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## **Composite Fiber Hazards**

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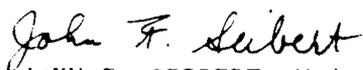
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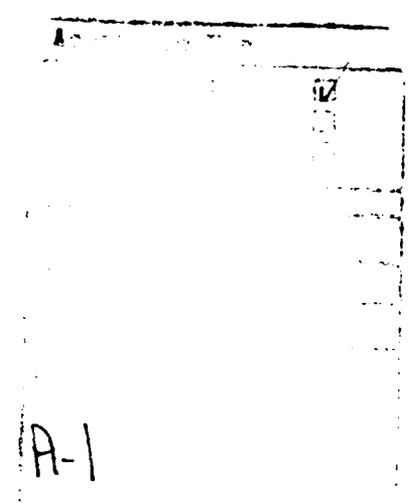
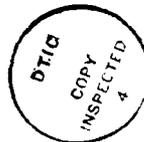
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## I. INTRODUCTION

A. Purpose: This report reviews potential health hazards from carbon/graphite and boron composite materials used in aircraft. While not including all available information on the topic, it serves as a basic introduction to composite materials.

B. Problem: Carbon and boron fibers are used as reinforcement in an epoxy matrix to form composite material aircraft parts. There is increasing concern over the potential health effects of these fibers released during sanding and grinding of composite parts in structural repair shops, and during clean up operations following aircraft accidents involving fire and/or breakage of composite parts.

C. Scope: Because of the improved performance of fiber-reinforced composite materials, their use in aircraft structures is increasing. Carbon/graphite fibers have been used in the Air Force F-15, F-16, F-117; and the Navy F-14, F-18, and AV-8B. Carbon/graphite is expected to be used in the B-2, V-22, C-17, ATF, and the Navy V-12 and ATA (A-12). Boron fibers have been used in the FB-111, F-15 and B-1B. Aircraft already containing large amounts of composite materials, such as the F-16, are being purchased in larger quantities for use in the Air Force Reserve and Air National Guard. Future aircraft are expected to use increasing quantities of carbon composites. With increased potential for exposure to composite materials, more personnel have become concerned with the potential health hazards from the fibers used in composites.

## II. DISCUSSION

A. Uses of Composites: Composite materials are used in aircraft manufacturing because they have a higher strength to weight ratio than metal components. Composites are composed of an epoxy resin matrix with a high strength fiber reinforcement. The most common composite material in civilian use is fiberglass (an epoxy or styrene resin matrix with glass fibers used as reinforcement). In military aircraft, fiberglass is used for low stress parts. Carbon and boron composites (epoxy resins reinforced with carbon or boron fibers) are being used more frequently. Kevlar fibers have also been used as a reinforcement fiber similar to carbon fiber.

1. Manufacturing: Carbon and boron composite parts are manufactured by laying "prepreg" tape or sheet on a mold. "Prepreg" tape has fibers oriented in a preselected pattern and is preimpregnated with the resin matrix. Additional layers of prepreg are added until the desired thickness and strength are achieved. Fiber laydown patterns are designed to give strength to the part in the direction of anticipated stress. The cured part is removed from the mold and machined with grinders, sanders and drills to prepare the part for mounting on the aircraft.

2. Maintenance: When carbon and boron composites crack or delaminate, the affected area is completely removed by grinding and sanding. New layers of fiber and epoxy are layered into the defective area, using the original manufacturing methods.

B. Toxicology of Fibers: The disease-producing potential associated with exposure to the fiber component of composite materials is a function of three major determinants: a) the dose, or amount of fiber deposited in the lung, b) physical dimension of deposited fibers, and c) fiber durability (lifetime) in the lung.

1. Particles with an Aerodynamic Equivalent Diameter (AED) above 10 micrometers ( $\mu\text{m}$ ) are considered "nonrespirable." They will impact in the nose, throat or tracheo-bronchiole tree, but will not deposit in the pulmonary gas exchange region. The AED of fibers are calculated from the formula:

$$D_e = D_f V_p (0.7 + 0.91 \ln \beta)^{1/2}$$

where:  $D_e$  = Aerodynamic Equivalent Diameter (AED) by sedimentation  
 $D_f$  = physical diameter of the fiber  
 $\rho_f$  = fiber material density  
 $\beta$  = ratio of fiber length to width (aspect ratio)

2. Fiber Dimension: Fibers in excess of 8  $\mu\text{m}$  in length and diameters less than 1.5  $\mu\text{m}$  have the greatest biological activity after deposited in the tissue. Animal experiments have consistently supported this "long, thin" hypothesis for development of malignant fibrous neoplasms.

3. Biological Durability: Fibers deposited in the lung may be rendered harmless through a) dissolving of the fiber in body fluids with no toxic end products, or b) changing the dimensions of the fiber (especially the length) such that normal clearance mechanisms can effectively remove it. Information on this subject in the scientific literature is lacking.

### C. Carbon and Graphite Fiber:

1. Background: Carbon and graphite fibers are man-made fibers of high carbon content formed from an organic precursor.(1,2) The terms "carbon fiber" and "graphite fiber" have been used to describe carbon fibers. In the strict sense, they are not the same material. Carbon and graphite fibers are manufactured similarly, except that carbon fibers are formed by heat treatment at 1000-1300°C and graphite fibers are heat treated at up to 3000°C. Graphite fibers are stronger, but more brittle, and are harder to bond to the epoxy matrix. As a result, graphite fibers are rarely used in composite aircraft parts. Carbon fibers are chemically inert (except with oxidants), heat resistant, have a low coefficient of expansion under changing temperatures, high electrical conductivity and high tensile strength. The carbon fibers manufactured for use in composites have a uniform diameter of 6 - 8  $\mu\text{m}$  and a semi-crystalline structure.

2. Respiratory Effects During Maintenance Activities: Research on potential respiratory effects of carbon fibers have centered in two areas: effects of the fibers based on their fiber shape, and effects of the nonfibrous carbon fragments based on their chemical composition.

a. Fiber Shape: The assumption is made that any fibers that have the same physical shape as asbestos will give the same effect. The focus is on fibers that are long and thin, with optimum effects expected from fibers 8  $\mu\text{m}$  long and 0.25  $\mu\text{m}$  in diameter (long & thin). These fibers are both

respirable and hard to clear from the alveoli. On the other hand, carbon fibers used in composite materials have a fiber diameter of 7.0  $\mu\text{m}$  and density of 1.8  $\text{mg}/\text{cm}^3$ . Assuming a minimum fiber length to width (aspect) ratio of 3:1, carbon fibers have a 12  $\mu\text{m}$  or greater AED and are considered non-respirable. They are caught in the throat and nose, with few making it to the alveoli. Only if they split lengthwise could they become thinner respirable fibers. During grinding on carbon fiber composites, most of the fibers fragment into a nonfibrous dust. Of those particles retaining a fibrous shape (length:width aspect ratio of  $>3:1$ ), only about 1% fulfill the "long & thin" criteria. Similarly, grinding on fiberglass composites also produces large quantities of nonfibrous glass dust, with  $<1\%$  of fiber shaped particles being long and thin. During burning of carbon composites, such as in aircraft crashes, it is much more likely that the fibers will become thinner (by splitting or by thinning out from the fire) and still remain long enough to be "long & thin" fibers. Therefore, during normal maintenance procedures, very few fibers of health concern are produced.

(1) Holt and Horne generated carbon fiber dust for animal exposure studies by feeding a polyacrylonitrile (PAN) based carbon fiber into a hammer mill.(3) Air samples were collected from the animal chamber and examined under a light microscope. Particle counts gave a concentration for nonfibrous particles of 370 particles/ $\text{cm}^3$ , for "black fibres" (probably carbon) of 2.9 fibers/ $\text{cm}^3$ , and for transparent fibers of 1.6 fibers/ $\text{cm}^3$ . Size distributions were not given, but Holt described four types of particles in the sample:

- (a) Non-respirable fibers with diameter 10 $\mu\text{m}$  and length  $>100 \mu\text{m}$ .
- (b) Nonfibrous particles with diameters from submicron to several microns.
- (c) Black fibers of diameter 1.0 - 2.5  $\mu\text{m}$ , and length up to 15  $\mu\text{m}$ .
- (d) Transparent fibers, typically 1.5  $\mu\text{m}$  diameter, up to 30  $\mu\text{m}$  long.

(2) Jones, et al., surveyed a "carbon fiber" continuous filament production facility to determine worker exposure to carbon fibers.(4) (They were probably graphite fibers, since the production process included temperatures up to 3000°C.) Air samples for dust were collected as "total dust" and "respirable dust" (using an elutriator with cutoff at 7  $\mu\text{m}$  Aerodynamic Equivalent Diameter), and were examined under a light microscope. None of the air samples indicated longitudinal fracturing of fibers. In the fiber production and winding area, dust samples contained carbon fibers of the parent diameter (8-10  $\mu\text{m}$ ), with some smaller particles suspected to be sizing material. Dust levels were higher in the laboratory, because carbon fiber-reinforced resins were being cut, ground and milled. Dust levels ranged from 0.08 - 0.39  $\text{mg}/\text{m}^3$  for total dust, and 0.03 - 0.16  $\text{mg}/\text{m}^3$  respirable dust.

(3) Mazumder, et al.,(5) collected air samples while grinding carbon composites, and chopping and grinding bundles of non-laminated carbon fibers inside of a 340-liter glove box. Dust from grinding of carbon

composites gave some free fibers, while other fibers were still bound to the epoxy. Epoxy was removed for detailed examination of the fibers by evaporating the epoxy at 400°C. Fibers were then examined under scanning electron microscope. Fibers underwent longitudinal splitting, leading to some fibrous fragments having diameters less than that of the parent fiber. The frequency distribution of fiber diameters was not given, but of the fibers with aspect ratio of 3 or greater, 52% were of reduced diameter. Of the reduced diameter fibers, only 3% had an aspect ratio greater than 8:1. Air samples from chopping parent carbon fibers were fed to a single-particle aerodynamic relaxation time (SPART) analyzer, giving a Mass Median Aerodynamic Diameter (MMAD) of 4.0 µm. Similar analysis of grinding of composites gave a MMAD of 2.7 µm. Microscopy was not performed to give relative ratios of fibrous to nonfibrous material. Mazumder stated that his results should be applicable to most commercially available carbon fiber types. He analyzed 6 types of carbon fiber from 4 manufacturers, finding parent fiber diameters in the range of 5.8 - 8.0 µm, and densities of 1.72 - 1.83 g/cm<sup>3</sup>.

(4) Eastes(6) collected air samples during cutting and grinding operations on a "graphite" fiber composite wing panel, and evaluated the samples with phase contrast microscopy. Of the 10 fibers selected for sizing, all graphite fibers had the diameter of the starting material (6.6 µm), with some binder material still attached. Some translucent fibers of smaller diameter were noted, but were attributed to being binder (epoxy) or fiberglass material. Three short-term (10-16 min) breathing zone samples showed graphite fiber levels of 0.4 to 4.6 fibers/cm<sup>3</sup>, and total fiber levels of 1.7 - 7.8 fibers/cm<sup>3</sup>. Non-fiber particulate counts were 2 - 180 particles/cm<sup>3</sup>. Eastes concluded that airborne graphite fibers did not pose a health problem, since 80% of the graphite fibers were non-respirable.

(5) Zustra(7) collected air samples during sanding and grinding of U.S. Coast Guard helicopter panels made up of PAN-based carbon fibers. He found airborne carbon fiber levels to be <0.07 fibers/cc, and total composite dust levels ranged from 1.25 to 2.81 mg/m<sup>3</sup>. Higher levels were reached when performing a simulated "worst case" sanding operation inside a 1.2m x 0.6m x 1.5m plexiglass chamber: fiber levels ranged from zero to 0.5 fibers/cc, and total dust levels were in the range of 31.9 to 96.6 mg/m<sup>3</sup>.

(6) A report from the U.S. EPA(8) stated that sawing with a hacksaw and drilling with carbide-tipped drills generated dust that contained large quantities of fibers about 50 -100 µm long and free of epoxy resin. Some longitudinal cleavage of fibers was found, with resulting fibers having diameters less than that of the 6 - 8 µm diameter parent fiber.

(7) Seibert(9) milled PAN-based carbon fibers and glass fibers in a ball mill to determine the potential for longitudinal splitting. He found a preponderance of nonfibrous carbon particles, with some fibers of reduced diameter. The smaller diameter fibers had low aspect ratios, with no fibers exceeding an aspect ratio of 10:1. Ground glass fibers gave similar results, with a preponderance of nonfibrous particles and smaller fibers of low aspect ratio.

b. Chemical Composition: The concern over the properties of the nonfibrous carbon dust centers on the polycyclic aromatic hydrocarbon (PAH) content of the original fibers. PAH's remain in the fiber (about 5% by

weight) as a byproduct of fiber production. Some have theorized that the PAH's can be desorbed by body fluids after the particles have deposited in the lungs. In this sense, carbon fiber fragments should have the same health effects as carbon black, since carbon black also contains about 5% PAH's as a byproduct of production. However, studies of PAH desorption from carbon fiber fragments have been aggressive studies, using benzene to extract the PAH's. Also, previous epidemiological studies that demonstrated health effects from carbon black did not take into account cigarette smoking or carbon monoxide exposure. The most recent studies on carbon black have recommended that it be treated as a nuisance particulate.

### 3. Potential Hazards Following Fires:

a. Mazumder, et.al., heated the dust from grinding carbon composites and found that at temperatures above 400°C the epoxy matrix begins to vaporize and release the fibers.(5) At temperatures above 850°C, carbon fibers begin to oxidize and become thinner, resulting in fibers of reduced diameter.

b. A report from the U.S. EPA stated that incineration of a carbon fiber/epoxy resin composite in a furnace at temperatures up to 1000°C destroyed the epoxy resin.(8) The fibers were left intact, with definite signs of pitting and thinning.

c. Zumwalde and Harmison performed a NIOSH review of available information on carbon fiber as of 1980.(10) The National Aeronautics and Space Administration (NASA) had performed a series of tests to determine the quantity and type of airborne carbon fibers generated from the burning of carbon fiber composites in an airplane crash. In a simulated aircraft fire, between 0.75% and 3.5% of the original fiber mass was released as single airborne fibers. The remaining fiber mass was consumed in the fire or remained in place. Airborne fibers averaged 2-3 mm long and 4-5 µm in diameter. A later analysis under different conditions gave average fiber diameters of 1.5 µm, and average length of 30 µm. It was concluded that heating the fibers reduces fiber diameter by partial oxidation and fibrillation (spitting). It was estimated that following an aircraft crash, in which carbon fiber composites burned, there would be a release of  $5 \times 10^{11}$  fibers (<3 µm diameter, >8 µm long) per kilogram of carbon fiber released. Air sampling in the smoke plume during a test burn showed fiber concentrations ranging from none detected to 0.14 fibers/cm<sup>3</sup>. All fibers were at least 5 µm in length, and 77% of the fibers were no more than 1.7 µm in diameter. The author concluded that, based on a lack of adequate toxicological data on carbon fiber, that it be treated and evaluated in the same manner as fibrous glass.

d. Air samples were collected following the 1988 crash of a McDonnell-Douglas AV-8B Harrier II at the Marine Corps Air Station, Cherry Point NC by Lt Formisano, U.S. Navy industrial hygienist.(11) Samples were collected using 25 mm cassettes with 0.8 µm mixed cellulose ester (MCE) filters and electrostatic extension cowls. Total fiber counts for breathing zones of workers cleaning up and moving burned carbon composites parts were between 0.2 and 3 fibers/cm<sup>3</sup> as an 8-hour time weighted average (TWA). Peak fiber levels as high as 6 fibers/cm<sup>3</sup> were noted. Fiber sizing was not performed to determine fiber diameter or respirability of fibers.

e. Following a Navy F-18 crash in a remote location, two of four individuals at the crash site complained of markedly reduced exercise capacity several days after the crash.(12) Medical examination of one individual showed an abnormal one second forced expiratory volume (FEV-1) which returned to normal after five months; reduced exercise capability; and a positive histamine challenge test. The investigator concluded that exposure to pyrolysis debris (i.e., cadmium fume condensed onto pyrolyzed graphite) can heighten airway reactivity in susceptible individuals. He recommended wearing SCBA during firefighting, and dust/fume respirators for follow on personnel.

4. Skin Effects: Carbon fiber appears to be similar to fibrous glass in causing physical irritation to the skin following rubbing of the fibers or composite material on the skin. The ability to irritate increases with increasing fiber diameter. Carbon fiber fragments splinter and easily become embedded in the skin. These splinters are hard to remove since they crumble easily when grasped with a tweezers.

#### D. Boron Fiber

1. Background: Boron fibers used in aircraft composites are formed as a boron coating on a tungsten core. Following heat treating, the boron combines with the tungsten. The resulting fibers are 100  $\mu\text{m}$  or 140  $\mu\text{m}$  in diameter of boron on a tungsten boride core, and appear more like fine wires than fibers. The fibers are combined with an epoxy matrix to form a prepreg tape (50% fiber, 50% epoxy by weight) used for composite lay-up operations.

2. Uses: Boron composites are used in aircraft parts requiring a high degree of stiffness. They have been used in the F-15 in the wing skin, horizontal stabilizer, vertical stabilizer and rudder. However, when these composite parts require repair, they can be replaced by carbon composites. Boron composite reinforcing tape is bonded to the side of the titanium dorsal longeron (structural element connecting the tail to the fuselage) as a stiffener for the B-1B bomber.

3. Health Hazard: When boron composites are machined, the boron fibers fragment into sharp needle shaped objects.(18) These pose a severe skin puncture hazard. Maintenance workers have expressed concerns over the possibility of fragments entering the blood stream and damaging the heart, lungs and liver.(19) There is no evidence to support this hypothesis. A respiratory hazard from boron fibers is not expected based on the nonrespirable size of the initial fibers and their fragments.

#### E. Other Fiber Types:

1. Glass: Glass fibers have been used and continue to be used as the reinforcing fiber in "fiberglass" composite panels. Matrix materials commonly used include polystyrene, epoxy and phenol/formaldehyde. The glass fibers used in composites are of uniform diameter of 6 - 8  $\mu\text{m}$ . Research by Seibert indicates glass fibers would break transversely into nonfibrous particles from machining of fiberglass composites.(9)

2. Kevlar: Kevlar<sup>R</sup>, a DuPont product has been investigated as a possible substitute for carbon fiber in aircraft composites. While initially

thought capable of completely replacing carbon, Kevlar's ability to wick water and delaminate the composite layers limits its use to special applications. Kevlar fibers have a uniform 12  $\mu\text{m}$  diameter, with a fibril substructure down to 0.1  $\mu\text{m}$ . Workplace air sampling by DuPont show Kevlar composites being machined will produce respirable size fibrils that carry significant static charge and clump together.(20) Air samples have shown levels  $<0.3$  fibrils/ $\text{cm}^3$  for all operations and typically  $<0.2$  fibrils/ $\text{cm}^3$  during machining. Some workers report itching at the wrists from accumulated Kevlar dust. Toxicological testing shows no potential for chemical sensitization. Inhalation testing with nonfibrous polymer particles indicate a lung reaction typical of "nuisance dust". Inhalation testing in rats at 285 f/ $\text{cm}^3$ , 6 hours/day, 5 days/week for 2 weeks showed lung fibrosis that shrunk when exposure was stopped. DuPont recommends an Acceptable Exposure Level (AEL) of 5 f/ $\text{cm}^3$  for an 8-hour TWA. DuPont also recommends various measures to minimize mechanical irritation caused by the fibers: nuisance dust mask, exhaust ventilation for individual operations, washing clothes regularly, showering after work, and wearing clothing with loose cuffs and collars.

#### F. Resin Matrix

1. Types: Although epoxy resin systems are the most common in aircraft composites, other thermosetting resins under investigation or use include polyester, polystyrene, phenolic, silicon and polyimide. Resin systems include a monomer as the basic building block, a curing agent (hardener) which connect the monomers to form long chained molecules, and various additives for the desired physical characteristics (hardness, color, etc.). Curing agents providing the most significant health effects include 4,4'-methylene dianiline (MDA), metaphenylene diamine, and the anhydrides. These agents are sensitizers and irritants. Substantially different from thermosetting plastics are the thermoplastic matrix materials currently under investigation for future aircraft composites. Thermoplastics are fully reacted, and are formed into composite parts by heating until they "flow" into the desired shape. They require no refrigeration, are more damage resistant, and damage can be repaired by heating and reforming to the necessary shape.

2. Usage: The choice of matrix system is based on its ability to adhere to the fibers, final cured strength, brittleness, temperature limits and other physical characteristics. After components are mixed together, epoxy systems transition through liquid, gel and solid stages ("A", "B" and "C" stages) while solidifying and curing. Composite suppliers provide "prepreg tapes" of unidirectional carbon fiber mats preimpregnated with epoxy. Prepreg tapes for carbon composites typically contain "B" stage epoxy that has partially cured and then frozen to halt further curing. The composite part must be heat cured to allow the epoxy matrix to fully react to its final state. Other information on resin systems is available in the pamphlet "Safe Handling of Advanced Composite Materials Components" from the Suppliers of Advanced Composite Materials Association (SACMA).(21)

3. Toxicology: The majority of the hazards associated with epoxy resins, curing agents, and the resultant composite materials involve manufacturing-type processes. Hazards associated with maintenance operations on Air Force bases include respiratory, skin, and eye exposure to epoxy liquids, epoxy vapors and binder agents. Prepregs contain  $<2\%$  solvents, are corrosive to the skin, eyes and mucous membranes, and can induce allergic

dermatitis. Potential outcomes include possible tumorigenesis, pulmonary irritation, eye irritation, skin irritation, and skin or systemic sensitization. The hazards of epoxy systems can, at best, be generalized unless the epoxy resins, binders, other additives, and fiber combinations are known. The Material Safety Data Sheet (MSDS) should be thoroughly reviewed to determine components that can cause irritation and sensitization.

4. Exposure Potential: During machining, sawing, and grinding operations, composite materials (carbon, graphite, and/or fiberglass fibers plus epoxy binders) may release particles coated with residues of binder chemicals which may vaporize and generate condensation aerosols. Research by Boatman, et al. has concluded that such dusts contained only small amounts of volatilizable chemicals.(22) Findings did not indicate a need for an occupational health standard more restrictive than the present nuisance dust standard. The authors are accomplishing a second phase of this study to examine the biological responses to the mixtures represented by these dusts.

5. Skin Effects: Skin irritation as well as skin sensitization has been frequently reported by workers in the composite materials industry. The most frequent problem experienced is direct skin contact with prepreg materials causing contact dermatitis. Protective gloves have successfully prevented dermatitis.

6. Liver Effects: An epoxy resin accelerator receiving special attention by McDonnell-Douglas Corp industrial hygienists is 4,4'-methylenedianiline (MDA).(23) Air sampling for combined levels of vapors and aerosol borne MDA during spraying of MDA-containing material in a spray booth gave levels in the 5 ppb range. MDA at levels below 5 ppb were also measured during cutting, trimming and hand lay up of composites. Skin absorption is also possible with MDA, and McDonnell-Douglas recommends protective gloves be worn when working with MDA containing materials. They have worked with glove manufacturers to produce a rubber coated cotton glove that is talc free and has less than 0.01 mg/in<sup>2</sup> of silicon and free hydrocarbons on the surface. This glove protects the workers' hands while not leaving a residue on the composites that could cause delamination.

7. Other Manufacturer Experiences: Boeing Aircraft composite workers complained of a variety of symptoms after starting work with a phenol/formaldehyde resin system.(25) The resin system gave off a strong unpleasant odor. Air sampling for phenol and formaldehyde by the industrial hygienist and NIOSH investigators showed levels well below the PEL. However, composite workers did not wear protective gloves, and cases of skin irritation were found. As complicating factors, management was behind schedule in producing the composite parts and composite workers were working seven days per week with one or two days off per month in a hot, poorly ventilated area. An investigation by a panel of physicians using a diagnostic interview schedule indicated over one-third of the workers had historical symptoms of skin or respiratory tract irritation related to work with the resin system. The majority of workers had symptoms related to sensory irritation (headache or mild nausea). Also, 73% of the workers examined met medical criteria for a diagnosis of anxiety (panic disorder) and depression. The physicians concluded "It is not clear whether the high prevalence of anxiety and depression seen in these workers is due to very low-level exposure to phenol, formaldehyde or organic solvents and associated sensory irritation of the

respiratory tract. It is possible that other sociological factors (such as fear, distrust, misinformation from health care providers, group interaction, attorney/media involvement, or labor-management problems) are playing a major role in producing or exacerbating these workers' symptoms...." Worker complaints subsided when Boeing switched to a polyester resin system.

## G. Standards

### 1. Fibers and Dust

a. ACGIH TLV: ACGIH does not have a TLV for carbon or glass fibers based on counting fibers. The TLV-TWA for nuisance particulates is  $10 \text{ mg/m}^3$ , for fibrous glass dust is  $10 \text{ mg/m}^3$ , and for carbon black is  $3.5 \text{ mg/m}^3$ .(13) While the sampling method for carbon black samples for "total dust," carbon black is completely respirable with all particle physical diameters less than  $0.6 \text{ }\mu\text{m}$ .(14)

b. OSHA PEL: OSHA does not have a separate standard for carbon or glass fibers. The 8-hour TWA PEL for inert or nuisance dust is  $15 \text{ mg/m}^3$  total dust, and  $5 \text{ mg/m}^3$  respirable dust.(15) The 8-hour TWA PEL for carbon black is  $3.5 \text{ mg/m}^3$ .

c. NIOSH: NIOSH gives a 8-hour TWA Recommended Exposure Limit (REL) for fibrous glass of 3 fibers/ $\text{cm}^3$  for fibers with length  $>10 \text{ }\mu\text{m}$  and diameter  $<3.5 \text{ }\mu\text{m}$ , and total fibrous glass dust of  $5 \text{ mg/m}^3$ .(16) NIOSH also recommends that the fibrous glass RELs be applied to other man-made mineral fibers until more information is available.

d. U.S. NAVY: The Navy has developed a PEL for carbon fibers of 3 fibers/ $\text{cm}^3$  for a 40-hour TWA with a ceiling limit of 10 fibers/ $\text{cm}^3$ .(14) Only fibers with length  $<10 \text{ }\mu\text{m}$  and diameter  $>3.5 \text{ }\mu\text{m}$  are counted (same as the NIOSH counting rules). The Navy PEL for total carbon fiber dust is  $3.5 \text{ mg/m}^3$  8-hour TWA, and  $7 \text{ mg/m}^3$  as a 15-minute STEL. In its analysis of potential hazards from carbon fiber, it considers the fibrous particles to be of similar hazard to fibrous glass, and the nonfibrous particles similar to carbon black.

e. U.S. Air Force: The Air Force does not have an AFOSH standard or policy regarding carbon fibers, glass fibers or carbon black. Carbon and glass fiber is considered a nuisance dust, and the ACGIH TLV-TWA of  $10 \text{ mg/m}^3$  is used.

2. Resin Matrix Systems: Material Safety Data Sheets (MSDSs) for each resin system must be reviewed to determine the chemical components and corresponding limits for each component. One component receiving recent attention is 4,4' methylenedianiline (MDA). OSHA has proposed an 8-hour TWA PEL for MDA of 10 parts per billion (ppb), and a 15-minute short-term exposure limit (STEL) of 100 ppb.(24) This PEL is designed to protect against suspected carcinogenicity in humans. Samples are collected on a sulfuric acid treated glass fiber filter and analyzed for total MDA.

## H. Policies & Procedures

### 1. Composite Manufacture or Maintenance

a. U.S. Air Force: USAF maintenance technical orders (T.O. 1F-16A-3-1, and T.O. 1-1-690, General Advanced Composite Repair Processes Manual) currently warn composite repair personnel to wear protective gloves when handling damaged graphite epoxy parts, to wear eye protection during drilling and to wear goggles, gloves and respirator when using solvents.

b. U.S. Navy: If airborne levels of dust exceed the PEL, and the dust is respirable, air purifying respirators with HEPA filters or positive pressure respirators are required. Local exhaust ventilation is required for all operations generating vapors and dust. Frequent vacuuming of the area with a HEPA vacuum is required. Dry sweeping and blowing with compressed air is forbidden. No smoking, eating or drinking is allowed in the work area; and hands and face must be washed prior to eating and at the end of the work shift. Waste composites and dust are double bagged, labeled as containing graphite/epoxy with skin and eye irritation resulting from contact, and disposed of as hazardous waste.

2. CORKER: In the late 1970s, the Air Force identified a potential electrical shorting hazard from airborne carbon fibers as a result of aircraft accidents involving burning of composite materials under the project name "CORKER." This hazard was identified after a manufacturer burned waste carbon composites in an incinerator, causing a nearby electrical substation to short out. The MITRE Corporation studied the potential further under project "HAVE NAME," concluding the potential for shorting out critical equipment on a typical air base to be insignificant.(26,27) HAVE NAME also concluded that a fire involving composites in tight quarters (i.e., inside a hanger or on an aircraft carrier) could be significant. Health effects were discussed in a cursory manner. As a result of HAVE NAME, special attention by the Air Force to aircraft fires involving composites was reduced and the term CORKER was discontinued.(28)

3. BROKEN ARROW: The BROKEN ARROW Guide for Bioenvironmental Engineers discusses hazards from burning composites following aircraft accidents.(29) It states that aerosols from composite fibers should be treated as nuisance dust. Protective equipment used to protect personnel from fire combustion products (SCBA) will be adequate protection for personnel in the immediate vicinity of the fire.

4. U.S. Navy Aircraft Crash Recovery Procedures: The Navy recommends SCBA for firefighters and rescue personnel as being adequate.(17,30,31,32) All cleanup and investigation personnel change clothing and shower prior to leaving work; and wash hands, forearms and face prior to eating, drinking or smoking. "Hold down" solution (acrylic acid or liquid floor wax with water) is sprayed on parts to reduce fiber releases. Personnel working directly with or within 10 feet of composites wear NIOSH approved half-mask respirators with cartridges for organic vapors (for protection from jet fuel) and dusts/mists/fumes (for carbon fiber). These personnel also wear leather gloves, impermeable Tyvek 1422A or 1443R or equivalent coveralls, steel toed shoes and disposable foot covers. Where boron/tungsten fibers are involved, shoes must also have steel shanks.

Personnel not within ten feet of the damaged parts may wear NIOSH approved disposable dust respirators and permeable coveralls, but must wear gloves and shoes as listed above. Additional protection is worn where contact with jet fuel and other hazards exist. Damaged composite parts are covered with adhesive or wrapped in plastic.

### III. CONCLUSIONS

A. Based on a review of current literature airborne dusts generated during machining of carbon composites contain fiber fragments and epoxy matrix dust. The fiber fragments typically occur as nonrespirable fibers, nonrespirable nonfibrous dust and respirable nonfibrous dust. Exposure to respirable fiber is unlikely. Carbon composite dust should be considered a nuisance dust. Dusts generated during machining of boron composites contain metallic dusts of boron and tungsten-boride, and epoxy matrix dust. The metallic dusts are considered nuisance dusts, with a TLV of 10 mg/m<sup>3</sup>. While the epoxy matrix dusts have been treated in the past as nonreactive chemicals, this has not been adequately addressed by toxicology research. Until such research is completed, occupational health personnel should be aware of possible sensitization reactions from exposure to the epoxy matrix. In the absence of sensitization to epoxy matrix dust, air sampling and the need for respiratory protection should be based on a comparison of airborne dust levels to the ACGIH TLV for nuisance dust of 10 mg/m<sup>3</sup>.

B. Direct skin contact with prepreg tapes can cause chemical irritation and sensitization. Skin contact can be prevented during lay up operations by use of chemical protective gloves.

C. Respirable fibers are generated from the burning of carbon composites in aircraft crashes. If the crash occurs in an open area, respirable fibers would be widely dispersed downwind in concentrations below the OSHA PEL for asbestos and below the NIOSH REL for man made mineral fibers. While the respirability of airborne fibers in the breathing zone of crash site clean up workers is unknown, heavier and nonrespirable fibers would be expected to remain at the crash site. The primary hazard during a cleanup operation would be puncture wounds to the skin from exposed fibers, and skin and eye irritation from residual dust and fiber fragments.

### IV. RECOMMENDATIONS

#### A. Workplace Evaluations:

1. Sample for nuisance dust, and compare the results to the ACGIH TLV of 10 mg/m<sup>3</sup>.

2. Determine, as completely as possible, the matrix formulation(s) for each prepreg component in use and potential health effects. Evaluate airborne levels and potential for skin irritation and sensitization for each component of the epoxy matrix system during the preparation, lay up, curing and machining of composite materials. Pay special attention to curing agents such as MDA.

B. Workplace Controls:

1. During sanding and grinding, wear goggles and puncture resistant gloves, and use vacuum attachments on grinders and sanders to reduce dust emissions. Keep the work area clean by routine vacuuming. Double bag composite waste and dust in impermeable bags and dispose of in a landfill. Make sure waste is not incinerated.

2. While handling prepreg tapes or matts, wear gloves specially selected for lay up operations (talc-free protective gloves with  $<0.01$  mg/in<sup>2</sup> silicon and free hydrocarbons).

C. Controls Following Aircraft Fires: Follow Navy Procedures during crash site clean up.

1. Firefighters, rescue and other personnel working in the smoke plume wear SCBA.

2. All cleanup and investigation personnel change clothing and shower prior to leaving work; and wash hands, forearms and face prior to eating, drinking or smoking. Personnel working directly with or within 10 feet of composites wear NIOSH approved half-mask respirators with cartridges for organic vapors (for protection from jet fuel) and dusts/mists/fumes (for carbon fiber). These personnel also wear leather gloves, impermeable Tyvek 1422A or 1443R or equivalent coveralls, steel toed shoes and disposable foot covers. Where boron/tungsten fibers are involved, shoes must also have steel shanks. Personnel not within ten feet of the damaged parts may wear NIOSH approved disposable dust respirators and permeable coveralls, but must wear gloves and shoes as listed above. Additional protection is worn where contact with jet fuel and other hazards exist.

3. Apply "hold down" solution (acrylic acid or floor wax and water) to reduce fiber releases, and then wrap parts in plastic. Dispose of composite parts as ordinary waste in a landfill.

D. Educate the work force to the potential health effects of composite materials used and the necessary protective measures to minimize these effects.

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