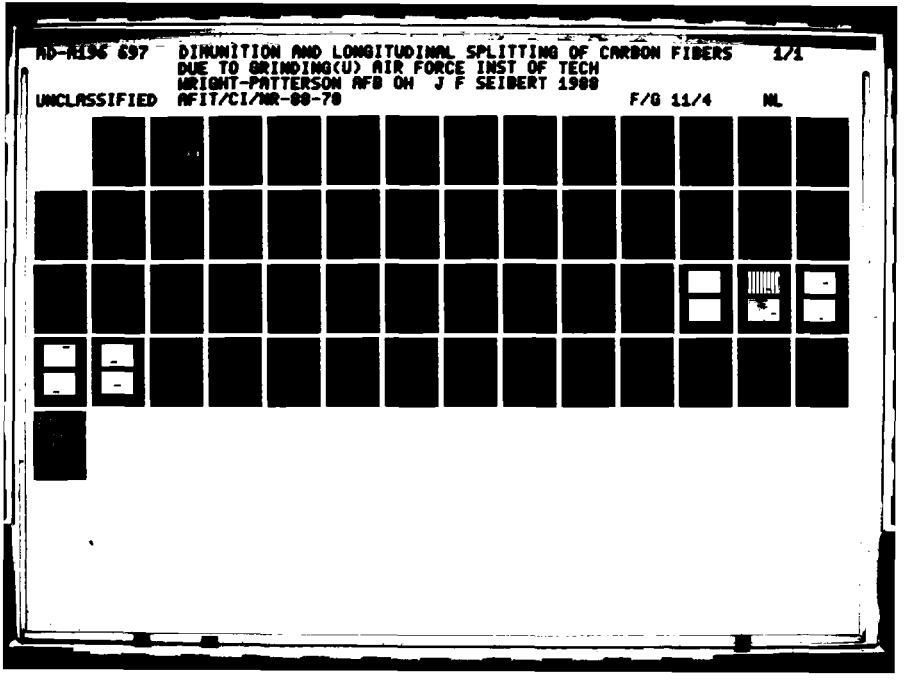
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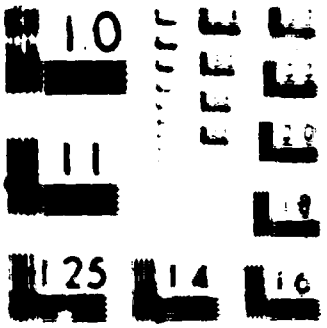
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DIMUNITION AND LONGITUDINAL SPLITTING OF CARBON FIBERS DUE TO GRINDING

by

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B.S. Electrical Engineering
Purdue University, 1977

Submitted to the Faculty of the
Graduate School of Public Health
in partial fulfillment of
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1987

Comminution and Longitudinal Splitting of Carbon Fibers due to Grinding

ABSTRACT

Lightweight composite materials composed of a carbon fiber/epoxy resin matrix are being used in increasing quantities in the aircraft production and the aerospace industry. The use of these composites is also expanding to the non-aerospace industries. Carbon fibers may become a potential airborne hazard during drilling and machining of composite materials. Air sampling by some investigators have indicated that all airborne fibers are of their original diameter (6-8 um), and are non-respirable, while others have noted longitudinal fracturing of fibers into smaller diameter respirable fibers. This research was performed to determine the degree of fracturing during grinding, and to compare this fracturing to that of glass fibers. Carbon and glass fibers without epoxy resin or sizing material were ground in a ball mill. The resulting particles were very similar for carbon and glass. While the particles were predominantly non-fibrous, fibers of reduced diameter were found for both carbon and glass fibers. The largest single size group of fibers were those fibers 0.5 um in diameter and 1.5 um long. It was determined that carbon and glass fibers fracture in a similar fashion, and would present similar probabilities of forming respirable fibers in typical workplace operations. The potential toxicity of dust from carbon composite machining was also reviewed. It is recommended that air sampling and medical evaluations consider airborne carbon fibers to be equivalent to glass fibers, and that non-fibrous carbon particles be considered as nuisance particulates.

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John E. Seibert, Capt, USAF, BSC
M.S. Hygiene, 1987
University of Pittsburgh

TABLE OF CONTENTS

TABLE OF FIGURES

TABLE OF TABLES

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ABSTRACT

Lightweight composite materials composed of a carbon fiber/epoxy resin matrix are being used in increasing quantities in the aircraft production and the aerospace industry. The use of these composites is also expanding to the non-aerospace industries. Carbon fibers may become a potential airborne hazard during drilling and machining of composite materials. Air sampling by some investigators have indicated that all airborne fibers are of their original diameter (6-8 um), and are non-respirable, while others have noted longitudinal fracturing of fibers into smaller diameter respirable fibers. This research was performed to determine the degree of fracturing during grinding, and to compare this fracturing to that of glass fibers. Carbon and glass fibers without epoxy resin or sizing material were ground in a ball mill. The resulting particles were very similar for carbon and glass. While the particles were predominantly non-fibrous, fibers of reduced diameter were found for both carbon and glass fibers. The largest single size group of fibers were those fibers 0.5 um in diameter and 1.5 um long. It was determined that carbon and glass fibers fracture in a similar fashion, and would present similar probability of forming respirable fibers in typical workplace operations. The potential toxicity of dust from carbon composite machining was also reviewed. It is recommended that air sampling and medical evaluations consider airborne carbon fibers to be equivalent to glass fibers, and that non-fibrous carbon particles be considered as nuisance particulates.

I. Introduction

With the increased use of carbon fiber as a reinforcing material in composite materials, there arises the question of possible adverse health effects from inhalation of airborne carbon fibers generated during fabrication and repair of composite material parts. If one assumes that the health effects of asbestos are due to a mechanical irritation of the critical tissue due to its physical shape and size, then one may, logically, be suspicious of other fibrous materials such as carbon fibers or fibrous glass. While the study of man-made fibers such as fibrous glass and carbon fibers may, as it has been claimed, only be "an etiological agent in search of a disease",[1] industrial hygiene practice requires, and prudence dictates, that we anticipate and correct hazards before a disease occurs.

The purpose of this thesis is to compare the size and shape of carbon fibers to fibrous glass under similar conditions of dimunition, so that a rough comparison can be drawn between their relative ability to generate airborne and respirable fibers during their use. The comparison was performed by grinding carbon fiber and fibrous glass in a ball mill, and comparing the relative size distributions of fibers following grinding. This gave a comparison of the relative abilities of carbon and glass fiber to generate respirable fibers during grinding and sanding operations. A previous comparison by Assuncao and Corn by milling fiberglass and asbestos indicated that asbestos fractured longitudinally to produce a higher proportion of respirable fibers, while glass fibers fractured transversely to give non-fibrous particulates.[1] This thesis also examined the potential toxicologic properties of carbon fiber following grinding, to develop a basis for a permissible exposure level for airborne carbon fiber dust.

II. Background of Carbon Fiber

A. Uses of Carbon Fiber

Carbon fiber is a man-made material of high carbon content formed from an organic precursor.[1,2] Carbon fiber manufacture can be tailored to individually optimize its properties of chemically inertness (except with oxidants), heat resistance, low coefficient of expansion, high electrical conductivity, and high tensile strength. Carbon fibers tailored for high tensile strength fiber have a uniform diameter and semi crystalline structure, and are often used as reinforcement in an epoxy resin matrix to form a composite material for parts requiring high strength and low weight. The carbon fibers are aligned within the composite matrix in the anticipated direction of stress. Because of their cost, carbon fiber composites are used primarily in the aerospace industry, where weight is critical. Carbon fiber composites are beginning to see use in the automotive industry whenever the savings in weight results in an overall reduction in manufacturing cost, or in a significant increase in the value of the product. The use of carbon fiber composites is expected to increase as the cost of producing carbon fiber drops, and as the composite manufacturing techniques improve.

B. Manufacture of Carbon Fiber

Carbon fibers have been formed from such diverse materials as: polyacrylonitrile (PAN), cellulose, pitch, asphalt, wool, lignin, polyvinyl chloride, polyvinyl alcohol and polyamide.[3] However, the greatest success in producing high modulus carbon fibers (those used in high strength composites) has been from a PAN precursor. Carbon fibers from PAN are formed in a 3 step process:

1. Formation of Precursor Fiber: PAN fibers are spun to provide the basic starting material and physical structure. The internal molecular structure of PAN fibers is one of long straight alkyl chains with cyanide groups attached. (Figure 1)

2. Oxidation: PAN fibers are heated to 200-250 C in air, creating oxygen cross-links between the straight chains (Figure 2). Some weight is lost in the form of gases, including cyanide. If oxidation were to take place without stretching, the straight chains would become twisted, thereby decreasing the desired longitudinal structure and the final strength of the fiber. Stretching during oxidation is controlled so that the chains are kept reasonably straight, but not stretched to the point where the fiber is damaged.

3. Carbonization: Fibers are heated to a temperature range of 1000-1500°C in an oxygen-free atmosphere to remove most of the non-carbon materials, while retaining the original shape and internal structure. The fiber loses up to 50% of it's weight, and shrinks in length and diameter. The internal structure

becomes one of crystalline carbon fibrils 0.0025-0.01 um wide, and 0.1 um or more long. The fibrils are relatively parallel, with an average deviation from the fiber axis of 10°. The voids between fibrils are believed to be filled with pores and a fine non-crystaline carbon.

Fibers that are further heated to 1700 - 2800°C are more properly referred to as "graphite fibers".[3] The higher temperatures remove all or most of the void between fibrils, and fibril orientation is essentially parallel to the fiber axis. These fibers have a higher tensile modulus (Young's modulus, less stretching when under load), but a lower tensile strength (lower maximum load-carrying capacity). Graphite fibers have not seen much use in aircraft composites, because graphite is harder to bond to the epoxy resin, thereby decreasing the final strength of the fiber/epoxy composite. The graphite fibers have more of a "slippery" surface due to the improved crystalline structure. The terms carbon fiber and graphite fiber have been used interchangably in the literature, so that one must review the final temperature used in fiber manufacture to be sure which material was actually being described. Carbon fibers are surface treated prior to use, to improve binding to the epoxy resin. Treatment takes the form of surface cleaning, mild etching, and the creation of active sites for epoxy bonding. There is no apparent loss of fiber strength from the treatment. This treatment is different from that used for fibrous glass, where a "sizing material" is coated onto the fiber to improve binding to the epoxy resin.

C. Aerodynamic Behavior of Carbon Fiber Dust

Dust from grinding carbon fibers can result in three types of particles:

1. Fibers having the diameter of the parent fiber (6 - 8 um), resulting from transverse fracture of the fiber.
2. Carbon particles (non-fibers having aspect ratios less than 3:1).
3. Fibers, having diameters smaller than that of the parent fiber, resulting from longitudinal fracture of the parent fiber.

It is important to raise the question of the relative importance of longitudinal vs. transverse fracturing because of the effect on aerodynamic behavior and the resultant inhalability. If carbon fibers fracture transversely, then the smallest particle that still appears as a fiber would have a diameter of approximately 7.0 um and length of 21 um. Burke and Esmen estimated the aerodynamic diameter of fibers for sedimentation and impaction:[5]

$$D_e = D_f \, p^{1/2} \, [0.7 + 0.91 \ln B]^{1/2}$$

$$D_i = D_f \, p^{1/2} \, (1 + 0.013(\ln B)^3) \, (0.71 + 0.91 \ln B)^{1/2}$$

where: D_e = aerodynamic equivalent diameter for sedimentation
D_f = fiber diameter
D_i = aerodynamic equivalent diameter for impaction
p = fiber density
B = fiber aspect ratio (fiber length/diameter)

Based on these formulas, a fiber with diameter of 7.0 um, density of 1.8 g/cm^3, aspect ratio of 3, and length of 21 um would have aerodynamic equivalent diameters of 12 um for both sedimentation and impaction. Based on the aerodynamic diameter, we would expect that almost all fibers of the parent diameter which become airborne would be removed primarily in the nose and throat, with no fibers reaching the more distal regions of the lung. Consequently, the only fibers of significance for deposition in the alveoli or bronchi would be those that result from longitudinal splitting of the fiber.

D. Workplace Experience

The concern for health effects from carbon fiber comes from the airborne dust produced during the manufacture or repair of composite parts. During production of composites, rough edges are smoothed by sanding or grinding, and holes are drilled or routed into the material. During repair of composites, the crack and adjacent material is sanded or ground out, and new material is laminated into the area. The dust generated during production or repair includes carbon fibers, carbon dust and epoxy resin dust.

Holt and Horne generated carbon fiber dust for animal exposure studies by feeding a PAN-based carbon fiber into a hammer mill.[6] An aerosol generator fed the resulting dust to an animal exposure chamber. 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/cm^3, for "black fibres" (probably carbon) of 2.9 fibers/cm^3, and for transparent fibers of 1.6 fibers/cm^3. Size distributions were not given, but Holt described 4 types of particles in the sample:

1. Non-respirable fibers with diameter 10um and length >100 um.
2. Nonfibrous particles with diameters from submicron to several microns.
3. Black fibers of diameter 1.0 - 2.5 um, and length up to 15 um.
4. Transparent fibers, typically 1.5 um diameter, up to 30 um long.

Jones, et.al., surveyed a "carbon fiber" continuous filament production facility to determine worker exposure to carbon fibers.[7] (They were probably graphite fibers, since the production process included graphitization of fibers at temperatures up to 3000°C.) Air samples for dust were collected as "total dust" and "respirable dust" (using an elutriator with cutoff at 7 um AED), 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 um), with some smaller particles suspected to be sizing material. Dust levels were higher in the laboratory, because carbon fibre-reinforced resins were being cut, ground and milled. Dust levels ranged from 0.08 -0.39 mg/m³ for total dust, and 0.03 - 0.16 mg/m³ respirable dust. 88 workers were given pulmonary function tests and chest x-rays. No evidence of ill effects attributable to carbon fiber were noted. However, the author admitted that the sample size was small, and the period of exposure was short. Only 31 workers had been working in the factory for more than 5 years, and the factory had been in operation for less than 14 years.

Mazumder, et al., collected air samples while grinding carbon composites, and chopping and grinding bundles of non-laminated carbon fibers inside of a 340-liter glove box.[8] Dust from grinding of carbon composites gave some free fibers, while other fibers were still bound to the epoxy. Epoxy was removed from the fibers by evaporating the epoxy at 400°C. Fibers were then examined under scanning electron microscope. Fibers underwent significant 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 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 MMAD of 4.0 um. Similar analysis of grinding of composites gave a MMAD of 2.7 um. Microscopy was not performed to give relative ratios of fibrous to non-fibrous material. Mazumder stated that his results should be applicable to most commercially available carbon fiber types. He analyzed 6 types from 4 manufacturers, finding fiber diameters in the range of 5.8 - 8.0 um, and densities of 1.72 - 1.83 g/cm³.

Eastes collected air samples during cutting and grinding operations on a "graphite" fiber composite wing panel, and evaluated the samples a with phase contrast microscope.[9] Of the 10 fibers selected for sizing, all graphite fibers had the diameter of the starting material (6.6 um), with some binder material still attached. Some translucent fibers of smaller diameter were noted, but thought to be 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/cc, and total fiber levels of 1.7 - 7.8 fibers/cc. Non-fiber particulate

counts were 23 -180 particles/cc. Eastes concluded that airborne graphite fibers did not pose a health problem, since 80% of the graphite fibers were non-respirable.

Zustra collected air samples during sanding and grinding of U.S. Coast Guard helicopter panels made up of PAN-based carbon fibers.[10] 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^3. 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 0 to 0.5 fibers/cc, and total dust levels were in the range of 31.9 to 96.6 mg/m^3.

Lurker reported air sample results from various sanding and grinding operations on carbon fiber composite panels of U.S. Air Force aircraft.[11] Initial sampling and analysis under electron microscopy indicated 99.89% of the particles were non-fibrous, and all of the fibers were of the original parent fiber diameter. Mean fiber concentration was 0.03 fibers/cc. Later samples from another facility indicated some fibers were generated with diameter less than the original 7 um diameter.

The U.S. EPA sawed, drilled and incinerated carbon fiber composites.[12] Sawing with a hacksaw and drilling with carbide-tipped drills generated dust containing large quantities of fibers about 50 -100 um long and free of epoxy resin. Some longitudinal cleavage of fibers was found, with resulting fibers having diameter less than that of the 6 - 8 um diameter parent fiber. Incineration of a carbon fiber/epoxy resin composite in a furnace at temperatures up to 1000°C destroyed the epoxy resin. The fibers were left with definite signs of pitting and thinning.

Zumwalde and Harmison performed a NIOSH review in 1980 of available information on carbon fiber.[13] The National Aeronautics and Space Administration (NASA) 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. Between 0.75% and 3.5% of the original fiber mass was released as single airborne fibers, and the rest was consumed in the fire or remained in place. Airborne fibers averaged 2-3 mm long and 4-5 um in diameter. A later analysis under different conditions gave average fiber diameters of 1.5 um, and average length of 30 um. It was concluded that heating the fibers reduces fiber diameter by partial oxidation and fibrillation. It was estimated that following an aircraft crash in which carbon fiber composites burned, there would be a release of 5 x 10^{11} fibers (<3 um diameter, > 8um long) per kilogram of carbon fiber released. Air sampling in the smoke plume during a test burn showed fiber concentration of none detected to 0.14 fibers/cm^3. All fibers were at least 5 um in length, and 77% of the fibers were no more than 1.7 um 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.

E. Epidemiology & Toxicology

Inhalation of carbon fiber and dust could cause adverse health effects from several mechanisms:

1. Long-thin fibers: One of the present theories holds that the effects of asbestos are due to the size and shape of the fibers. If carbon fibers are of the same size and shape, then diseases similar to asbestosis, bronchogenic carcinoma and mesothelioma may be considered to be possible consequences from exposure to a sufficent dose of carbon fibers.

2. Polycyclic Aromatic Hydrocarbon (PAH) induction of cancer: Carbon fiber material contains some PAH residue from production processes. If lung fluids are able to desorb significant levels of PAH's, then enhancement of lung cancer risk from direct contact with PAH's might be expected.

3. Respirable dust exposure: Sufficient dust loading of the lungs may lead to a form of pneumoconiosis.

Holt and Horne exposed guinea pigs to the carbon fiber dust for up to 104 hours, then sacrificed the animals at intervals of up to 144 days. Lungs were excised, stained, sectioned, and examined for particle size and morphology under a light microscope. The lung section of one animal exposed for 7 hours and killed after 1 day showed non-fibrous dust within macrophage cytoplasm. The researchers suspected extracellular dust had been washed out by tissue preparation, since a separate section of frozen tissue demonstrated extracellular dust particles. Some macrophages were attached to alveolar walls, and some were embedded in thickened alveolar wall. Frequency of dust-filled macrophages increased to a peak for animals killed at 109 days. Interalveolar tissue showed some thickening with time, but no fibrosis was found. Almost all fibrous particles longer than 6 um were extracellular. No fibers were found that were less than 0.5 um in diameter and longer than 10 um in length.

Ballantyne performed a dermal tumorigenicity study on the benzene extract of carbon fiber fragments of four carbon fiber types.[25] The skin of mice developed local tumorigenic effects with pitch-based carbon fibers, but not with pitch-based MAT fibers or with PAN-based or PAN-oxidized fibers. Further testing supported a hypothesis that the pitch-based carbon fiber initiated a tumorigenic response, and physical irritation promoted development of tumors. Ballantyne concluded that, due to the extreme test conditions, there was an insignificant risk of skin tumors from chronic skin contact with carbon fibers.

III. Background on Similar Materials

A. Fibrous Glass Epidemiology and Toxicology

NIOSH issued a criteria document for fibrous glass which reviewed epidemiology and toxicology data.[26] It recommended control of airborne respirable glass fibers (<3.5 diameter, >10 um long) to less than 2 fibers/cc. The control decision was based on the belief that health effects observed from asbestos exposure were caused by the physical size and shape of asbestos fibers. It was concluded that glass fibers had the potential of occuring in the same size and shape as asbestos. Investigators have conflicting opinions of whether workplace inhalation of fibrous glass induces lung cancer typical of that found with asbestos exposure. Confounding variables included smoking and worker exposure to asbestos. Also, worker exposure to respirable fibers has been orders of magnitude lower for fibrous glass than for asbestos.

Fiberglass was not considered a significant hazard by Gross in the review of a group of international epidemiological studies of the health effects of fibrous glass.[1] He concluded that the studies had failed to demonstrate that exposure to fibrous glass is associated with a significantly increased risk of death from lung cancer or nonmalignant respiratory disease. He pointed out that workers in these studies were exposed to airborne fibrous glass at much lower levels than were asbestos workers who developed lung cancers and nonmalignant respiratory disease. Therefore, fibrous glass could be an unrealized hazard due to presently low exposure levels.

B. Carbon Black Epidemiology and Toxicology

Numerous studies were reviewed by NIOSH in formulating a criteria document for workplace exposure to carbon black.[14] The primary effects of carbon black noted were pneumoconiosis and pulmonary fibrosis. Functional changes included decreases in vital capacity, respiratory minute volume, maximum ventilatory capacity, FVC and FEV_1. Secondary effects noted were skin irritation and specific dermatoses, cardiovascular dysfunction. Shortfalls of the studies included failure to account for the effects of workplace carbon monoxide exposure or smoking, and the lack of air sampling data for carbon black. Some workplace data was available for "total dust", and indicated workplace levels ranging from 8.2 - 1000 mg/m^3. NIOSH indicated that the presence of polycyclic aromatic hydrocarbons adsorbed on the carbon black was the primary hazard from workplace exposures.

Crosbie studied the pulmonary effects on workers in carbon black factories, specifically addressing the effects of carbon black dust exposure vs. smoking.[15] Although quantitative airborne levels of carbon black were not available, workers were grouped into four exposure groups based on qualitative assessment of carbon black exposure. Crosbie administered questionaires, and

performed spirometry and chest radiography. Exposure to dust had the primary effect on forced vital capacity and symptoms of chronic cough and phlegm production. Smoking was associated with decrease in maximum mid-expiratory flow, forced expiratory flow, and symptoms of wheezing. Both dust and smoking were associated with decrease in forced expiratory volume in 1 second (FEV_1). A "lung deterioration index (LDI)" was used that gave a numerical rating to the combined results of pulmonary function tests and symptoms. This LDI indicated that smoking was the primary factor in pulmonary effects. Radiography indicated that less than 1% of the workers showed pneumoconiosis, with no association with pulmonary dysfunction. The author concluded that exposure to carbon black would only lead to simply pneumoconiosis, and that it should be treated as a "nuisance dust".

Robertson and Ingalls performed a cohort study of workers in four U.S. carbon black factories to examine the effects of carbon black on cancer and heart disease.[16] They compared mortality rates of all employees at carbon black factories to those of the surrounding population and found that the observed deaths in carbon black workers due to cancer or heart disease were not significantly in excess of the expected rate. They also found no increase in cancer with increasing length of employment. A marginally significant ($0.05<p<0.10$) increase in heart disease was found for increased length of employment. The study did not account for smoking, or measure the relative exposures of carbon black. A later study by Robertson and Ingalls compared the total dust exposure of carbon black workers with selected circulatory, malignant and respiratory diseases with matched disease-free controls. They found that the workers with disease had comparable dust exposure to those without disease, except for diseases of the circulatory system. For these diseases, the workers with disease had a significantly lower exposure to dust than did the disease-free workers. This study did not account for smoking, and estimated past dust exposures based on current air sampling and a history of where the person worked. The authors felt that these would not adversely affect the conclusions that carbon black should be considered a nuisance dust.

Hodgson and Jones performed a mortality study of carbon black workers to determine whether exposure to carbon black was related to increased lung cancer.[18] They noted an increase in lung cancer, but it was not statistically significant. This study was not conclusive due to mortality data missing from two of the five factories studied.

IV. Present Health Standards

ACGIH, OSHA, U.S. Air Force and General Dynamics Corp consider carbon composite particulates to be an inert nuisance dust.[9,10,19,20] The U.S. Air Force uses the ACGIH standard of 10 mg/m³ total dust and 5 mg/m³ respirable dust, while OSHA uses 15 mg/m³ total dust and 5 mg/m³ respirable dust.

The U.S. Navy permissible limit for carbon fibers is 3 fibers/cc for an 8-hour time weighted average (TWA), with a ceiling limit of 10 fibers/cc.[21] The Navy also recommends maximum total dust levels of 3.5 mg/m³ for an 8-hour TWA, and 7 mg/m³ for a 15-min short term excursion limit (STEL). The fiber limit is based on the assumption that carbon fiber behaves similarly to fibrous glass. This limit reflects the NIOSH recommended limit for fibrous glass exposure. This appears to be a fair comparison. Carbon fiber and fibrous glass share the same attributes:

1. The parent fiber is of an aerodynamic size that is relatively non-respirable.
2. The fibers have similar physical strengths, and are used in similar applications in composites.

Similarly, the Navy limit for carbon fiber "total dust" levels are based on the NIOSH recommended limit for carbon black, since both carbon black and carbon fiber contain residual PAH's from the manufacturing process. NIOSH recommended in their criteria document that exposure to carbon black be evaluated by collecting air samples for total dust. Since most carbon black dust is less than 0.3 um, and the dust in carbon black factories is predominately carbon black, most of the dust collected would be respirable carbon black. NIOSH additionally recommends that the air samples should contain a total PAH concentration less than 0.1 mg/m³, based on the cyclohexane extract of the carbon black dust. The Navy comparison of carbon fiber to carbon black may not be as firm. The relative PAH content of carbon fiber and carbon black is highly variable and dependent on the manufacturing process. The relative ability of lung tissue to desorb the PAH's has not been addressed. The largest difference is that while carbon black is almost completely respirable, the dust from carbon fibers is of larger sizes typical of that produced from machining operations. I feel that basing an allowable limit for airborne carbon fiber dust on the current standard for carbon black is inappropriate at this time. Since NIOSH issued its criteria document and ACGIH issued its TLV for carbon black, three epidemiological studies have concluded that carbon black should be treated as a nuisance dust. The standard for carbon fiber should not rely on the carbon black standard until the results of these studies are addressed.

V. Experimental Procedures

A. Grinding Theory

"Grinding" generally refers to the reduction of a solid material to smaller sizes by mechanical forces.[22] The term communition is more accurate, and describes the sum of events in size reduction: cutting, tearing, rubbing, compressing or impacting. During ball milling of material, particle size is reduced by particle-to-ball friction, particle-to-particle friction, and crushing between balls or between balls and walls. The contribution of each process to the size reduction process is determined by mill size, ball size, particle size, properties of the material, mill speed and ball and mill roughness. The chemical and mining industry and its researchers have attempted to predict and optimize the energy expenditure required to achieve a given size reduction. They have relied heavily on experimentation to determine the most efficient way to produce material of the desired size distribution from a parent size distribution. Communition theory holds that energy applied to a material will take one of eight forms:

A. Material being crushed
    1. Lattice rearrangements
    2. Surface energy
    3. Elastic deformation
    4. Plastic deformation
B. Crusher and interparticle effects
    1. Friction
    2. Kinetic energy
    3. Electric effects
    4. Sound

The desired effect on the material is to create reorientation of the crystalline structure, and to form cracks by breaking bonds in the structure. Cracks are first formed in imperfections in structures, such as the the locations of impurities. Cracks continue to grow as more energy is imparted to the material. The particle is broken into smaller pieces when the crack(s) have sufficiently propagated.

Ball milling was chosen as a method of communition for carbon fiber for several reasons. Primarily, it is easily performed in a laboratory with a minimum of time and equipment set-up. Also, ball milling appears to be a heavily stochastic form of communition, that will yield basic information about the ability of a material to withstand fracturing. While not giving precise information about the underlying crystalline structure of the material, it will give a crude understanding of how the crystalline structure responds to the spectrum of comminution forces. Performing simulated grinding of a carbon fiber composite material gives a good deal of information on the material being tested under the specific conditions used in the simulation. However, it gives only inclinations of what can be expected from other composite materials using different fiber orientation within

the composite matrix, or different epoxy resin formulations. Grinding the nude fiber under the random orientations present in a mill gives a broad-brush 'feel' of the basic fracture characteristics of the material. If ball milling is performed for a large number of materials, such as various types of asbestos, glass fiber, boron fiber and carbon/graphite fibers, a rough comparison can be drawn of the relative ability of each material to retain a fibrous shape following machining operations or physical deterioration. The milling of fibrous glass and chrysotile asbestos by Assuncao and Corn was one such comparison, which elucidated why fibrous glass air samples seemed to contain fewer fibers than did asbestos air samples.[2]

B. Initial Sizing & Pycnometry

Carbon and glass fibers were sized prior to grinding by cutting the fiber tows with a scissors. The cut pieces were mounted on a glass slide in oil, covered with a cover slip, and sized with a Zeiss microscope. Total magnification was 2000X, by using 100X objective with oil immersion and numerical aperature of 1.23. Theoretical resolution, assuming a light wavelenth of 0.55 um, was 0.22 um.[23]

Density of the initial carbon fiber material was measured with a 2 mL water pycnometer. The pycnometer was filled with water and weighed when the water level dropped to a reference point in the capillary column. A weighed amount of material was added to the pycnometer, and the pycnometer reweighed at the same reference point on the capillary column. The density of the material was determined from the formula:

$$D_m = W_m * D_w / (W_m - W_c)$$

Where: D_m = density of material being tested

W_m = weight of material added to pycnometer

D_w = density of water at current temperature

W_c = change in weight of pycnometer from addition material

C. Milling Procedures

M-63 carbon fiber material (deLorme Marketing Corp., Capistrano Beach, California: a woven tow, with approximately 100 fibers/tow) was cut with a scissors into lengths of approximately 1 cm, to yield 1 gram of fiber for grinding. The cut fiber was weighed before grinding and was dispersed by hand inside a 1 liter ceramic ball mill with 33 each 2.6 cm ceramic balls. The mill was closed, and the material milled at 71 rpm for times ranging from 5 to 30 minutes. Since the grinding process is stochastic, an average effect for each grind time was achieved by grinding three

sets of fiber for each grind time. The mill was allowed to cool for about 2 hours following each grind before opening the lid. Ground material was extracted wet from the mill jar with distilled water. A prelimenary test grind performed without allowing the mill to cool, and removal of dust by dry brushing, showed a fine particulate cloud leaving the mill. This cloud was probably composed of the smallest aerodynamic diameter particles. To extract the material, water was poured into the mill, and each ball was wet brushed with a soft tooth brush and rinsed with water to remove ground material. The walls of the mill were also wet brushed. The mill was thoroughly rinsed, and all rinse waters consolidated as the sample for that grind. After removal of the ground material, the mill was washed by replacing the balls in the mill, adding water and laboratory glassware soap, and milling for about 5 minutes. The mill and balls were thoroughly rinsed with water, and air dryed with compressed air.

D. Grinding Efficiency

The resulting samples of ground fiber in water was filtered through a sieve with Tyler #8 mesh (opening size 0.24 cm). The fiber collected in the sieve was taken as a rough measure of the amount of the original cut fiber mass that remained "unground". The filtered fiber was placed in an aluminum drying dish, and dried by placing the dish on a hot plate at about 120°C. A drying dish half full of water was also placed on the hot plate as a control. When all of the water had evaporated from the control dish, the dish with fiber was removed, allowed to come to room temperature, and weighed. "Unground fiber" weight was determined from the weights of the dish with and without fiber. The original weight of fiber used in a grind was compared to the weight of "unground fiber" to estimate the "percent ground" for each grind time. Recovery efficiency for "unground fiber" was measured by putting fiber samples through the grinding and recovery process, except that no grinding was performed.

E. Fiber Counting

Ground material from each of the three grinds at 5, 15 and 30 minutes were mounted on slides for optical microscopy. After removal of "unground fiber" by sieving, the dust/water suspension was shaken to give a homogenous mixture, and a sample withdrawn from the center of the sample jar with a glass medicine dropper. A drop was placed on the microscope slide, covered with a cover slip, and the cover slip sealed along the edges with clear fingernail polish. The particles on the slide were allowed to sediment within the water before examination. Attempts to size the particles on the slide immediately after mounting were futile due to Brownian motion of the particles.

Sizing was done with a Zeiss microscope using a 100X objective with oil immersion (numerical aperature-N.A. of 1.25), 2X optovar and 10X eyepiece. This gave a total of 2000X magnification, and resolution of 0.22 microns.[23] Diameters and

lengths were measured to the nearest 1 division with a 100 division eyepiece graticule ruler. The graticule was calibrated with a stage micrometer, giving dimensions of 0.51 um per ruler division. Slides were scanned through the area of highest particle density, if possible. Each sample slide was placed on a white background to determine if there was a region on the slide dense with particles (appearing as a dark gray area). If a dense area was found, the slide was examined under the microscope by scanning through the center of the dense region. If no dense area was found, the slide was scanned across the center of the cover slip. Each slide was scanned once from left to right across the full width of the cover slip. Only fibers with a length:diameter ratio (aspect ratio) of at least three were recorded. Both length and diameter were recorded for analysis of diameter, length and aspect ratio. Three slides were prepared and counted from each fiber grind. If less than 100 total fibers were counted from the three slides, three additional slides were mounted and counted to increase the total fiber count to over 100.

Glass fibers were ground, filtered and sized using the same procedures as for carbon fiber. Glass fibers were ground only for times of 5, 15 and 30 minutes. Microscopy was also identical, except that high particle densities were visible as a white spot on a black background; and the microscope objective was 100X with a numerical aperature of 1.30, giving a theoretical resolution of 0.21 um.

F. Data Analysis

The fiber diameter and length data was summarized in two ways: the fiber diameter cumulative frequency distribution; and grouping of fiber counts to show fiber length and diameter frequency.

The cumulative frequency distribution of fiber diameter for each grind was calculated from a count of fibers for each diameter for all slides from a particular grind. An average frequency distribution for each grind time was calculated from the arithmetic mean of the frequency distributions of the three grinds.

Fiber length and diameter size grouping was performed by counting the number of fibers in each diameter range and length range for each grind. The percent of total fibers was calculated in each size group for that grind. The average frequency of each size group for a grind time was calculated from the arithmetic mean of the frequencies for each grind of that grind time.

The ability of the mill to grind the fiber material was reviewed by measuring the percent of unground fiber vs. grind time. The percent of unground fiber was calculated by dividing the amount of filtered fiber recovered from the sieve by the amount of fiber originally placed into the mill. The percent of unground fiber was corrected for recovery by dividing all values

VI. Results and Discussion

A. Carbon Fiber

The initial carbon fibers were very uniform in diameter, with 7.1 um count median diameter (CMD) and geometric standard deviation (GSD) of 1.1.(Figure 3) Carbon fiber density was 1.60 g/cm^3 from pycnometry. Grinding of carbon fiber gave a preponderance of non-fibrous carbon particles. Identifying fibers for sizing and counting required a high degree of particle rejection.

The size distributions for different grind times show that increasing the grinding time from 5 to 30 minutes shifted the size distribution to smaller sizes, with the shape of the distribution remaining substantially the same. The shape of the size distribution suggested a bimodal distribution composed of the sum of two size distributions: fibers of the original diameter, and fibers of reduced diameter. Attempts at separating the two distributions were successful. The CMD and GSD for reduced fiber diameters, with their fraction of the total fiber count, were calculated.(Table XV) These values were recombined with the size distribution for the original fiber diameter fibers to check the theoretical estimates. The theoretical recombined distributions showed a high degree of fit when graphed with the experimental data (Figure 6), showing that the total fiber size distribution was bimodal. As expected, the CMD for the reduced fibers decreased and their fractional contribution to the total fiber count increased with increasing milling times. The GSD showed no trend with increasing milling times.

A further analysis of fiber size distributions by accumulated length diameter was considered, but was infeasible to perform. While data for fiber length was measured for the smaller diameter fibers, many fibers of the original diameter were only recorded as being >50 um long. Also, 'unground' fibers removed by filtration were unsized. An accumulated length diameter distribution would only have meaning if all fibers of the original diameter were ground into reduced diameter sizes. Based on the extensive grinding time, the results would not be comparable to workplace conditions.

A review of the diameter vs. length tables shows that the most significant number of fibers seen were in the size group with 0.5 um diameter and 1.5 um length.(Tables IX-XII) This single size group comprised 31%, 38% and 46% of all fibers counted for grind times of 5, 15 and 30 minutes respectively. The physical appearance of these fibers was more ellipsoidal than cylindrical. Of the 0.5 um diameter fibers, no fibers over 5.5 um were found. Also, of the 1 - 2 um diameter fibers, no fibers longer than 10.5 um were found. This indicates that finding long and thin respirable fibers is a rare event. The ability of carbon particles to retain a fibrous shape at diameters less than 0.25 um can only be hypothesized without performing electron microscopy.

Figure 8 shows the fraction of unground fibers as a function of grinding time. This figure suggests that the percent of total fibers remaining unground decreased exponentially with increasing grinding time. Assuming an exponential function:

$$P/P_0 = EXP(-at)$$

where: P_0 = initial weight of material
P = weight of unground material at time 't'
a = exponential decay rate
t = grinding time in minutes

Using the carbon fiber data, we find that a = 0.034 ± 0.010. It appears that as grinding time was increased, fibers were removed from a 'reservoir' of unground fibers of the original diameter, and the transition was at a relatively constant rate through the intermediate diameters to submicron diameters. This behavior is expected because of the stochastic nature of the grinding process.

B. Glass Fiber

Sizing of the initial glass fibers showed them to be also very uniform, with 6.3 um count median diameter (CMD) and geometric standard deviation (GSD) of 1.1.(Figure 3) This glass fiber was chosed as being the closest in size to the carbon fibers being studied.

The results from grinding glass fiber were very similar to carbon fiber. Ground glass fiber gave a preponderance of non-fibrous particles. Also observed were a number of translucent particles that did not appear to be glass. These could have been bacteria or other non-glass materials. If not following the pattern of glass particles, they were not counted. It is possible that some of the smaller particles counted as glass (i.e. 0.5 um X 1.5 um) were actually bacteria. This problem of separating fibers from extraneous material did not occur for carbon fiber sizing, since the carbon particles were opaque and easily separated from bacteria, glass and cellulose.

Increasing the grinding time from 5 to 30 minutes did not shift the glass fiber size distribution to smaller sizes (Figure 3), but this could have been due to the large variance in the 5 minute grind data.(Table VIII) Extraction of the size distribution for reduced fiber diameters was also successfull, with a tight fit between the reconstructed size distributions and observed data.(Figures 8-10) However, the CMD showed no trend with grinding time, and the fraction of reduced diameter fibers decreased with increased grinding time.

The largest diameter/length size group of fibers were in the size range of 0.5 um by 1.5 um, comprising 41%, 31% and 39% of all fibers for the 5, 10 and 15 minute grinds respectively.(Tables XII-XIV)

The percent of 'unground fiber' for glass fiber also decreased with increasing grinding time, having values within the same range as for carbon fiber (Figure 8). This suggests that the physical properties of glass and carbon fiber are very similar, or that the parameters of the ball mill control the rate of grinding the fiber.

C. Comparison to Other Studies

Finding carbon fibers of reduced diameter after grinding agrees with the findings of all investigators except two. Jones found no longitudinal splitting in a carbon fiber manufacturing facility. Eastes also found no splitting during graphite composite machining, but microscopy was performed under 45X10 magnification. If we assume the microscope objective was a 45X with numerical aperature of 0.75, the theoretical resolution would be 0.37 um. Many of the small fibers seen after milling of carbon fiber would not be visible. Also, Eastes examined the size of only 10 fibers, reducing the overall precision of any findings.

Assuncao and Corn studied the effects of milling on a wool type fibrous glass and chrysotile asbestos.[2] After milling, 20% of glass fiber diameters were at or below 1.0 um. However, the glass and chrysotile fiber diameters before milling were not measured to determine the original size distribution. Instead, they performed prelimenary milling, and sized the "starting material" before commencing with more milling. A comparison to the starting material to final milled material showed no decrease in fiber diameter for glass, but a significant decrease for chrysotile. Their comparison, coupled with this comparison of carbon fibers to glass fibers, indicates that carbon and glass fibers have a tendency to fracture transversely at first. Then, the smaller fragments will begin to fracture longitudinally. The final result is that carbon and glass will fracture into fibers, but that these fibers have low aspect ratios (<10). In contrast, chrysotile will fracture longitudinally into fibers of reduced diameter with aspect ratios exceeding 10.

Schneider et.al.(24) evaluated the size distribution of airborne fibers as measured in workplace air samples. They determined that the air samples will show an overall reduction in fiber count median diameter due to the effects of sedimentation and ventilation systems. They did not take into effect any reduction in fiber diameter due to longitudinal splitting.

If we were to size the ground glass fiber according to NIOSH analytical method #7400 (counting only fibers > 10 um long and <3.5 um diameter), we find that about 1% of the total carbon and glass fibers would be counted. If we consider the NIOSH counting criteria to be an accurate measure of respirable and biologically significant fibers, then very few of the total fibers are significant. We would expect that workplace air sampling would also show very low levels of countable fibers when compared to the total number of airborne fibers.

VII. Recommendations for Further Work

Little data is available on workplace levels of respirable carbon fibers and non-fibrous carbon dust. More data needs to be collected so that workplace carbon fiber exposure can be compared to currently available glass fiber data to test the hypothesis that similar fiber exposure levels are generated in carbon and glass fiber opeations.

PAH desorption from carbon fiber debris in lung tissue and fluids needs further review. Testing to date has been with organic solvents such as benzene, and has not addressed the ability of body fluids to desorb PAH's from carbon particles.

VIII. Conclusions

Milling of carbon and glass fiber gives fibers of reduced diameter. These fibers, while being respirable, have an aspect ratio less than 10. If we follow the hypothesis that only "long and thin" fibers are important, then these fibers have a low potential for adverse health effects.

Carbon and glass fibers responded in an equivalent manner to ball milling. Airborne levels of fibers and non-fibrous particulates from workplace grinding and sanding operations should also be similar for carbon and glass fiber. If it is assumed that health effects are related only to the physical size and shape of the particulates, then similar health effects would result. Following these assumptions, it is appropriate to evaluate carbon fiber exposure by using the NIOSH exposure criteria and counting method for glass fiber.

Inhalation toxicology data on non-fibrous carbon particles indicate a low potential for adverse health effects. Carbon particles should be considered as nuisance particulates during workplace and medical evaluations.

I feel that an appropriate standard for workplace exposure to carbon fibers and dust would be:

Fibers: Use the NIOSH recommended standard for fibrous glass of 3 fibers/cc (fiber defined as >10 um long and <3.4 um diameter) as an 8-hour TWA.

Dust: Use the ACGIH standard for "nuisance particulates" of 10 mg/m^3 total dust and 5 mg/m^3 respirable dust as an 8-hour TWA.

IX. Summary

Ball milling of carbon and glass fiber gave a preponderance of small non-fibrous particles, and fibers of reduced diameter. Wide variations in fiber size distributions were noted between grinds. However, most fibers of reduced size were less than 1.5 um in diameter. Fibers with 0.5 um diameter and 1.5 um length comprised 31-46% of the total fiber count. Fibers of reduced diameter were found to have an aspect ratio less than 10:1. Only 1% of the total carbon fiber count would have been counted if NIOSH analytical method #7400 had been used, and only 1% of all glass fibers would have been counted. Since most of the ground particles were non-fibrous, air sampling and toxicity testing of carbon fiber composite dust should address both fibrous and non-fibrous components.

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Figure 1

Molecular Structure
of PAN Precursor Fiber

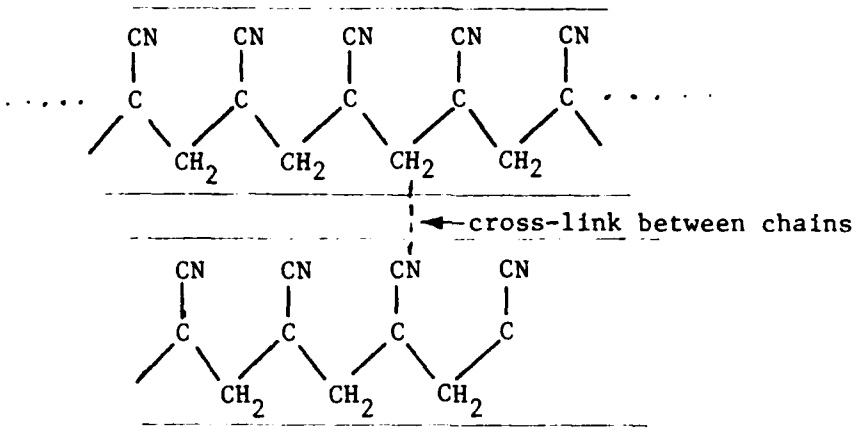


Figure 2

Molecular Structure
of Oxidized PAN Fiber

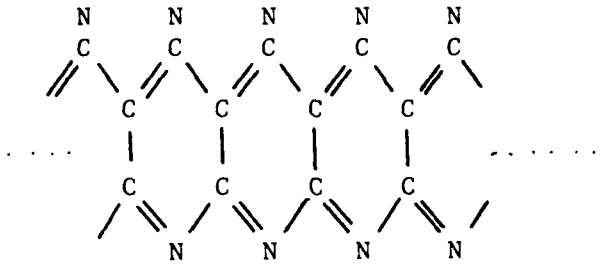


Figure 3

Fiber Size Before Grinding

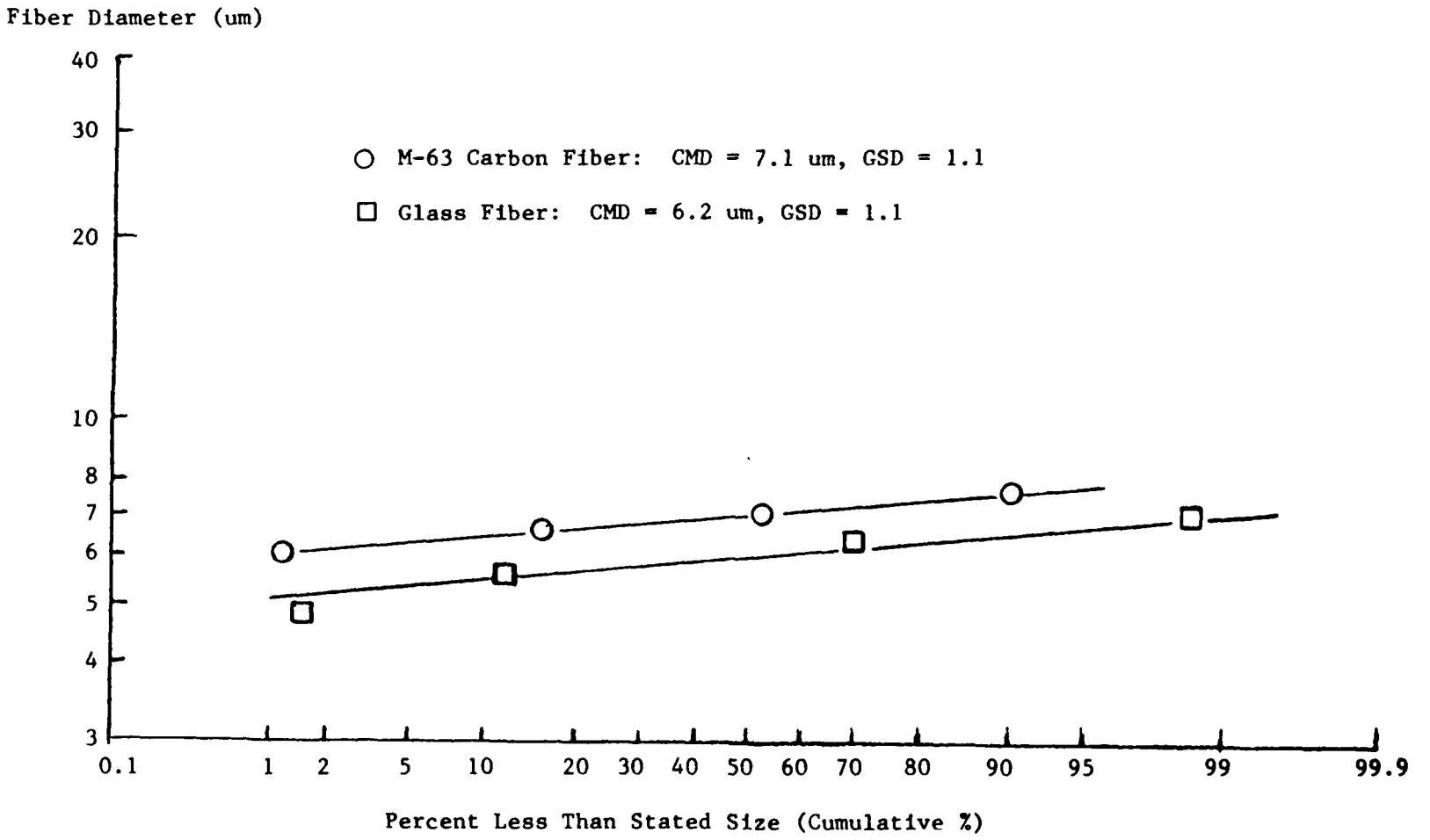


Figure 4

Distribution of Fiber Diameter for
Ground M-63 Carbon Fiber

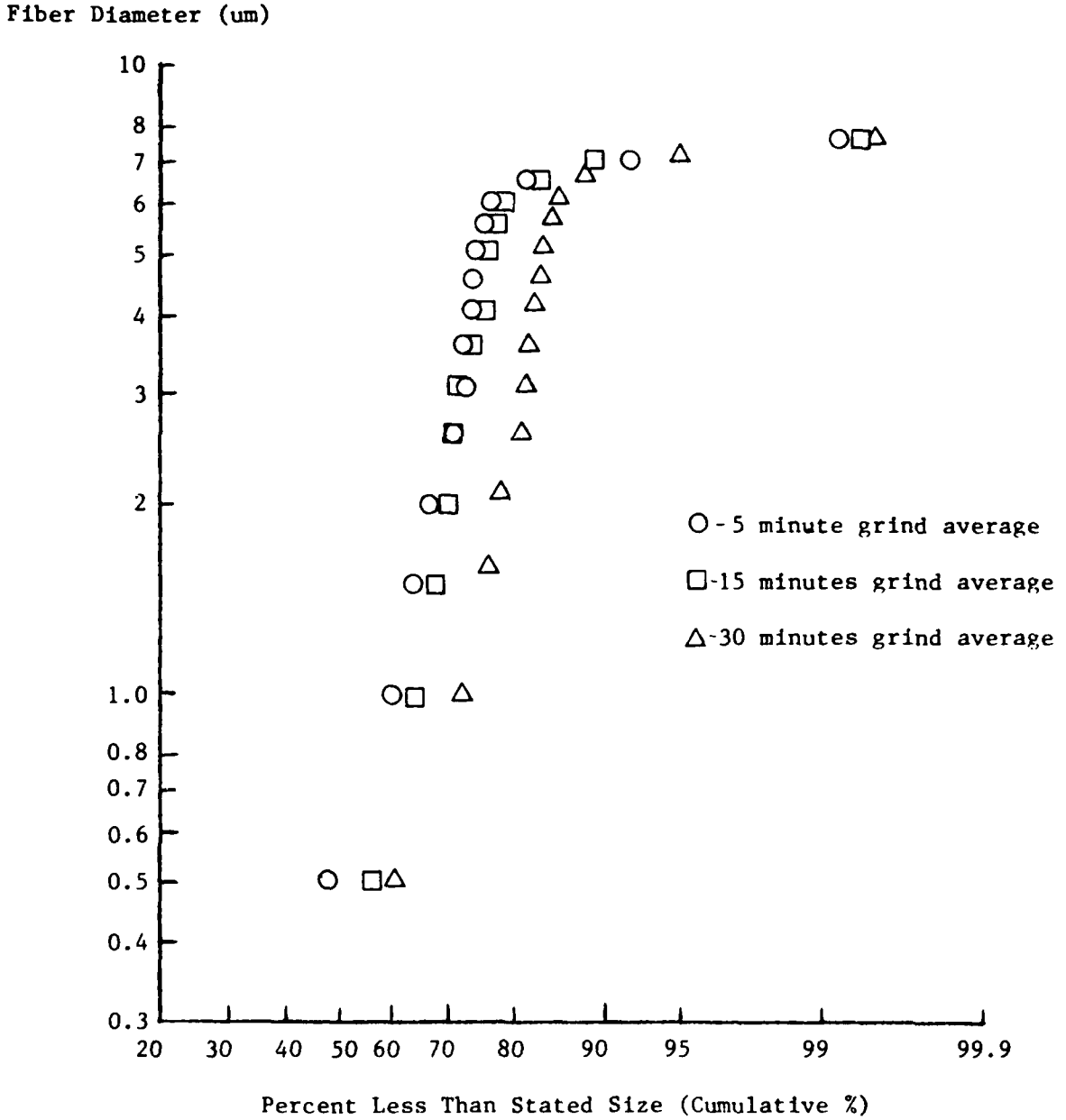


Figure 5

Distribution of Fiber Diameter for
Ground Glass Fiber

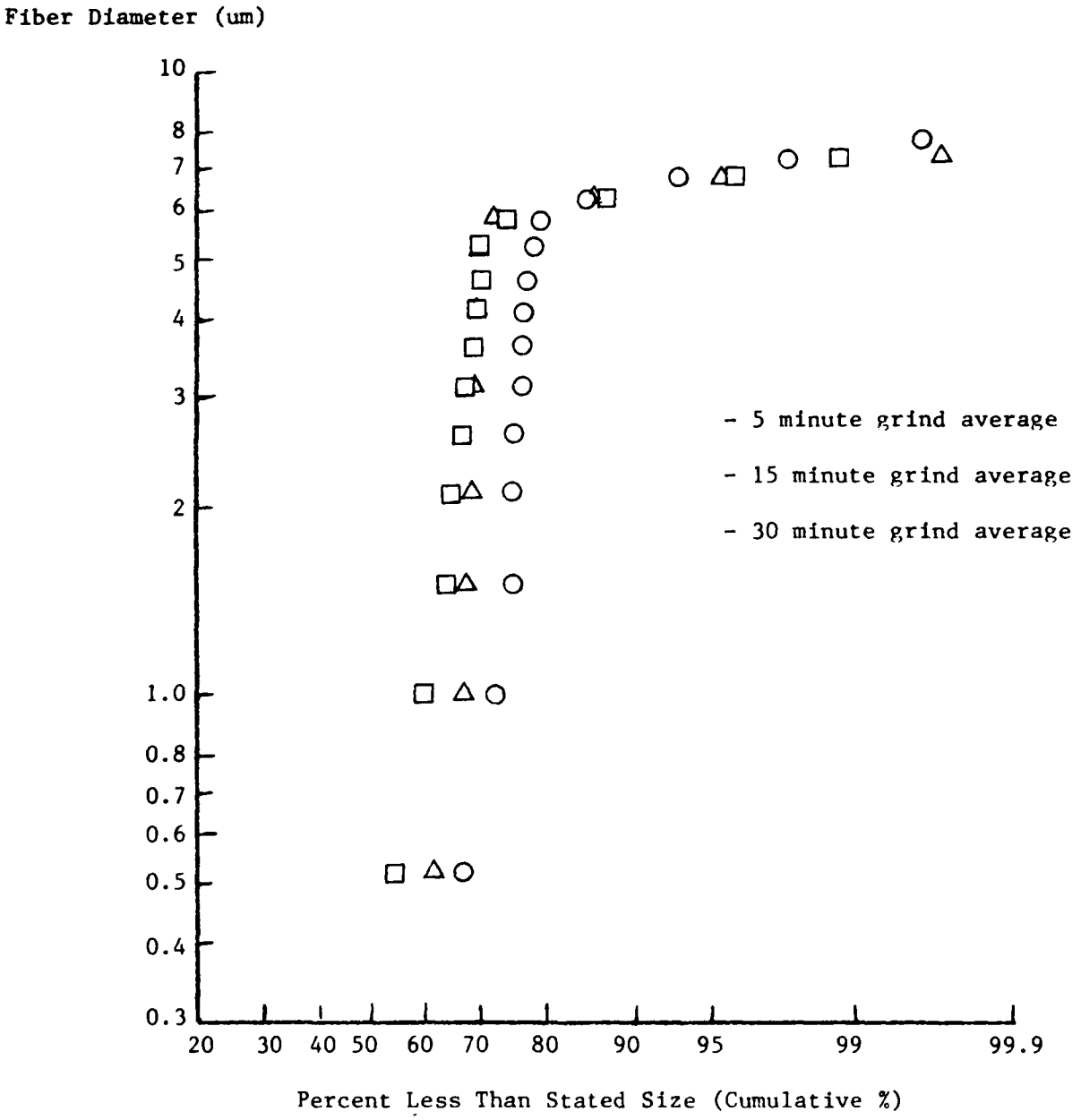


Figure 6

Reconstructed Theoretical Fiber Diameter
Size Distribution and Experimental Data Points
for Carbon Fiber Ground X5 Minutes

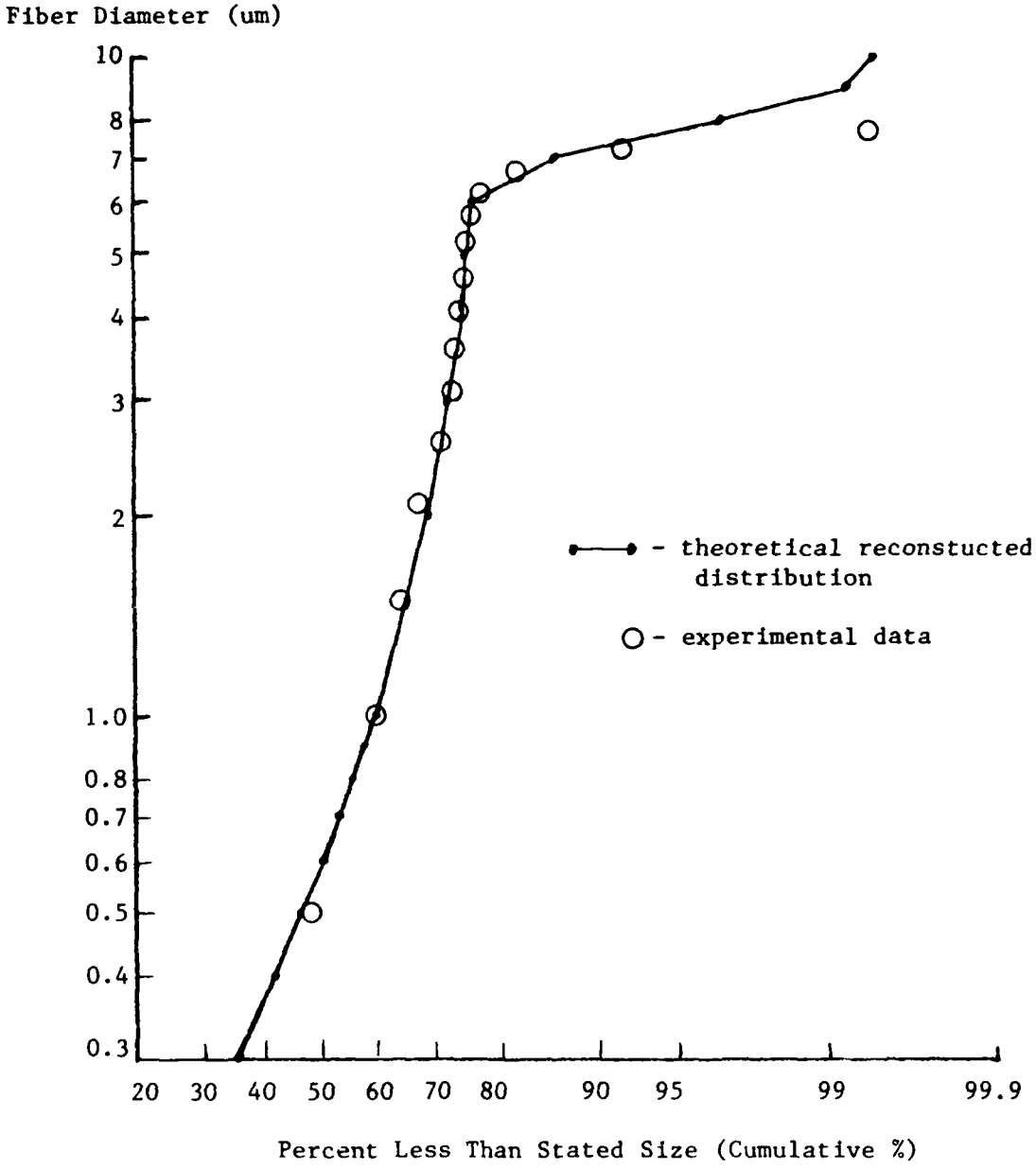


Figure 7

Reconstructed Theoretical Fiber Diameter
Size Distribution and Experimental Data Points
for Glass Fiber Ground X5 Minutes

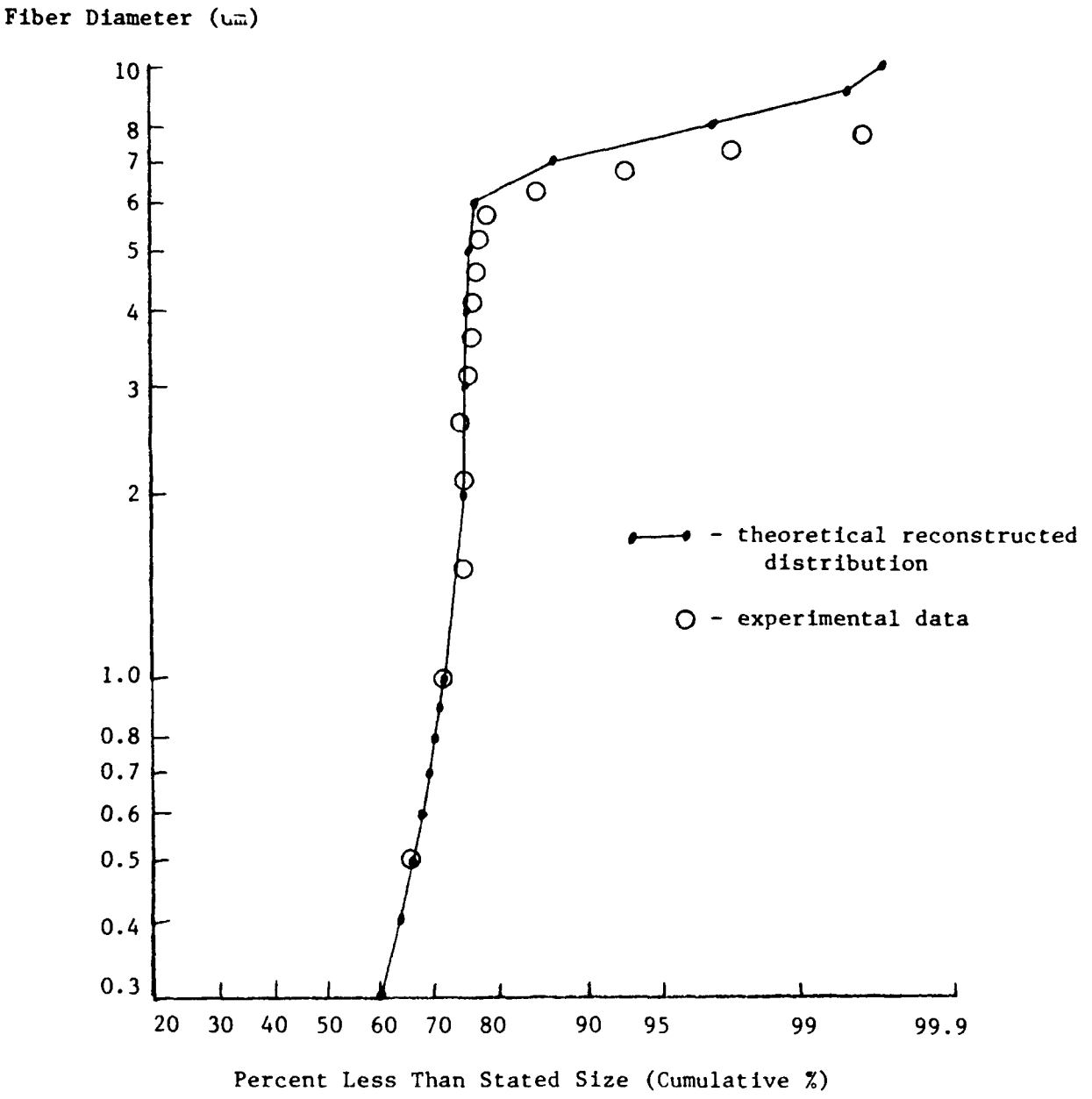
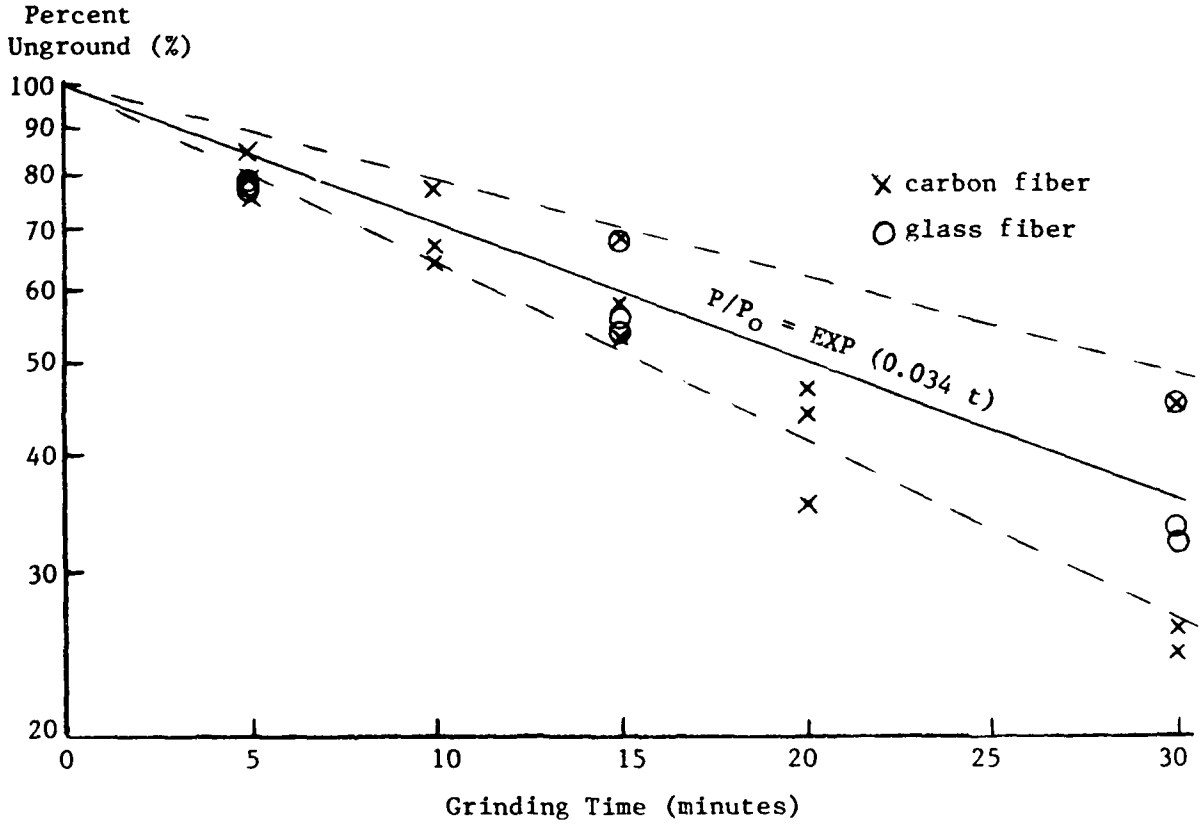


Figure 8

Percent Unground Fiber vs. Grind Time
for Carbon and Glass Fiber



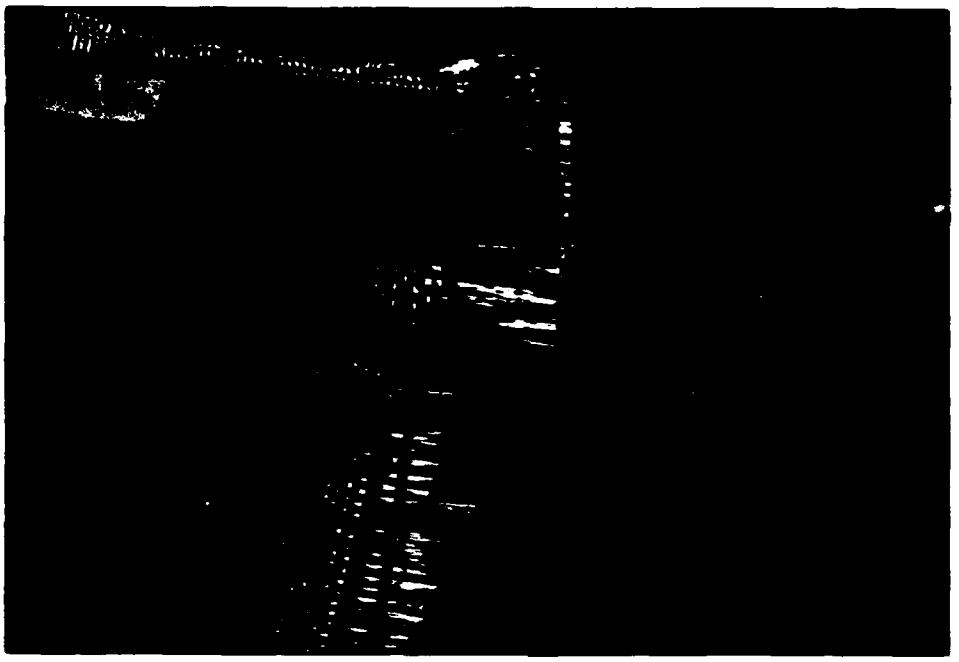


Figure 9
M-63 Carbon Fiber Cloth Used for Grinding

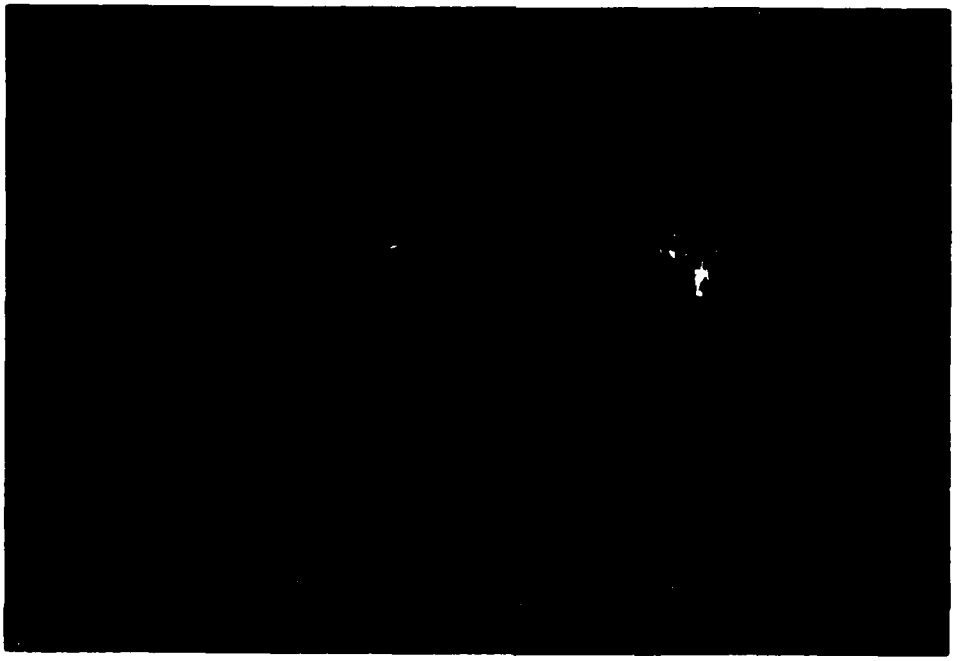


Figure 10
Carbon Fiber Cut into Approx. 1 cm Lengths
in Preparation for Milling

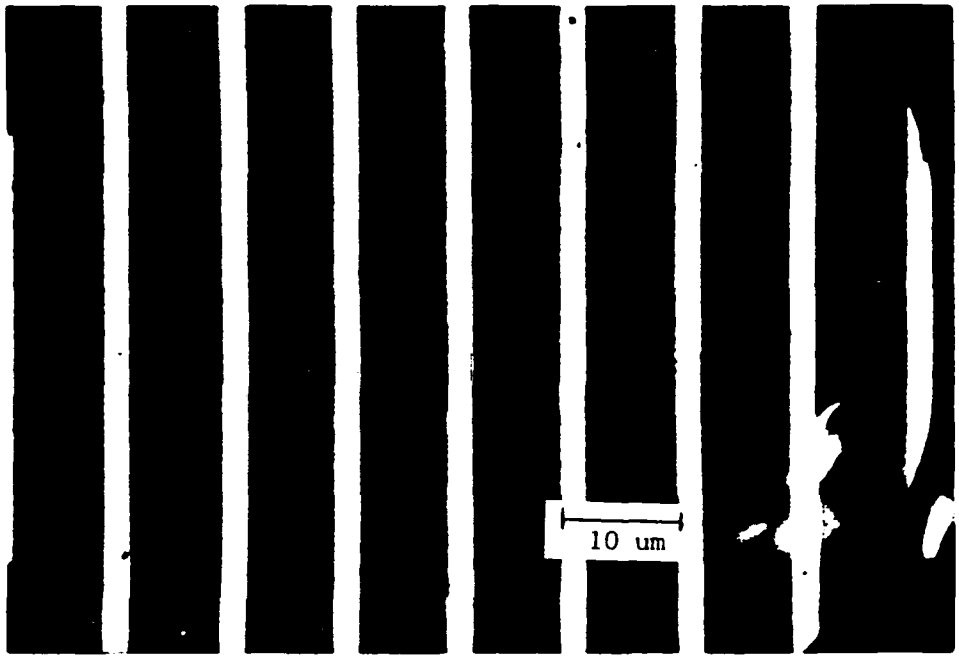


Figure 11
Calibration of 0-100 Eyepiece Graticule Ruler
Stage Micrometer at 10 um per White Line

Figure 12
Measuring Diameter of Carbon Fiber
with Eyepiece Ruler

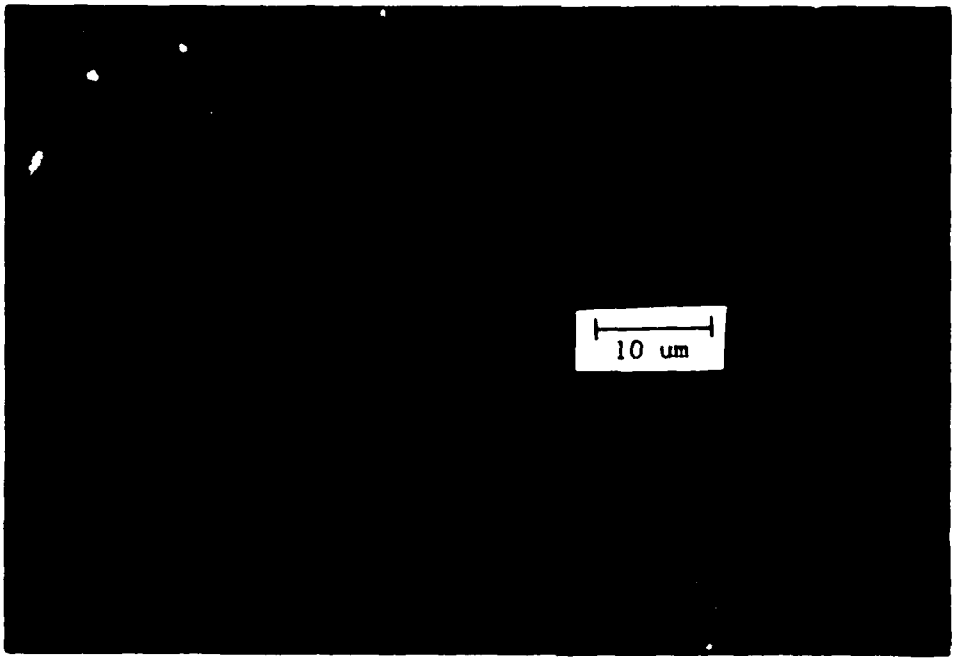


Figure 13
0.5 X 3.0 um Carbon Fiber

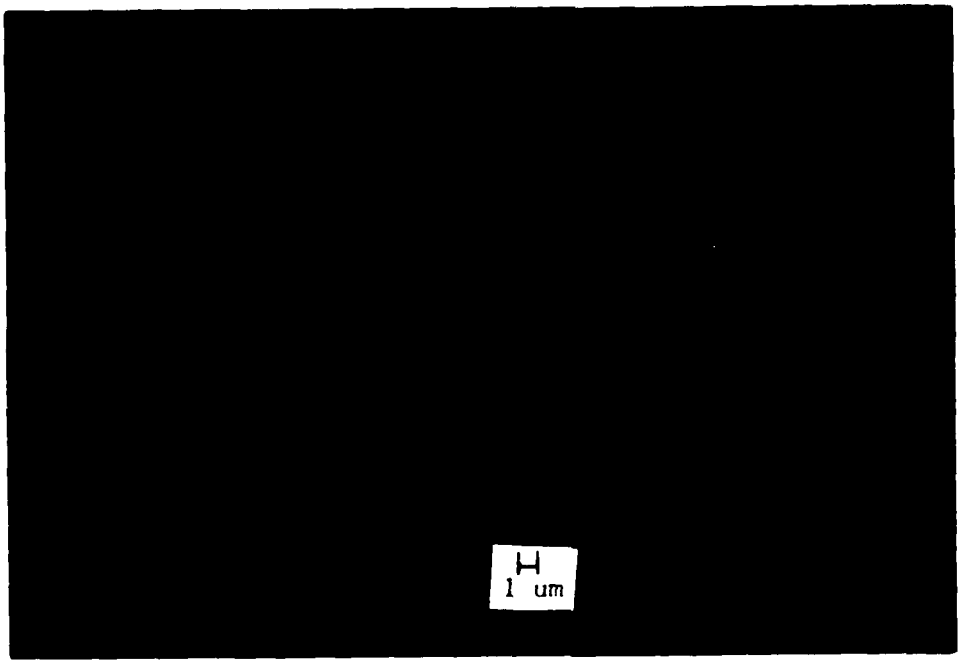


Figure 14
0.8 X 2.4 um Carbon Fiber

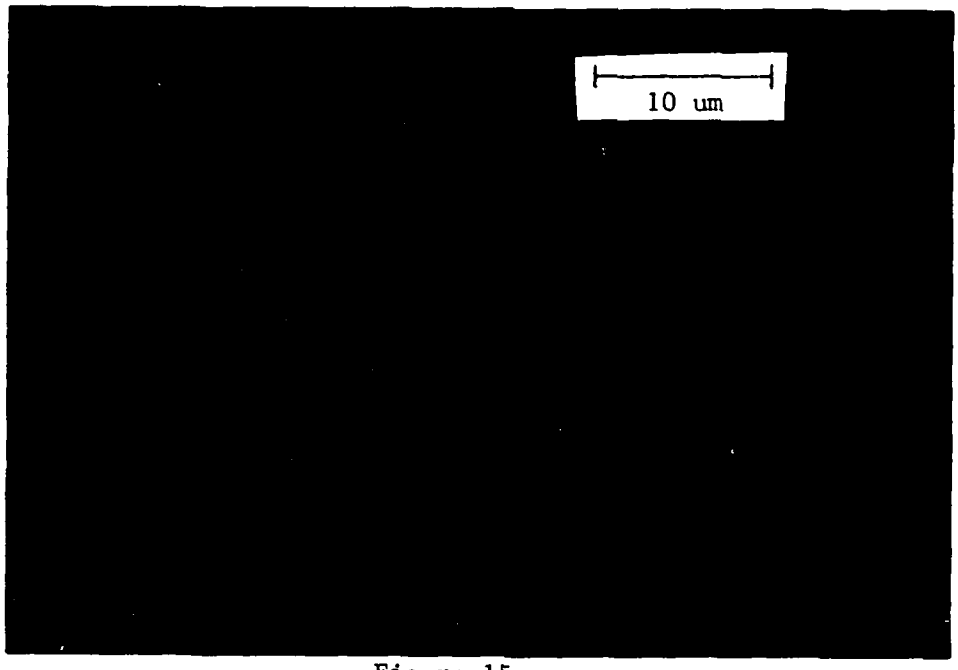


Figure 15
7.9 um Diameter Fiber of Original Diameter

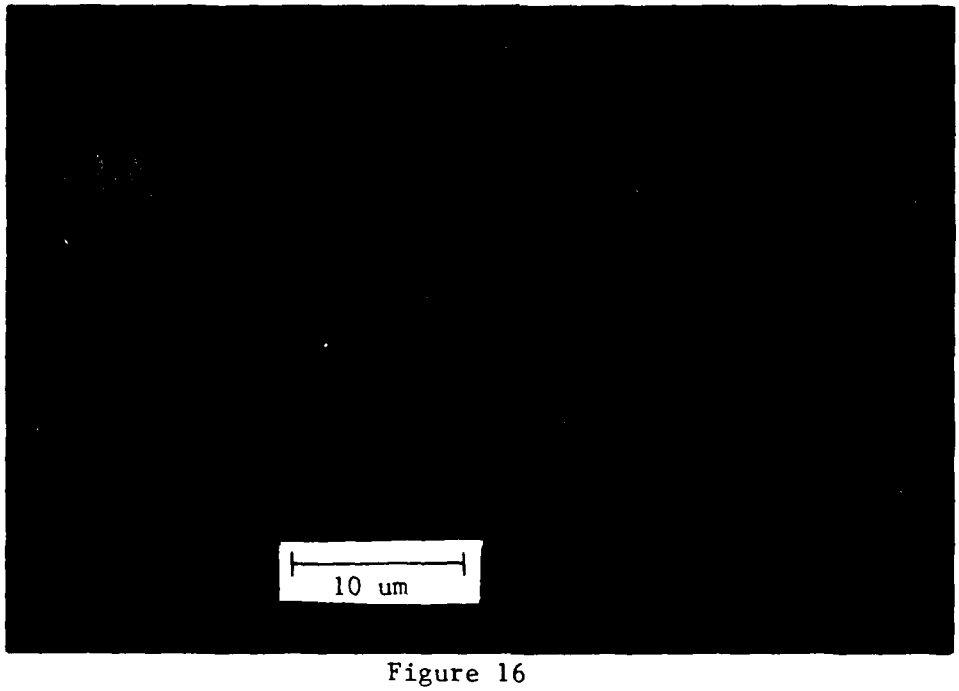


Figure 16
Glass Particles with a 0.8 X 5.8 um Glass Fiber

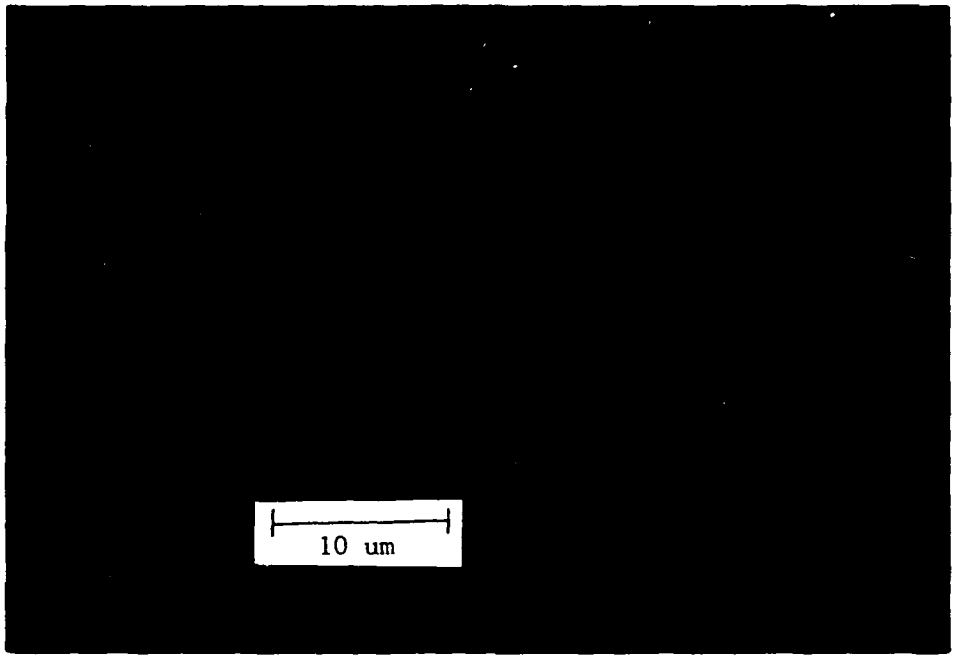


Figure 17
Non-Glass Fiber Ignored in Counting

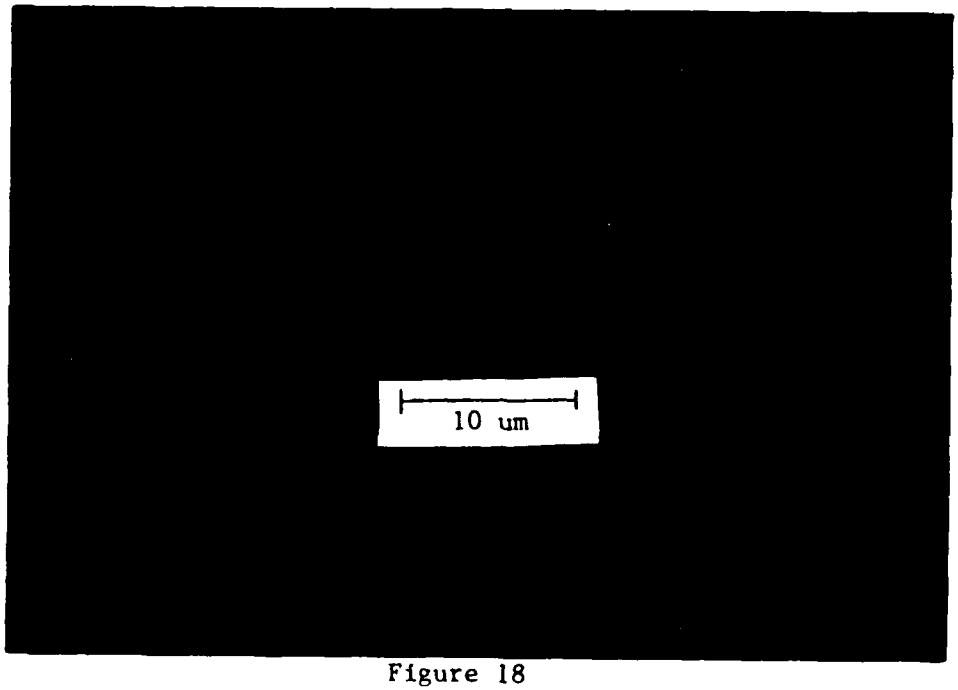


Figure 18
Appears as Cluster of Bacteria
Not Counted as Glass Fiber

TABLE V

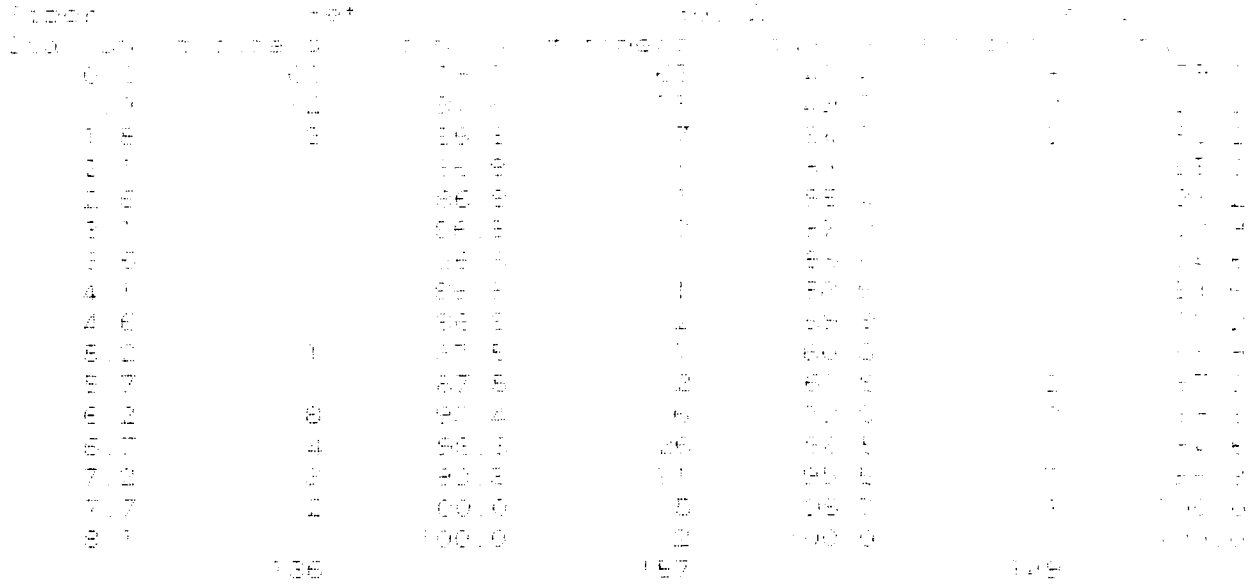


TABLE VI

Fiber Diameter Distribution
Glass Fiber Ground Pile Mixture

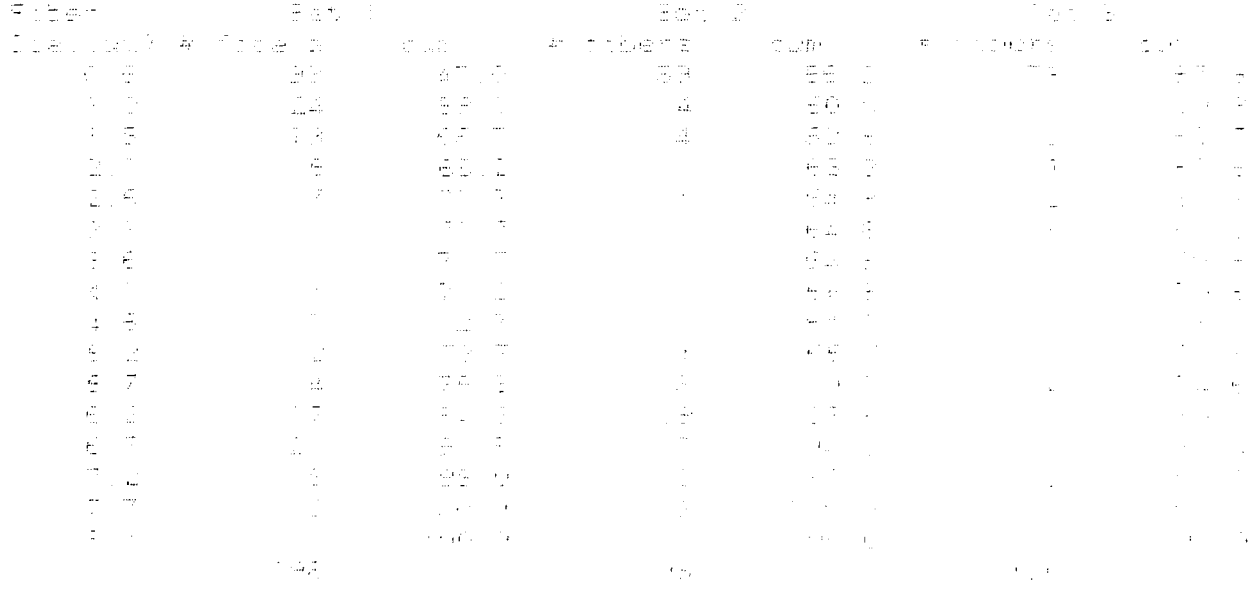


TABLE VII [illegible]

[illegible]

[illegible]

Fiber Diam. (um)	Set # fibers	cum %	# [illegible]	cum %	# [illegible]	[illegible]
0.5	[illegible]	[illegible]	7	[illegible]	[illegible]	[illegible]
1.0	[illegible]	[illegible]	[illegible]	79	[illegible]	[illegible]
1.5	1	57.[illegible]	[illegible]	78.7		[illegible]
2.1	2	[illegible]	1	[illegible]		[illegible]
2.6		[illegible].7		79.2		[illegible]
3.1	[illegible]	[illegible].5	3	[illegible].2		[illegible]
3.6		59.5		[illegible]		[illegible]
4.1	[illegible]	60.[illegible]		[illegible]		[illegible]
4.6		60.[illegible]		80.[illegible]		[illegible]
5.2		[illegible]		[illegible].2	[illegible]	[illegible]
5.7	4	63.5	4	[illegible]	[illegible]	[illegible]
6.2	19	77.8	22	[illegible]	[illegible]	[illegible]
6.7	[illegible]	92.1	8	[illegible]	[illegible]	[illegible]
7.2	[illegible]	100.0	4	[illegible]	[illegible]	[illegible]
7.7		100.0	2	100.0		[illegible]
8.1		100.0		100.0		100.0
	136		207		[illegible]	

TABLE VIII
Average of 4 [illegible]
Glass Fiber

Fiber Diam. (um)	6 min grind cum %	std dev	10 min grind cum %	std dev	[illegible] grind cum %	std dev
0.5	46.7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1.0	71.2	18.2	[illegible]	[illegible]	[illegible]	[illegible]
1.5	74.7	17.9	64.[illegible]	[illegible]	[illegible]	[illegible]
2.1	74.[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
2.6	75.[illegible]	[illegible]	67.2	[illegible]	[illegible]	[illegible]
3.1	75.[illegible]	18.2	[illegible]	[illegible]	[illegible]	[illegible]
3.6	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4.1	[illegible]	18.7	[illegible]	[illegible]	[illegible]	[illegible]
4.6	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5.2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5.7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
6.2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
6.7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
7.2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
7.7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
8.1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table IX

Percent of Total Fibers in Each
Length and Diameter Size Group

Carbon Fiber Ground for 5 Minutes
Average of Sets 1,2,3

Fiber Length (um)	Fiber Diameter (um) 0.25-0.75	0.76-2.3	2.4-4.3	4.4-6.3	> 6.3	Sum %	Cum %
1.3-1.75	30.7	-	-	-	-	30.7	30.7
1.76-2.8	17.4	-	-	-	-	17.4	48.1
2.9-5.3	0.7	15.3	-	-	-	16.0	64.1
5.4-10	-	4.6	2.9	-	-	7.5	71.6
11-25	-	-	4.3	1.6	2.3	8.2	79.8
26-50	-	-	-	1.4	8.0	9.4	89.2
> 50	-	-	-	-	10.9	10.9	100.1
Sum %	48.8	19.9	7.2	3.2	21.2		
Cumulative %	48.8	68.7	75.9	78.9	100.1		

Table X

Percent of Total Fibers in Each
Length and Diameter Size Group

Carbon Fiber Ground for 15 Minutes
Average of Sets 1,2,3

Fiber Length (um)	Fiber Diameter (um) 0.25-0.75	0.76-2.3	2.4-4.3	4.4-6.3	> 6.3	Sum %	Cum %
1.3-1.75	37.9	-	-	-	-	37.9	37.9
1.76-2.8	17.9	-	-	-	-	17.9	55.8
2.9-5.3	2.4	11.2	-	-	-	13.6	69.4
5.4-10	-	2.7	2.0	-	-	4.7	74.1
11-25	-	-	4.4	2.4	2.1	8.9	83.0
26-50	-	-	0.2	0.3	5.1	5.6	88.6
> 50	-	-	-	0.2	11.0	11.2	99.8
Sum %	58.2	13.9	6.6	2.9	18.2		
Cumulative %	58.2	72.1	78.7	81.6	99.8		

Table XI

Percent of Total Fibers in Each
Length and Diameter Size Group

Carbon Fiber Ground for 30 Minutes
Average of Sets 2,3,4

Fiber Length (um)	Fiber Diameter (um) 0.25-0.75	0.76-2.3	2.4-4.3	4.4-6.3	> 6.3	Sum %	Cum %
1.3-1.75	46.1	-	-	-	-	46.1	46.1
1.76-2.8	17.1	-	-	-	-	17.1	63.2
2.9-5.3	1.4	16.6	-	-	-	18.0	81.2
5.4-10	-	0.6	2.1	-	-	2.7	83.9
11-25	-	-	2.4	2.4	2.4	7.2	91.1
26-50	-	-	-	0.4	4.1	4.5	95.6
> 50	-	-	-	0.3	4.4	4.7	100.3
Sum %	64.6	17.2	4.5	3.1	10.9		
Cumulative %	64.6	81.8	86.3	89.4	100.3		

Table XII

Percent of Total Fibers in Each
Length and Diameter Size Group

Glass Fiber Ground for 5 Minutes
Average of Sets 1,2,3

Fiber Length (um)	Fiber Diameter (um) 0.25-0.75	0.76-2.3	2.4-4.3	4.4-6.3	> 6.3	Sum %	Cum %
1.3-1.75	41.2	-	-	-	-	41.2	41.2
1.76-2.8	20.9	-	-	-	-	20.9	62.1
2.9-5.3	3.6	7.5	-	-	-	11.1	73.2
5.4-10	-	1.8	0.7	-	-	2.5	75.7
11-25	-	-	1.1	2.9	0.8	4.8	80.5
26-50	-	-	-	2.5	5.7	8.2	88.7
> 50	-	-	-	2.9	8.6	11.5	100.2
Sum %	65.7	9.3	1.8	8.3	15.1		
Cumulative %	65.7	75.0	76.8	85.1	100.2		

Table XIII

Percent of Total Fibers in Each
Length and Diameter Size Group

Glass Fiber Ground for 15 Minutes
Average of Sets 1,2,3

Fiber Length (um)	Fiber Diameter (um) 0.25-0.75	0.76-2.3	2.4-4.3	4.4-6.3	> 6.3	Sum %	Cum %
1.3-1.75	30.5	-	-	-	-	30.5	30.5
1.76-2.8	21.1	-	-	-	-	21.1	51.6
2.9-5.3	2.3	9.1	-	-	-	11.4	63.0
5.4-10	-	2.5	1.5	-	-	4.0	67.0
11-25	-	-	2.5	5.4	2.2	10.1	77.1
26-50	-	-	-	6.1	3.8	9.9	87.0
> 50	-	-	-	6.6	6.8	13.4	100.4
Sum %	53.9	11.6	4.0	18.1	12.8		
Cumulative %	53.9	65.5	69.5	87.6	100.4		

Table XIV

Percent of Total Fibers in Each
Length and Diameter Size Group

Glass Fiber Ground for 30 Minutes
Average of Sets 1,2,3

Fiber Length (um)	Fiber Diameter (um) 0.25-0.75	0.76-2.3	2.4-4.3	4.4-6.3	> 6.3	Sum %	Cum %
1.3-1.75	38.8	-	-	-	-	38.8	38.8
1.76-2.8	21.4	-	-	-	-	21.4	60.2
2.9-5.3	2.2	4.7	-	-	-	6.9	67.1
5.4-10	-	1.2	0.2	-	-	1.4	68.5
11-25	-	0.3	0.7	2.0	0.9	3.9	72.4
26-50	-	-	-	5.0	4.2	9.2	81.6
> 50	-	-	-	9.5	8.9	18.4	100.0
Sum %	62.4	6.2	0.9	16.5	14.0		
Cumulative %	62.4	68.6	69.5	86.0	100.0		

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