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General Electric Corporation, Evendale, Ohio

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GENERAL ELECTRIC CORPORATION
EVENDALE, OHIO**

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SUMMARY

On September 27, 1988, the National Institute for Occupational Safety and Health (NIOSH) received a request from the United Auto Workers Local 647 for a health hazard evaluation (HHE) at General Electric (GE), Evendale, Ohio. The union was concerned with the removal of a fluoroelastomer coating from aircraft parts and the machining of prototype aircraft engine parts made of a graphite composite material. Specific union concerns at the fluoroelastomer operation included the adequacy of the existing standard operating procedures for removal of the coating, potential employee exposures during this removal operation, and the necessity for additional ventilation and housekeeping procedures. Employee concerns with the machining of aircraft parts made from a graphite composite included suspected cases of work-related dermatitis among workers in the Development Manufacturing Operations (DMO) area and the possible presence of unreacted methylenedianiline (MDA) in the cured graphite composite.

An initial industrial hygiene and medical survey was conducted on November 3, 1988. A follow-up medical survey was conducted on March 14, 1989, during which 31 employees, identified by union officials as having experienced skin problems in the DMO area, were interviewed. A follow-up industrial hygiene survey was conducted in the DMO area on August 25, 1989, to collect bulk samples of composite-based particulate and to conduct air sampling for airborne dust and fibers. Air sampling was not conducted at the fluoroelastomer removal operation.

No residual MDA was detected from an analysis of a bulk sample of graphite composite particulate (the limit of detection for this method was 0.8 parts per million [ppm], expressed in a weight to weight ratio). A bulk sample of composite particulate was analyzed by polarized light microscopy to determine dust morphology. The results indicated that the sample consisted mostly of black, opaque, elongated graphite fibers with a somewhat consistent diameter (approximately 8 micrometers). The fiber sides on undamaged pieces were smooth and parallel, while the terminations were somewhat pointed. The graphite fibers were embedded in parallel array in a matrix (the composite resin material). In one instance the texture of the matrix was serrated. Seven personal breathing-zone (PBZ) and general area (GA) air samples collected in the DMO area and analyzed by phase contrast microscopy (PCM) contained no airborne fibers. The limit of detection (LOD) for this sample set was 7 fibers per square millimeter. Concentrations of total and/or respirable particulate in the DMO area were very low, ranging from 0.01 to 0.06 milligrams per cubic meter (mg/m^3) for respirable particulate and from 0.07 to 0.17 mg/m^3 for total particulate. All of these results were well below the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) of 5 mg/m^3 for respirable particulate and the Swedish exposure standard for composite dust of 3 mg/m^3 .

Most interviewed employees had histories consistent with possible work-related skin disorders. These disorders consisted of pruritus (itching) and redness of the skin; the parts of the body most commonly affected were the hands and arms. Some workers also experienced rashes on the ankles, legs, and back of the neck, and on the face around the edges of respirators. One worker related that, upon coming home from work, his children developed rashes when they sat in a chair that he had sat in while wearing his work clothes. The rash-causing agent was suspected to be cured composite dust in most instances.

Employees who wore gloves felt that the gloves decreased the frequency of skin disorders. Some of the employees who wore sleeves and paper overalls provided by the company felt that this equipment decreased the frequency of skin disorders. However, most workers stated that the sleeves were a safety hazard, and that the composite dust penetrated the sleeves and overalls. Barrier creams and moisturizing lotions were used infrequently and respirators were worn occasionally.

NIOSH investigators have determined that a potential hazard existed to the exposed, unprotected skin from the handling of the graphite composite particulate. The morphology of the graphite fibers imbedded in the resin matrix suggests that mechanical irritation of the skin could be responsible for the itching and redness described by some of the workers in the DMO area. Some of the recommendations which have been made in this report include changes in the type of protective clothing used when handling or machining graphite composite parts and an increased use of local exhaust ventilation when machining composite components without the use of cutting fluids.

KEYWORDS: SIC 3724 (Aircraft engines and engine parts), PMR-15, composite, dermatitis, MDA, 4,4'-methylenedianiline, CAS No. 101-77-9, graphite.

INTRODUCTION

On September 27, 1988, the National Institute for Occupational Safety and Health (NIOSH) received a health hazard evaluation (HHE) request from United Auto Workers Local 647, concerning two areas of the General Electric (GE) aircraft engine facility located in Evendale, Ohio. The request pertained to two operations: (1) the removal of Viton®, a fluoroelastomer coating covering some aircraft engine components; and (2) the grinding, milling, and cutting of PMR-15, a graphite composite material used in some prototype aircraft engine parts.

The union was specifically concerned about the adequacy of the existing GE standard operating procedures (SOPs) for removal of a fluoroelastomer coating, an activity which was performed on a very intermittent schedule. Specific union concerns included the possible exposure of workers other than the grinder (who wore a disposable half-mask respirator) in the immediate work area and whether the underlying metal alloy was also being removed during the grinding of the fluoroelastomer coating. Other union concerns included the necessity of installing local exhaust ventilation and developing procedures for safely cleaning the work area after the fluoroelastomer coating had been removed. On the subject of the PMR-15 graphite composite, the union was concerned about suspected cases of work-related dermatitis among employees in the Development Manufacturing Operations (DMO) and the presence (if any) of unreacted methylenedianiline (MDA) in the cured graphite composite.

An initial industrial hygiene and medical survey was conducted on November 3, 1988. A follow-up medical survey was conducted on March 14, 1989. A follow-up industrial hygiene survey was conducted in the DMO area on August 25, 1989.

BACKGROUND

The GE-Evendale facility designs and manufactures jet engines for commercial and military use. Since this evaluation was limited to two departments (the removal of the fluoroelastomer coating from aircraft components and the machining of prototype graphite composite jet engine components in the DMO area), only these activities are described in detail.

REMOVAL OF FLUROELASTOMER COATING FROM JET ENGINE COMPONENTS

This operation was performed very infrequently. According to company and union representatives, some metal parts used in jet engines are covered with Viton®, a fluorinated synthetic rubber manufactured by Du Pont. Although no classified materials are handled in this operation, how the Viton® coating is actually attached to the metal engine components is classified. Because of Department of Defense (DOD) security requirements, the removal of the elastomeric coating was performed in a secure area with a minimal number of employees in the room. During the walk-through on November 3, 1988, no grinding was being done and, for DOD security reasons, the fluoroelastomer-coated engine parts were covered with tarpaulins.

Based on information provided by GE, the first step in salvaging or repairing Viton®-coated engine parts requires the removal of the fluoroelastomer coating. This is manually performed using small, hand-held grinders or sanders. According to company and union representatives, the grinding and sanding activities were precise and generally did not involve removal of a large amount of Viton®. Smoking was not permitted during the grinding and sanding of the coating and the machinists were required to wear a 3M® Model 9920 disposable respirator while grinding or sanding on the Viton®.

DEVELOPMENT MANUFACTURING OPERATIONS (DMO)

Employees in the DMO area machine a variety of prototype aircraft parts, some of which are made of a graphite composite material called PMR-15, a polyamide resin-based material manufactured by the Fiberite Corporation. The adjacent chart outlines the basic steps involved in producing the PMR-15 graphite composite and the subsequent manufacturing of engine components.

As of 1989, composite work accounted for approximately 10-15% of the work performed by DMO machinists. In a walk-through survey of the DMO operations area on

November 3, 1988, cured PMR-15 composite material of varying shapes and sizes was being machined, both with and without the use of coolant. A large, moveable dust collector provided local exhaust ventilation (LEV) when the composite material was machined dry.

1. Extremely high purity (99.9%) carbon is woven in various widths ranging from 1 to 6 feet.
2. The carbon cloth is impregnated with PMR-15 resin (a polyamide resin precursor solution) and kept frozen with dry ice until used. It should be noted that Steps 1 and 2 were not performed at the Evendale facility.
3. After shipping to GE-Evendale, the frozen impregnated carbon sheets are thawed and then manually formed to create the composite aircraft parts. These formed parts are then autoclaved to set the resin. The forming and autoclaving of the uncured composite material was performed in a GE-Evendale laboratory that was not part of this evaluation.
4. The autoclaved (or cured) composite components are then transferred to the DMO area for final machining (such as grinding, drilling, and end milling).

EVALUATION METHODS

INDUSTRIAL HYGIENE EVALUATION

Table 1 summarizes the sampling methods used in the DMO area to analyze bulk samples of cured PMR-15 composite particulate and to measure airborne dust and fiber levels in this department. For the fluoroelastomer removal operation, no air sampling was scheduled because this activity was performed so infrequently.

MEDICAL EVALUATION

The medical survey conducted on March 14, 1989, consisted of private interviews with 31 current GE employees who had been identified by union officials as having experienced skin problems while working in the DMO area.

EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by work place exposures, NIOSH field staff employ evaluation criteria for the assessment of a number of chemical (and physical) agents. The primary sources of environmental evaluation criteria for the work place are the following: (1) NIOSH Criteria Documents and Recommended Exposure Limits (RELs), (2) the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs), and (3) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values® (TLVs).^{1,2,3} The objective of these criteria for chemical agents is to establish levels of inhalation exposure to which the vast majority of workers may be exposed without experiencing adverse health effects.

Full-shift and shorter duration inhalation criteria are available depending on the specific physiologic properties of the chemical substance. Full-shift limits are based on the time-weighted average (TWA)

airborne concentration of a substance that most workers may be repeatedly exposed to during a normal eight or 10-hour day, up to 40 hours per week for a working lifetime, without adverse effect. Some substances have recommended short-term exposure limits (STELs) or ceiling limits which are intended to supplement the full shift criteria where there are recognized irritative or toxic effects from brief exposures to high airborne concentrations. STELs are based on TWA concentrations over 15 minute time periods, whereas ceiling limits are concentrations which should not be exceeded even momentarily.

Occupational health criteria are established based on the available scientific information provided by industrial experience, animal or human experimental data, or epidemiologic studies. Differences between the NIOSH RELs, OSHA PELs, and ACGIH TLVs may exist because of different philosophies and interpretations of technical information. It should be noted that RELs and TLVs are guidelines, whereas PELs are standards which are legally enforceable. OSHA PELs are required to take into account the technical and economical feasibility of controlling exposures in various industries where the agents are present. The NIOSH RELs are primarily based upon the prevention of occupational disease without assessing the economic feasibility of the affected industries and as such tend to be conservative. A Court of Appeals decision vacated the OSHA 1989 Air Contaminants Standard in *AFL-CIO v OSHA*, 965F.2d 962 (11th Circuit, 1992); and OSHA is now enforcing the previous 1971 standards (listed as Transitional Limits in 29 CFR 1910.1000, Table Z-1-A).² However, some states which have OSHA-approved State Plans will continue to enforce the more protective 1989 limits. NIOSH encourages employers to use the 1989 limits or the RELs, whichever are lower.

It is important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these occupational health exposure criteria. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, previous exposures, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other work place exposures, or with medications or personal habits of the worker (such as smoking, etc.) to produce health effects even if the occupational exposures are controlled to the limit set by the evaluation criterion. These combined effects are often not considered by the chemical specific evaluation criteria. Furthermore, many substances are appreciably absorbed by direct contact with the skin and thus potentially increase the overall exposure and biologic response beyond that expected from inhalation alone. Finally, evaluation criteria may change over time as new information on the toxic effects of an agent become available. Because of these reasons, it is prudent for an employer to maintain worker exposures well below established occupational health criteria.

COMPOSITE MATERIALS

Composite materials are combinations of resin systems and fibrous materials. Approximately half of all advanced composite resin systems are epoxy resin-based.⁴ 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.⁴

There is a great deal of information on the health effects of various components of composite materials as they exist in the *uncured* state. Many of these components, such as formaldehyde and styrene, are irritants. Other ingredients, such as toluene diisocyanate, are allergens as well as irritants. Some composite agents, such as glycidyl ethers and MDA, have adverse systemic effects or are suspect human carcinogens.⁴

There is not much known, however, about the health effects of composite components as they exist in the *cured* state. Most research on the medical hazards of cured composite have involved investigations into possible pulmonary (lung) toxicity. Results from some studies suggest that the bulk of the composite dust is particulate in nature.⁵ Results of morphological/chemical studies suggest that the composite dust is lower in desorbed and/or reactive decomposition products than most other plastic products, and that over-exposure to decomposition products during activities such as milling, grinding, sanding, or drilling, is unlikely to occur.⁵

Sweden is the only country that has established a standard for composite dust. This value, 3 milligrams per cubic meter (mg/m³) for total dust, includes "dust with or without fiberglass from set or non-set plastic material..."⁵ Morphologically, composite dust has been compared more closely to epoxy dust than to natural graphite or fiberglass.⁵

The Material Safety Data Sheet (MSDS) supplied by the Fiberite Corporation for PMR-15 did not list any hazards associated with the cured product. However, a MSDS from Armco Inc. for a similar product that was also used by this GE facility stated that "in the unlikely event of exposure to high concentrations of resin vapors, eye, nasal, and respiratory irritation may result in some people" and that "hypersensitive individuals may experience dermatitis from dusts produced during the grinding, buffing, and cutting of fully cured resins."

4,4'- METHYLENEDIANILINE (MDA)

Methylenedianiline is an aromatic amine curing agent used in the manufacture of the PMR-15 graphite composite material. Although residual MDA levels may vary with resin system and cure conditions, no free (unreacted) MDA is likely to be detected in the cured composite laminate.⁴ In animal studies, chronic exposure to MDA caused liver and possible kidney damage. In observational occupational studies, MDA has been shown to cause liver damage (jaundice) in humans after oral or dermal exposure.⁶ Based on the finding of thyroid and liver tumors in both sexes of rats and mice, the National Toxicology Program (NTP) determined MDA to be a carcinogen.^{7,8} An epidemiological study of MDA-exposed workers has been conducted by NIOSH.⁹ Among these exposed workers, an excess of bladder cancer-related deaths over the expected proportion was found.

NIOSH considers MDA to be a suspect human carcinogen and recommends exposures be kept at the lowest feasible concentration.¹⁰ The OSHA PEL for MDA is 10 parts per billion (10 ppb) as an 8-hour TWA, or a STEL of 100 ppb.¹¹ 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 also considers MDA to be a suspect human carcinogen.

VITON®

Viton®, a fluorinated synthetic rubber manufactured by the Du Pont Company, is used in a variety of industrial applications as well as in personal protective equipment (such as gloves and aprons). Its physical appearance can be in the form of pellets, chips, and sheets. According to MSDS No. VIT006 supplied by Du Pont, Viton® has no hazardous components. While there are no OSHA PELs, NIOSH RELs, or ACGIH TLVs pertaining to Viton®, the Du Pont MSDS states that if Viton® is heated to temperatures above 600°F, decomposition products such as hydrogen fluoride (HF) and perfluoroolefins may be formed.

DERMATITIS

Skin rashes are the most commonly reported occupational illness. Approximately 95% are due to "contact dermatitis." This is a kind of rash that results from chemicals or other substances coming into direct contact with the skin. There are two major types of contact dermatitis, those caused by "irritants" and those caused by "allergens." An irritant is a substance, usually a chemical, that damages the skin at the point of contact. Any chemical, in sufficient concentration and under the right conditions, can cause irritation. An allergen is a substance, usually a chemical, that causes damage to the skin by inducing an "allergic reaction." Only certain chemicals are allergens, and only a small proportion of workers are susceptible to them.

Based on the results obtained from employee interviews and from analyses of air and bulk material samples, NIOSH investigators concluded that allergens were not responsible for the dermatitis problems

experience among DMO workers. For this reason, allergens are not discussed in further detail in this report. The following section, however, discusses irritants.

Irritants

An irritant is a substance, usually a chemical, that damages the skin at the point of contact. Almost any chemical, in sufficient concentration and under the right conditions, can cause irritation. "Strong irritants are intrinsically damaging, corrosive substances that rapidly injure anyone's skin immediately following contact. Mild (or moderate) irritants are less toxic substances that in normal usage cause irritation in only a small percentage of exposed persons."¹²

Workers are especially susceptible to irritants when their skin: (1) has lacerations (even small ones, into which irritant materials can enter), (2) is subject to friction (such as that which occurs when operating grinding machines and other equipment), and (3) is covered with clothing that has been contaminated with irritant chemicals. Working in environments in which there is excessive heat or low humidity also facilitates the development of rashes.

In irritant dermatitis, initially the skin turns red. Soon thereafter, small, oozing blisters and "bumps" appear. After several days, crusts and scales form. Stinging, burning, and itching may accompany the rash. If there is no further contact with the irritant, the rash disappears in 1-3 weeks. In chronic cases, workers develop hardening, discoloration, and cracking of the skin.

Exposed areas of the skin, such as hands and forearms, which have the greatest contact with irritant chemicals, are most commonly affected. The backs and sides of the fingers, hands, and forearms are especially susceptible. (Palms, which are protected by a particularly strong layer of skin, are usually spared.) If the irritant gets on clothing, it produces rashes at areas of greatest contact, such as the anterior thighs, upper back, armpits, and feet. Irritant dust produces rashes at areas where dust accumulates and is held in contact with the skin, such as under the collar and belt, at the tops of shoes, and in flexural areas (i.e., areas that bend, such as the front of the elbow and the back of the knee). Irritants may also be transferred to the genitalia (by the hands), and rashes may appear in areas that are not thoroughly cleaned, such as under rings and between fingers. Irritant dermatitis does not usually spread to parts of the body other than those in direct contact with the offending substance.

RESULTS

DMO AREA

Bulk Sample Analysis of Particulate to Measure Residual Methylenedianiline (DMO Area)

An analysis of the graphite composite bulk sample for residual MDA determined that the amount of MDA present was *less* than the limit of detection (LOD) for the method (the LOD is 0.8 parts per million [ppm]), expressed in a weight to weight (w/w) ratio. The limit of quantitation (LOQ) for this analysis was 2.4 ppm (w/w).

Polarized Light Microscopic Analysis to Determine Particulate Morphology (DMO Area)

A bulk sample of composite particulate was analyzed by polarized light microscopy (PLM) to determine dust morphology. The results indicated that the sample consisted mostly of black, opaque, elongated fibers that were likely graphite. The diameter was a very consistent 8 micrometers (varying by no more than 0.75 micrometers from particle to particle). The sides on undamaged fibers were smooth and parallel, while the terminations were somewhat pointed. The graphite fibers were embedded in parallel array in a matrix (the composite resin material). In one instance the texture of the matrix was serrated.

Phase Contrast Microscopic Analysis to Measure Airborne Fibers (DMO Area)

The results of seven personal breathing-zone (PBZ) and general area (GA) air samples collected in the DMO area and analyzed by phase contrast microscopy (PCM) are shown in Table 2. No airborne fibers were detected in any of these samples. The LOD and LOQ for this sample set were 7 fibers per square millimeter (f/mm²) and 100 f/mm², respectively.

Total and Respirable Particulate Sampling (DMO Area)

The results from the six PBZ and GA air samples collected for total and/or respirable particulate are shown in Table 3. The concentrations were very low, ranging from 0.01 to 0.06 mg/m³ for respirable particulate and from 0.07 to 0.17 mg/m³ for total particulate. All of these results were well below the OSHA PEL of 5 mg/m³ for respirable particulate and the Swedish exposure standard for composite dust of 3 mg/m³.

MEDICAL EVALUATION

Interviews conducted on March 14, 1989, with 31 employees identified by union officials as having experienced skin problems yielded the following information:

- < Some employees had histories consistent with possible work-related skin disorders.
- < The disorders consisted of pruritus (itching) and redness of the skin.
- < The parts of the body most commonly affected were the hands and arms. Some workers also experienced rashes on the ankles, legs, and back of the neck, and on the face around the edges of respirators. One worker related that, upon coming home from work, his children developed rashes when they sat in a chair that he had sat in while wearing his work clothes.
- < The rash-causing agent was suspected by the affected employees to be cured composite dust.
- < Some employees also complained that they frequently got splinters from handling cured composite, and that these splinters were difficult to remove.

The following observations were noted concerning personal protective equipment and barrier creams:

- < Some employees who wore gloves felt that they decreased the frequency of skin disorders. Most said that gloves were very difficult to use because they presented a safety hazard and because the nature of the work required employees to frequently "feel what they were working on." One person commented that thin surgical gloves were not practical because they ripped easily. Another person commented that composite dust "seemed to go right through" cloth gloves.
- < Some employees wore sleeves and paper overalls provided by the company and felt that they decreased the frequency of skin disorders. Most said that sleeves were a safety hazard, and that the composite dust penetrated the sleeves and overalls.
- < Barrier creams and moisturizing lotions were used infrequently.
- < Respirators were worn occasionally.
- < In general, the gloves, barrier creams, and lotions were not readily available.

DISCUSSION

DMO AREA

Industrial Hygiene

The results of the air sampling did not identify employee exposures which exceeded any NIOSH, OSHA, or ACGIH exposure criteria. For example, the particulate generated from the machining of cured PMR-15 composite parts did not contain any residual, unreacted MDA. This is consistent with the information provided by GE management that the amount of residual MDA in cured PMR-15 composites had been continually reduced, through manufacturing and quality control improvements, since this operation was first introduced in the Evendale plant. A morphological examination of the particulate generated by machining on composite components revealed that it contains carbon fibers of a somewhat uniform diameter (approximately 8 micrometers). This finding is consistent with other researchers who have found fibers from cured composite materials typically ranging in size from 7 to 8 micrometers in diameter.¹³ Only fibers with diameters of less than 3.5 micrometers are considered respirable (small enough to enter the lungs).¹⁴ Levels of total and respirable dust were well below the OSHA PELs for "nuisance" particulates. If compared to the more stringent Swedish composite dust standard of 3 mg/m³, the particulate levels in the DMO area on the day of sampling were still very low.

Perhaps of more significance are the remaining results obtained from the morphological examination of the composite particulate. The microscopic analysis revealed that the terminations of the individual fibers were often somewhat pointed. Additionally, in several particulate samples the matrix (the resin holding the fibrous composite together) had a serrated texture. These findings suggest that the sharp points and serrated edges observed on some of the fibers and the matrix could be capable of causing the skin irritation described by some DMO machinists.

The GE-SOP for machining cured composites in the DMO area is summarized in the adjacent chart.

Ventilation

A portable LEV system was available for use whenever composite parts were machined "dry" (without coolant). During this evaluation only one portable LEV system was located in the DMO area. According to DMO employees, there were occasions where several composite were machined at the same time. Under these circumstances dry machining of composite parts could be performed without the benefit of LEV.

SOP for Machining Cured Composites

Vacuum Used:

- ! Coolant is not be used.
- ! Personal protective devices such as face mask, protective clothing, etc., are optional.

Vacuum Not Used:

- ! Part must be flooded with coolant.
- ! Face mask (respirator) is mandatory.
- ! Personal protective equipment other than face mask is optional.
- ! Spray mist is not acceptable on cured composites.

Waste Cured Composites:

- ! Place in 55 gallon steel drum with plastic liner and label "waste cured composites."
- ! Drum is to be stored at Building 500 dump station near COL A-26.

Procedure for Securing Face Mask:

- ! Foreman will fill out form GT-9219 "Request for Respirator" for each employee.
- ! Send employee to dispensary for instruction on use of respirator and type (3M® 9920 dust-fume mask, IME crib # 2s420445). Nurse will sign form and give form back to employee.
- ! Employee then takes form to nearest crib to get respirators.
- ! Protective clothing and gloves are available from the DMO crib or facility crib.

Adjacent Areas:

- ! If personnel in areas adjacent to machining on cured composites are getting cured composite dust on them, they can get respirators or protective clothing.

Spot checks (using ventilation smoke tubes) of the portable LEV system on milling machines nos. 10189 and 19444 in the DMO area revealed excellent capture of particulate during machining operations. A panel fan (used for personal cooling) positioned near a horizontal boring machine (no. 10434), however, created very turbulent air which disrupted the LEV effectiveness on the machines in this area.

FLUOROELASTOMER REMOVAL OPERATION

Based on information contained in the MSDS provided by the Du Pont Company, along with description of the coating removal process provided by management and workers, it would appear that employee exposures during this activity would be minimal, assuming that the Viton® coating is not heated to above 200°C (392°F). According to Du Pont, hydrogen fluoride (HF) could be present as a decomposition product if Viton® is heated above 200°C without adequate ventilation. Since the actual removal operation was not observed during this survey, the company should conduct air monitoring to characterize exposures. The air sampling recommendations contained in this report were selected based on the possible decomposition products from heating Viton® and the possibility of removing metal (along with the Viton® coating) during sanding. This exposure assessment would document whether a respirator should be used by employees when removing the coating.

CONCLUSIONS

The morphological examination of the particulate generated during the machining of prototype composite aircraft engine components in the DMO area revealed individual fibers which were often somewhat pointed. In addition, these fibers were imbedded in a resin matrix which, in several instances, had a serrated texture. These findings suggest that the symptoms described by DMO employees could be a result of mechanical irritation to the skin and other surfaces exposed to the composite particulate.

Personal protective equipment in the DMO area, while generally available, was not always satisfactory. For example, according to some DMO employees, the cloth work gloves worn were not effective in preventing skin contact with the composite particulate. Barrier creams were used infrequently. Finally, some of the DMO workers stated that the composite dust penetrated the protective arm sleeves and coveralls provided by the company.

The portable LEV system used on some of the machines in the DMO area which handled composite parts appeared effective (based on a visual examination during this survey). However, the use of panel fans did reduce the effectiveness of the LEV in at least one instance.

RECOMMENDATIONS

GENERAL SAFETY AND HEALTH RECOMMENDATIONS

Appendix A contains information on the use of skin cleaners, protective clothing, and barrier creams. In addition, the following recommendations would be applicable in any situation where employees are handling materials which may cause skin irritation or sensitization.

1. Workers should be periodically educated about the effects of the chemicals which they work with and the types of work practices that will minimize their exposure to them.
2. Good factory housekeeping should be emphasized.
3. Any skin problem should be immediately reported to the medical department.

DMO AREA

1. Gloves should be worn at all times when handling or machining composite components to minimize skin contact with the potentially irritating particulate. Based on responses from the workers in the DMO area, cotton or cloth gloves were insufficient in protecting their skin from the graphite particulate. To increase the protection from the particulate, a nitrile-laminated fabric may be preferable. These gloves, available from a variety of manufacturers, are flexible, allowing employees to "feel their work."
2. Protective coveralls and sleeve protectors should be worn if particulate contamination on the clothing is determined to be a significant problem. During the employee interviews conducted by NIOSH in March 1989, one worker related that his children had developed rashes when they sat in a chair that he had sat in while wearing his work clothing. Disposable protective garments that "breathe", such as Comfort-Gard I® (manufactured by the Scott Paper Company), KleenGuard® (manufactured by Kimberly-Clark), and Durafab® (manufactured by Durafab), offer an effective, tear-resistant barrier against particulates and liquids.
3. The use of floor, wall, or ceiling-mounted panel fans (used primarily for operator comfort) should be discouraged since the air turbulence generated by these fans can reduce LEV effectiveness.
4. If dry machining on composite materials will involve more than one machine at a time, additional LEV systems should be purchased for the DMO area. An alternative to the portable LEV system currently in use would be to flood the composite part with synthetic coolant during machining to reduce dust levels.

FLUOROELASTOMER REMOVAL OPERATION

1. Based on information obtained during this evaluation, we recommend that GE conduct PBZ and GA air sampling for inorganic acids (specifically HF), metals, and both total and respirable particulate when Viton® is being removed with a grinder or sander. Although overexposures are not anticipated based on a description of this process, this monitoring would serve to objectively characterize worker exposures. The NIOSH Sampling and Analytical Methods appropriate for each sample category are as follows:
 - a. Inorganic acids (including hydrofluoric acid) by NIOSH Method No. 7903.
 - b. Metals (including nickel, chromium, and cobalt) by NIOSH Method No. 7300.
 - c. Respirable and/or total particulate by NIOSH Methods Nos. 0500 and 0600.
2. Based on the results from personal breathing-zone air samples collected during the Viton® removal operation, the requirement for the operator to wear a respirator while sanding or grinding on the fluoroelastomer coating can be reevaluated.

REFERENCES

1. CDC [1988]. NIOSH recommendations for occupational safety and health standards 1988. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health. MMWR 37 (supp. S-7).
2. Code of Federal Regulations [1989]. 29 CFR 1910.1000. Washington, DC: U.S. Government Printing Office, Federal Register.
3. ACGIH [1992]. Threshold limit values and biological exposure indices for 1992-1993. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
4. SACMA [1989]. Safe handling of advanced composite materials components: health information. Published by the Suppliers of Advanced Composite Materials Association, Arlington, VA.
5. Bourcier DR [1989]. Exposure evaluation of composite materials with emphasis on cured composite dust. Applied Industrial Hygiene (Special Issue), Cincinnati, OH. Vol. 12 (pp. 40-46).
6. Kopelman H, et al [1966]. The epping jaundice. British Journal of Medicine, Volume 1:514-516.
7. Lamb JC, et al [1986]. Carcinogenesis studies of 4,4'-methylenedianilinedihydrochloride given in drinking water to F344/N rats and B6C3F1 mice. Journal of Toxicology and Environmental Health, Vol. 18:325-337.
8. NTP [1986]. Toxicology and carcinogenesis studies of dichloromethane (methylene chloride)(CAS No. 75-09-2) in F344/N rats and B6C3F1 mice (inhalation studies). National Toxicology Program Technical Report No. 306.
9. NIOSH [1982]. Health hazard evaluation report no. 82-146-1388, Boeing Vertol Company, Philadelphia, PA. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health.

10. CDC [1992]. NIOSH recommendations for occupational safety and health: compendium of policy documents and statements. Atlanta, GA: 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. 92-100.
11. Code of Federal Regulation [1993]. 29 CFR 1910.1050. Methylenedianiline. Washington, DC: U.S. Department of Labor, Occupational Safety and Health Administration, U.S. Government Printing Office.
12. Adams R [1983]. Occupational skin diseases. Grune and Stratton, New York, New York.
13. Thomson SA [1989]. Toxicology of carbon fibers. Proceedings of the Conference on Occupational Health Aspects of Advanced Composite Technology in the Aerospace Industry 164-176. National Technical Information Service. Springfield, Virginia.

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Copies of this report have been sent to:

1. General Electric, Evendale, Ohio
2. UAW Local 647, Evendale, Ohio
3. IAM Local 912, Evendale, Ohio
4. OSHA Region V

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.

Table 1
Sampling and Analytical Methods
General Electric, Evendale, Ohio
HETA #89-0001

Sampling Method (NIOSH Method No. where applicable)	Collection Device	Sampling Flow Rate	Analytical Method	Comments
Fiber Count using Phase Contrast Microscopy (NIOSH Method No. 7400)	37 mm mixed cellulose-ester filters, 0.8 micron pore size	2.0 lpm	Analysis of filters by phase contrast microscopy (PCM) to count total fibers.	Sample preparation and analyses were done following procedures outlined in NIOSH Method No. 7400. A Zeiss PCM, with a magnification of 400X, was used.
Microscopic analysis of graphite composite particulate by Polarized Light Microscopy	Bulk sample of PMR-15 graphite composite dust obtained from the DMO area	Not Applicable	A portion of the dust was immersed in a Cargille liquid to enhance contrast and then mounted on a glass slide. No mechanical mixing of any kind was done so as not to alter the true particulate morphology. The dust samples were analyzed at a variety of magnifications and light types on an Olympus PLM.	Photomicrographs (in slide format) were made of the magnified images.
Determination of residual MDA from graphite composite particulate	Bulk sample of PMR-15 graphite composite dust obtained from the DMO area	Not Applicable	NIOSH Sampling and Analytical Method No. 5029 for MDA was modified to test for residual MDA in the particulate from the cured PMR-15 composite. The modification involved extracting the bulk samples with 8 mL of a 0.1 N methanolic sodium hydroxide. After agitation for 1 hour in a sonic bath, the samples were filtered and analyzed by HPLC.	The bulk samples of composite particulate were obtained from the DMO area following machining on PMR-15 composite parts.
Gravimetric analysis for total particulate (NIOSH Method No. 0500) and for respirable particulate (NIOSH Method No. 0600)	Tared, 37 mm PVC filters, 5 micron pore size	3.0 lpm (for total particulate) 1.7 lpm (for respirable particulate)	Gravimetric analysis for total particulate	

Abbreviations and Comments:

lpm = liters of air per minute	MDA = Methylene dianiline
DMO = Development Manufacturing Operations	PMR-15 = A polyamide resin-based graphite composite
PVC = Polyvinyl chloride	HPLC = High performance liquid chromatography

Source for analytical methods:

Eller PM, ed. [1989]. NIOSH manual of analytical methods. 3rd rev. ed. 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)

Table 2
Microscopic Analysis of Air Samples Collected in Development Manufacturing Operations
Plant: General Electric, Evendale, Ohio
Date: August 25, 1989
HETA #89-0001

Sample No.	Sampling Location	Sample Type	Sampling Period	Sampling Flow Rate	Particulate Loading	Fibers per square millimeter (f/mm ²)	General Comments																
25163	Operator of Machine No. 10420, Vertical Turret Lathe	PBZ	0756 to 1409	2.0 lpm	Moderate	ND	Operator was wearing a 3M Model 9920 Respirator																
25423	Area between columns A-22 and A-23	GA	0810 to 1443	2.0 lpm	Moderate	ND	General area sample																
25184	Operator of Machine No. 10434, Horizontal Boring Mill	PBZ	0817 to 1109	2.0 lpm	Moderate	ND	Operator was wearing a Tyvek® shirt and using a 3M 9920 respirator																
25195	Operator of Machine No. 10189, Milling Machine	PBZ	0836 to 0841	2.0 lpm	Extremely Light	ND	Counter boring one composite grommet pad. Operator using LEV at the point of dust generation.																
25197	Operator of Machine No. 10433, Horizontal Boring Mill (HBM)	PBZ	0907 to 1411	2.0 lpm	Light	Trace	Drilling and tapping on a composite aft case. Used "portable" LEV system with flexible exhaust duct.																
25153	Near column D-31, on top of storage cabinet near Machine No. 10433 (HBM)	GA	0857 to 1425	2.0 lpm	Moderate	ND	General area sample near the horizontal boring mill																
25164	Near column D-36, on top of work bench near Machine No. 10433 (HBM)	GA	0904 to 1422	2.0 lpm	Moderate	ND	General area sample near the horizontal boring mill																
Limit of Detection						7 fibers per mm ²																	
Limit of Quantitation						100 fibers per mm ²																	
<p>Abbreviations:</p> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%;">lpm = liters of air per minute</td> <td style="width: 10%;"></td> <td style="width: 10%;">PBZ =</td> <td style="width: 50%;">Personal breathing-zone air sample</td> </tr> <tr> <td>GA = General Area air sample</td> <td></td> <td>ND =</td> <td>Concentration below the minimum detectable concentration</td> </tr> <tr> <td>LEV = Local exhaust ventilation</td> <td></td> <td>Trace =</td> <td>Between the minimum detectable and minimum quantifiable concentrations</td> </tr> <tr> <td>mm² = square millimeter</td> <td></td> <td></td> <td></td> </tr> </table>								lpm = liters of air per minute		PBZ =	Personal breathing-zone air sample	GA = General Area air sample		ND =	Concentration below the minimum detectable concentration	LEV = Local exhaust ventilation		Trace =	Between the minimum detectable and minimum quantifiable concentrations	mm ² = square millimeter			
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APPENDIX A

Use of Skin Cleaners, Protective Clothing, and Barrier Creams

Skin Cleaners

Skin cleaners remove dirt, grease, and hazardous substances from the skin. Unfortunately, detergents in the cleaners can act as irritants. In addition, the cleaners sometimes contain mild abrasives and proteolytic enzymes which are added to improve cleaning and which can also act as irritants. "Following repeated use of skin cleaners, especially those with abrasive substances, the skin barrier may be broken down, leading to penetration through the epidermis of any potentially harmful substance that the worker may be using. This is the major cause of industrial irritant hand dermatitis and is a frequent background condition upon which contact allergic sensitization develops."¹ The backs of the hands and forearms (where the protective layers of the skin are relatively thin compared to that of the palm) are particularly susceptible to irritant dermatitis. Cleaners that contain abrasives are best used on the palm and even there, sparingly.

Waterless hand cleaners are skin cleaners that work without water. They are formulated to remove difficult oil and grease stains that can not be easily removed with ordinary cleaners. The cleansing agent in a waterless hand cleaner can be a solvent, an organic amine or an anionic detergent. Some of these agents can be irritating. Solvent-containing products are the most irritating. Those which contain anionic detergents are less irritating. In general, waterless hand cleaners are less irritating to the skin than cleaners that contain abrasives. However, those that contain solvents should be used sparingly during the day and after use, the potentially irritating residual film should be washed off with mild soap and water. Waterless hand cleaners must be removed from the skin after use. If towels are used to remove these waterless cleaners, they may contain significant amounts of irritating materials by the end of a shift. Thus, towels should be replaced at frequent intervals; better still, disposable towels should be provided.

The following general rules are appropriate for many occupational exposures.²

- < Use the mildest soap for skin cleansing which will do the job.
- < Use waterless hand cleaners instead of abrasive soaps for removing difficult oil and grease stains on the backs of hands and forearms.
- < Use abrasive soaps only for removing difficult oil and grease stains on palmar skin.
- < Use waterless cleaners and abrasive soaps sparingly and only when necessary. Do not, however, use them on inflamed skin.
- < Wash the residual film of waterless hand cleaner off the skin with mild soap and water.
- < Use a skin moisturizer after contact with soap or detergent, particularly if frequent hand washing or contact with industrial detergent is unavoidable. This will help combat the skin-drying effect of the detergent.

Protective Clothing

Manufacturers of protective clothing provide guidelines for selection of materials for various types of exposure. However, these recommendations are qualitative and imprecise and almost never indicate the criteria upon which the evaluations were made. For example, aprons should cover the front of the body (to below the knees), be washable and lightweight, have heat-sealed seams without cloth stitching, and contain a trough at the base to prevent spillage onto footwear. They may need to be laundered daily.

Leather and canvas gloves can be used for handling dry materials. (Liquids make leather slippery and cause it to deteriorate.) Rubber and plastic gloves -- which come in surgical, household, and industrial varieties -- can be used for liquids. Natural rubber gloves can be made out of latex that contains isoprene and several additives. Synthetic rubber gloves may be made out of butyl rubber, neoprene, fluorocarbon rubber (such as Viton®), nitrile rubber, and styrene

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butadiene rubber. Plastic gloves may be made out of ethylene methyl acrylate, ethylene vinylacetate, polyethylene, polyvinyl alcohol, and polyvinyl chloride.

There is a great variation in the resistance of these gloves to specific chemicals. In addition, there can be significant differences in performance between glove materials of the same nominal composition from different manufacturers.³ As with other types of personal protective equipment, maintaining a variety of sizes and models improves the selection, fit, protection, and comfort afforded workers.

In general, gloves should cover at least one-third of the forearm and fit snugly. Rubber and plastic gloves should be lined with cloth or another sweat-absorbing material. If they are worn for an entire shift, they should periodically be taken off to allow the skin to "breathe." This is especially true for finger cots, which are very occlusive. Surgical gloves should not be worn more than once and other gloves should be replaced if they become torn or if the insides become contaminated. (Insides can become contaminated if workers allow their bare hands to contact the substances they are working with and then place their hands inside clean gloves. This can be avoided by **always** wearing gloves when dealing with potentially hazardous agents.)

It should be noted that gloves can sometimes **cause** skin problems, such as itching, excessive sweating, and rashes. Possible causes for this include allergenic substances in the glove material, powder and linings, and occlusion effects.

Sleeves should cover the entire arm, including the wrist, and should be worn over the tops of gloves, rather than being tucked into them. Like aprons, they may need to be laundered daily.

Barrier Creams

Barrier creams are creams applied to the skin to protect it from hazardous substances. They are used when gloves or other protective clothing can not be safely or conveniently utilized. Barrier creams are either nonspecific (i.e., broad-purpose) preparations or specific chemical neutralizers. The nonspecific preparations include vanishing creams, water-repellent creams, oil/solvent-repellent creams, and ionic exchangers.

Vanishing creams are somewhat effective against dust, glass fibers, and heavy oils, but not against water-soluble substances, many oils, and solvents. Water-repellent creams offer protection against water-soluble substances, acids, alkalis, soaps and detergents, but not against oils or solvents. A major problem with them, however, is that they are very greasy and slippery. Oil/solvent-repellent creams are useful against dusts, oils, solvents, and resins. Unfortunately, since they are water soluble, they tend to come off with perspiration.

The primary question is whether barrier creams can prevent or decrease the incidence of skin disease when used under working conditions. Unfortunately, the answer to this question is still unknown in most instances and, in fact, many barrier creams evaluated have not demonstrated substantial efficacy.⁴ In addition, barrier creams provide a false sense of security, trap hazardous chemicals on the skin and/or increase their penetration, and may contain preservatives, fragrances, soaps, and other substances that may be irritants or allergens in some individuals.⁴

1. Adams R [1983]. Occupational skin diseases. Grune and Stratton, New York, New York.
2. Mathias CGT [1986]. Contact dermatitis from use or misuse of soaps, detergents, and cleansers in the workplace. Occupational Medicine: State of the Art Reviews, Vol. 1(2):205-218.
3. Tewari J [1980]. Differences in the extent of solvent penetration through natural rubber and nitrile gloves from various manufacturers. American Industrial Hygiene Journal 41:527-528. Akron, Ohio.
4. Orchard S [1984]. Barrier creams. Dermatologic Clinics, Vol. 2(4):619-629.