastic is placed over the part, additional foam is applied, and the box is closed and sealed. A typical packaging operation requires about five minutes to complete. Since the foam is only applied during a brief portion of the packaging operation, released chemicals, such as MDI, enter the work area as a point source emission, and any exposure would be intermittent.

The packaging system is located in the Shipping department. Generally one worker performs the foaming operation although three or four other workers may be in the immediate area. Adjacent to this area is a garage door that is opened on a frequent basis.

## METHODS

### June 16-17, 1999, Site Visit

During the NIOSH site visit, after meeting with Future Aviation, Inc., management and an employee representative, a walk-through survey was conducted to review various operational parameters, and to collect bulk samples from both wash tanks in the Test Area. During the walk-through survey, work practices, and the use of personal protective equipment were observed. Written safety procedures, policies, and employee training programs were also reviewed.

#### ***Bulk Samples***

Bulk samples from both of the cleaning tanks in the Test Area were collected and shipped separately to the NIOSH contract laboratory. Samples were collected in clean, unused containers. Because some of the petroleum naphtha used was a recycled product, an additional bulk sample of the naphtha was obtained and analyzed by gas chromatography-mass spectroscopy (GC-MS) at the NIOSH analytical laboratory (Cincinnati, Ohio) to identify the primary constituents.

#### ***Industrial Hygiene Sampling: Naphtha and Recycled Solvents***

Environmental monitoring was conducted to assess worker exposures to petroleum solvents. Full-shift personal breathing zone (PBZ) samples for petroleum naphtha were collected on five workers. A 1.5 hour PBZ sample was also collected on one worker while he cleaned a wheel hub with solvent in a wash tank to determine “peak” exposure during this presumably worst-case exposure task. The samples were collected with SKC Pocket Pump™ low-flow sampling pumps. Nominal flow rates of 50 cubic centimeters per minute (cc/min) were used to collect the full-shift samples. A flow rate of 100 cc/min was used to collect the 1.5 hour sample. All pumps were pre- and post-calibrated with a BIOS Dry-Cal Lite primary standard.

Standard charcoal tubes (100 milligrams front section/50 milligrams backup) were used to collect the samples. After collection, the samples and blanks were placed in a refrigerator until the naphtha bulk analysis was available, after which they were shipped via overnight delivery to the NIOSH contract laboratory. The major compounds identified in the bulk sample (toluene and total hydrocarbons) were selected for quantitative analysis on the charcoal tubes via NIOSH Manual of Analytical Methods, fourth ed. # 1550.

#### ***Ventilation Evaluation***

Local exhaust ventilation (LEV) was evaluated by measuring air velocity at the duct or hood face using a factory calibrated TSI Velocicalc® model 8360 anemometer. This instrument measures air velocity in feet-per-minute (fpm). For each system evaluated, multiple measurements in a grid-like pattern were obtained and the results averaged to obtain the mean velocity. The following LEV systems were evaluated: Varsol hoods 1 and 2, paint hood in the Cleaning Area, the non-destruct test hood, and the exhaust duct scavenger in the Nickel Plating Shop. Work practices during the use of these hoods were observed.

### October 19, 1999, Site Visit



NIOSH industrial hygienists conducted both PBZ and area air sampling for the isocyanate-containing compounds used in the foam packaging and spray painting operations.

### ***Industrial Hygiene Sampling: Polyurethane Spray Painting***

The isocyanate exposure assessment consisted of PBZ air sampling on the painters, and area air sampling near the spray painting hood, curing oven, and adjacent areas. The air samples were collected to determine short term, task-based inhalation exposures and airborne concentrations of the isocyanate-containing compounds found in the polyurethane paints. All air samples were collected using a 37-millimeter (mm) quartz fiber filter (QFF) impregnated with 1-(9-anthracenylmethyl) piperazine (MAP).<sup>1</sup> Battery-operated sampling pumps calibrated to a nominal flow rate of 1.5 liters per minute (Lpm) 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 milliliters (mL) of a MAP in acetonitrile solution. All samples were shipped and stored in a cold environment prior to analysis.

The QFF 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. Upon receipt at the analytical laboratory, 10 microliters of acetic anhydride were added to each QFF sample. The acetic anhydride was allowed to react with the excess MAP overnight. Each QFF sample solution was filtered and concentrated to 1 mL. The HPLC analysis used a 150 x 4.6 mm C8 Inertsil column containing 5 micron particles, and the mobile phase flow rate was 1.5 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. 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 average (mean) sample volumes from the PBZ and the area air sampling data. These sample volumes were 27.3 and 137.1 liters, respectively. The LODs and MDCs for these air samples are in Table 1.

### ***Industrial Hygiene Sampling: Polyurethane Foam Packaging***

Isocyanate exposures occurring during foam packaging were assessed using PBZ and area air samples. Ten-minute PBZ samples were collected on the foamer while he was packaging parts in polyurethane foam. Full-shift area air samples were collected to map out MDI concentrations in the nearby work area and to measure short-term (peak) concentrations while the foamer was using the foam-in-place system. In an attempt to determine the worst-case exposure, a single (serial) sample was collected in the foamer's breathing zone only when MDI was being dispensed. MDI and MDI-based polyisocyanates were collected and analyzed using the same methods described above for HDI and HDI-based polyisocyanates sampling (referred to as the "MAP method").<sup>1</sup> The LODs and MDCs for these air samples are 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 assessment

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

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs),<sup>2</sup> (2) the American Conference of Governmental Industrial Hygienists' (ACGIH®) Threshold Limit Values (TLVs®),<sup>3</sup> and (3) the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs).<sup>4</sup> Employers are encouraged to follow the OSHA limits, the NIOSH RELs, the ACGIH TLVs, or whichever are the more protective criterion.

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

hazards, even in the absence of a specific OSHA PEL.

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

## Naphthas

Petroleum naphtha is comprised mainly of aliphatic hydrocarbons.<sup>5</sup> Effects from exposure to these solvents are primarily acute, unless significant amounts of substances that have chronic toxicity are present, such as benzene or glycol ethers. Epidemiologic studies have shown that exposure to similarly refined petroleum solvents (i.e., mineral spirits, Stoddard solvent) can cause dry throat, burning or tearing of the eyes, mild headaches, dizziness, respiratory irritation, and dermatitis.<sup>6</sup>

Since naphtha's are mixtures of aliphatic hydrocarbons, the evaluation criteria are based upon the most commonly available varieties (petroleum ether, rubber solvent, varnish makers' and painters' [VM&P] naphtha, mineral spirits, and Stoddard solvents). The NIOSH REL for petroleum distillates (naphtha) is 350 milligrams per cubic meter (mg/m<sup>3</sup>) of air as a TWA exposure.<sup>2</sup> In addition, a ceiling concentration limit (15 minutes duration) of 1800 mg/m<sup>3</sup> is stipulated. The OSHA PEL for petroleum distillates (naphtha) is 1600 mg/m<sup>3</sup> TWA, while the PEL for Stoddard solvents is 525 mg/m<sup>3</sup>.<sup>4</sup> ACGIH has also established a TLV of 525 mg/m<sup>3</sup> for Stoddard solvents.<sup>3</sup> NIOSH, ACGIH, and OSHA have evaluation criteria for *n*-hexane of 180 mg/m<sup>3</sup> TWA.<sup>2,3,4</sup> The NIOSH REL for toluene is 100 parts per million (ppm) as a full-shift TWA.<sup>2</sup>

## 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 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 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.<sup>7</sup> 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 the 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 consistent 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 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.

Exposure to isocyanates is irritating to the skin, mucous membranes, eyes, and respiratory tract.<sup>8,9</sup> 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).<sup>9,10,11</sup> Contact dermatitis can result in symptoms such as rash, itching, hives, and swelling of the extremities.<sup>8,9,11</sup> 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.<sup>8,10,11</sup> 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.<sup>8,10,12,13,14</sup> 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).<sup>10,13</sup> The late asthmatic reaction is the most common, occurring in approximately 40% of isocyanate sensitized workers.<sup>15</sup> An improvement in symptoms may be observed during periods away from the work environment (weekends, vacations).<sup>8,10,13</sup> 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.<sup>16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32</sup> 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<sup>12,33</sup> to 25% in polyurethane production plants<sup>34,33</sup> and 30% in polyurethane seatcover operations.<sup>35</sup> The scientific

literature contains some animal data suggesting that dermal exposure to diisocyanates may produce respiratory sensitization.<sup>36,37,38,39</sup> 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.<sup>13</sup> 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.<sup>40,41,42,43</sup> 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.<sup>11</sup> 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.<sup>10,11</sup> 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.<sup>10,11</sup> 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.

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 MDI and HDI were evaluated using the NIOSH RELs, which are ceiling limits of 200 and 140 microgram per cubic

meter ( $\mu\text{g}/\text{m}^3$ ), respectively.<sup>8</sup> The exposure evaluation criterion for HDI-based polyisocyanate used by the NIOSH investigators is the Swedish National Board of Occupational Safety and Health's ceiling limit of  $200 \mu\text{g}/\text{m}^3$ .<sup>44</sup> No specific exposure evaluation criteria exists for MDI-based polyisocyanates.

## Respiratory Protection

NIOSH recommends that respiratory protection be used for worker protection only when engineering controls are not technically feasible, during the interim while the controls are being installed or repaired, or when an emergency and other temporary situations arise.<sup>45</sup> Respirators are the least preferred method of worker protection to air contaminants because it places the burden of protection on the worker and there are inherent limitations to respirators. An effective respiratory protection program must be implemented to increase the reliability of the protection, and the cooperation of the workers to adhere to the elements of the program is critical for respirators to afford adequate protection.

There are two general classes of respiratory protection, **air-purifying respirators** which remove contaminants from the ambient air before it is inhaled, and **air-supplied respirators** which deliver an independent source of respirable air (other than the surrounding atmosphere).<sup>46</sup> Both types of respirators can be subclassified based on the type of inlet covering (facepieces, helmet/shroud, suit, etc.) and the mode of operation. Regardless of the subclassification, air-purifying respirators only remove contaminants from the air and air-purifying respirators must not be used in oxygen deficient atmospheres. It is essential to fully characterize the hazardous atmosphere that respirators will be used in, including the identity and concentration of the air contaminants and the oxygen level.

## Ventilation

LEV is commonly used to control contaminants at the point of generation to reduce the potential for

employee exposure. Ventilation assessments, in conjunction with exposure monitoring results, help determine the adequacy of controls at a workstation. This information also assists with deciding if additional controls, or modification of existing controls, is warranted. The principle design parameter for LEV systems is capture velocity. Capture velocity is the velocity necessary to overcome opposing air currents and capture contaminated air by causing it to flow into the exhaust hood. Recommended capture velocities will vary depending on the contaminant's toxicity and volatility, the manner in which the material is used (e.g., heated, agitated), and room conditions (e.g., air currents). Criteria commonly used for evaluating LEV systems are from the ACGIH publication, *Industrial Ventilation: A Manual of Recommended Practice*.<sup>47</sup>

## RESULTS

### Air Sampling – Naphthas

Air sampling to assess exposure to solvents was conducted on June 17, 1999. On the day of monitoring, Future Aviation, Inc., personnel indicated that production activity was that of a typical work day. The major compounds identified in the bulk sample (toluene and total hydrocarbons) were selected for quantitative analysis on the charcoal tubes. VM & P Naphtha was used as a reference standard for the total hydrocarbon analysis.

As shown in Table 2, all measured concentrations of total hydrocarbons and toluene were below the applicable REL on the day of monitoring. The highest full-shift total hydrocarbon concentration ( $57.1 \text{ mg}/\text{m}^3$ ) was from the worker cleaning generators in the Test Area. The highest partial shift total hydrocarbon concentration ( $211.5 \text{ mg}/\text{m}^3$ ) was measured on the worker cleaning the wheel hub. The REL for total hydrocarbon is  $350 \text{ mg}/\text{m}^3$ . The highest full-shift toluene concentration ( $7.8 \text{ mg}/\text{m}^3$ ) was measured on the worker cleaning wheels. The highest partial shift toluene concentration ( $15.4 \text{ mg}/\text{m}^3$ ) was found on the worker cleaning a

wheel hub (1.5 hour PBZ sample). The REL for toluene is 375 mg/m<sup>3</sup>.

## Workplace Observations

During the June 16, 1999, NIOSH survey, the garage door in the shipping department was open from approximately 8:00 a.m. to 5:30 p.m., which provided for additional ventilation at the packaging operation. The safety equipment worn by the worker during a packaging operation consisted of eye protection and a half mask air purifying organic vapor cartridge respirator. The worker did not wear gloves while preparing foam packages.

A comprehensive program for proper selection and use of gloves has not been established. Gloves were observed in work areas that were not cleaned or stored properly. In some areas, gloves were re-used repeatedly without proper decontamination and inspection, which could result in additional exposure. Skin contact can be a significant route of exposure to solvents, and prevention of skin contact is the primary control focus for preventing solvent-related skin disorders. Although a complete review of the hazard communication program was not conducted, MSDSs were not updated and complete for all chemicals currently in use in the facility.

Management has instituted a requirement for respirator use for certain processes. However, a respiratory protection program (RPP) has not been established (e.g., exposure assessment, written program, training, fit-testing, *etc.*) and exposure monitoring supporting the need for respiratory protection has not been conducted.

Compressed air functions as a venturi to draw VM & P Naphtha out of a container and dispense onto parts. Although this activity is conducted in a ventilated hood (Varsol booth), the pressure of the compressed air sprayer in the Varsol booth appears too high, as considerable aerosol was dispersed outside the hood from the velocity of the dispensed solvent.

The small-scale plating operation involves high speed nickel plating on a rotating flange. Several chemical solutions are manually applied to the rotating part

throughout the process. One operator performs this task, which is conducted intermittently. The labeling of the chemicals present on the work bench in the Nickel Plating Shop was insufficient (no identification or hazard warning). A spill cleanup protocol has not been established.

## Ventilation

The average face velocities on the Varsol hoods were 61 feet per minute (ft/min) (Hood 1) and 100 ft/min (Hood 2). No sash was present on the front of the hood in the Non-Destruct Test room. Noise levels were noticeably increased (communication was difficult) due to fan turbulence when the hood was on. The mean velocity at the face of this hood was 165 ft/min. At the Nickel Plating Station, a local exhaust ventilation system, consisting of a 6 inch open duct, is positioned over the area where solution is applied to the rotating part. There was a direct connection of a round duct to a square duct in this system which is considered an inefficient transition that decreases the performance of the ventilation. The average velocity measurement of the duct opening was 1614 ft/min.

Noise levels in the Test Area were such that communication was difficult; noise measurement data were not available. Although a hearing conservation program has not been established (monitoring, audiometric testing, worker training) workers were required to wear hearing protection in the Test Area.

## Polyurethane Spray Painting

The data from the PBZ and area air sampling are in Table 3. Two PBZ exposure measurements were collected from the painter during the spray painting of aircraft parts. The measurements were task-based and simultaneous, collected from the right and left shoulder. No HDI was detected in either of these samples. The painter's HDI-based polyisocyanate exposure was 10.7 and 5.1 µg/m<sup>3</sup>.

Area air samples were located at the hood face, at the doors to the curing oven, on cabinets 6 feet behind

the painter, on a work bench 15 feet behind the painter, and on a work bench 20 feet from the painter. HDI was detected in only one of the seven area air samples collected during spray painting; a concentration of  $0.4 \mu\text{g}/\text{m}^3$  was found at the curing oven doors.

Figure 1 is a schematic showing the layout of the spray painting area and the location of these area sampling devices. Figure 2 is a similar schematic, but the sample numbers have been replaced with the HDI-based polyisocyanate concentration measured at the given sample location during spray painting. The area HDI-based polyisocyanate concentrations ranged from below the MDC to  $1.6 \mu\text{g}/\text{m}^3$ . Finally, an outside (ambient) air sample was collected in the parking lot adjacent to the facility. No HDI or HDI-based polyisocyanate was detected in this air sample.

## Polyurethane Foam Packaging

The data from the PBZ and area air sampling for MDI and MDI-based polyisocyanates are in Table 4. Foam packaging occurred during three distinct times during the day. A 10-minute PBZ exposure measurement was collected each time the foam-in-place system was used. MDI-based polyisocyanate was not detected in any sample. The foamer's MDI exposures were  $3.5 \mu\text{g}/\text{m}^3$ ,  $5.2 \mu\text{g}/\text{m}^3$ , and "none detected" ( $< 2.6 \mu\text{g}/\text{m}^3$ ). The foaming task typically was completed in less than 3 minutes. In an attempt to determine the worst-case exposure, a single (serial) sample was collected in the foamer's breathing zone only when MDI was being dispensed. These sampling times included short samples during each of the three packaging jobs, and a one-minute period that began when the gun malfunctioned and a small volume of MDI spilled into a box. The results of this sampling indicate an average peak exposure of  $7.5 \mu\text{g}/\text{m}^3$ . These exposure concentrations are all well below the NIOSH REL of  $200 \mu\text{g}/\text{m}^3$ .

Area air samples were collected to the east and west of the foam-in-place station at distances of  $2\frac{1}{2}$ , 5, and 10 feet, and an additional sample was collected to the east at a distance of 20 feet. These samples were

collected as a means for mapping MDI and MDI-based polyisocyanate concentrations in the work area surrounding the foam packaging station. Neither MDI nor MDI-based polyisocyanates were detected at any of these sampling locations. No LEV is present on the packaging system and service or calibration records for the system were not available.

## DISCUSSION AND CONCLUSIONS

An industrial hygiene evaluation was conducted to help determine if reported health problems (headaches and eye irritation) were associated with exposure to petroleum solvents or other chemical contaminants in the workplace. All measured exposures to toluene and total hydrocarbons were well below the applicable REL during the June 16-17, 1999, survey. Although the monitoring results did not indicate the need for respiratory protection, respirators were being worn by some workers, and some employees may wish to continue using respirators for certain tasks. If employees choose to wear respirators on a voluntary basis, certain elements of a respiratory protection program are necessary. The new OSHA regulations require a complete respirator program whenever respirator use is required by the employer. However, when respirators are used voluntarily by employees, the employer needs only to establish those respirator program elements necessary to assure the respirator itself is not a hazard. The exception is that filtering facepiece respirators can be used without any respirator program when used voluntarily. Although there are no known studies of such voluntary respirator use, NIOSH supports OSHA's voluntary use provisions because they provide safe ways, not previously available, to use respirators to reduce exposure well below established exposure limits.<sup>48</sup> Elements of a respiratory protection program include a written program, training, fit testing, medical clearance, cleaning, regular inspection, and maintenance. The requirements for a respirator program are described in the OSHA regulation 29 CFR 1910.134.

Personal protective equipment (primarily glove use) practices were inadequate. Skin contact can be a significant route of exposure to solvents, and contact dermatitis of the hands and forearms can be a problem for workers exposed to these chemicals. During the NIOSH evaluation, skin contact with solvents was observed, and this contact could be decreased with appropriate work practices and glove use. The glove program was found to be ineffective primarily because of the lack of worker training and failure to uniformly enforce the use of protective gloves.

LEV was generally adequate. A couple of deficiencies were found in The Non-Destruct Test room (sash missing, increased noise levels due to fan turbulence) and the Nickle Plating Station (inefficient transition).

In the Test Area, noise levels made communication difficult (strained communication is often an indicator of inappropriate noise levels). A noise survey is necessary to determine if a hearing conservation program (monitoring, hearing protection, audiometric testing, worker training) is appropriate.

These spray painting data indicate that the painter's isocyanate inhalation exposures and the area concentrations were at low to trace levels. This probably indicates that the spray painting hood effectively captures and removes these contaminants from the workplace. Also, the area monitoring indicates that isocyanate-containing compounds are not migrating to nearby areas and rooms.

In addition, the painter is also protected from inhalation exposures by wearing the air-purifying respirator with combined particulate and organic vapor cartridges. Recent studies have shown that organic vapor cartridges effectively remove isocyanate-containing compounds from inhaled air.<sup>49,50,51</sup> Unfortunately, none of these cartridges have an end-of-service-life-indicator (ESLI), 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.

Currently, NIOSH recommends that all workers with a potential for exposure to isocyanate-containing compounds be provided with and wear supplied-air respiratory protection.<sup>8</sup> However, there may be situations when this is not practical. OSHA states that when an ESLI is not available for the given exposure and cartridge combination, an air-purifying respirator can still be used if the "employer implements a change schedule for canisters and cartridges that is based on objective information or data that will ensure that canisters and cartridges are changed before the end of their service life."<sup>52</sup> OSHA provides information on change-out schedules at their Internet homepage (Internet address: [http://www.osha-slc.gov/SLTC/respiratory protection](http://www.osha-slc.gov/SLTC/respiratory%20protection)). Since isocyanate-containing compounds are irritating to the eyes, and there is a potential for the painter to be accidentally sprayed in the eyes, the painter should wear a full-face respirator. 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.<sup>53,54</sup>

NIOSH also recommends that efforts should be taken to prevent dermal exposures to isocyanate-containing substances.<sup>8</sup> The employer should provide protective clothing and gloves that are impervious to isocyanate-containing compounds. The gloves should be elbow-length and made of a permeation-resistant material, such as nitrile rubber, butyl rubber, or neoprene. Face-shields and aprons should be used whenever there is a possibility of a splash or a spill of isocyanate containing liquids. The openings at the interface between different forms of protective clothing should be sealed (taped) to prevent exposure through the interface.

In the interim letter dated May 19, 2000, the NIOSH investigators stated they may conduct a return site visit to conduct additional isocyanate air sampling. This decision was based on the finding of low isocyanate exposures and area concentrations from



the foam packaging and spray painting operations, and on a previous finding that the MAP method may experience analyte loss during sample storage prior to analysis. Recently, the NIOSH chemist responsible for the MAP method determined that the loss of analyte was attributed to problems with the analytical instruments used to analyze a different set of samples, and not an inherent problem in the MAP method. It was also determined that the instrumentation problems were not present when analyzing the Future Aviation isocyanate samples. Hence, a return site visit was not conducted, and the NIOSH investigators believe the isocyanate exposure and area concentration data are valid.

## RECOMMENDATIONS

1. Proper PPE use should be mandatory when dispensing or using chemicals. Dermal contact with solvents should be reduced as much as possible by the use of appropriate personal protective equipment and modification of work practices. For certain tasks, (e.g., cleaning wheels), employees should be required to wear rubber gloves that cover the forearm and a rubber-front apron. A comprehensive personal protective equipment program should be implemented. The elements of an effective program include:

**Written Procedures:** Define the necessary PPE and ensure it is properly and consistently used and maintained. The use of PPE should be mandatory in certain areas.

**Proper Selection and Use:** There are many gloves available which provide adequate protection and still allow considerable dexterity. Gloves should be individually assigned.

**Inspection and Maintenance:** PPE should be inspected before and after each use, cleaned prior to removal and replaced frequently. After cleaning, it should be stored properly.

2. Eye protection designed for chemical splashes should be worn when working with chemicals. A

permanent eye-wash station should be installed at the Cleaning Tank Area and Nickel Plating Shop.

3. A complete, written, hazard communication program should be implemented. Refer to OSHA 1910.1200 for a description of the requirements of a hazard communication program.

4. The possibility of skin contact with isocyanate-containing compounds should be minimized by using proper personal protective equipment. Workers should wear gloves (e.g., nitrile rubber, butyl rubber, polyvinyl chloride, and flexible laminates Viton™, 4H™ [PE/EVAL], Silver Shield™) at all times during the foaming and painting operations.

5. As discussed in this report, exposures to isocyanate-containing compounds may result in respiratory problems among some workers. If a worker develops respiratory problems which may be related to the work environment, the worker should be removed from all diisocyanate exposure until evaluated and diagnosed by an occupational medicine physician with experience in diagnosing isocyanate-induced respiratory conditions.

6. Reduce the pressure in the Varsol spray gun to less than 30 psi to minimize over spray. Educate users regarding the need to confine spraying within the hood.

7. Engineering controls (e.g., containment, ventilation) or work practice changes (eliminating use of compressed air, depressurization, etc.) should be a first consideration to reduce the potential for exposure. If respirators are necessary for worker protection, or until engineering controls are implemented, a comprehensive written respiratory program is necessary. The requirements for a respirator program are described in the OSHA regulation 1910.134. Note that OSHA requires the employer to provide respirators when required, at no cost to the worker.

8. A noise survey should be conducted and a hearing conservation program established if necessary.

## REFERENCES

1. Streicher RP, Arnold JE, Ernst MK, Cooper CV [1996]. Development of a novel derivatization reagent for the sampling and analysis of total isocyanate group in air and comparison of its performance with that of several established reagents. *American Industrial Hygiene Association Journal* 57:905–913.
2. NIOSH [1992]. Recommendations for occupational safety and health: compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92–100.
3. ACGIH [2001]. 2001 TLVs® and BEIs®: threshold limit values for chemical substances and physical agents. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
4. CFR [1997]. 29 CFR 1910.1000. Code of Federal Regulations. Washington, DC: U.S. Government Printing Office, Office of the Federal Register.
5. Browning E [1965]. Toxicity and metabolism of industrial solvents. New York, NY: Elsevier, pp 141–144.
6. NIOSH [1977]. Criteria for a recommended standard: occupational exposure to refined petroleum solvents. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77–192.
7. Woods G [1987]. The ICI Polyurethanes Book. New York, NY: ICI Polyurethanes and John Wiley & Sons. Inc.
8. NIOSH [1978]. Criteria for a recommended standard: occupational exposure to diisocyanates. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 78-215.
9. NIOSH [2000]. Pocket guide to chemical hazards. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 90–117.
10. NIOSH [1986]. Occupational respiratory diseases. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 86–102.
11. Levy BS, Wegman DH, eds. [1988]. Occupational health: recognizing and preventing work-related diseases. 2<sup>nd</sup> ed. Boston/Toronto: Little, Brown and Company.
12. Porter CV, Higgins RL, Scheel LD [1975]. A retrospective study of clinical, physiologic, and immunologic changes in workers exposed to toluene diisocyanate. *American Industrial Hygiene Association Journal* 36:159-168.
13. Chan Yeung M, Lam S [1986]. Occupational asthma. *American Review of Respiratory Disease* 133:686–703.
14. NIOSH [1981]. Technical report: respiratory and immunologic evaluation of isocyanate exposure in a new manufacturing plant. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 81-125.
15. McKay RT, Brooks SM [1981]. Toluene diisocyanate (TDI): biochemical and physiologic studies. *American Review of Respiratory Disease*

123:132.

16. Harries M, Burge S, Samson M, Taylor A, Pepys J [1979]. Isocyanate asthma: respiratory symptoms due to 1,5-naphthylene di-isocyanate. *Thorax* 34:762–766.

17. Woolrich PF [1982]. Toxicology, industrial hygiene and medical control of TDI, MDI, and PMPPi. *American Industrial Hygiene Association Journal* 43:89–98.

18. Mobay Corporation [1983]. Health & safety information for MDI, diphenylmethane diisocyanate, monomeric, polymeric, modified. Pittsburgh, PA: Mobay Corporation.

19. Berlin L, Hjortsberg U, Wass U [1981]. Life-threatening pulmonary reaction to car paint containing a prepolymerized isocyanate. *Scandinavian Journal of Work, Environment and Health* 7:310–312.

20. Zammit-Tabona M, Sherkin M, Kijek K, Chan H, Chan-Yeung M [1983]. Asthma caused by diphenylmethane diisocyanate in foundry workers. *American Review of Respiratory Disease* 128:226–230.

21. Chang KC, Karol MH [1984]. Diphenylmethane diisocyanate (MDI)-induced asthma: evaluation of immunologic responses and application of an animal model of isocyanate sensitivity. *Clinical Allergy* 14:329–339.

22. Seguin P, Allard A, Cartier A, Malo JL [1987]. Prevalence of occupational asthma in spray painters exposed to several types of isocyanates, including polymethylene polyphenyl isocyanate. *Journal of Occupational Medicine* 29:340–344.

23. Nielsen J, Sungo C, Winroth G, Hallberg T, Skerfving S [1985]. Systemic reactions associated with polyisocyanate exposure. *Scandinavian Journal of Work, Environment and Health* 11:51–54.

24. Alexandersson R, Gustafsson P, Hedenstierna G, Rosen G [1986]. Exposure to naphthalene-diisocyanate in a rubber plant: symptoms and lung function. *Archives of Environmental Health* 41:85–89.

25. Mapp CE, Chiesura-Corona P, DeMarzo N, Fabbri L [1988]. Persistent asthma due to isocyanates. *American Review of Respiratory Disease* 137:1326–1329.

26. Liss GM, Bernstein DI, Moller DR, Gallagher JS, Stephenson RL, Bernstein IL [1988]. Pulmonary and immunologic evaluation of foundry workers exposed to methylene diphenyldiisocyanate (MDI). *Journal of Allergy and Clinical Immunology* 82:55–61.

27. Keskinen H, Tupasela O, Tiikkainen U, Nordman H [1988]. Experiences of specific IgE in asthma due to diisocyanates. *Clinical Allergy* 18:597–604.

28. Cartier A, Grammar L, Malo JL, Lagier F, Ghezzi H, Harris K, Patterson R [1989]. Specific serum antibodies against isocyanates: association with occupational asthma. *Journal of Allergy and Clinical Immunology* 84:507–514.

29. Mobay Corporation [1991]. Hexamethylene diisocyanate based polyisocyanates, health and safety information. Pittsburgh, PA: Mobay Corporation.

30. Vandenplas O, Cartier A, Lesage J, Perrault G, Grammar LC, Malo JL [1992]. Occupational asthma caused by a prepolymer but not the monomer of toluene diisocyanate (TDI). *Journal of Allergy and Clinical Immunology* 89:1183–1188.

31. Vandenplas O, Cartier A, Lesage J, Cloutier Y, Perrault G, Grammar LC, Shaughnessy MA, Malo JL [1992]. Prepolymers of hexamethylene diisocyanate as a cause of occupational asthma. *Journal of Allergy and Clinical Immunology* 91:850–861.

32. Baur X, Marek W, Ammon J, Czuppon AB, Marczynski B, Raulf-Heimsoth M, Roemmelt H, Fruhmann G [1994]. Respiratory and other hazards of isocyanates. *International Archives of Occupational and Environmental Health* 66:141–152.
33. Weill H [1979]. Epidemiologic and medical-legal aspects of occupational asthma. *The Journal of Allergy and Clinical Immunology* 64:662-664.
34. Adams WGF [1975]. Long-term effects on the health of men engaged in the manufacture of tolylene diisocyanate. *British Journal of Industrial Medicine* 32:72-78.
35. White WG, Sugden E, Morris MJ, Zapata E [1980]. Isocyanate-induced asthma in a car factory. *Lancet* i:756-760.
36. Karol MH, Hauth BA, Riley EJ, Magreni CM [1981]. Dermal contact with toluene diisocyanate (TDI) produces respiratory tract hypersensitivity in guinea pigs. *Toxicology and Applied Pharmacology* 58:221–230.
37. Erjefalt I, Persson CGA [1992]. Increased sensitivity to toluene diisocyanate (TDI) in airways previously exposed to low doses of TDI. *Clinical and Experimental Allergy* 22:854–862.
38. Rattray NJ, Bothman PA, Hext PM, Woodcock DR, Fielding I, Dearman RJ, Kimber I [1994]. Induction of respiratory hypersensitivity to diphenylmethane-4,4'-diisocyanate (MDI) in guinea pigs. Influence of route of exposure. *Toxicology* 88:15–30.
39. Bickis U [1994]. Investigation of dermally induced airway hyperreactivity to toluene diisocyanate in guinea pigs. Ph.D. Dissertation, Department of Pharmacology and Toxicology, Queens University, Kingston, Ontario, Canada.
40. Baur X, Dewair M, Rommelt H [1984]. Acute airway obstruction followed by hypersensitivity pneumonitis in an isocyanate (MDI) worker. *Journal of Occupational Medicine* 26:285–287.
41. Yoshizawa Y, Ohtsuka M, Noguchi K, Uchida Y, Suko M, Hasegawa S [1989]. Hypersensitivity pneumonitis induced by toluene diisocyanate: sequelae of continuous exposure. *Annals of Internal Medicine* 110:31–34.
42. Selden AI, Belin L, Wass U [1989]. Isocyanate exposure and hypersensitivity pneumonitis – report of a probable case and prevalence of specific immunoglobulin G antibodies among exposed individuals. *Scandinavian Journal of Work, Environment and Health* 15:234–237.
43. Vanderplas O, Malo JL, Dugas M, Cartier A, Desjardins A, Levesque J, Shaughnessy MA, Grammar LC [1993]. Hypersensitivity pneumonitis-like reaction among workers exposed to diphenylmethane diisocyanate (MDI). *American Review of Respiratory Disease* 147:338–346.
44. Swedish National Board of Occupational Safety and Health [1996]. Occupational exposure limit values, AFS 1996:2. Solna, Sweden: Swedish National Board of Occupational Safety and Health.
45. NIOSH [1987]. NIOSH respirator decision logic. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87–108.
46. NIOSH [1987]. NIOSH guide to industrial respiratory protection. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-116.
47. ACGIH Committee on Industrial Ventilation [1992]. ACGIH industrial ventilation: a manual of recommended practice. 20th Ed. Lansing, Michigan: American Conference of Governmental Industrial Hygienists.

48. NIOSH [1999]. NIOSH Respirator Use Policy, August 1999. In: NIOSH policy statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health.

49. Giardino N, England E, Doddridge J, Greebon K, Carlton G [1999]. Application of Cohen and Garrison's respirator service life prediction model to 1,6-hexamethylene diisocyanate monomer. *Applied Occupational and Environmental Hygiene* 15:245–248.

50. Vasta J [1985]. Respirator cartridge evaluation for isocyanate containing Imron and Centari-Enamels. *American Industrial Hygiene Association Journal* 46:39–44.

51. Rosenberg C, Tuomi T [1984]. Airborne isocyanates in polyurethane spray painting: determination and respirator efficiency. *American*

*Industrial Hygiene Association Journal* 45:117–121.

52. OSHA [1998]. Respiratory protection. Title 29 Code of Federal Regulations Part 1910.134.(d)(3)(iii)(B)(2). Washington, DC: U.S. Department of Labor, Occupational Safety and Health Administration.

53. NIOSH [1987]. NIOSH guide to industrial respiratory protection. Cincinnati, Ohio: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87–116.

54. OSHA [1998]. Respiratory protection. Title 29 Code of Federal Regulations Part 1910.134. Washington, DC: U.S. Department of Labor, Occupational Safety and Health Administration.

**TABLE 1**  
**Limits of Detection and Minimum Detectable Concentrations for the Isocyanate Monitoring**

Analyte	Sample Type	LOD <sup>1</sup>	MDC <sup>2</sup>
HDI	Impregnated Filter, PBZ Air Sampling	0.024	0.88
HDI-based Polyisocyanate	Impregnated Filter, PBZ Air Sampling	0.024	0.88
HDI	Impregnated Filter, Area Air Sampling	0.024	0.18
HDI-based Polyisocyanate	Impregnated Filter, Area Air Sampling	0.024	0.18
MDI	Impregnated Filter, PBZ Air Sampling	0.025	2.6
MDI-based Polyisocyanate	Impregnated Filter, PBZ Air Sampling	0.025	2.6
MDI	Impinger & Filter in Series, Area Air Sampling	0.025	0.05
MDI-based Polyisocyanate	Impinger & Filter in Series, Area Air Sampling	0.025	0.05

<sup>1</sup> LOD = limit of detection in micrograms per sample.

<sup>2</sup> MDC = minimum detectable concentration in micrograms of analyte per cubic meter of air.

**TABLE 2**  
**Personal Air Samples for Solvents**

Sample #	Task	Time (min)	Concentration Detected in mg/m <sup>3</sup>			
			Toluene	TWA	Total HC	TWA
CT-1	Starter Generators: cleaning with solvents, enamel painting	08:24–12:04 (220)	5.13	4.8	(27.9)	(17.7)
CT-10		12:05–15:36 (211)	4.42		(7.1)	
CT-2	Wheels: cleaning with solvents	08:25–11:57 (212)	8.54	7.8	113.7	84.7
CT-7		11:59–16:16 (257)	6.43		33.4	
CT-3	Starter Generators: cleaning with solvents, enamel painting	08:26–12:03 (217)	6.26	7.2	97.4	(57.1)
CT-9		12:03–16:14 (251)	7.99		(20.0)	
CT-4	Assembly: assembling and testing parts	08:30–12:00 (210)	2.90	4.1	4.35	4.1
CT-8		12:01–15:37 (216)	5.24		3.8	
CT-12	Wheels: cleaning with solvents	13:50–15:34 (104)	15.4	NA	211.5	NA
NIOSH Recommended Exposure Limit				375		350

mg/m<sup>3</sup> = milligrams of contaminant per cubic meter of air sampled

TWA = time-weighted average concentration calculated as follows:

$$TWA = \frac{C_1T_1 + C_2T_2}{T_1 + T_2}$$

Where: C = concentration detected during the sampling period T

Total HC = total hydrocarbons detected on the sample

NA = Not Applicable

Measurements in parenthesis were between the analytical limit of detection and analytical limit of quantitation

**TABLE 3**  
**PBZ and Area Air Sampling Data for the Spray Painting Operation**

Sample # – Sample Location	Sample Type <sup>1</sup>	Sample Time <sup>2</sup>	Sample Volume <sup>3</sup>	[HDI] <sup>4</sup>	[HDI-Based Polyisocyanate] <sup>4</sup>
1 – Painter, left shoulder	PBZ	1026–1044	27.0	ND	10.7
2 – Painter, right shoulder	PBZ	1026–1044	27.6	ND	5.1
3 – Right side of hood face, level with the painter’s breathing zone	AAS	1028–1048	30.6	ND	ND
4 – Left side of hood face, level with the painter’s breathing zone	AAS	1028–1048	30.8	ND	ND
5 – Curing oven doors	AAS	1035–1505	399.6	0.4	ND
6 – 6' behind and to the right of the painter	AAS	1028–1048	30.1	ND	1.2
7 – 6' behind and to the left of the painter	AAS	1028–1048	30.1	ND	1.4
8 – 15' behind painter on work bench	AAS	1029–1044	22.9	ND	(1.3)
9 – 20' to the left of the painter on work bench	AAS	1029–1044	15.4	ND	(1.6)
10 – Ambient air sample from the parking lot	AAS	0907–1457	537.3	ND	ND
NIOSH REL – Ceiling Limit				140	
Swedish Standard – Ceiling Limit					200

<sup>1</sup> PBZ = personal breathing zone air sample

AAS = area air sample

ND = none detected

<sup>2</sup> Sample times are in military time.

<sup>3</sup> Sample volumes are in liters of air.

<sup>4</sup> Airborne concentrations are in micrograms of analyte per cubic meter of air. Concentrations in parentheses are between the MDC and MQC for the analytical method, and should be considered semi-quantitative.



**TABLE 4**  
**PBZ and Area Air Sampling Data for the Foam Packaging Operation**

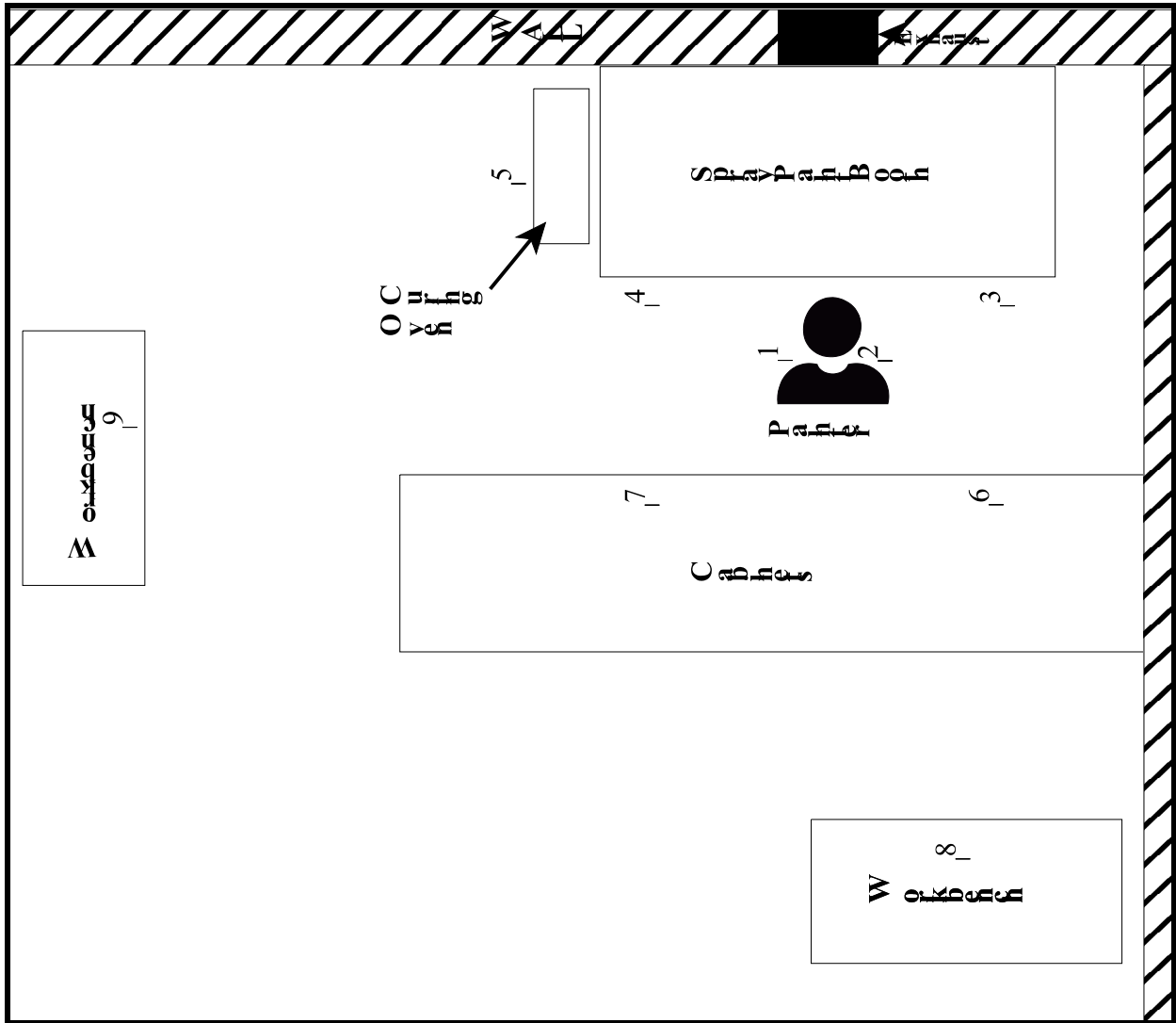
Sample Location	Sample Type <sup>1</sup>	Sample Time <sup>2</sup>	Sample Volume <sup>3</sup>	[MDI] <sup>4</sup>		[MDI-Based Polyisocyanate] <sup>4</sup>
				short-term	full-shift	
Foamer, breathing zone	PBZ	0954–1004	9.8	ND	–	ND
Foamer, breathing zone	PBZ	1338–1348	9.8	5.2	–	ND
Foamer, breathing zone	PBZ	1706–1716	9.8	3.5	–	ND
Foamer, breathing zone	PBZ	0955–0957 1314–1315 1339–1341 1706–1709	8.6	7.5	–	ND
2½' west of foaming station	AAS	0904–1716	480	–	ND	ND
5' west of foaming station	AAS	0904–1716	470	–	ND	ND
10' west of foaming station	AAS	0904–1716	460	–	ND	ND
2½' east of foaming station	AAS	0904–1716	470	–	ND	ND
5' east of foaming station	AAS	0904–1716	500	–	ND	ND
10' east of foaming station	AAS	0904–1716	460	–	ND	ND
20' east of foaming station	AAS	0911–1716	480	–	ND	ND
NIOSH REL				200	50	

<sup>1</sup> PBZ = personal breathing zone air sample    AAS = area air sample    ND = none detected

<sup>2</sup> Sample times are in military time.

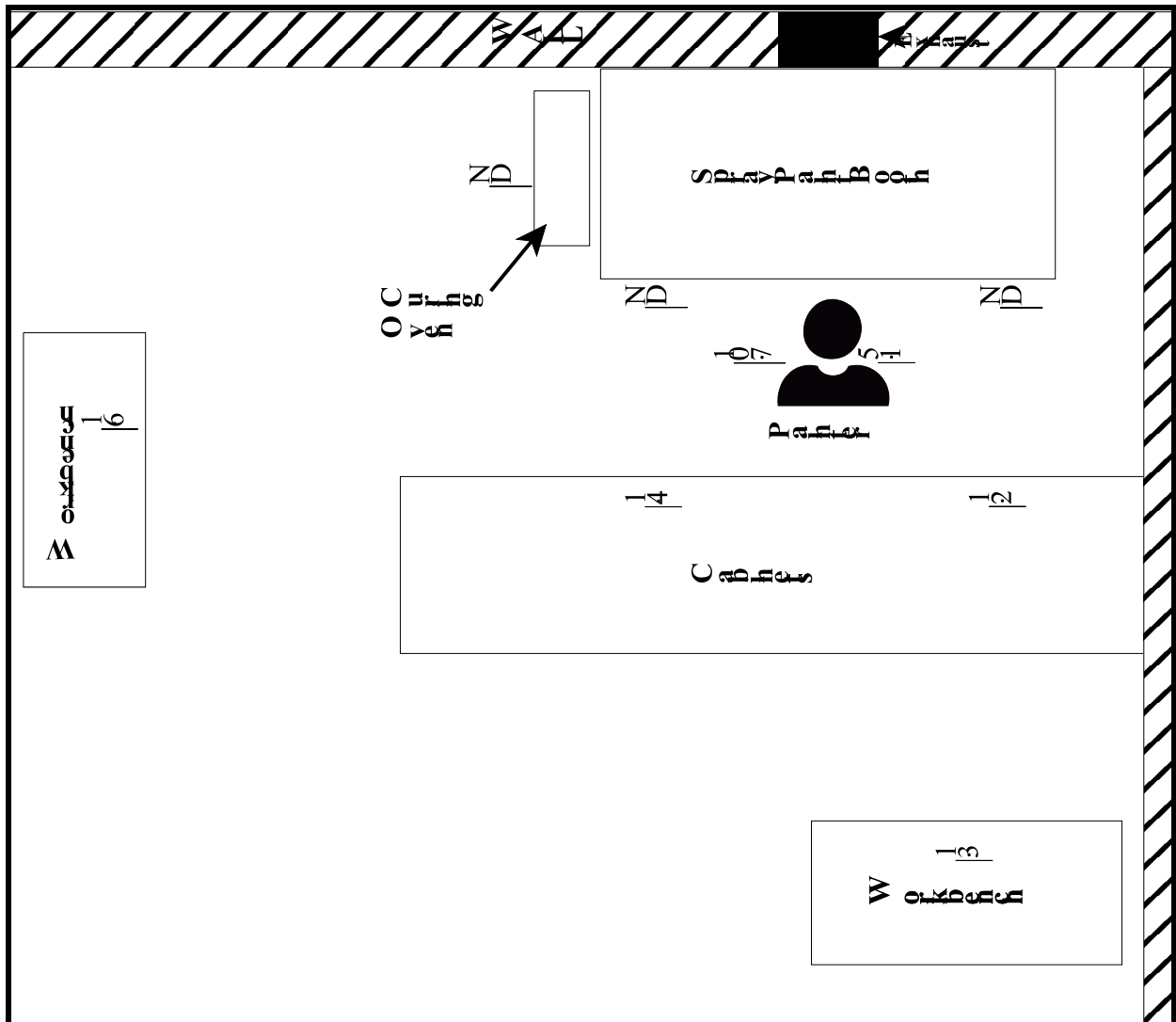
<sup>3</sup> Sample volumes are in liters of air.

<sup>4</sup> Airborne concentrations are in micrograms of analyte per cubic meter of air.



**Figure 1: Layout of the Spray Painting Area and Location of the Air Samples**

The above numbers correspond with the sample numbers shown in the first column of Table 3.



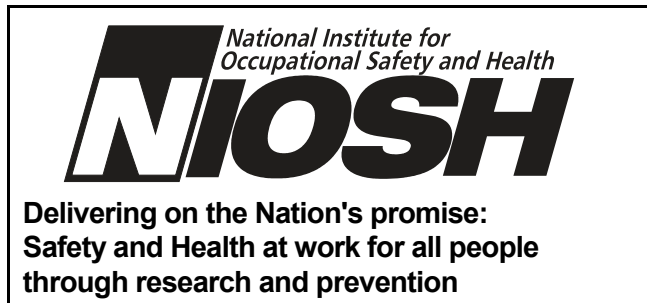
**Figure 2: HDI-Based Polyisocyanate Concentrations by Sample Location**

Concentrations are in micrograms per cubic meter of air; ND = none detected.

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