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**HETA 98-0263-2817**  
**General Electric - Evendale**  
**Cincinnati, Ohio**

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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 Gregory Burr and Loren Tapp of HETAB, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Field assistance was provided by Steven Ahrenholz. Desktop publishing was performed by Robin Smith. Review and preparation for printing were performed by Penny Arthur.

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# Highlights of the NIOSH Health Hazard Evaluation

## Methanol and 4,4'-MDA Exposures to SPO Technicians

At the request of the IAM, Local Lodge 912, NIOSH industrial hygienists measured exposures to methanol and 4,4'-methylenedianiline (4,4'-MDA) among SPO workers during the lay-up of uncured PMR-15 graphite composite. Prior air monitoring by GE had measured very low concentrations of 4,4'-MDA, but occasional high concentrations of methanol. A NIOSH medical officer conducted confidential interviews with SPO employees and examined occupational injuries and illness records.

### What NIOSH Did

- # We took full-shift air samples for methanol and 4,4'-MDA on SPO workers.
- # We talked to seven SPO employees.
- # We looked at the medical records of some SPO employees.

### What NIOSH Found

- # All of the 4,4'-MDA concentrations were very low and similar to those measured previously by GE.
- # Methanol concentrations were also very low.
- # SPO employees we spoke with mentioned ergonomic problems, fatigue, and sore throats.
- # Recent process changes in vane lay-up appeared to reduce worker's exposure to methanol.
- # We briefly smelled an odor similar to vehicular exhaust odor in the SPO area. Employees thought it came from a nearby delivery truck.

### What SPO Managers Can Do

- # Continue to check SPO workers' exposures to 4,4'-MDA by collecting air samples.
- # Use a high efficiency particulate air (HEPA)-filtered ventilated hand tool for cutting and trimming the uncured PMR-15 composite.
- # Continue training on work practices to reduce potential dermal exposure.
- # Consider adding urine monitoring for 4,4'-MDA as part of the medical surveillance program for employees who work directly with 4,4'-MDA.
- # Find the source of the sporadic exhaust odors in the SPO area.

### What SPO Employees Can Do

- # Use the rod and clamp assembly to hold uncured laminate while spraying methanol.
- # Always move your tool stand as close as possible to the high efficiency particulate air (HEPA)-filtered exhaust.



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**Health Hazard Evaluation Report 98-0263-2817  
General Electric  
Evendale, Ohio  
November 2000**

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## **SUMMARY**

In July 1998, the National Institute for Occupational Safety and Health (NIOSH) received a health hazard evaluation (HHE) request from the International Association of Machinists (IAM), Local Lodge 912 concerning the Special Product Operations (SPO) at General Electric (GE) plant in Evendale, Ohio. The request concerned the lay-up of uncured PMR-15, a graphite composite material used to make jet engine parts. Potential exposures included methanol and 4,4-methylenedianiline (4,4'-MDA), a component in the PMR-15 composite material. The union suspected higher 4,4'-MDA exposures in the "case room." Prior air monitoring by GE industrial hygienists had measured very low concentrations of 4,4'-MDA, but occasional high concentrations of methanol (ranging from 160 to 180 parts per million [ppm]).

In March 1999, personal breathing-zone (PBZ) air samples for 4,4'-MDA and methanol were collected by a NIOSH industrial hygienist and a NIOSH medical officer conducted confidential interviews with SPO employees. The Occupational Safety and Health Administration (OSHA) Log and Summary of Occupational Injuries and Illnesses, Form 200 (OSHA 200 log), and company injury reports from the preceding three years were reviewed. The company medical records of 19 SPO employees, including 12 of the 14 employees listed as currently working in the lay-up area, were reviewed. All interviewed employees were included in the medical record review.

The concentration of 4,4'-MDA ranged from trace amounts (defined as between 0.015 and 0.062 parts per billion [ppb] for this sample set) to 0.42 ppb, as time-weighted averages (TWA). All of these results were well below the OSHA Permissible Exposure Limit (PEL) of 10 ppb and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV<sup>®</sup>) of 100 ppb, TWA over an 8-hour work day. NIOSH recommends that exposures be kept as low as feasible. Methanol concentrations ranged from 4.4 to 22 ppm, all of which were well below the NIOSH recommended exposure limit (REL), OSHA PEL, and ACGIH TLV of 200 ppm, TWA over an 8- to 10-hour work day.

Six of 14 SPO current lay-up employees and one former lay-up employee were interviewed. The remaining SPO lay-up employees were unavailable or declined the interview. Five of the seven employees reported musculoskeletal disorders, two reported fatigue, and two reported sore throat with methanol and/or a decontamination solution use. Concerns of the interviewed employees included: lack of solvent handling and ergonomic training, ventilation in the SPO lay-up area, adequacy of personal protective equipment (PPE), and lack of representative air sampling due to the daily variability of work activities. Additional concerns included exposure to 4,4'-MDA (both airborne and dermal) in the lay-up area, and the lack of biological monitoring (urine testing) for 4,4'-MDA in the company medical surveillance program.

Company medical records of 19 employees working in SPO were reviewed, including the seven workers who had been interviewed. Not all of the 19 were working with 4,4'-MDA at the time of the review. Of the 19, three had a history of abnormal liver function tests, two had a history of hematuria (blood in the urine), and two had a worsening of dermatitis that began prior to their working with 4,4'-MDA. Fourteen of the 19 charts indicated visits for musculoskeletal complaints. The liver and renal problems appeared to be due to non-occupational causes. The OSHA 200 logs from 1996 through October 1998 were also reviewed. Of

22 injuries and/or illnesses recorded for SPO workers during this time period, one involved a heart arrhythmia potentially aggravated by methanol exposure and 10 involved cumulative trauma disorders (CTD's) of the upper extremity.

NIOSH investigators determined that a health hazard did not exist from airborne exposures to either 4,4'-MDA or methanol at the time of this evaluation, although two employees had reported health effects possibly related to excessive short-term exposure to methanol in the past. No documented evidence of work-related liver or renal abnormalities was found, and the use of PPE to prevent dermal exposure was appropriate. Recommendations are included on methanol spraying techniques and biological monitoring to more thoroughly assess workers' exposures to 4,4'-MDA.

Keywords: SIC 3724 (Aircraft engines and engine parts), PMR-15, composite, dermatitis, MDA, 4,4'-methylenedianiline, methanol, ergonomics.

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## INTRODUCTION

In July 1998, the National Institute for Occupational Safety and Health (NIOSH) received a health hazard evaluation (HHE) request from the International Association of Machinists (IAM), Local Lodge 912 concerning the Special Product Operations (SPO) at the General Electric (GE) aircraft engine facility in Evendale, Ohio. The request concerned the lay-up and machining (grinding, milling, and cutting) of composite aircraft engine components made of PMR-15, a graphite composite material.

The union was specifically concerned about the following issues: (1) the safe use of methanol (reagent grade methanol is used during the lay-up process to keep the uncured composite pliable and slightly tacky); (2) the adequacy of skin and respiratory protection from exposure to 4,4'-methylenedianiline (4,4'-MDA), a component in the PMR-15 composite material; (3) suspected higher 4,4'-MDA exposures in the "case room," and (4) the absence of biological monitoring for 4,4'-MDA exposure among SPO workers as part of their medical surveillance program. Prior air monitoring by GE industrial hygienists in the SPO area found very low concentrations of 4,4'-MDA but, in some instances, high concentrations of methanol (ranging from 160 to 180 parts per million [ppm]).

An initial opening conference with management and union representatives and a walk-through of the SPO area was conducted in October 1998. A follow-up industrial hygiene survey was conducted on March 12 and 18, 1999, during which personal and area air sampling was conducted for 4,4'-MDA and methanol on SPO technicians.

## BACKGROUND

The GE-Evendale facility designs and manufactures jet engines for commercial and military use. Since this evaluation was limited to the manufacture of composite aircraft parts in the SPO area, only these activities are described in detail.

Composite materials are combinations of resin systems and fibrous materials, with the majority of all advanced composite resin systems being epoxy

resin-based.<sup>1</sup> Other resin systems of importance include phenol-formaldehyde resins, isocyanate resins, and polyamide resins. The common fibrous materials used are fibrous glass and fiber-reinforced graphite.<sup>1</sup> In the SPO operations at GE, fiber reinforced graphite and polyamide resins (containing 4,4'-MDA) were in use.

Access to the SPO composite lay-up area is restricted due to both Department of Defense (DOD) security requirements and Occupational Safety and Health Administrations (OSHA) regulations which require GE-Evendale to control occupational exposure to 4,4'-MDA by establishing restricted exposure areas. In the SPO operation, approximately six to ten technicians and mechanics per shift manually lay-up composite aircraft components, which range in size from small jet engine vanes to much larger pieces such as jet engine housings (referred to as "cases"). At the time of this evaluation there were two shifts. The smaller aircraft engine vanes are manufactured on a daily schedule and can be assembled more quickly than the larger engine cases, which can take two technicians several days to complete. Since case lay-up occurred so infrequently, SPO technicians were requested to arrange their work schedule slightly to accommodate the sampling performed in this evaluation.

The uncured PMR-15 polyamide composite material used in the SPO area is received already impregnated with 4,4'-MDA by the manufacturer. The PMR-15 laminate is kept frozen until use. After it is thawed, reagent grade methanol is hand-sprayed onto the sheets of PMR-15 by SPO technicians during the manual lay-up of the composite sheets. The methanol is primarily used to keep the composite material tacky during the build-up of the composite part. For quality assurance, both the temperature and relative humidity in this department are controlled (70° F and 13%, respectively).

The technicians working in the SPO area use protective gloves when handling the PMR-15; at the time of this evaluation the workers were wearing RollPruf® gloves, a polymer blend of natural, nitrile, and neoprene rubber. This brand of gloves had been in use since approximately 1991. In addition to gloves, SPO workers are required to wear disposable coveralls and shoe covers, and all workers have been

fit-tested for a respirator. Respirator use in the 4,4'-MDA-restricted areas is optional.

In addition to the OSHA regulations which require the establishment of a restricted area to limit exposure to 4,4'-MDA, there were other aspects of this evaluation which complicated both the collection of air samples and the evaluation of worker activities. For example, because of DOD security requirements, only one of the NIOSH investigators had the appropriate security clearance to actually observe all of the work practices. In addition, no photographs were permitted, and any items (such as notebooks and writing instruments) which could not be suitably decontaminated (because of the potential presence of 4,4'-MDA) were required to remain in the restricted area for subsequent disposal. As a result of this latter restriction, notebooks were not taken in the restricted SPO area by NIOSH investigators, and sampling pumps were placed beneath the disposable coveralls worn by the workers.

## METHODS

### Environmental

Full-shift personal breathing zone (PBZ) air samples were collected for 4,4'-MDA and methanol during two activities of particular interest to the SPO workers, "vane lay-up" and "case lay-up." Air samples for 4,4'-MDA were collected following NIOSH Sampling and Analytical Method No. 5029 on 37 millimeter (mm) glass fiber filters which had been previously treated with sulfuric acid. An air flow rate of 2 liters per minute (Lpm) was used. Immediately following sampling, the treated glass fiber filters were transferred to glass vials containing potassium hydroxide in methanol. Analysis was by high performance liquid chromatography, with the following modifications: a Supelcosil LC-18, 4.6 X 250 mm, 5 micrometer ( $\mu\text{m}$ ) column was used; the column temperature was 40°C; the mobile phase used acetonitrile with a buffer; and the flow rate and injection volume were 1.0 milliliter (mL)/minute and 25 microliters ( $\mu\text{L}$ ), respectively.<sup>2</sup>

Full shift PBZ samples for methanol were collected using silica gel tubes according to NIOSH Sampling and Analytical Method No. 2000. An air flow rate of 50 cubic centimeters per minute (cc/min) was used.

Analysis for methanol was done using gas chromatography according to NIOSH sampling Method No. 2000, with the following modifications: a 30 meter X 0.52 mm fused silica capillary column coated internally with 7  $\mu\text{m}$  of RTX-1 was used; the oven temperature was programmed from 40°C (held for 5 minutes) to 200°C, at a rate of 60°C per minute.<sup>2</sup>

### Medical

Confidential interviews were offered to all 14 employees listed by GE as currently working in the lay-up area. The OSHA Log and Summary of Occupational Injuries and Illnesses Form 200 (OSHA 200 log), and company injury reports from the past three years were reviewed. Company medical records of SPO employees, including those currently working in lay-up, were reviewed.

## 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 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),<sup>3</sup> (2) the American Conference of Governmental Industrial Hygienists' (ACGIH®) Threshold Limit Values (TLVs®),<sup>4</sup> and (3) the OSHA Permissible Exposure Limits (PELs).<sup>5</sup> Employers are encouraged to follow the OSHA limits, the NIOSH RELs, the ACGIH TLVs, or whichever are the more protective criteria.

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.

## **4,4'- Methylene dianiline (4,4'-MDA)**

Methylene dianiline is an aromatic amine used as a curing agent in the manufacture of the PMR-15 graphite composite material. Although 4,4'-MDA levels may vary with resin system and cure conditions, no free (unreacted) 4,4'-MDA is likely to be detected in the cured composite laminate.<sup>1</sup> In animal studies, chronic exposure to 4,4'-MDA caused liver and possible kidney damage. Occupational exposure studies have found 4,4'-MDA slightly irritating to skin and mucous membranes.<sup>6</sup> 4,4'-MDA has been shown to cause liver damage (jaundice) in humans after oral or dermal exposure.<sup>1,6,7</sup> Based on the finding of thyroid and liver tumors in both sexes of rats and mice, the National Toxicology Program (NTP) determined 4,4'-MDA to be a carcinogen.<sup>8,9</sup> A NIOSH

epidemiological study of 4,4'-MDA-exposed workers found an excess of bladder cancer-related deaths.<sup>10</sup>

NIOSH considers 4,4'-MDA to be a suspect human carcinogen and recommends exposures be kept at the lowest feasible concentration.<sup>3</sup> The OSHA PEL for 4,4'-MDA is 10 parts per billion (ppb) as an 8-hour TWA, with an STEL of 100 ppb.<sup>11</sup> The ACGIH has adopted a TLV® for this chemical of 100 ppb for an 8-hour TWA, with a notation that a significant contribution to a worker's overall exposure can occur by the cutaneous (skin and mucous membranes) route. The ACGIH considers 4,4'-MDA to be a suspect human carcinogen.

## **Methanol**

Methanol, a clear, highly flammable liquid also known as wood alcohol and methyl alcohol, is used as an industrial solvent, in windshield washer fluid, and in the production of paints, cements, inks, and other products. Methanol is quickly absorbed after ingestion or inhalation, and the most characteristic effects of methanol poisoning include visual changes and metabolic acidosis (a systemic lowering of the pH of the blood). Historical evidence suggests that long-term exposure to concentrations ranging from 1200 to 8300 ppm can cause impaired vision, while exposures to methanol vapors ranging from 360 to approximately 4000 ppm may cause blurred vision, headache, dizziness, and nausea.<sup>12,13</sup> The NIOSH REL is 200 ppm for up to a 10 hour TWA, with a STEL of 250 ppm. The OSHA PEL for methanol is 200 ppm, TWA for up to an 8 hour exposure.<sup>5</sup> The ACGIH TLV® for methanol is similar to the NIOSH REL (200 ppm for up to an 8-hour TWA exposure, with a short-term excursion limit of 250 ppm.) Both NIOSH and the ACGIH have a skin notation for methanol, meaning that appropriate protection must be used to avoid skin exposure.

# **RESULTS**

## **Environmental**

As shown in Table 1, the concentration of 4,4'-MDA in the PBZ samples ranged from trace amounts (trace concentrations defined as between 0.015 and 0.062 ppb for this sample set) to 0.42 ppb. The highest concentration (0.42 ppb) was measured during case lay-up. All of these results were well below the OSHA PEL of 10 ppb and ACGIH TLV of 100 ppb, TWA over an 8-hour work day. NIOSH recommends that exposures be kept as low as feasible. The PBZ concentrations found by NIOSH appeared to be slightly higher than those measured by GE industrial hygienists between February 24, 1999, to March 18, 1999, which ranged up to 0.15 ppb.

Table 2 presents the results of the PBZ sampling for methanol. Concentrations ranged from 4.4 to 22 ppm. As with the 4,4'-MDA samples, the highest concentrations were measured during case lay-up. However, all of these concentrations were well below the NIOSH REL, OSHA PEL, and ACGIH TLV of 200 ppm, TWA over an 8- to 10-hour work day. These concentrations were similar to those measured by GE industrial hygienists between February 24, 1999, to March 18, 1999, which ranged from <0.065 to 33 ppm.

On the days of this evaluation SPO technicians were observed wearing appropriate protective equipment, including gloves (polymer blend of natural rubber, nitrile, and neoprene) and disposable coveralls and shoe covers while working in the 4,4'-MDA restricted areas. No SPO technicians were observed spraying methanol near their face or upper torso during this survey and in fact only a minimum amount of methanol was actually observed being sprayed onto the composite laminate. Finally, an odor similar to vehicular exhaust was detected by NIOSH investigators at approximately 8:00 a.m. on March 12, 1999. The SPO technicians suspected that exhaust from a truck delivering nitrogen to a nearby autoclave was being drawn into the outside air intake.

## Medical

## Interviews

Six of 14 current SPO lay-up employees and one former lay-up employee were interviewed. The remaining lay-up employees were either not available or declined the interview. The average age of the seven interviewed workers was 41 years (range: 37 to 45 years). The average length of time these seven had worked in the SPO area was 2.5 years (range: 5 months to 7 years). Six of the seven employees reported work related health problems; five reported musculoskeletal disorders, two reported fatigue, two reported sore throat after using methanol and/or DeCon Solution (a decontamination solution containing glutaraldehyde), and one reported pre-existing dermatitis that was aggravated by work exposures.

Concerns of the interviewed employees included the following: lack of solvent handling and ergonomic training; ventilation in the SPO lay-up area; adequacy of personal protective equipment; and lack of representative air sampling due to the daily variability of work activities. Additional concerns included the level of exposure to 4,4'-MDA (both airborne and dermal, the latter from coming in contact with potentially contaminated work surfaces in the lay-up area), and the possible need for the company to implement biological monitoring for 4,4'-MDA.

## Medical Record Review

The medical surveillance program for SPO employees includes a medical history, physical examination, urinalysis, blood tests for liver and renal function testing, and pulmonary function testing and is performed annually. Biological monitoring for 4,4'-MDA is not included in the program.

Company medical records used for routine medical surveillance and work-related health visits were reviewed for 19 SPO employees; 12 of 14 current SPO lay-up employees and 7 employees recently working in SPO lay-up with potential work related health problems based on information obtained in the employee interviews. Records for all 7 of the interviewed employees were among the reviewed records. Among the 19 employee records that were reviewed, three had a history of abnormal liver

function tests (LFT's); all had medical problems unrelated to work which could explain the abnormalities. Two employees had a history of hematuria; one was diagnosed with a condition not related to work, the other was to undergo further testing by his private physician. Two medical visits involved methanol exposure; one for a methanol splash to the eye, and another for symptoms of burning eyes and fatigue which would resolve over the weekends when away from work. Two workers had pre-existing dermatitis that had worsened after working in SPO lay-up. Fourteen of the 19 charts revealed visits for musculoskeletal complaints, 10 of which were repetitive strain injuries.

### **OSHA 200 Logs and Company Injury Records**

The OSHA 200 logs from 1996 through October 1998 were reviewed. Of eight recorded injury and/or illness entries for SPO employees in 1996-1997, four entries were for cumulative trauma disorders (CTD's). Non-recordable injury records for 1997 revealed two additional SPO workers with CTD's. Of 14 recorded entries for SPO workers in 1998, one concerned a heart arrhythmia potentially aggravated by methanol exposure and six involved CTD's of the upper extremity. Of the 18 non-recordable injuries, two entries involved methanol exposure (one splash to the eye, the other with symptoms of eye burning and fatigue) and one involved a CTD.

## **DISCUSSION**

Exposure to methanol and 4,4'-MDA were among the chief concerns of employees. However, the measured 4,4'-MDA concentrations were below the OSHA PEL and ACGIH TLV. Likewise, methanol concentrations were well below its NIOSH REL, OSHA PEL, and ACGIH TLV. Although interviews and medical records indicated that some employees had experienced symptoms consistent with excessive methanol exposure, the PBZ air concentrations suggest that workers are exposed to very low concentrations of methanol when measured over the course of an entire work-day. While GE exposure data collected prior to this evaluation suggested that much higher short-term exposures to methanol had occurred (possibly when the hand spray bottle was held too close to the employees breathing-zone), the

addition of two process changes in vane lay-up (using a rod and clamp assembly to hold uncured composite laminate and the repositioning of three tool stands nearer the ventilation system) should reduce the frequency of these higher short-term worker exposures to methanol.

Based on observations from this evaluation and interviews with employees, it appeared that the greatest work-related health problem found in the SPO lay-up employees was repetitive motion injuries. According to workers, an ergonomic evaluation was conducted July 1998 by a GE consultant and recommendations were made; however, few of the recommended changes had been implemented at the time of this survey.

Another question posed by some SPO workers to NIOSH investigators during this evaluation concerned the benefit of using bio-monitoring to assess 4,4'-MDA exposure. At the time of this NIOSH evaluation bio-monitoring for 4,4'-MDA was not being done. In a study of 4,4'-MDA exposure and the use of urine bio-monitoring in three aerospace industry facilities, researchers found that the total mass of 4,4'-MDA excreted in the urine of exposed workers was appreciably greater than the mass inhaled.<sup>14</sup> In that study, the employees working exclusively with wet 4,4'-MDA-containing materials, in an area where air sampling indicated essentially no airborne analyte, had the highest concentrations of 4,4'-MDA detected among the collected urine samples.<sup>14</sup> The researchers concluded that skin exposure appeared to play an important role in 4,4'-MDA exposure and that this exposure may have been overlooked. Skin contact with contaminated tools or work surfaces was mentioned as a potential source of 4,4'-MDA exposure in those employees not directly working with the substance.

## **CONCLUSIONS**

P Air concentrations of 4,4'-MDA and methanol measured on SPO technicians during this survey were well below the applicable OSHA PELs and ACGIH TLVs. NIOSH recommends that exposures to 4,4'-MDA be kept as low as feasible, however.

- P At the time of the review, the annual surveillance exams of employees in the SPO lay-up area did not reveal evidence of laboratory abnormalities attributable to occupational exposure to 4,4'-MDA or methanol, despite the lack of routine 4,4' MDA monitoring to assess dermal exposure.
- P The two process changes in vane lay-up made prior to this evaluation appeared to be effective in reducing methanol exposures. The first involved using a rod and clamp assembly to hold uncured composite laminate while spraying with methanol. The second change repositioned each of the three tool stands (there was one worker per tool stand) closer to the high efficiency particulate air (HEPA)-filtered exhaust.
- P No SPO technicians were spraying methanol near their face or upper torso during this survey and only a small amount of methanol was actually applied to the composite laminate by the workers. However, some SPO employees sprayed larger amounts of methanol onto their work table tops at the end of the day as part of their routine clean-up activities. Based on the sample results, however, this did not result in elevated methanol exposures when averaged over the entire work day. Finally, several SPO technicians mentioned methanol vapor migrating over a partial wall which surrounded case lay-up and into the surrounding vane lay-up areas. No strong methanol odors were detected in or around case lay-up by NIOSH investigators on the days of this survey, however.

## RECOMMENDATIONS

1. Use a HEPA-filtered ventilated hand tool for cutting and trimming the uncured PMR-15 composite.
2. SPO technicians should use the rod and clamp assembly to hold uncured composite laminate while spraying it with methanol.
3. Continue to assess workers' exposures to 4,4'-MDA by air sampling.

4. To assess exposure from both inhalation and dermal routes, which air sampling alone will not detect, incorporate urine monitoring for 4,4'-MDA into the medical surveillance program for employees who work directly with 4,4'-MDA or are potentially exposed to 4,4'-MDA by skin contact with contaminated tools and work surfaces. Although a correlation between the level of 4,4'-MDA exposure and the concentration of 4,4'-MDA in urine has not been determined, urine monitoring for this substance has been used effectively to demonstrate dermal exposure not otherwise recognized. See the Appendix for further guidelines in 4,4'-MDA urine monitoring.
5. Continue training in work practices to reduce potential dermal exposure.
6. Investigate the source of the vehicular exhaust odors in the SPO, including determining the appropriateness of the location of the outside air intakes for the SPO area and the effectiveness of any existing restrictions on the operation of gas or diesel powered equipment while loading or unloading material.
7. Implement the approaches to reduce musculoskeletal stress outlined in the ergonomic report issued by the GE ergonomic consultant to reduce the upper extremity, neck, and back discomfort reported by SPO technicians. This would include the development of tools to reduce the grip forces used by the workers during the manual lay-up of the composite.

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**Table 1**  
**Results of Personal Breathing Zone Samples for 4,4-methylenedianiline (4,4'-MDA)**  
**Samples Collected in the Special Product Operation (SPO) Area**  
**General Electric, Cincinnati, Ohio (HETA 98-0263-2817)**

Activity	Sample Number	Sample Time (min)	Sample Volume (liters)	Concentration (ppb)	Comments
				4,4'-MDA	
Sampling Date: March 12, 1999					
Case Work	GB-2	147	294	0.32	Sampling pump failure after 147 minutes
Case Work	GB-3	429	858	0.19	Sample removed during lunch
Case Work	GB-10	177	354	0.42	Pump failure, replacement pump used
Vane Work	GB-5	379	758	Trace	Sample removed during lunch
Vane Work	GB-4	379	508	Trace	Worker ended early for the day
Vane Work	GB-1	399	798	0.14	Sample removed during lunch
Sampling Date: March 18, 1999					
Vane Work	GB-13	202	404	Trace	Worker ended early for the day
Vane Work	GB-14	439	878	0.27	Sample removed during lunch
Vane Work	GB-15	435	870	Trace	Sample removed during lunch
Ultrasonic Knife	GB-19	421	842	0.074	Sample removed during lunch
MDC			800	0.015	
MQC			800	0.062	
NIOSH Recommended Exposure Limit				LFC	
OSHA Permissible Exposure Limit				10	
ACGIH Threshold Limit Value				100	

Trace = Concentration is between the MDC and the MQC  
MDC = Minimum detectable concentration for the sample set  
MQC = Minimum quantifiable concentration for the sample set  
ppb = sample concentrations are reported in parts per billion  
LFC = lowest feasible concentration

**Table 2**  
**Results of Personal Breathing Zone Samples for Methanol**  
**Samples Collected in the Special Product Operation (SPO) Area**  
**General Electric, Cincinnati, Ohio (HETA 98-0263-2817)**

Activity	Sample Number	Sample Time (min)	Sample Volume (liters)	Concentration (ppm)	Comments
				Methanol	
Sampling Date: March 12, 1999					
Case Work	GB-8	147	--	Pump failure	Pump failed, no sample collected
Case Work	GB-7	429	21.5	12	Sample removed during lunch
Case Work	GB-11	177	8.9	22	Pump failure, replacement pump used
Vane Work	GB-9	379	19	3.6	Sample removed during lunch
Sampling Date: March 18, 1999					
Vane Work	GB-17	202	10.1	5.2	Worker ended early for the day
Vane Work	GB-18	439	22	6.8	Sample removed during lunch
Vane Work	GB-16	435	21.8	4.4	Sample removed during lunch
MDC			20	0.03	
MQC			20	0.11	
NIOSH Recommended Exposure Limit				200	250 ppm for a short term exposure
OSHA Permissible Exposure Limit				200	
ACGIH Threshold Limit Value				200	250 ppm for a short term exposure

MDC = Minimum detectable concentration for the sample set  
MQC = Minimum quantifiable concentration for the sample set  
ppm = sample concentrations are reported in parts per million  
LFC = lowest feasible concentration

# APPENDIX

## Protocol for Biological Monitoring for 4,4'-Methylenedianiline (4,4'-MDA)

The following are minimal guidelines proposed by the authors of this report for biological monitoring and surveillance of 4,4'-methylenedianiline (4,4'-MDA). In workplaces where there is potential for occupational exposure to 4,4'-MDA, management has the primary responsibility for setting up 4,4'-MDA hazard controls and for maintaining a proper medical program, and management is responsible for all costs of the biological monitoring and surveillance programs. The National Institute for Occupational Safety and Health (NIOSH) does not have an official recommendation regarding biological monitoring for 4,4'-MDA, and the American Conference of Governmental Industrial Hygienists (ACGIH) has not set biological exposure indices (BEI) for 4,4'-MDA. However, the absence of these limits should not preclude the use of biological monitoring for helping to control exposure, particularly where absorption of the material can occur by non-inhalation routes.<sup>1</sup> Additionally, more stringent guidelines should be continued if already in place to further minimize potential health effects related to occupational exposure.

The following recommendations are based on existing scientific information concerning occupational exposure to 4,4'-MDA as well as other well-accepted occupational health guidelines.

1. A program of biological monitoring and medical surveillance should be made available to all employees who work directly with 4,4'-MDA or are potentially exposed to 4,4'-MDA by skin contact with contaminated tools and/or work surfaces. The purpose of this program is to prevent (or to detect at an early stage) both the acute and chronic adverse health effects resulting from exposure to 4,4'-MDA. This program consists of periodic urine 4,4'-MDA tests and medical evaluation.
2. Medical and work histories (including previous exposure to 4,4'-MDA or other occupational exposures) should be taken for each worker assigned to work with or around 4,4'-MDA prior to job placement; medical and work histories should be updated periodically. The health care professional responsible should be familiar with the adverse health effects of excessive exposure to 4,4'-MDA and provided with an estimate of the worker's potential for exposure to 4,4'-MDA, including any available workplace sampling results and a description of any protective devices or equipment the worker may be required to use. A pre-placement evaluation should take place and focus particular attention to the liver and skin, as well as to the urinary and endocrine systems, as these are most likely to be affected by 4,4'-MDA.<sup>2</sup> The pre-placement examination should include liver and renal function tests, and urinalysis. The medical evaluation, including history, physical examination, and laboratory testing, should be repeated annually. Workers who report symptoms suggestive of 4,4'-MDA health effects at any time should be offered a repeat medical examination.
3. A baseline 4,4'-MDA urine level should be established before beginning work. Urine samples (to determine 4,4'-MDA levels) also should be collected at regular intervals, as determined by a qualified physician familiar with 4,4'-MDA bio-monitoring, from all employees who are exposed to 4,4'-MDA. Workplace exposures may comprise both inhalation and dermal routes of exposure, potentially resulting in a biphasic pattern of elimination. In other settings, biological monitoring of 4,4'-MDA-exposed workers has revealed a temporal pattern of urine 4,4'-MDA levels whereby, if exposure is likely to be via inhalation, post-shift samples should be collected, and if exposure is likely via the skin, pre-shift samples the next day are more appropriate.<sup>1,3</sup> This pattern occurs because of the more rapid absorption and elimination of 4,4'-MDA with inhalation exposure compared to the slower uptake of the substance with dermal exposure. Initially, this periodic sampling should consist of samples collected at the end of the working shift (post-shift) and again on the next day (pre-shift) before work begins. The decision on when to collect urine samples for further monitoring should take into account the major route of 4,4'-MDA exposure and the results of the initial testing.

Other investigators have suggested that 50 nanomole 4,4'-MDA per millimole creatinine (nmol 4,4'-MDA/mmol creatinine) be used as a “yardstick” of potential overexposure in the absence of a biological exposure standard.<sup>1</sup> They found that among workers using appropriate work practices, regardless of the route of exposure, urinary 4,4'-MDA concentrations were kept below 50 nmol 4,4'-MDA/mmol creatinine. If the urine 4,4'-MDA level is above 50 nmol MDA/mmol creatinine, an industrial hygiene assessment should be made regarding exposure levels, use of personal protective equipment, and work practices, and measures should be taken to reduce exposure.

4. Excessive 4,4'-MDA absorption has been well established to cause liver toxicity in humans regardless of the route of exposure, and has also been associated with skin irritation.<sup>4</sup> Medical removal is a means of protecting workers when, for whatever reasons, other methods, such as engineering controls, work practices, protective clothing, and respirators, have failed to provide adequate protection. Medical removal involves the temporary removal of a worker from his regular job to a place of significantly lower exposure. The need for medical removal should be determined by a physician knowledgeable of exposure and health issues related to 4,4'-MDA. During the period of medical removal, workers must be provided with appropriate follow-up medical surveillance to determine when the employee can be safely returned to his/her usual job.

Medical removal should not be a substitution for other, more effective methods of protecting workers (such as engineering controls). If workers are medically removed from their usual job duties, they should retain their wages, seniority, and benefits to which they would be entitled had they not been reassigned. Also, when medically eligible to return to their former jobs, workers should be entitled to the position, wages, and benefits they would have had had they not been removed.

5. All employee health information must be kept confidential and maintained in a secure location. This information should be released only when it is required by law or preempted by public health concerns; when the information is requested by other health professionals for relevant reasons; and when provided to specific individuals at the employee's request. Employers may be advised about an employee's medical fitness to work but not to specific diagnoses or specific details of their medical care, except in conformity with other laws and regulations. Each employer that retain health records should designate a guardian of the records through whom access may be obtained.<sup>5</sup> All records of biological monitoring and medical examinations should be kept for at least 30 years after termination of employment of the worker.<sup>6</sup>

6. Physicians with expertise in occupational medicine should provide guidance in developing a medical surveillance program. The medical aspects of the surveillance program may be delivered by other physicians or other health care professionals, and if results indicate a health problem in the workplace, physicians trained in occupational medicine should be consulted to help resolve the problem.<sup>7</sup>

7. The data generated under the occupational medical surveillance program should be recorded in a systematic manner. The data should be analyzed periodically in an epidemiologically meaningful manner, such as by job title or work area. The data should be made available for use by OSHA and NIOSH.<sup>8</sup>

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