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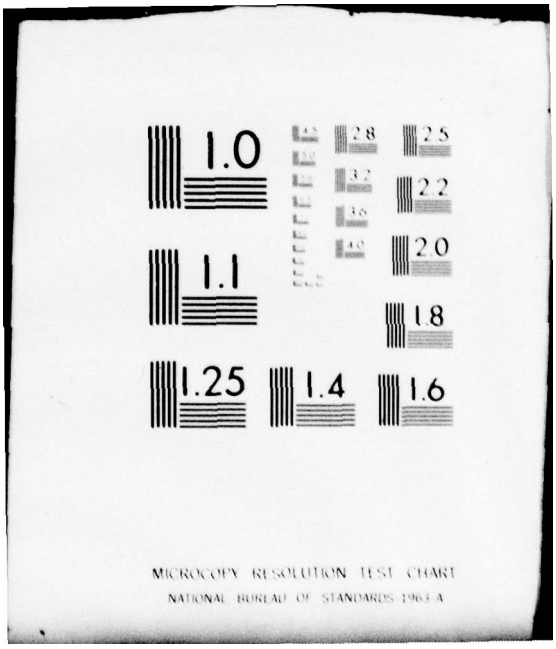
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CARBON FIBER ELECTRICAL RESISTANCE MODIFICATION- ITS RELATIONSHIP TO ELECTRICAL EQUIPMENT MALFUNCTION.

Office of Naval Research Carbon Fiber Study Group

1 Sept 1978

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Final Report.

GIDEP

E134-1524

Prepared for

OFFICE OF NAVAL RESEARCH
METALLURGY AND CERAMIC PROGRAM

Arlington, Virginia 22217

265 250

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* See Box 15	** See Box 15	

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Examines the problem of carbon fibers which come in contact with critical electrical circuits when accidentally dispersed into the air. A Carbon Fiber Study Group was convened to consider whether or not the electrical resistance of carbon fibers could be increased to acceptable levels without altering other desirable characteristics. The group considered (1) the magnitude of resistance changes required to minimize electrical equipment malfunction, (2) whether or not carbon fibers can be modified to meet these requirements, (3) the ease of hardening confined spaces, and (4) the disposal of carbon fibers and composites after use.

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16. KEY WORDS FOR INDEXING
Carbon Fibers; Electrical Equipment; Electrical Resistivity; Carbon-Carbon Composites; Fire; Explosion; Carbon-Organic Matrix Composites; Airborne Carbon Fibers; (Doc Des--P)

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PREFACE

The work described in this report is the result of the contributions of the following members of The Office of Naval Research Fiber Study Group:

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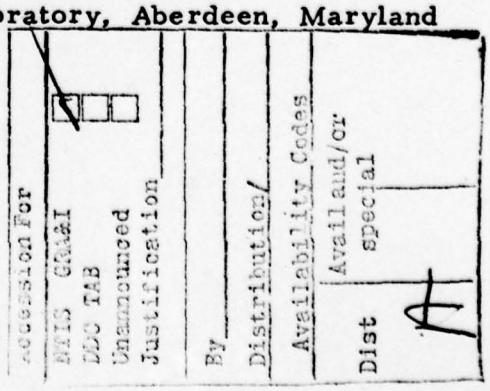

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I. INTRODUCTION

Individual carbon fiber filaments can be released from carbon-fiber reinforced composites when the latter are subjected to severe environmental conditions such as fire, explosion, impact, and wear. The highly electrically conductive fibers, so released, can interact with electrical equipment and cause their malfunction by such phenomena as short circuits, arcs, and coronas.

Because of the increased use of carbon fibers for aerospace and automotive applications and for a variety of consumer products, the chances of contamination by airborne fiber are also increasing. Furthermore, because the fibers are stiff, strong, and have low density, they are used in composites to reduce weight, which is an important factor in conserving energy. Industries have already committed large capital expenditures and are planning further expansions provided that the potential threat of air-borne fibers can be controlled.

A Carbon Fiber Study Group was convened by the Office of Naval Research (ONR) to consider whether or not the fiber resistance of carbon fiber could be increased sufficiently to minimize the hazards to electrical equipment. The group considered whether or not the modifications to the fiber resistance could be accomplished without undue sacrifice to the modulus and strength.

The objective of the study was to define research approaches that might alleviate the potential problems. The conclusions and recommendations are based on discussions with experts in fiber manufacturing, fiber utilization, and the influence of fibers on electrical equipment malfunctions. The effects of variations in the composition and morphology of the fiber on the electrical resistance and mechanical properties were also considered. The conclusions were made largely on the basis of unpublished information and on analyses performed by committee members.

The results of the study are published as two separate reports: The Executive Summary, 039-160-1 (TR-0078(3721-11)-1), and The Executive Summary combined with supportive information, 039-160-2 (TR-0078(3721-11)-2). Sections I and VI of this report also appear in The Executive Summary as Sections I and II.

II. BACKGROUND INFORMATION

As they become more useful in many different applications, composite materials are of growing importance to the entire national industrial economy; they offer an improvement in performance and weight over metals they replace. Federal research and development programs, notably within the National Aeronautics and Space Administration (NASA) have focused on expanding the use of composites in the civilian aviation field; Federal procurement and development programs, particularly within the Department of Defense (DoD), have specified these high-performance, lightweight materials; and Federal automotive fuel consumption standards virtually require conversion from present metals to new lighter-weight materials. Furthermore, the use of carbon composites will help alleviate the availability problem of certain metals. A typical carbon fiber has a strength of approximately 2.7 GPa (400×10^3 psi), a modulus of approximately 207 GPa (30×10^6 psi) to 620 GPa (90×10^6 psi), and a density of 1.80 g/cm^3. These fibers are well suited for reinforcing lightweight low-modulus plastics or resins. Structural parts produced from these components have strength and modulus properties equivalent to metal parts but are at a quarter of the total weight. The replacement of metal structures by carbon-fiber-reinforced plastics on all moveable parts results in substantial potential weight reduction and thus substantial reduction in the energy required to overcome inertia and maintain velocity. A recent market survey prepared for NASA indicated that by 1990 the production of carbon fibers could be 5×10^5 kg/yr (10^6 lb) for aerospace applications, 5×10^8 kg/yr (10^9 lb) for automotive applications, and 5×10^5 kg/yr (10^6 lb) in the remaining areas of use.[1] Marketing experts are now predicting an increase of more than 400% in the worldwide carbon fiber demand and production by 1980. Such increases depend, in part, on further development of low-cost,

[1] Preliminary Economic Evaluation of the use of Graphite Materials in Surface Transportation, NASA report 77-165-1, ECON, Inc., Princeton, New Jersey (11 July 1977).

continuous, high-modulus carbon fibers and the use of carbon fiber technology not only in the aerospace and defense areas but also in the automotive industry. For the latter, forecasts of the amount of carbon fibers that are predicted to be used vary by a factor of 40 or more. Thus, there will undoubtedly be large increases in the amount of fibers to be used, but exact amounts are difficult to predict.

By 1985, industry will likely be consuming large volumes of carbon fibers. Applications of carbon fibers in the aircraft and aerospace industries are expected to increase, particularly for structural load-bearing applications. The aircraft industry is expected to be the major user of carbon composites until the period of 1985. Some predictions indicate that the volume of non-military aerospace use is expected to increase by about a factor of 5 every five years until 1990.[2] Other authorities in the aircraft industry indicate that the amount of fibers used in 1975 was about 5×10^4 kg (10^5 lb), which may triple in 1980 and increase to 5×10^5 kg/yr (10^6 lb) by 1985. But beyond 1985, the major user of carbon composites is predicted to be the ground transportation industry.

The interest in carbon composites for automotive manufacturing has increased largely because of the pressure to reduce gasoline consumption in accordance with national policy. Several automotive components produced from carbon fiber composites are now found in test vehicles: leaf springs, drive shafts, door intrusion beams, and truck frame elements. Ford Motor Company has produced a demonstration automobile in which the use of carbon fibers has contributed to a 35% weight reduction, which is equivalent to approximately 640 kg (1400 lb). Future application may include push and connecting rods, rocker arms, oil pans, shafts, axles and axle housings, and secondary body components. It has been predicted that, by 1985, the average automobile will contain about 2.3 kg (5 lb) carbon composites. Representatives from Ford are quick to add, however, that any predictions beyond 1985

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[2] "Carbon Fiber Study," NASA Technical Memorandum 78-718 (May 1978).

must await the results obtained between now and 1985. Other estimates of 40 kg (90 lb) per average car in 1990 are based on a technical review by the Department of Transportation. For an estimated production rate of 10 million cars in 1990, the projected consumption of composites would be 4×10^8 kg/yr (450,000 tons) in 1990, or about 2×10^8 kg (225,000 tons) of fibers.[2]

The major current use of carbon fiber is in such consumer products as tennis rackets, fishing rods, and golf clubs. Also, carbon fiber composites are being used in selected industrial applications for such products as gears, flywheels, and structural members. Although it is extremely difficult to acquire definitive data on current and projected use of carbon fiber composites, it is estimated that 23,000 kg/yr (50,000 lb) are now being used, and this may increase to 46,000 to 68,000 kg/yr (100,000 to 150,000 lb) by 1980.

The use of carbon fibers will undoubtedly increase the chances of an accidental release of carbon fibers, which could result in the malfunctioning of electrical equipment. The electrical hazard of carbon fibers first came to light during pilot plant manufacturing of carbon fibers, whether from rayon precursors, acrylic precursors (the Orlon, Acrilan, and Courtelle-type fibers), or pitch precursors. During these early production stages, it was noted that the strong but brittle fibers were easily damaged during handling operations, and aerosol dispersion of short fibers was produced. The airborne fibers could interact with electrical equipment and cause shutdown. The occurrences varied from the mildly annoying and relatively inexpensive to major disruptions and costly outages. Carbon fiber manufacturers and personnel responsible for handling the material during composite fabrication had to "harden" their equipment in order to prevent the airborne fibers from contacting such electrical equipment as terminals, contacts, and bus bars. Since carbon fibers were not intended for use alone but rather as the reinforcing agent in a composite, manufacturers that experienced the difficulties reasoned that once the fibers were encapsulated within a composite,

the hazard no longer existed. Subsequently, several events occurred that caused a reevaluation of the possible hazards when these or similar fibers became dispersed into the atmosphere outside the confines of a manufacturing facility. On 12 May 1972, a cardboard carton containing untwisted carbon fiber filaments was inadvertently placed in an incinerator at the Union Carbide facility in Fostoria, Ohio. Within minutes, individual fibers were being discharged from the chimney of the incinerator. Fibers were observed floating in the air, settling on roof tops, wires, and in the yard area. Two electrical power substations in the plant area downwind and one-half mile from the chimney were shorted out 25 to 60 min after the carton was placed in the incinerator. Later, a third substation shorted out, but eight other open-air substations downwind from the chimney did not short out. Electrical outage problems occurred in two other manufacturing sites six miles downwind, and the Ohio Power Company experienced a number of outages on 12 and 13 May, which resulted in blackouts in Fostoria. It should be noted that the fibers placed in the incinerator were loosely packed in the cardboard container and were not encapsulated into a matrix; hence, it was still believed that composite materials were hazard free. However, a series of aircraft crashes with ensuing fires at Miramar Naval Air Station, California, motivated concern over the possibility of carbon fiber release from composites being used or soon to be used on DoD and civilian aircraft. On 29 October 1975, an F14 Tomcat fighter plane threw a turbine blade shortly after takeoff, burst into flames, and crashed; the fire was extinguished before the aircraft came to rest. The horizontal stabilizer, a large control surface in the rear of the aircraft, is a structure that contains boron fiber embedded in an epoxy matrix. Although the fire lasted only a few seconds, approximately 30% of the boron fibers was released and scattered over an area of about 230 m^2 (2500 ft^2). On 21 June 1976, a second F14 crashed at Miramar and approximately 50% of the boron fibers was released. On 23 June, while the accident investigation team was on-site, yet another F14 crashed and fibers were scattered over an area of about 900 m^2 (10, 000 ft^2). Each accident occurred at great distances from

other equipment without any side effects. However, in view of the known high conductivity of carbon fibers and the much slower settling rate when compared to boron (because of the finer diameter and lower density of the carbon fibers), a natural concern is for the consequences if released carbon fibers are allowed to interact with aircraft avionics or airport radar installations.

The events described above indicate that, with increased use of carbon fiber materials in aircraft, sporting goods, and automobiles (the carbon fiber worldwide production rate of nearly one billion pounds per year predicted by 1990), the occurrence of fires involving composites and hence the incidence of accidental dispersion should also increase. Although there have been no reports of accidental release of carbon fibers from composite materials by means of fire that have resulted in electrical breakdown of nearby equipment, there is good reason to consider methods for reducing this potential risk.

Because of the relative scarcity of data concerning the inadvertent release of carbon fibers from composite materials, their dissemination in the atmosphere, the ways in which fibers in the atmosphere reach electronic and electrical components likely to be affected, and the severity of damage likely to be produced, it is almost impossible to predict the rate of carbon-fiber-induced electrical incidents. Both NASA and DoD are conducting experimental test programs and risk analyses in efforts to improve the capability of making such predictions. However, time is required to obtain and verify the reliability of test results under real-life conditions. In the meantime, alternative approaches and solutions need to be investigated.

The electrical hazards created by carbon fibers could be ameliorated by three general methods: (1) protection of equipment, (2) limiting dissemination of hazardous fibers, and (3) modification of the hazard-causing material. In order to reduce the potential electrical hazards for cases 2 and 3, several approaches can be taken:

1. Significant reduction of carbon fiber conductivity
2. Development of matrices that either do not burn or resist dispersal of fiber
3. Development of fiber coatings that can survive fire environments and prevent electrical interaction
4. Development of gel coats for the composite that hold the composite intact when placed in a fire environment or
5. A combination of the above approaches.

In this report, the primary emphasis is on recommendations for changing the electrical resistance without adversely altering other desirable properties or materially increasing manufacturing costs. The basic hypothesis is that, if reasonable methods can be found to eliminate the problem at the source, then a large variety of matrix materials can be used in composite design. Indeed, commercial articles are currently available in which generic matrix materials such as epoxies, polyimides, and polysulfones are used, and others are being developed for a variety of uses.

Attention was given to the feasibility of modifying the resistance of the fibers, including surface coatings or treatment of the fibers. This ONR study appears to complement work by NASA, who has the prime responsibility for investigating alternative materials. The NASA programs concern such aspects as methods for bonding the fibers together during a fire or explosion or both and thereby inhibit the fibers from becoming airborne. The NASA approach will likely result in the earliest success, whereas the modification of fibers will be a longer-term approach because of the three or more years usually required to develop a production process and qualify the new fibers. Furthermore, any change in fibers or matrices will be resisted by manufacturers because of the costs of requalification.

Finally, the committee considered not only the feasibility of changing the electrical conductivity of the fibers, but also the amount of change required to reduce the possibility of electrical equipment malfunction because of airborne fibers.

III. EFFECTS OF CARBON FIBERS ON ELECTRICAL EQUIPMENT

A. MAGNITUDE AND TRENDS OF THE PROBLEM

The problem of contamination of electrical and electronic systems by means of aerosols and airborne particulates has existed throughout the development of such systems. The problem is not confined to conducting particulates. Insulating particles and fibers can cause considerable malfunction in electromechanical devices by preventing circuit closure at low voltage switch contacts – a typical problem in telephone systems. Organic vapors can cause problems when catalyzed at switch and relay contacts, particularly platinum-coated contacts, to yield carbonaceous particles, which enhance low current arcs. Dust can cause breakdown in high electric fields by creating field intensification sites; moreover, many dust-laden atmospheres are highly explosive (witness the many catastrophic explosions in grain silos caused by electrostatic discharges).

The problem considered here is therefore not fundamentally new but is accentuated by certain characteristics of these carbon fibers:

1. High electrical conductivity
2. High thermal conductivity
3. Reasonably high temperature properties (nonself-sustaining burning temperatures in the range of 350 to 700°C, in air, compared with the sublimation temperature of pure graphite, approximately 3650°C)
4. Low mass density (approximately 1.5 to 1.9 g $(cm)^{-3}$)
5. Small diameter (approximately 7 to 22 μm)
6. High chemical stability (not biodegradable)
7. High tensile strength and Young's Modulus
8. For low heat treatment fibers, a negative temperature coefficient of resistance at low temperatures

The combination of low mass density and small diameter allow the fibers, as short dipoles, to become airborne easily (Fig. 1) and, furthermore, to be re-entrained by surface air turbulence after they have settled on the terrain. The persistance of the problem is indicated by the fact that 0.64- and 1.3-cm (0.25- and 0.5-in.) fibers released over desert terrain about three years ago are still being resuspended and detected many miles from the original source.

On the other hand, for lengths much greater than about 1 cm, the fibers tend to form clumps, depending on the surface finish and subsequent history. These clumps have considerably larger fall velocities than those of single fibers. Clumping is not a peculiar problem of these fibers alone. All particulate suspensions tend to clump or aggregate when their concentration is high enough to permit near-neighbor interactions. The short-range forces may involve coulomb and van der Waals attractive forces. Considerable research has been undertaken to study the frictional and contact electromechanical effects of carbon fibers.[3] Thus, for lengths greater than about 1 cm, the hazard to enclosed systems from carbon fibers is minimal not only because of the ease of air filtering, but also simply because, in still air or low wind conditions, the fibers settle quickly and within a confined area. However, in a "fire storm," where high wind shears exist, long fibers and aggregates of fibers may travel considerable distances. Limited laboratory and field experience with carbon and graphite powders indicate that the problem is reduced as the particles become smaller and more spherial, which means that there is a range of lengths at which fibers are most detrimental to electrical equipment.

B. DEFINITION AND SCOPE OF THE VARIABLES

The carbon fiber contamination problem has been demonstrated to exist at all voltages above 2 or 3 V and all frequencies from dc to high radio frequencies (rf) in use if there is penetration to exposed electrodes or intense

[3] I. C. Roselman and D. Tabor, "The Friction of Carbon Fibres," J. Phys: D. App. Phys. 9, 2517 (1976).

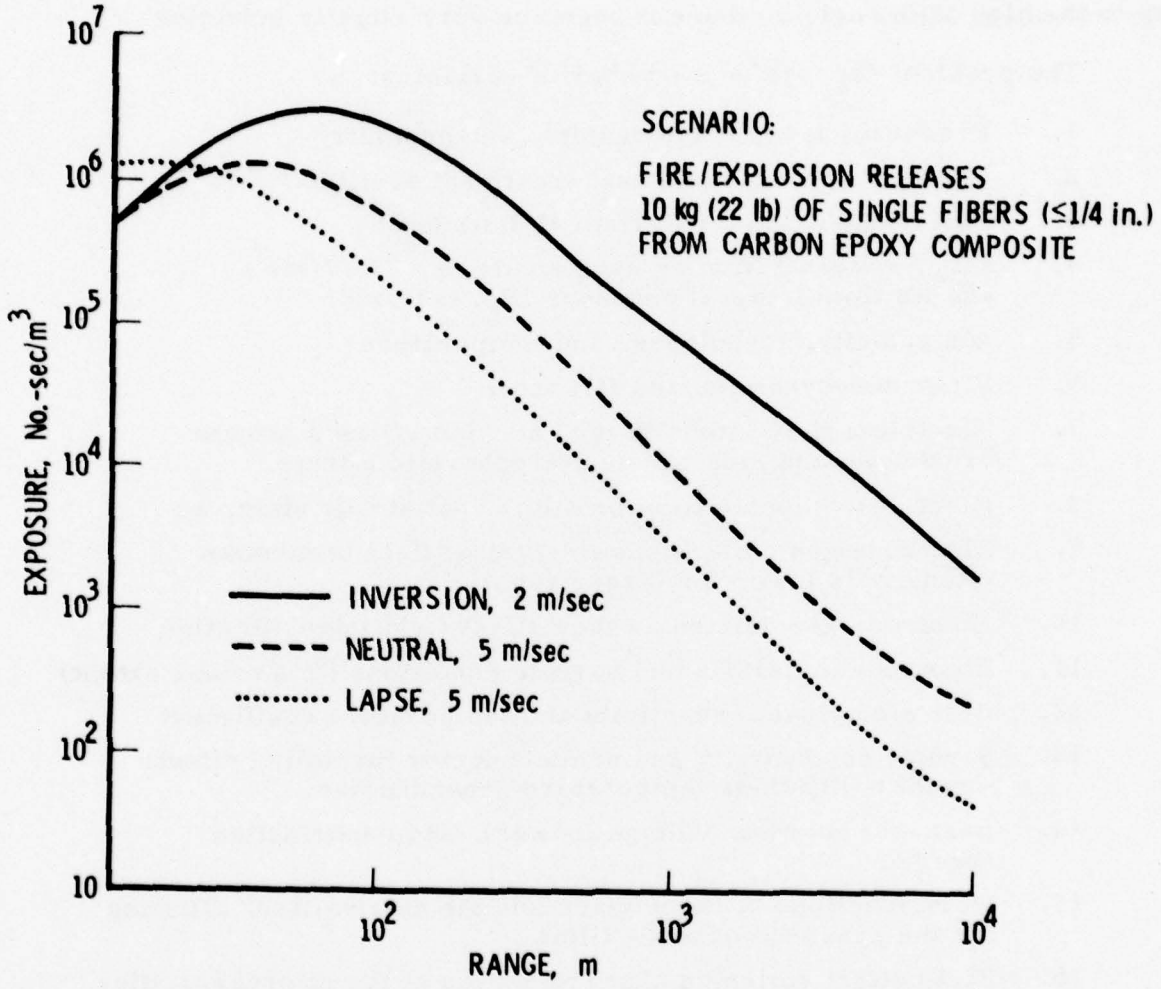

Figure 1. Exposure of Single Fibers from Composite Accident. Vertical isopleth.

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electric fields or both. The fiber acts as a resistor, and laboratory experiments indicate that the fiber impedance remains almost purely resistive up to the high MHz region, where it becomes very slightly inductive.

The problem depends on a number of variables:

1. Precursor type, mass density, and geometry
2. Pyrolysis process and heat treatment profile
3. Fiber length and its statistical distribution
4. Fiber concentration or number density (No. $/(m)^3$) and its time integral exposure (No. -sec/m^3)
5. Air velocity, turbulence, and temperature
6. Fiber aerodynamics and fall rates
7. Electrical field intensity (dc, ac, and rf) as it affects breakdown and electro/dielectrophoretic effects
8. Electrical impulse time profile; if not steady state, ac
9. Electrode gap dimensions (electrical field breakdown intensity is lower for larger gaps)
10. Electrode geometries as they affect field intensification
11. Electrode materials and surface conditions (to a minor extent)
12. Bulk electrical conductivity and temperature coefficient
13. Surface conductivity and semiconductor tunnelling effects together with their temperature dependencies
14. Burn-out current, voltage (power), and vaporization energy
15. Work functions of the surface and the extremities, allowing for the presence of oxide films
16. Field effect emission characteristics at the microasperities of the fiber ends
17. Exoelectrons from freshly broken fibers
18. Coronal jet reaction forces, which are asymmetric (positive corona occurs at a lower voltage than does negative corona at standard temperature and pressure (STP)
19. Coulomb and van der Waals forces
20. Polluted system electromagnetic characteristics such as energy, power, and internal impedance.

C. AERODYNAMICS

Because the hazard is contingent upon the dispersal of carbon fibers, the aerodynamic parameters have received considerable attention as the primary factors, even though there are situations where aerodynamic and electrodynamic forces can be in sharp competition or cooperation. Several models of varying scope and complexity have been developed to describe the atmospheric diffusion of low Reynolds number particulates. These characteristics have been studied extensively* and, since the fiber parameters cannot be altered sufficiently to cause significant changes, the aerodynamic details will not be discussed here.

D. ELECTRICAL EFFECTS CRITERIA

From a general overview of the problem, the electrical effects may be separated somewhat arbitrarily into the following three regimes:

1. Low voltage: ~2 to 18 V
2. Medium voltage: ~18 to 500 V
3. High voltage: greater than 500 V

1. LOW-VOLTAGE REGIME

The lower bound is several volts because of the presence of barrier or semiconductor films on both the fiber and the electrode surfaces. The voltages used in typical solid-state circuits (5 to 18 V) are usually more than enough to achieve "punch-through" of surface barriers; thus, access to the conducting planes of the carbon fiber is achieved.

In practical tests of transistor-transistor logic (TTL) boards, instantaneous effects are generally not observed, but in time, malfunctions do occur. Typical hitherto unpublished susceptibility data are given in Table 1. In extreme cases, fibers have been found trapped beneath plug-in chip sockets,

*R. I. Gray, Carbon Fiber Hazard Criteria, TR-3837, Naval Surface Weapons Center, Dahlgren, Virginia (in preparation).

Table 1. Typical Susceptibility of Solid-State Circuits[a]

Circuit Type	Fiber Types				
	AS	T300	GY 70	TP 4104/B	TP 4104/B(I)
Transistor-Transistor Logic (TTL)	18				1-8
TTL, low-current TTL (L)	18	2		3-10	1-8
Complementary Metal-Oxide Semiconductors (CMOS)	18		9	5	

[a] $E_o \times 10^{-5}$ (No. sec m^{-3}), where E_o is exposure from the negative exponential distribution function.

and decontamination by air blast, washing, and spraying has usually been ineffective. The problem is particularly detrimental because many of the effects are transient and subtle. The existence of spurious conductors in TTL systems may make them "illogical." It is therefore reasonable to consider that the fibers fall across circuit components to cause circuit perturbations by impedance changing or switching. In order for the perturbations to be significant, the linear fiber resistance must be comparable to the circuit component impedances, e.g., metal oxide semiconductor field effect transistor (MOSFET), approximately 10^{14} ohm complementary metal oxide silicon semiconductor (CMOS), approximately 10^{6} ohm; and bipolar transistor, approximately 10^{3} ohm, each with a standard solder-pin gap of 0.25 cm (0.1 in.). All smaller spacings are on the chip and sealed inside the can or molding. These are fiber linear resistance values near 10^{15}, 10^{7}, and 10^{4} ohm/cm, respectively, for comparable impedances to perturb the circuit. One saving feature is that the higher-impedance devices are often driven by low-impedance generators. Because MOSFETS are used mainly in

research equipment (electrometers, isolation, and other operational amplifier applications), and because this problem cannot be solved unless fiber materials such as glass, quartz, or unpyrolyzed polymers are considered, this rather special case must be set aside.

For solid-state devices and circuits in everyday use, approximately 10^6 ohm/cm may therefore be taken as a design goal lower bound. These data are not likely to change significantly in the immediate future. This method of approach is vulnerable, however, to the criticism that several fibers may fall across the same pair of conductors and thereby reduce the safety factor. Moreover, under conditions of high exposure, where total surface coverage is significant, protection may only be obtained by total exclusion of fibers. Under such conditions, deep potting (conformal coatings), hermetical sealing, and air filtration have promise as protective measures, but may be very costly.

2. MEDIUM-VOLTAGE REGIME

In this regime, individual fibers are generally burned or vaporized on contact, and the source may have sufficient power (or energy) combined with a sufficiently low internal impedance to generate and possibly sustain damaging metal-vapor arcs. Fibers may bridge contacts either singly or by forming contiguous chains (not chain-linking phenomena involving long sparks between fibers as discussed later). Such arcs may permanently damage insulation surfaces by carbon tracking. In this voltage regime, terminal equipment operating at consumer power frequencies of 60 and 400 Hz, electrical and electronic equipment (power packs), generators, alternators, and motors and motor generators together with their solid-state equivalents are potentially susceptible. For such equipment, the fiber resistance is not the only controlling parameter; work functions, field emission, vaporization energy, vaporization by-products, and photoionization may also play important roles. Because of the heating effects, room-temperature fiber properties no longer apply, and the dynamic values should be used in the analyses.

For the medium voltage regime, it is desirable to derive criteria, if possible, for fiber linear resistance, which is more meaningful than bulk resistivity. There are three principal zones to be considered: fiber burnout, arc initiation, and arc maintenance.

Because of the statistical nature of electrical breakdown processes, which involve a wide range of physical properties (e.g., initial electrons, formulative lag-times, surface work-functions usually determined by oxides, precursor avalanche effects, primary and secondary ionization coefficients, ion/electron recombination rates, and plasma physics), it is extremely difficult to achieve good replication of experimental results, even under well-controlled conditions. It is therefore usually very difficult to establish criteria for the occurrence of events.

It is possible, however, to establish, with fairly high precision, the criteria for the impossibility of occurrence of such events. Accordingly, arc maintenance will not be addressed here, but the two sets of threshold criteria for fiber burnout and the nonoccurrence of arcs will be established. Fortunately, there is a single, well-tried model that can be used for both of these criteria: the theory of polluted insulator flash-over and scintillation, which has been studied in detail since before World War II and has been more than adequately validated by experiment. This approach has been applied to the carbon fiber problem.* The conclusion is that linear resistance on a scale of 10^6 to 10^7 ohm/cm is required in order to significantly reduce the probability of arc initiation.

3. HIGH-VOLTAGE REGIME

In the kilovolt range, the predominant effects are flash-over and arcing across air gaps and over the surfaces of insulators, usually culminating in

*R. I. Gray, Carbon Fiber Hazard Criteria, TR-3837, Naval Surface Weapons Center, Dahlgren, Virginia (in preparation).

permanent tracking in the latter case. "Chain-linking" occurs in which gaps between adjacent fibers are comparable with fiber length. Large air gaps break down at lower electric field intensities than do small air gaps because of the mean-free path criterion for secondary ionization. Furthermore, coronal ion jets tend to counteract dielectrophoretic and electrophoretic forces. Therefore, as the concentration of fibers increases, the point is ultimately reached where breakdown between gaps occur, usually before the fibers touch. As the first gap breaks down, the others follow in rapid succession because of the step-functions in local gap fields. Fibers migrate toward the zones of increasing field intensity. Corona occurs at the sharp asperities that exist at fiber extremities, and the Fowler-Nordheim equation applies for these excellent cold, field-effect emitters,[4,5] which are used in electron microscopes and other applications. Field emission on the order of microamperes occur in average fields of a few kilovolts per centimeter, but the local fields are greatly enhanced by the tip asperities, which have radii on the order of nanometers. The effect of surface oxides also lowers the work function from about 4.6 to 1 or 2 eV. Exoelectrons may also be emitted from the freshly broken ends of fibers. Runaway current phenomena occur unless limited by high impedance circuits. The physics become dynamically complex because the fields are perturbed by the discharge products. Space-charge fields tend to inhibit further breakdown, and Trichel pulses are observed in dc fields. The Raether/Loeb/Meek streamer theory and photoionization mean-free-paths (approximately 0.16 cm) predominate in determining breakdown criteria and streamer discharges. In this regime, the bulk resistivity of the fiber plays a negligible

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[4] F. S. Baker, A. R. Osborn, and J. Williams, "The Carbon-Fibre Field Emitter," J. Phys. D: Appl. Phys. 7, 2105 (1974).

[5] E. Braun, J. F. Smith, and D. E. Sykes, "Carbon Fibres as Field Emitters," Vacuum 25 (9/10), 425, (1975).

part in the onset criteria, although it does limit the subsequent current. For example, corona can be produced by such materials as glass, wool, and ice. Usually, there is sufficient energy available to vaporize carbon fibers that act as precursors for a normal metal-vapor fed arc in air across large gaps.

Although increasing fiber resistance cannot solve the high-voltage problem, it is possible to use the corona off-set/on-set threshold as a criterion to determine the associated fiber resistance that will prevent a transition from corona to spark or arc. For very large gaps greater than 90 cm, or for the idealized, infinitely sharp point, the corona off-set curve is a constant at 4.82 kV/cm.[6] Toward the small gap limit (1 to 2 cm), the corona and spark curves coalesce at the triple point, and the upper bound for breakdown in air at STP is usually assumed to be approximately 32 kV/cm as for plane electrodes. If a maximum field of 32 kV/cm is assumed, the associated fiber resistance that will just not cause a flash-over is about 10^8 ohm/cm.*

In summary, the lower bounds are as follows:

Low voltage: $>10^6$ ohm/cm
Medium voltage: $>10^6$ ohm/cm
High voltage: $>10^8$ ohm/cm

E. STATUS OF ELECTRICAL PROPERTIES OF CARBON FIBERS

In order to have significant impact on the problems in question, a solution involving only the increase in fiber resistance would require values at least as high as those given in the preceding listing. Typical values for fiber

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*R. I. Gray, Carbon Fiber Hazard Criteria, TR-3837, Naval Surface Weapons Center, Dahlgren, Virginia (in preparation).

[6]H. Norinda and O. Salka, "Mechanism of Positive Spark Discharges with Long Gaps in Air at Atmospheric Pressure," Arkiv För Fysik Band 3 nr 19, 347 (1950).

Table 2. Fiber Conductivities

Manufacturer	Precursor[a]	Designation	Fiber Resistance, ohm $(cm)^{-1}$	Conductivity, $(ohm\text{-}cm)^{-1}$
Celanese	PAN	GY 70	640-1,700	770-3,440
Hercules	PAN	AU/AS	3,950-4,900	220-520
	PAN	HMS	1,700-2,550	631-1,300
Union Carbide	R	VYB 105	10,740-14,700	50-130
	R	Thornel 50	2,330-3,100	960-1,000
	R	Thornel 75		630-1,400
	P	VM 0034	54-150	~5,000
	P	TP 4101	180-303	~5,750
	P	TP 4104B	~90	~4,900
Great Lakes	PAN	Fortafil 3-T	~2,670	~300
	PAN	Fortafil 4-T	~1,950	~1,030
	PAN	Fortafil 5-T	~1,690	~1,160
HITCO	R	HMG 25	~2,700	~1,020
	R	GY 2-1	~7,690	~170
Carborundum	R	GSGY 2-10	~6,700	~220
Stackpole	PAN	30/A	~4,000	~570
Courtaulds	PAN	HM	~1,490	~2,020
	PAN	HT	1,570-2,150	1,000-1,[illegible]0
RAE Farnborough	PAN	2500	~2,450	~670

[a]PAN: acrylic fiber; R: rayon fiber; P-pitch fiber

bulk, longitudinal conductivity $(\text{ohm-cm})^{-1}$, and linear resistance (ohm/cm), for a number of fibers used in the last six years of research are given in Table 2. The scatter in these results reflects not only the variation in product control, but also the scatter in experimental techniques of measurement. Both four-probe and two-terminal methods were used by various researchers, but the four-probe technique has yielded much more reliable data. However, it will be seen that the range of values is not very large when considering the possible need for several orders of magnitude increase in resistance. The fundamental question, then, is whether or not we can anticipate an increase in fiber resistance to acceptable values by altering fiber preparation or processing techniques or both.

The electrical properties of PAN-base fibers have been studied in detail.[7,8] The variations of longitudinal resistivity, thermoelectric power, magnetoresistance and the resistance ratio measured at 77 and 500 K were derived as functions of heat-treatment temperature (HTT). An important change in electronic structure for HTT 1700 to 1800°C was reported. At higher HTT, the resulting fibers behave as highly graphitic material. The emergence of large g-anisotropy in electron spin resonance measurements is a positive indicator of the onset of the graphitic band structure and is caused by the very large effect of spin-orbit coupling in the presence of a band degeneracy (i.e., a zero-gap semiconductor with small band overlap resulting in semimetallic behavior). The principal evidence of the onset of semimetallic behavior is the change in sign of the thermoelectric power at HTT near 1750°C. No fiber has both g-anisotropy and a negative Seebeck coefficient. Although the change in electronic structure clearly occurs near

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[7] D. Robson, F. Y. I. Assabghy, and D. J. E. Ingram, "An Electron Spin Resonance Study of Carbon Fibers Based on Polyacrylonitrile," J. Phys. D: Appl. Phys. 4, 1426 (1971).

[8] D. Robson, F. Y. I. Assabghy, and D. J. E. Ingram, "Some Electronic Properties of Polyacrylonitrile-Based Carbon Fibers," J. Phys. D: Appl. Phys. 5, 169 (1972).

1750°C, the longitudinal resistivity varies only very smoothly through this region. The general trend in present commercial fibers is toward higher resistivity for low HTT, but the effect is relatively small, variation of only about a factor of 3 from 1000 to 2800°C.

F. SUMMARY

In summary, with the present commercial processing conditions, it does not appear possible to achieve dramatic changes in resistivity through standard HTT. Techniques will have to be developed and used for maintaining significant numbers of electronic traps (e.g., nitrogen) in the fiber, which raises the resistance without decreasing mechanical properties beyond acceptable limits. These results require further investigation.

The problem of fiber resistance may be ameliorated by producing a fiber with linear resistance in the lower bound of approximately 10^7 ohm/cm. The problem can be eliminated solely in terms of fiber resistances only if very high resistances are used, say 10^{20} ohm/cm.

IV. DELINEATION OF SOLUTION METHODS

The methods for solving the problem of free-flying carbon fibers have been arbitrarily categorized as near-term and long-range. The near-term includes methods that could be applied to this problem immediately; the long-range includes practices that might impact the problem within four or more years.

A. NEAR-TERM APPROACHES

The electrical, electronic, and communication industries have a long-standing awareness of environmental hazards to the functioning of equipment. Historically, the hazards have included intrusions of moisture, corrosive contamination, particulates, and explosive vapors. Codes of the National Electrical Manufacturers Association (NEMA), for example, give guidance in the construction of buildings and facilities under a variety of circumstances of exposure. Similarly, the American Telephone and Telegraph Company has issued instructions to the operating telephone companies concerning the construction and ventilation of buildings. Manufacturers of large-scale computing equipment have developed engineering criteria for the environmental protection of their equipment by means of filtered ventilation systems and humidity control.

The national engineering organizations, testing laboratories, and electrical and electronics industries have not yet addressed the specific effects of carbon fibers on electrical equipment. The current trends toward extreme miniaturization are compelling new concerns over the role of the environment. Modern integrated circuits have high level of electronic functions in very small spaces: a circuit with several thousand equivalent transistors on an area one-tenth the size of a postage stamp is now within the state of the electronic art, and major extensions of this technology are in development. The interconnection of such solid-state circuits demands

great concentrations of conductors spaced at close intervals. Current technology, for example, makes common use of conductors that are only 0.008 to 0.013 cm (0.003 to 0.005 in.) wide and spaced 0.013 cm (0.005 in.) apart. Technology in the near future is expected to yield a scale of interconnections two or three times as dense as this present level.

Because the investment in fabrication is extremely high per unit of circuit, and because reliability at every level of integration is acutely demanded, measures to protect these systems from their environment have always been regarded as cost-effective. Quite apart from the potential new threat from carbon fibers, the environment in which these systems must operate is already amply hostile and has been the cause for close attention. The chief enemy is humidity, with attending problems of the deposition of water and corrosive salts on electrically active circuit paths. The protective technology has therefore striven to provide encapsulation of integrated circuits and cover coating to protect these systems from attack. Furthermore, the building environments in computing centers and telephone offices are appropriately air-conditioned to reduce humidity to acceptable levels. Control of particulates through air filtration is also mandatory for such systems. The present state of technology appears to be sufficient to protect miniature circuits against the invasion of carbon fibers.

Several manufacturers of carbon fibers* have reported that they are routinely able to minimize electrical outages from conducting particles and fibers within their own facilities. Construction practices often involves the use of NEMA-12 standards, which provide for design of indoors dust- and drip-tight facilities. This level of protection is substantially less demanding than are the codes specified for hazardous vapors or outdoor installations. On the scale of conventional electrical circuits, the present measures of building and maintenance practices appear to be sufficient to protect against

*Private communication with ONR Carbon Fiber Study Group, April 1978, by representatives from Union Carbide Corporation, Great Lakes Carbon Research Corporation, and Stackpole Carbon Company.

the intrusion of carbon fibers, even though fiber concentration exposure levels are relatively high in these manufacturing facilities (10^5 to 10^7 fibers/m^3 which corresponds to 10^{10} fibers sec/m^3/8 hr), and certainly higher than would be expected in most other industrial facilities or residential areas.

Airborne fibers can be effectively removed by ordinary furnace filters. Precautions should also be taken to prevent leakage around these filters by properly sealing them with tape. The National Bureau of Standards has information on the performance of air filters. The approach of industries that require air filtration has, however, been largely empirical. Systems of filtration are commercially available, with engineering specifications, for the treatment of environments under widely diverse conditions. The use of these filtration systems to deal with airborne carbon fibers appears to offer no new building or facility adaption problems.

Further information is required in order to more accurately determine the risks involved and the means for preventing accidental release of fibers. Therefore it is recommended that a specific effort be undertaken to gather information concerning events that contribute to industrial or consumer-related accidents. This effort should involve industrial groups such as fiber producers and users of fibers such as sporting goods, aircraft, and automotive manufacturers. From such information, other near-term approaches toward the amelioration of the flying fiber problem might be derived.

B. LONG-RANGE APPROACHES

Even though it appears to be relatively easy and inexpensive to protect electrical equipment that is contained within a closed environment, there are situations where such procedures may not be practical: high-voltage transmission lines, exposed antennas, electrical substations, and aircraft during maintenance procedures (when in flight service condition, aircraft avionics are usually in a controlled atmosphere). Therefore, it is mandatory to

consider alternative methods for reducing a potential hazard by highly conducting airborne carbon fibers.

This committee and the NASA Workshop held in March 1978 concluded that there are no quick-fix methods for eliminating the potential hazard of airborne carbon fibers other than exclusion. In all probability, a combination of near-term preventive measures and the long-range approach of modifying the fibers or composites or both will be used. Modification in any of the materials now being used in composites will require several years for development, evaluation, and requalification before the composite can be certified. In some instances, the problem of requalification does not exist. For example, in automotive uses, design studies are still under way, the present cost of fibers is too high for wide-scale use, and the manufacturing capability for further reducing the cost of the fibers does not yet exist. Therefore, sufficient time is available to alter the fiber and resin properties and qualify these materials prior to extensive use in automobiles.

Some possible long-range approaches for reducing the effect of the accidental release of conducting fibers from composite materials are discussed here. The information presented is a compilation of the conclusions and recommendations of the March 1978 NASA-sponsored workshop and recommendations that were submitted to the Defense Director of Research and Engineering (DDR&E) by the Naval Surface Weapons Center (NSWC), the Naval Research Laboratory (NRL), the Army Materials and Mechanics Research Center (AMMRC), the Army Research Office (ARO), and by members of this committee.

1. CARBON FIBER MODIFICATIONS

Efforts to prepare PAN-type fibers with low thermal conductivity, but reasonable strength and modulus, has resulted in fibers that also have low electrical conductivity. This was achieved by careful processing of the fibers at below normal temperatures, and fibers with large amounts of nitrogen were produced. Both the low-temperature processing and the

inclusion of noncarbon atoms within the fiber structure can result in higher carrier scattering and hence higher resistivity. The surface of the fiber can be altered by oxygen or fluorine treatment to reduce its π-bond nature. Some type of catalyst might induce rapid low temperature oxidation of the fibers. Modifications are discussed in more detail in Section V.

2. ALTERNATIVE FIBER MATERIALS

The problem can also be eliminated by replacing the highly conducting carbon fiber with low-conducting materials, including glass fibers (170 GPa, 25×10^6 psi, modulus; 1.7 GPa, 250 ksi, tensile strength); some five different high-modulus organic fibers (140 to 170 GPa, 20 to 25×10^6 psi, modulus; 2.7 GPa, 400 ksi, tensile strength, 1.2 to 1.5 g/cm^3 density); boron nitride fibers (properties similar to carbon fibers except for extremely high resistivity); α-Al_2O_3 fibers (low strength, high density, low cost); and SiC fibers (high modulus, high strength, reasonable cost). The boron carbide fibers are not now being investigated; however, the mechanical properties are reported to be similar to carbon fibers.

3. FIBER COATINGS

Coating the fibers with insulative layers has been suggested by both government and industrial researchers. Such coatings might include glass, silicon carbide, boron, boron nitride, and SiO_2. In each case, the compatibility of these types of coatings would have to be evaluated with respect to the matrix that bonds the fibers.

It may also be possible to coat the fibers with organic coatings that have special characteristics. For example, in the case of fire, if the coating has a high char yield, and the formation of heavy clumps of fibers is enhanced, the distribution of single fibers is inhibited. Or the coating might swell into a foam-type layer when it is heated, thereby forming a high-resistance layer. Further discussion is presented in Section V.

4. HYBRID COMPOSITES

Composites are now being produced with several types of fibers to take advantage of the best attributes of each type of fiber. These multi-component or hybrid composites may also provide another method of containing the airborne carbon fibers. For example, a combination of glass and carbon fibers is being considered for use in automotive drive shafts. It appears that the carbon fibers will be the small fraction of the total fibers in the part. Consequently, in a fire situation, the glass could melt and help contain the carbon fibers.

Perhaps other hybrid composite concepts can be designed to contain an inactive material that causes little or no alteration in composite performance under normal situations. However, when the composite is burned, the material would become active and prevent dispersal of airborne carbon fibers. The available intumescent paints might perform this function.

5. EPOXY RESIN MODIFICATION

The epoxy resins now being used in composite applications have been "fine tuned" to achieve optimum performance at minimum cost. The addition of fillers or comonomers such as phosphorous compounds or organic phosphinates to increase char formation will alter the current properties of the composites such as fracture toughness, strength, and modulus. Consequently, modifications to this resin system should be considered as if a new material system were being developed where requalification, process reproducibility, cost, and other factors must be evaluated. Significant work toward this end is under way or is being considered by NASA and its contractors. Therefore, the present study has been intentionally limited to modifications of the fibers and their surfaces.

6. EPOXY RESIN REPLACEMENT

In view of the potential technological and economic impact of airborne carbon fibers, it may be desirable to consider organic matrices that are developed especially to alleviate the problem but not at the expense of such

properties as strength and modulus. Careful consideration should be given to the selection of candidate materials in order to minimize the number of combinations of generic types that should be formulated and evaluated.

As pointed out earlier, no specific recommendations concerning matrices are presented here. However, it should be emphasized that the interrelationship between the matrix and fiber was considered to be an important aspect of the total problem.

C. SUMMARY

There is a general concensus that there is no short-term solution that uniquely solves the fiber release problem either by the development of special materials or by operational procedures.

However, in the near term, standardized industrial practices do provide for protection against the possibility of equipment malfunctions from airborne fibers. The extent to which these measures will alleviate the problem needs to be more completely evaluated as soon as possible.

The long-term approaches involve the development and qualification of new or drastically modified materials. In all probability, four or more years will be required in order to identify a meaningful approach in the laboratory, to scale-up the process to manufacturing quantities, and to qualify the material. Alterations to the fiber or matrix may significantly change the advantageous physical properties of the existing composites or increase the production costs such that carbon fibers may not be used.

The combination of near- and long-term approaches may alleviate the problem. Awareness of the problems of good housekeeping and relatively inexpensive hardening of equipment can be undertaken immediately. This, together with the long-term development of new material concepts, should help solve the problem.

Both analytical and experimental approaches that will help solve the airborne carbon fiber problem should be defined. Without a clear plan, some industrial manufacturers who produce or use carbon fibers are delaying their expansion plans in this area of technology.

V. CARBON FIBER MODIFICATION

High-performance carbon fibers attain high modulus and high strength as a direct result of the anisotropy in the graphite crystal structure. Examination of single crystals of graphite indicates that modulus values as high as 1000 GPa (146 million psi) are theoretically possible in the direction parallel to the graphite planes. However, the single-crystal tensile modulus perpendicular to the graphite planes and the shear moduli are approximately 400 times lower than the in-plane moduli. The single-crystal modulus is drastically reduced, however, when a stress is applied at an angle to the in-plane direction (Fig. 2).

The electrical properties of single-crystal graphite are also highly anisotropic; the conductivity parallel to the graphite planes is 20,000 times higher than that in the perpendicular direction. The conductivity (Fig. 3) with direction of applied field decreases much more slowly than does modulus, if we assume that a parallel model is correct. Hence, control of the orientation of the graphite planes is more important for mechanical properties as compared to electrical conductivity.

In contrast to the single crystal described above, a carbon fiber is composed of crystallites such that properties are determined by the (preferred) orientation of these crystallites. Although the details are different from the single crystal, and results will depend on microstructure, high modulus is again more dependent on a high preferred orientation of the crystallites than is electrical conductivity.

The properties of carbon fibers are affected by foreign atoms and structural defects as well as preferred orientation. Foreign atoms such as boron and nitrogen may be substituted into the carbon lattice. Boron would increase the number of charge carriers and therefore does not appear to be desirable. Nitrogen may be effective for compensation or scattering and

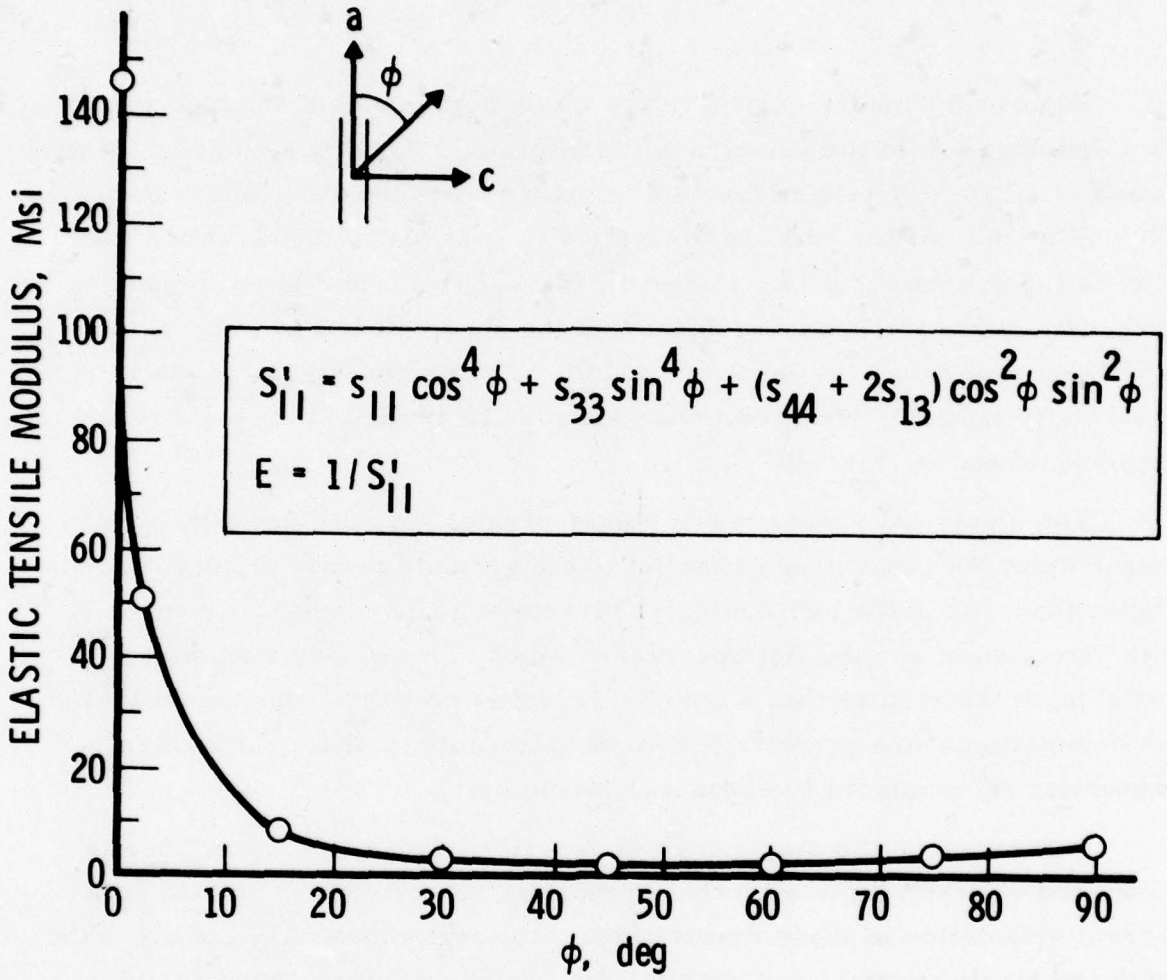

Figure 2. Tensile Modulus of a Graphite Single Crystal as a Function of Angle of Applied Stress

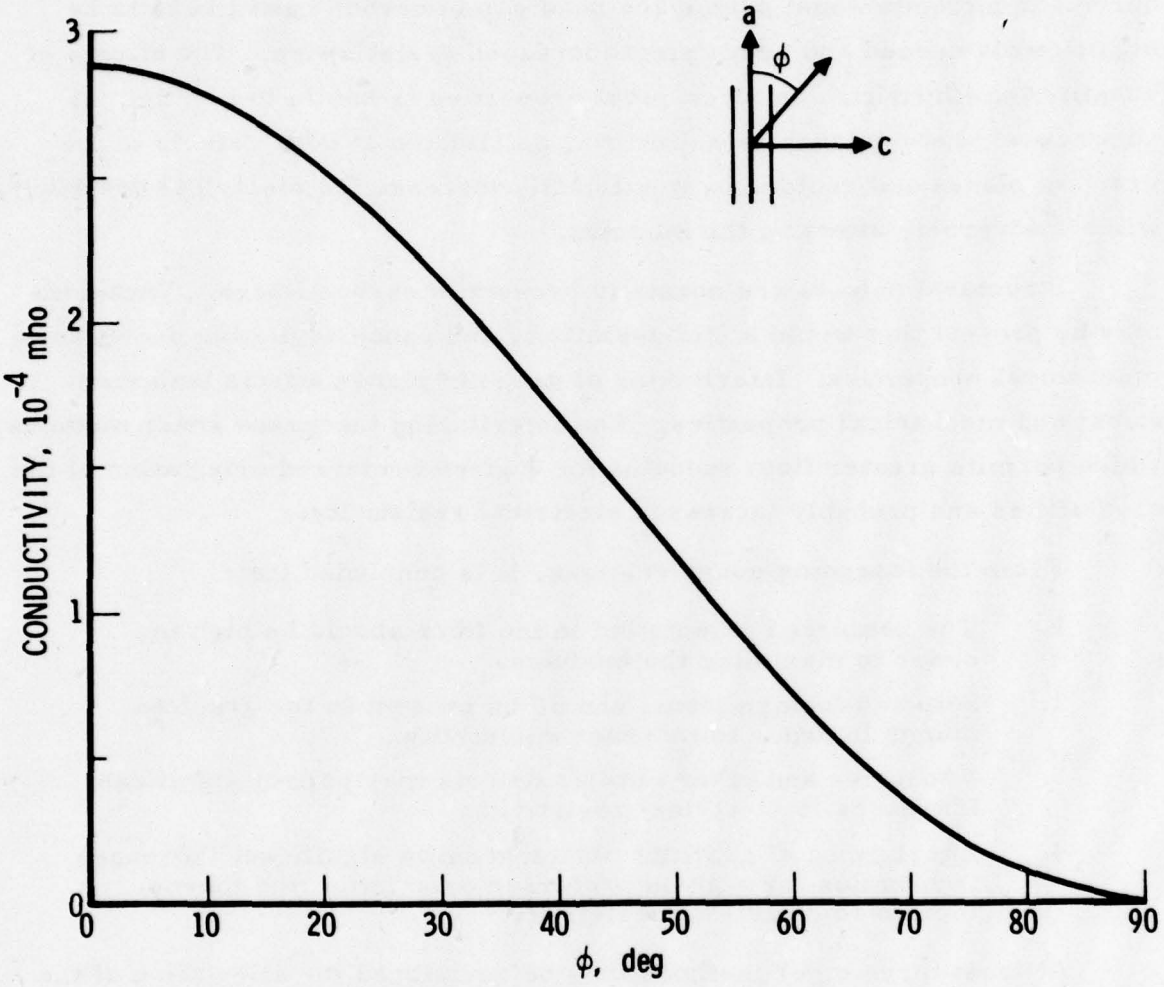

Figure 3. Electrical Conductivity of an Infinite Graphite Single Crystal as a Function of Angle of Applied Voltage

may significantly change the electrical resistivity. The proper addition of boron and nitrogen would permit the band gap in carbon base fibers to be significantly opened and hence yield increased resistivities. The effects of substituting impurities on mechanical properties is known to be minimal. Other foreign atoms such as sulfur may be situated at edge defects in the graphite planes and could also significantly increase the electrical resistivity without adversely affecting the modulus.

Structural defects are normally present in carbon fibers. Vacancies may be present that would affect resistivity and cause negligible decrease in mechanical properties. Interlinking of graphite planes affects both electrical and mechanical properties. The interlinking increases shear modulus, which permits greater fiber modulus for a given preferred orientation of the crystallites and probably increases electrical resistivity.

From the foregoing considerations, it is concluded that:

1. The preferred orientation in the fiber should be high in order to maximize the modulus.
2. Selected foreign atoms should be present in the graphite planes in order to increase resistivity.
3. Vacancies and other similar defects may permit significant increases in electrical resistivity.
4. Interlinking of graphite planes permits significant increases in modulus for a given preferred orientation and maybe increased electrical resistivity.

At least three other methods may be envisioned for alleviation of the carbon fiber problem: (1) destruction by oxidation, (2) immobilization, or (3) insulation. Commercial carbon fibers vary in oxidation rate by three orders of magnitude. Hence, the rate of fiber oxidation can be altered by varying the concentration of defects within the fibers and by catalysts. Catalytic oxidative destruction in an oxygen-poor atmosphere requires the presence of an internal oxidizer in the composite that may

be unsatisfactory from the standpoint of safety. Immobilization and insulation are desirable because they can be achieved without much change to existing composite systems or manufacturing methodology.

A. POTENTIAL METHODS FOR CHANGING THE ELECTRICAL CONDUCTIVITY OF CARBON FIBER

The techniques used to produce carbon fiber from PAN and pitch precursors are described in the open literature. Process studies usually emphasize the development of molecular order within the fibers and how the order affects the mechanical characteristics. The various potential methods for changing the electrical characteristics of the fibers without adversely affecting their mechanical properties are discussed here.

Because carbon fibers inherently tend to have low resistivity, the techniques used to change the resistivity must result in either a poorly carbonized fiber or a doped- or surface-treated fiber. Possible methods of achieving these results include the following:

1. Substitution of nitrogen or other atoms in the carbon lattice
2. Reaction of foreign atoms on edge sites
3. Preparation of fibers with high preferred orientation and high defect structure
4. Intercalation
5. Surface treatments and coatings

1. SUBSTITUTION OF NITROGEN OR OTHER ATOMS IN THE CARBON LATTICE

The substitution of nitrogen into the carbon lattice may increase resistivity significantly. Nitrogen, however, is unstable in the carbon lattice at temperatures where diffusion is rapid ($> 2000^{\circ}C$). Most likely, the incorporation of nitrogen into the carbon lattice would be made in the precursor material or possibly during low-temperature processing stages. Although it may be possible to introduce nitrogen into all carbon fiber precursors,

the large amount of nitrogen in PAN fibers, and the present use of PAN fibers as a precursor make it most desirable for use in evaluating the advantages of nitrogen substitution.

The development of graphitic-like sheet structures in PAN precursor and, hence, the development of graphitic-like electrical characteristics. begins to occur at temperatures as low as 400 to 600°C.[9] Dehydrogenation of adjacent stabilized PAN molecules could result in the formation of graphitic-like structures. At temperatures greater than 600°C, the nitrogen becomes unstable and denitrogenation reactions occur.[9-12] This results in extensive lateral molecular growth of graphitic sheets, particularly among closely spaced adjacent species. As the molecular growth occurs, the electrical resistance begins to decrease drastically. Recent results strongly indicate that a high-resistance fiber can be produced if some nitrogen is maintained in the fibers while the mechanical properties are developed. The characteristics of these high-resistivity fibers are listed in Table 3. These values were derived by optimizing the processing variables and maintaining the heat-treatment temperature below 1000°C in order to maintain > 5% of nitrogen in the fibers and still achieve adequate levels of mechanical properties for many applications. The nitrogen, as part of the carbon structure, may act as an electron trap and, as such, be responsible for the relatively high electrical resistance. If the fiber at any time experiences temperatures greater than 1000°C, whether intentional, by fire, or from carrying more than approximately 1 W/cm of power, the nitrogen in the fiber will become unstable, and the resistance will decrease.

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[9] W. Watt et al., in Proceedings of International Conference on Carbon Fibres, Plastics Institute, London (1974).

[10] W. Watt, Nature 236 (physical science section), 10 (1972).

[11] W. Watt, in Proceedings of International Conference on Carbon Fibres I, Plastics Institute, London (1971).

[12] J. Bromley, in Proceedings of International Conference on Carbon Fibres I, Plastics Institute, London (1971).

Table 3. High-Resistivity Fibers

Designation	Resistance, ohm-cm	Resistivity, μohm-cm	Modulus	
			× 10^6 psi	GPa
DG110	139,000	79,000	20	140
DG111	156,000	77,000	21	145
DG112	12,800	7,000	25	170
DG113	17,600	8,000	31	215
Type A (control)		2,000	30	210

This method of obtaining higher resistance carbon fibers has been demonstrated to be effective and is useful for the production of fibers for applications where low and intermediate up to about 200 GPa (30 million psi) modulus fiber is required. It is not yet possible to produce high modulus (> 240 GPa, > 35 million psi) carbon fiber with high nitrogen content and high resistance. Further research and development are needed on this subject. It may be possible to incorporate other atoms into the PAN or pitch precursor materials and retain them in the fibers after high heat treatment in order to improve fiber resistance and permit desired mechanical properties.

2. REACTION OF FOREIGN ATOMS

The unsaturated bonds at the edges of the graphite planes will react with atmospheric gases and other atoms to yield substantial increase in charge carriers. Resistance may be improved if these edge sites are reacted with suitable foreign atoms. The magnitude of this increase is not known, but may be important in the more poorly structured carbon fibers produced at low temperatures and that presumably have more edge sites and other defects.

3. PREPARATION OF FIBERS WITH HIGH PREFERRED ORIENTATION AND HIGH DEFECT CONCENTRATIONS

The introduction of vacancies, dislocations, and other similar defects, as well as the interlinking of the graphitic planes should significantly increase the electrical resistivity of the carbon fibers. Potential methods of introducing these defects and the interlinking involve modifying the precursor fiber, changing the processing, and using low-temperature heat treatments that retain these defects and substitutional nitrogen. The low processing temperatures that result in a high concentration of defect and retained nitrogen occur in a regime where the carbon structure is being drastically changed and where several events occur simultaneously. It may be that the increased resistance is due to processes not related to nitrogen, i.e., nitrogen content is only an accompanying result and not the primary factor.

Low-temperature heat treatment usually results in lower fiber modulus and therefore requires precursor and processing modifications that maximize preferred orientation. Furthermore, as was pointed out earlier, a high preferred orientation is important for optimizing the tradeoff between high modulus and high electrical resistivity. Changes in precursor molecular configurations and conformations are expected to permit improved preferred orientations and to prevent relaxation of this orientation in the subsequent stabilization and carbonization processes. Areas of investigation that may result in improvement of properties include: stereoregular polymers, controls of molecular weight and molecular weight distributions, and precursor chemistry. Improved preferred orientations and subsequent processing may be obtained by improving spinning and drawing. The inhibition of relaxation during stabilization and carbonization has resulted in significantly higher modulus in some systems for a given final heat treatment temperature.[13] Higher electrical resistivity has been observed in these fibers.

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[13] W. Watt and W. Johnson, Nature 220, 835 (1968).

Precursor systems that appear to allow graphite plane interlinking should be investigated, as the modulus of fiber produced from these precursors is higher for a given preferred orientation than that from precursors that produce noninterlinked planes. In Fig. 4, the higher moduli obtainable with PAN-base precursors are shown as compared with pitch and rayon precursors for a given preferred orientation.[14] Although both PAN and pitch can use low temperature final heat treatments, the chemistry of PAN decomposition as compared with pitch may produce a more highly interlinked graphite planar structure. Variations in precursor chemistry and fiber processing should be considered for maximization of graphite layer interlinking, which would increase fiber modulus. Other changes can be made to precursors that may significantly change the defect structures and hence the electrical and mechanical properties.

One method considered for producing high-modulus carbon fiber with a relatively high electrical resistance involves changing the fibrillar network or domain size of the precursor fiber. The objective of this approach is to develop as high a level of mechanical properties as possible with heat-treatment temperatures less than 1000°C.

When PAN is wet-spun into a coagulating bath, the PAN molecules form fibrils, which then join together to form a fibrillar network within each individual filament. The length of the fibrils between network junctions is markedly affected by the coagulant temperature, the bath composition, extrusion rate, and takeup rate.[14-17] Since carbon fiber is composed of a mass of undulating fibrillar ribbons, there is a high probability that these ribbons will form on the skeleton of the precursor fibrillar network.

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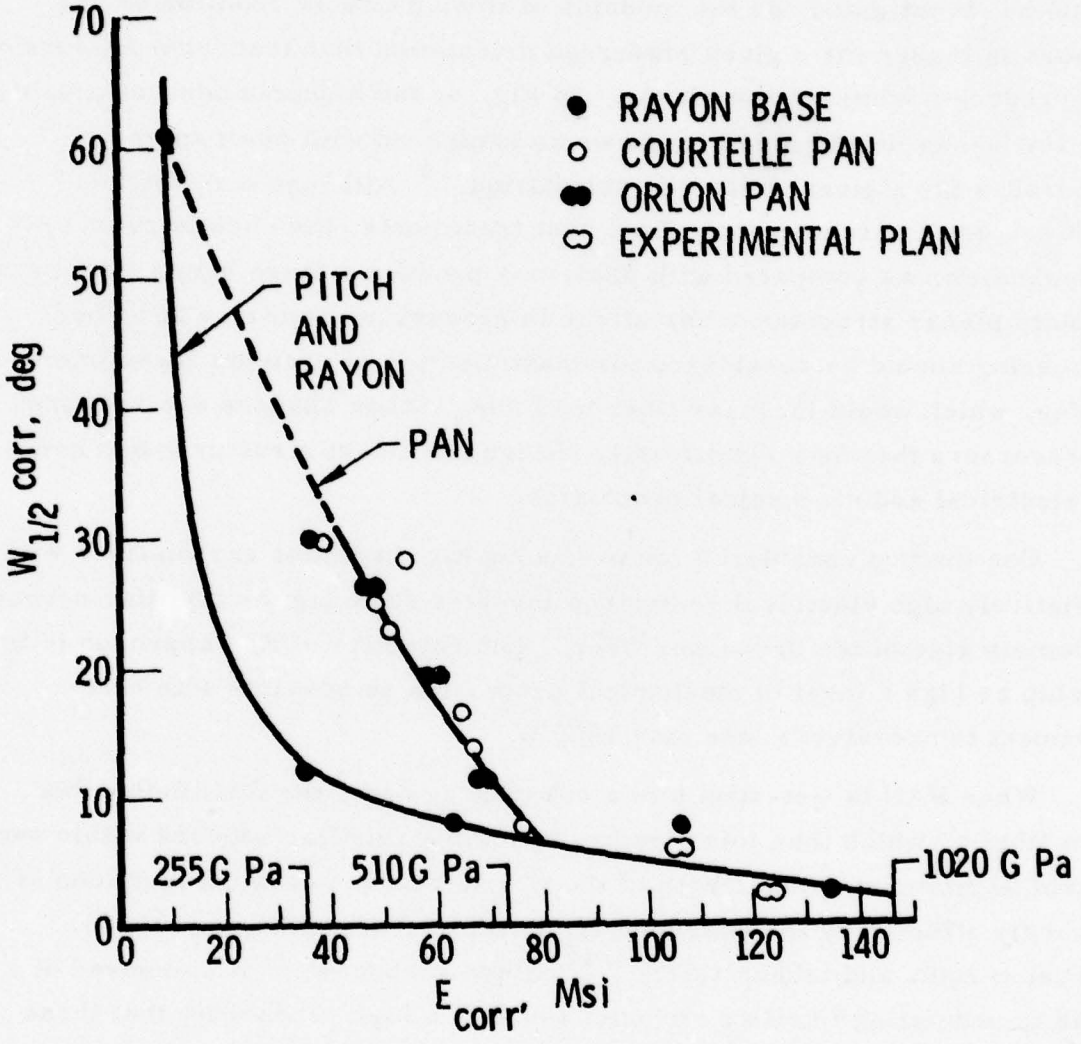


Figure 4. Index of Preferred Orientation $W_{1/2}$ vs Carbon Fiber Modulus. The results indicate that PAN precursor fibers can have a higher modulus for a given preferred orientation ($W_{1/2}$) than pitch or rayon precursor fibers.

Because the dimensions and structure of the carbonized ribbons significantly affect the mechanical properties of the carbon fibers, by varying such parameters as the network tightness and fibrillar dimension of the as-spun fiber, the dimensions and structure of the carbonized ribbons should be significantly changed, which would affect the mechanical properties of carbon fiber.

The effect of altering the precursor fibrillar network or domain size on the mechanical and electrical properties of fibers heat-treated at temperatures below 1000°C is not known. This method of changing the electrical resistivity while enhancing the mechanical properties is worthy of investigation.

4. INTERCALATION

Graphite intercalation compounds are formed by the insertion of atomic or molecular layers of a different chemical species between layers in a graphite host material. Intercalation is known to occur in carbon fibers, and the degree of order increases with increasing order of the host fiber. Intercalation introduces large relative changes in the carrier concentration, typically by one or two orders of magnitude or greater. Thus, intercalation results in major changes in the transport properties.

Because in-plane resistivity for bulk graphite decreases on intercalation for all common intercalate species, it should be expected that the electrical resistivity of carbon fiber will also decrease with intercalation. This expectation is confirmed by results for carbon fibers intercalated with potassium, where as much as 20 fold decreases in resistivity have been observed.

In addition to the changes in electrical resistivity, graphite intercalation compounds are generally very reactive and must be stored in an inert atmosphere. This reactivity should be considered when selecting a composite matrix for intercalated carbon fibers. Furthermore, because

desorption of the intercalate is greatly increased by heating, a fire would reduce the intercalate concentration and increase the electrical resistivity.

In summary, intercalation is a promising method for decreasing the electrical resistivity of carbon fibers, but has little promise for increasing resistivity. It is possible that intercalation processes may result in a stable material with higher resistivity such as the preparation of graphitic oxide.

5. GRAPHITIC OXIDE

Another method for altering the electrical resistivity of the fiber, and perhaps particularly the surface, involves the conversion of the carbon sheets to graphitic oxide. This can be accomplished rapidly and with little hazard according to the reaction

$$\underset{\text{(carbon sheets)}}{\text{Graphite}} + H_2SO_4 + KMnO_4 + NaNO_3 \longrightarrow \text{graphitic oxide}$$

The oxygen is covalently bonded to the carbon and the bonding appears to be similar to that of an epoxy group. The change in resistivity is dramatic as the oxygen content of the fibers increases (Table 4). The effect of the formation of graphitic oxide on the mechanical properties of the fibers is unknown. It has been speculated that the mechanical properties may not be adversely affected if the graphitic oxide coating is thin.

An advantage to this technique is that oxide layers of variable thicknesses can be formed. Surface treating the fibers to form graphitic oxide appears to be inexpensive. Mechanical characterization of the fibers, thermal stability of the oxide, and the long-term stability of the fibers need to be investigated.

Table 4. Graphite Oxide Properties[a]

Carbon/Oxygen	Resistivity, ohm-cm
3.0	10^7
3.5	4000
4.3	250
7.1	0.4
12.0	0.2
21.0	0.05
Graphite	0.023

[a]Presented by F. L. Vogel at NASA-Langley meeting, March 1978.

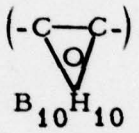
6. FIBER IMMOBILIZATION AND INSULATION

The release of carbon fibers from composites exposed to fire apparently results from the selective combustion of the organic polymer, leaving free carbon fibers. An obvious way to prevent dispersal of the free fibers is to "glue" them together and, by so doing, increase their mass/area ratio. The "glue" required for this process could be char that results from the incomplete oxidation of the matrix or a material initially applied to the fibers as a thin coating. The proper choice of char type could also provide electrical insulation on the fibers surface.

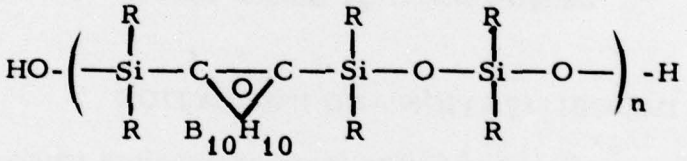
A number of organic flame retardant compounds produce a carbon char. The retardants usually contain halogen or phosphorus (or both) and may produce toxic combustion products. The phosphorous-modified resins used in ablatives produce a residue that retains the phosphorous temperatures below 1200°C. A polymeric fiber coating could perhaps be developed

which thermally decomposes to produce an inorganic char or residue capable of holding neighboring fibers together and at the same time provide electrical insulation.

Carboranylpolysiloxanes are silicone polymers that contain the carboranyl group in the polymer backbone. Soluble and thermoplastic



polymers can be prepared that can be crosslinked to form tough and flexible films and have high thermal stability (up to 300 to 400°C in air).



R = alkyl, aryl or similar group

Upon heating a carboranylpolysiloxane in air, the polymer melts then burns to form a residue that contains oxides and carbides of silicon and boron. If the polymer contains chemically combined nitrogen, a voluminous residue is produced that resembles a "blown" polyurethane polymer and contains boron nitride in addition to the oxides and carbides. Since the side-chains of carboranyl polysiloxane polymers can be varied at will, compatibility with the organic resins should be possible with little or no compromise of overall physical properties or current manufacturing techniques.

A charring silicone coating may also be applied to the fibers. If the composite should become involved in a fire, a nonconducting silicon-carbon

char would develop on each filament. In order for a material to be an effective coating, it would necessarily have to have a high char yield, a high char electrical resistivity, and provide an effective fiber-matrix bond.

The oxidation and fluorination of carbon fiber surfaces is a means of disrupting the π-electron system present in the fiber surface. Whereas partial oxidation could result in fibers with pendant carboxyl groups that are compatible with a polar polymer, fluorination would result in C-F bonds (re "Teflon") with little affinity for a polar polymer, and poor fiber adhesion would likely result. Fluorination, or perhaps high-temperature chlorination followed by hydrolysis of the C-F or C-Cl bonds with water vapor at high temperatures, should produce a carbon surface with pendant -OH groups, which could provide polymer adhesion and an interrupted π-electron system with increased resistance.

The formation of inorganic coatings on the graphite fibers can be accomplished in a number of ways; e.g., chemical vapor deposition, thermal degradation of organometallic polymer coatings, and high-temperature carbon carbon metal oxides at elevated temperature. Some candidate inorganic materials and their resistivities are given in Table 5.

Table 5. Inorganic Materials and Their Resistivity

Material	Resistivity, ohm-cm
TiC	10^{-4}
B_4C	5×10^{-1}
B	7×10^{3}
SiC	10^{3}-10^{5}
BN	10^{13}
Si_3N_4	10^{17}

Studies are under way at several industrial laboratories to develop coating technologies for carbon. Critical issues to be addressed include the dielectric breakdown properties of the coatings, the effect of the coating on the fiber mechanical properties, the chemical stability of the coating, the "clumping potential," the cost of applying the coating, and the settling behavior of the coated fibers.

The introduction of scattering centers and disorders into the fibers also appears promising for increasing the electrical resistivity of the fibers and should be investigated further. Increasing the disorder may increase the mechanical properties of the fiber as well.

Finally, it is recommended that a number of approaches be combined. Different techniques result in small changes in resistivity, but a combination of techniques may result in large changes.

VI. CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

The extent of the problem of carbon fiber release as a hazard to the operation of electrical equipment and its relationship to major disruptions has not been fully evaluated and indeed may be overstated.[2] The severity of the hazards needs to be ascertained by means of a risk analysis with appropriate experimental data.

It is technically feasible and routine in most industrial plants, particularly those involved in the production and handling of carbon fibers, to protect electrical equipment against carbon fiber intrusion. The balance between the cost of protection and the potential hazard must be evaluated for each situation. A combination of awareness of the problem, good housekeeping, hardening of equipment, and reduction of the release of highly conducting fibers will reduce the hazard to acceptable levels relative to the benefits to be derived from the use of carbon-fiber-reinforced plastics and resins.

Analysis of the breakdown of electrical circuits indicates that three voltage ranges might be considered: low (less than 18 V), medium (18 to 500 V), and high (greater than 500 V). In the high-voltage regime, the high conductivity of carbon fibers does not present any additional hazards other than those already experienced by other high-voltage pollutants such as sea or road salt, cement dust, and bird droppings.

Hazards in all voltage regimes might be reduced by several methods, for example, the prevention of accidental dispersion of fibers by containment,

the use of nonflammable matrices in composites, and the catalysis of low-temperature oxidation of fibers. In the low and medium voltage regimes, coating the fibers with an insulating material or increasing the resistance of the fibers can also reduce the hazards. In theory, it is possible to increase the settling rate of dispersed fibers by increasing the diameter; in practice, only small increases in diameter and hence settling rates can be achieved.

A serious problem might arise in disposing of scrap, broken, or obsolete parts. This problem may exceed that generated by accidental release in service. The burning of junked items under uncontrolled conditions is a principal cause for concern.

There are no "quick-fix" solutions for reducing or eliminating the potential hazard occasioned by dispersed carbon fibers by modifying the materials used in composites. Any such modifications will require, at best, several years for development, evaluation, and requalification before the composite can be certified for use.

In the low voltage regime ($\leq$18 V) an important parameter is the contact resistance and associated punch-through phenomenon in addition to fiber bulk resistance. Punch-through, the penetration of surface barrier films by the fibers, can occur at about 2 V. Surface resistances greater than 10^6 ohm/cm would significantly reduce the hazard for single-fiber bridgings.

No general conclusions can be made concerning fiber resistance requirements independent of circuit impedance to minimize the problem in the medium voltage regime (18 to 500 V) because of the many diverse applications involved. However, preliminary studies indicate that bulk resistances greater than 10^5 or 10^7 ohm/cm significantly reduce the probability of arc initiation, and resistances greater than 10^4 ohm/cm reduce the danger of shock to personnel.

Fiber resistance is considered to play an important part in causing equipment failure. Typical commercial fiber resistances range from 90 to 15,000 ohm/cm with many near 2000 to 8000 ohm/cm.

Current evidence indicates that resistances of about 10^6 ohm/cm can probably be attained. Polyacrylonitrile (PAN)-base carbon fibers can now be produced with 4.07 GPa (30×10^6 psi) modulus, 2.07 GPa (300×10^3 psi) tensile strength, and 2×10^5 ohm/cm by retaining appreciable nitrogen. The extent of improvement that can be obtained and the effects of fire on the fiber resistance is not yet certain. Further research is required.

The preparation of intercalation compounds from carbon fibers to increase the electrical resistivity while maintaining the high modulus offers little potential for reducing the airborne fiber hazard. The use of intercalation processes to prepare stable materials with high resistivities may, however, be possible. Because many materials intercalated or otherwise placed into carbon fibers tend to be unstable, composite aging problems and the degradation of interfacial bonding may result.

Examination of available resistivity-modulus-strength data for various fiber types indicates that the PAN-base fibers appear to offer the most promising compromise for ameliorating the airborne fiber problem. The available pitch fibers are much more conducting at equivalent moduli. However, because research on increasing the resistance of pitch-type fibers is not as advanced as that on PAN-base fibers, these should not be eliminated from consideration as alternative fibers for the airborne fiber problem.

A low-temperature processing approach appears to have merit in increasing resistance because of the retention of foreign atoms and increased disorder of the crystallites in both PAN- and pitch-base fibers. However, it has not been established whether or not acceptable fiber mechanical properties can also be maintained by this method.

The application of a coating to fibers appears to be a promising approach for either increasing the surface resistance or preventing dispersal of free-flying fibers. Care must be taken to ensure that the desirable properties of the fiber or the adjacent matrix are not degraded.

Insufficient information exists about the electrical and mechanical properties as well as the surface and bulk morphology of fibers released from multicomponent composites after exposure to different types of severe

environments such as impact and fire or explosion or both. Such information is necessary for risk analysis calculations in order to evaluate more accurately the effectiveness of any proposed material modifications.

B. RECOMMENDATIONS

The recommendations given here are not ranked by priority within each category.

1. GENERAL CONSIDERATIONS

a. Risk analysis must be expanded to include all current and potential major applications. Sources for the utilization of fibers considered should include automotive and industrial applications, sporting goods, and aerospace applications. Consideration should be given to release mechanisms of fiber other than by burning or explosion or both, e.g., wear-erosion of carbon-carbon brakes.

b. In order to prevent duplication of efforts, an information and coordination system should be established among those organizations concerned with the problem of airborne carbon fibers.

c. Information on the potential hazards in the use and disposal of carbon fibers should be communicated to the users of carbon fibers by the manufacturer.

d. Methods should be developed and evaluated for the disposal of carbon fiber in a manner that is safe now and in the future.

2. SPECIFIC RESEARCH APPROACHES

a. Work should be carried out on matrix systems to minimize fiber dispersal. The objective would be to limit the dispersion of fibers by providing better fiber/matrix bonding and higher char yield to hold fibers together. Char on the fiber may also enhance its surface resistance. Consideration should also be given to the development of special matrices to enhance the oxidation of the fibers when exposed to fire.

b. The retention of nitrogen in the PAN-base carbon fibers has been shown to yield increased resistance. The extent to which resistance can be increased without sacrifice of mechanical properties should be examined.

c. Because nitrogen retention yields increased resistance, other foreign atoms should be considered for incorporation into the carbon structure in order to obtain desired properties.

d. More intensive work should be directed toward the coupling of mechanical, electrical, and morphological properties of the fibers. Most studies have concentrated on either the combined mechanical-morphological or the electrical-morphological properties but not on the coupled interactions. The coupled interactions should also be studied in cases where intercalation processes result in stable carbon compounds.

e. Alteration of various processing conditions prior to heat treatment, including precursor modifications, fiber spinning, and stabilization conditions should be undertaken for both PAN and pitch precursors in order to optimize fiber properties.

f. The application of coatings to fibers that form either insulating chars or high-resistance fibers on exposure to fires should be investigated. A promising coating system appears to be based on a carborane-siloxane system.

g. Detailed evaluations should be made of the fibers that are released from composites that have been exposed to environmental conditions such as impact and fire. These evaluations should include values of surface and bulk electrical conductivity, morphology, and in particular their surface conditions. This information would be used in risk analysis for determining the probability for disabling equipment. Particular attention should be given to investigation of the condition of the fibers after the incident.

C. DISCUSSION OF RECOMMENDATIONS

The paragraphs presented here are keyed to the corresponding recommendation presented in the preceding section.

(1a) The risk analyses thate are now available and in preparation are mostly concerned with the application of carbon fiber technology to aircraft and aerospace vehicles. Carbon fibers may well find wide use in the automotive industry and are being used in other civilian-oriented markets such as sporting goods and industrial equipment. Consequently, risk analyses should be expanded to include the manufacture, use, and planned or accidental

destruction of such items as automobiles and tennis rackets. The use of carbon-fiber-containing products by the military is subject, in principle, to tight control of use and disposal. This control is not available for the use and disposal of carbon fiber products by the population at large. Misguided or negligent manipulation of carbon fibers could result in serious problems. A survey should be made and kept current to identify other potential and actual uses of fibers and the risks involved in their application. Continuous use of carbon fiber products will also result in the dispersal of fibers by wear and erosion mechanisms. An example is carbon fiber aircraft brakes, which, under use, may emit a fine powder of carbon. Clearly, this and other mechanisms for dispersal must be examined and included in the analysis.

(1b) In order to prevent duplication of efforts, an information exchange and task coordination system should be established. At a recent meeting held by NASA, 52 companies, 8 universities, and 22 government installations were present and reported involvement in various aspects of the carbon fiber problem. This roster of interested and involved organizations will undoubtedly continue to expand, and the generation of new concepts, analyses, and materials will expand accordingly. Coordination of this information flow is essential for the expeditious development of the overall program and awareness by the public use and potential hazards of carbon fibers. A leading organization in the field of carbon fiber technology should take responsibility for the dissemination of information.

(1c) The many users of fibers with diverse end-item application must be made aware of the risks to electrical equipment. Only a few manufacturers include a "potential hazard" label on packages of

carbon fibers. More awareness of the risks should be noted by including detailed instruction for proper disposal on all fiber packages shipped to customers. Some consideration should be given to the larger question of whether or not all carbon fiber products should contain warning labels concerning their proper disposal.

(1d) Methods for the disposal of carbon fibers present a problem because of their resistance to oxidation and the ease with which they can be dispersed in the air. A common method of disposal is to bury plastic bags of fibers in a controlled land fill. No information is available about the subsequent degradation or potential dispersal within such sites. Other methods of disposing of fibers and parts containing fibers should be investigated before the problem becomes acute or extremely expensive or both because of the lack of proper containment.

(2a) Carbon fibers are released from composite matrices by failure of the fiber matrix bond on impact and explosion or by the preferential combustion of the matrix in a fire. Consequently, desirable matrices would be those impact-resistant materials that give the required structural properties of the system coupled with enhanced or tumescent char yields during combustion. The preferential combustion of matrices could be mitigated by the synthesis of polymers that have good fiber coupling and fire-retardant properties and produce a tumescent char during combustion. It is well within the present state of polymer science to approach these problems with some assurance of success, and such efforts of this sort should be emphasized.

(2b) It has been noted that PAN-base fibers processed at low temperatures to give reasonable strength and modulus values also give higher resistance. Further research and development are

necessary in order to determine the limits of the method for optimizing the resistance versus the mechanical properties of these fibers.

(2c) If the improved resistance of PAN-base fibers is a direct result of nitrogen retention, other types of additives should be investigated to determine if they can be incorporated into the carbon fiber structure in order to increase resistance while retaining suitable mechanical properties and matrix adhesion. Additives that are stable at high processing temperatures and can withstand exposure to fire would be highly desirable.

(2d) In order to obtain optimum fiber properties, a somewhat disordered microstructure may be desired. Highly conducting carbons have a very highly ordered carbon microstructure. Studies on the electrical characteristics of carbon fibers have usually been carried out with the use of commercially produced materials. There is very little data available on the influence of processing conditions on both mechanical and electrical properties. Such studies should be undertaken.

(2e) More sophisticated uses of carbon fibers may require physical properties than can only be attained from one of the precursor fibers. For example, there are certain applications for the military where a modulus near 683 GPa (100 × 10 psi) is required. This value indicates consideration of a pitch- rather than a PAN-base fiber. In contrast, PAN-base fibers can be produced with a higher electrical resistance and still retain a higher modulus value as compared to a pitch-base fiber. Consequently, no class of fibers should be eliminated and considered unsatisfactory. Rather, tradeoffs may have to be made and more knowledge obtained about the interactions between properties. In considering these precursors, practically no effort has been made to

modify the composition or structure or both of the precursor materials used in PAN- or pitch-base fibers to enhance resistance yet retain good mechanical properties of the resulting carbon fibers. Furthermore, if low-temperature processing is the correct method of increasing fiber resistance, modifications in the as-spun fiber structure should have marked effects on the ultimate carbon fiber properties. Many carbon fibers have a highly ordered, conductive skin with a less-ordered, less-conductive core. Adjustments in the fiber formation and fiber stabilization processes may alter the fiberial structure and skin-core gradients and yield improved overall properties. There is little published evidence available on how the fiber formation and the stabilization processes influence subsequent processing and properties of carbon fibers. Little effort has been directed toward determining the influence of processing conditions, morphological changes, and intercalation on the combined mechanical and electrical properties of carbon fibers. Such studies should be encouraged.

(2f) Coating the fibers with a highly insulative layer is one way to reduce the electrical hazard. The insulation can be obtained by using coating materials such as oxides and carbides or with chars that have high resistance or become low-density foams that spatially insulate the fiber. Other types of coatings might be beneficial, such as polymeric materials that thermally decompose to produce a char or residue capable of holding fibers together and provide electrical insulation. Polymetric coatings may also be effective for landfill disposal. Any coating selected should be tested to determine its effect on composite properties and whether or not it remains effective after dispersion.

The effectiveness of carbon fibers in causing the disruption of electrical equipment depends on their bulk and surface resistance. Furthermore, the properties of fibers expelled from the composite may differ significantly from the morphological, electrical and mechanical characteristics of the original fibers. Studies should therefore be undertaken to determine these characteristics. Such information will be particularly useful in the risk analysis. Methods for characterization must be carefully selected in order to preserve the post-environmental test character of the fibers.

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