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CARBON FIBER MODIFICATION

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Final Report
Covering the Period 23 October 1978 to 1 August 1979

9 November 1979

By: Thomas E. Thompson, Senior Research Physicist
Engineering Sciences Laboratory

Prepared for:

National Aeronautics and Space Administration
Ames Research Center
Moffett Field, California 94305

Attn: C. Frederick Hansen, MS 223-6

NASA Contract NAS 2-10091

SRI Project 7976

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I INTRODUCTION

This is the final report of a six-month project to investigate methods of reducing the electrical conductivity of commercial carbon fibers. This work was motivated by a major concern throughout several agencies of the Federal Government over the fact that carbon fibers can cause short circuits, arcing, and even fires in electrical equipment. A 1978 NASA study indicated that more than a dozen such incidents had occurred since 1970 in industrial plants producing or using carbon fibers. Since composite materials containing carbon fibers have come to play a major role in several industries--most notably aerospace--immediate attention was given to the potential of a major problem caused by the release of carbon fibers into the air.

The work reported here, the result of a project contracted by the Ames Research Center, is a direct attempt to reduce the electrical conductivity of carbon fibers without significantly altering their tensile strength or stiffness.

Our approach was based on the fact that the desirable mechanical properties of carbon fibers result from sp^2-bonds (σ-bonds) which develop between carbon atoms during the carbonization process while forming the fibers, whereas the electrical properties result from the p_z electrons (π-electrons) which remain as a result of the σ-bonding. It is known that intercalation processes can increase the electrical conductivity of carbon fibers by altering the number and nature of these π-electrons. We attempted to reduce the electrical conductivity of the fibers by oxidative reactions with these π-electrons that would reduce their effectiveness as charge carriers.

A variety of carbon fibers made from both polyacrylonitrile (PAN) and pitch-based precursor materials were obtained from Union Carbide Corp., Celanese Corp., and Hercules Inc. Reactions between the fibers and $TiCl_4$, $FeCl_3$, $AlCl_3$, and an HNO_3/H_2SO_4 mixture were attempted, followed in some cases by a further oxidation at an elevated temperature in air. The experiments were successful to a limited degree, since in most cases we were able to produce 10 to 50 percent increases in the fiber resistivities. In one case, pitch fibers in an HNO_3/H_2SO_4 mixture showed an increase in resistivity by a factor of 16. These increases in resistivity indicated that our approach was generally valid. However, NASA scientists felt that resistivity increases by a factor of 1,000 would be necessary to eliminate the electrical shorting problem which originally motivated the study.

Section II of this report contains detailed descriptions of the procedures and a comprehensive tabulation of the results of our experiments. A summary and discussion is presented in Section III.

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II EXPERIMENTAL PROCEDURES AND RESULTS

A. Measurement Techniques

1. Electrical Resistivity

These measurements were made with a small digital multimeter (Triplett 3400) which uses a probe current of 23 μA or less. Individual fibers were laid out on a piece of white paper with a grid drawn on it. Using special large-diameter copper-tipped probes that minimized fiber damage, resistivities were measured for several lengths of the fiber, usually from 7 cm to 1 cm, and a programmable calculator was used to make a least-squares fit to the data to determine the resistance per unit length, R_ℓ, and the resistance for zero length. The latter quantity was a test for contact resistance, which was found to be negligible.

To determine the resistivity of a fiber, the cross-sectional area has to be known, so the fiber diameter was routinely measured using a 400-power optical microscope (Unitron TMD-3069). This method, however, has limited precision (5 to 10 percent) and does not apply to fibers with irregular cross sections. Careful shape and dimension determinations were made with a scanning electron microscope (SEM) to corroborate the optical microscope measurements.

Since the fibers are produced as yarns containing several thousand individual fibers, measurements were always made on at least half a dozen individual fibers, and the resistance and resistivity values were determined by a statistical analysis of all this data.

2. Mechanical Testing

Stiffness and strength tests were performed on an Instron mechanical-testing machine using a type-A load cell with a 50-g full-scale sensitivity. Each fiber to be tested was mounted with red wax (Dennisons, NO. 14A) on a 2 X 0.5 X 0.014 inch^3 stiff paper card. The card had a 1-inch oblong hole punched in its center and the fiber was mounted over this hole. The purpose of the card was to provide support for the fiber while it was being mounted and aligned in the rubber jaws of the Instron. Once the fiber was in place, the two supporting edges of the paper card were burned away with a hot Nichrome wire, leaving a one-inch length of fiber for testing. A tracing of the stress/strain curve of one of the highest strength fibers is shown in Figure 1. The initial part of the curve shows a slight bowing that could be a result of slippages in the support and clamping of the fiber, as well as slippage and straightening

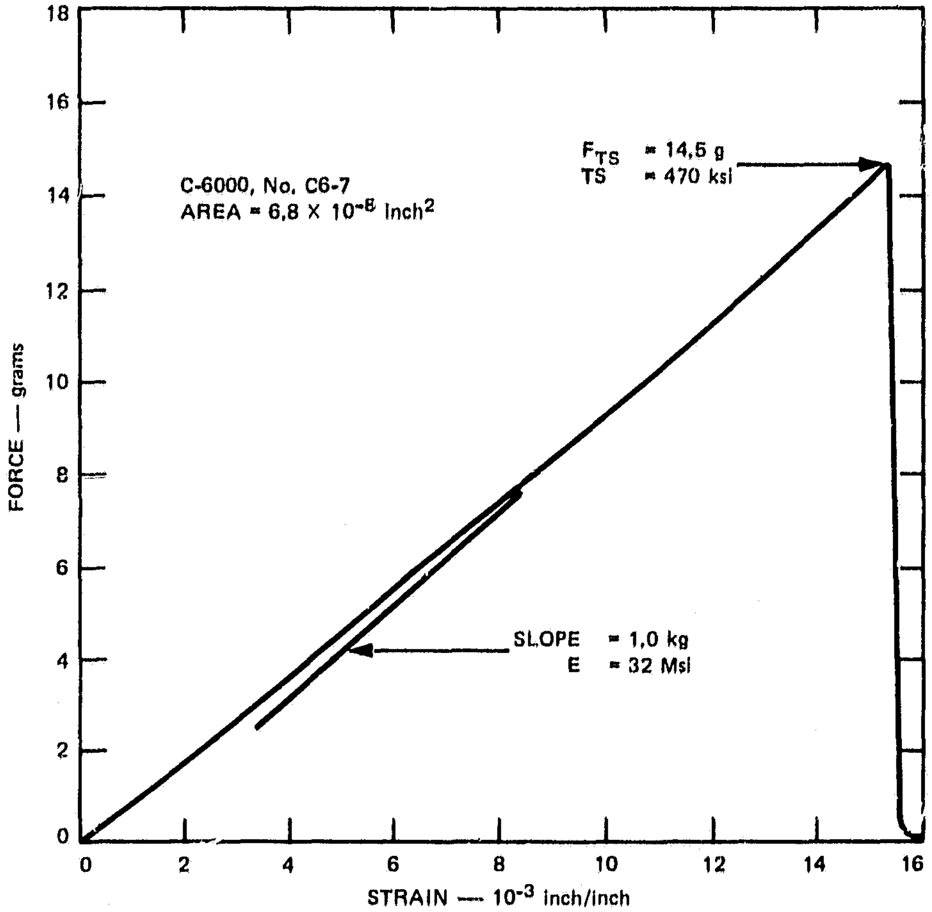


FIGURE 1 STRESS/STRAIN CURVE FOR A CELION 6000 CARBON FIBER WITH A VERY HIGH TENSILE STRENGTH (TS) — THE SHAPE OF THE CURVE IS TYPICAL

of the microfibriles which make up the fiber itself. This slippage does not affect the value found for the tensile strength (TS) which is simply the breaking-point force divided by the cross-sectional area. Young's modulus, E, is found from the slope of the upper half of the stress/strain curve.

B. Characterization of Unreacted Fibers

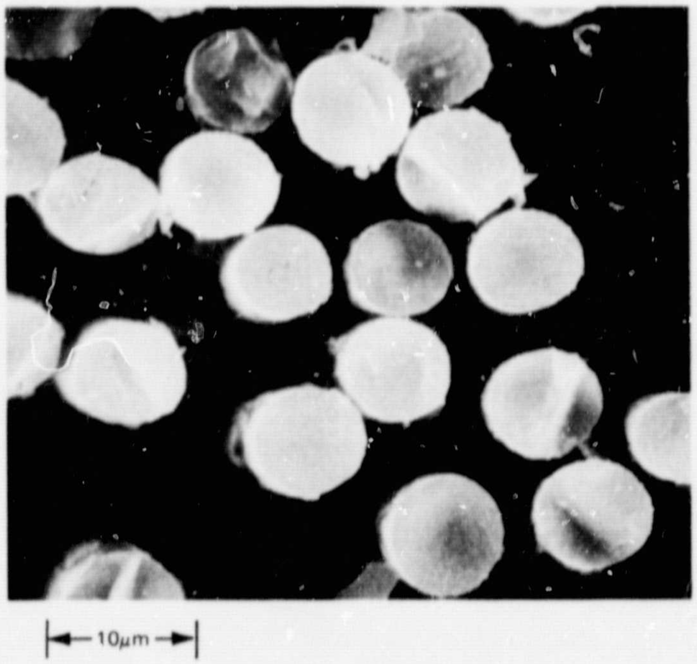
Ten different carbon-fiber samples were obtained from three different companies, Union Carbide Corp., Celanese Corp., and Hercules, Inc. Two samples from Union Carbide were made from pitch-based polymers, the rest from polyacrylonitrile (PAN). (We note that none of the companies produces all of the fibers by themselves, but they have various licensing and production agreements with other companies: Union Carbide with Toray Industries of Japan, Celanese with Toho-Beslon Co. of Japan, and Hercules with Courtaulds, Ltd. of Great Britain.)

The details of the ingredients and processing of the fibers are proprietary to the individual manufacturers. However, we do know that high-strength, medium-modulus carbon fibers like Union Carbide's Thornel 300 (T-300) and Celanese's Celion 6000 (C-6000) are produced with heat-treatment temperatures between 1300 and 1500°C and they can contain up to 10 percent noncarbon residual. High-stiffness fibers are treated at considerably higher temperatures, up to 3000°C, and have a lower noncarbon content. Another unknown aspect of the fibers is surface treatment. Various proprietary coatings and/or oxidation treatments are used to enhance the adhesion of the fibers to epoxy resins for the production of composite materials. We ordered uncoated materials, but even with coated materials we didn't notice any effect on electrical measurements except that sometimes the electrode had to be moved slightly to achieve a good contact.

Figures 2 through 4 and Table 1 summarize the characteristics of the starting fibers. All of the fibers have round cross sections except the T-50, T-300, and GY70, as can be seen in the SEM micrographs. We previously mentioned that high stiffness materials (E > 50Msi) are associated with high temperature treatments and have higher carbon content. Table 1 shows that these materials also have lower electrical resistivities.

C. Chemically Treated Fibers

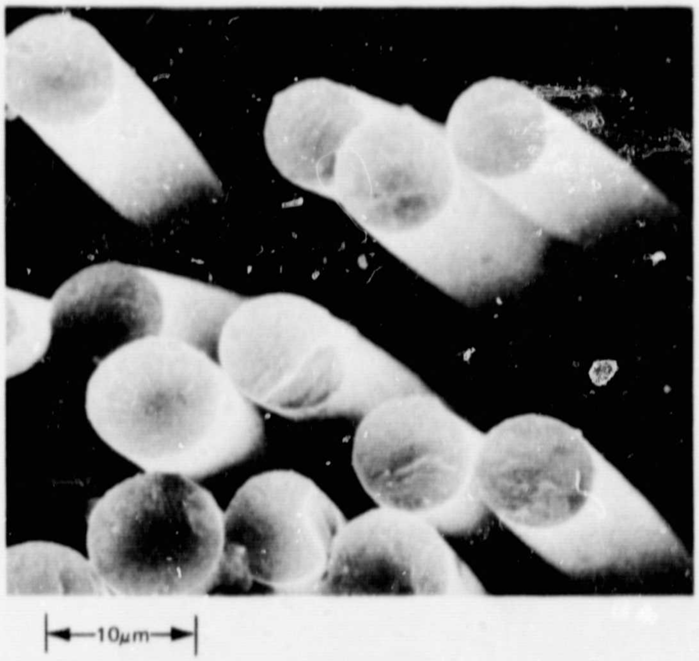
Four different reactants, $TiCl_4$, $FeCl_3$, $AlCl_3$, and a HNO_3/H_2SO_4 mixture were chosen because of their known reactions with graphite. We initially thought that the chlorides would interact to produce a fiber with reduced resistance, but that a further oxidation would produce the bonding of the π-electrons necessary to increase the resistance. The reaction with the nitric acid mixture was chosen because government reports indicated that it could produce a factor-of-700 increase in the resistivity of T-300 fibers.



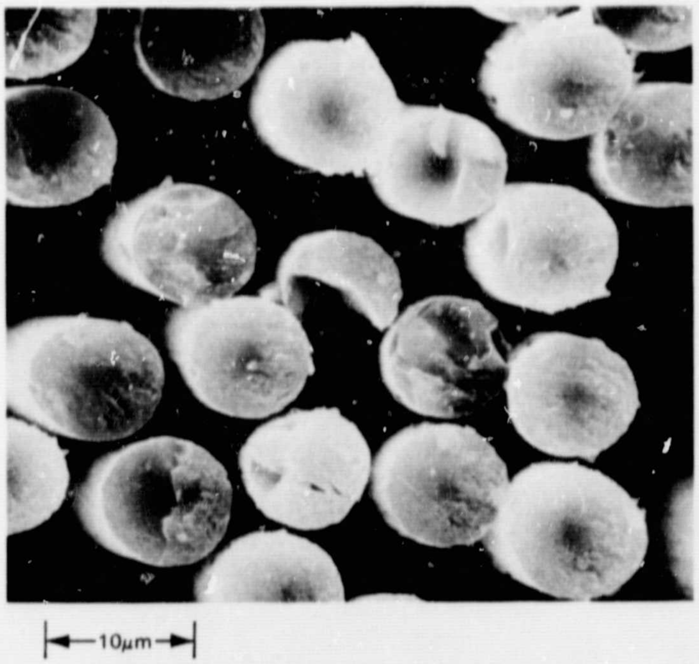
(a) CELION 6000

(b) GY70SE

FIGURE 2 SEM MICROGRAPHS OF CARBON FIBERS FROM CELANESE CORPORATION

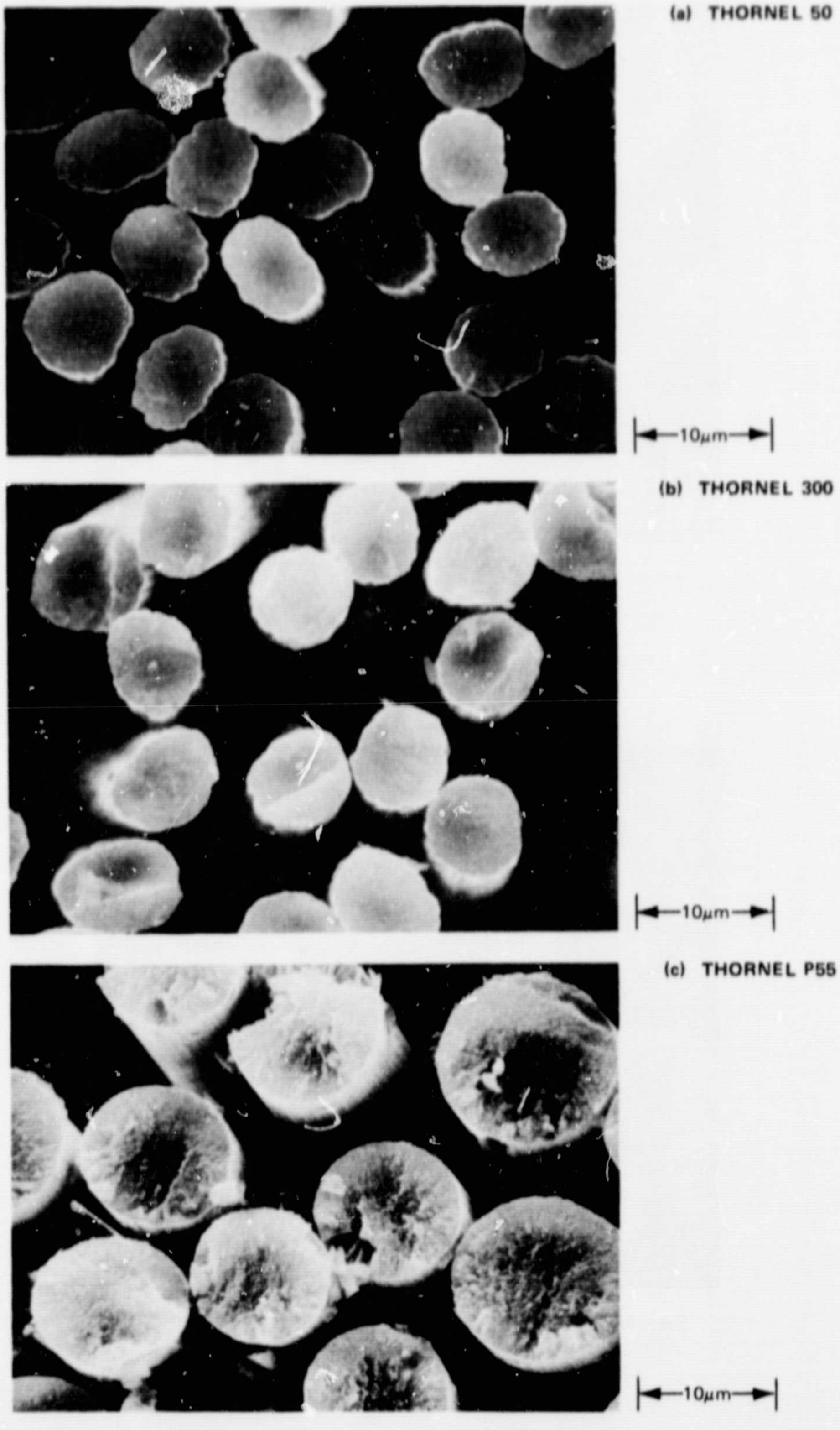


(a) HERCULES HTS2



(b) HERCULES HMS

FIGURE 3 SEM MICROGRAPHS OF CARBON FIBERS FROM HERCULES INCORPORATED



(a) THORNEL 50

(b) THORNEL 300

(c) THORNEL P55

FIGURE 4 SEM MICROGRAPHS OF CARBON FIBERS FROM UNION CARBIDE CORPORATION: (a) AND (b) ARE FROM PAN PRECURSORS, (c) FROM PITCH

Table I

A SUMMARY OF THE MECHANICAL AND ELECTRICAL PROPERTIES OF TEN DIFFERENT COMMERCIAL CARBON FIBERS

Fiber	Diameter (μm)		Area (μm²)		Density (g/cm³)	Percent Carbon	E* (Msi)		TS† (ksi)		R_ℓ‡ (kΩ/cm)		ρ§ (μΩ-cm)		Comments
	Manuf. Data	Our Meas.	Manuf. Data	Our Meas.			Manuf. Data	Our Meas.	Manuf. Data	Our Meas.	Manuf. Data	Our Meas.	Manuf. Data	Our Meas.	
Union Carbide															
T-300, WYP 15	7.0	7.2±0.3■	38.7	41±3	1.73	92	33	32± 3	390	300±100	4.65	4.8 ±0.1	1800	1970±180	PAN, made by Toray (Japan) 6000 filaments
T-50, WYR 15	6.5	6.7±0.2■	33.3	35±2	1.81	99	57	54± 7	320	380± 50	2.85	2.8 ±0.2	950	990± 90	PAN 6000 filaments
P 55, VSB-32	10-11	10.5±1.0	85	86±8	2.02	99	55	58±10	300	314± 73	0.88	0.77±0.02	750	660± 65	Pitch 2000 filaments
Type P, VSA-11	—	13.0±0.8	—	134±16	—	—	—	36± 5	—	186± 20	—	0.69±0.08	—	924±155	Pitch, old product, discontinued
Celanese															
Celion 6000	7.1	7.5±0.5	40	44± 3	1.76	—	34	32± 4	400	400±160	3.8	3.6 ±0.3	1500	1580±150	Made by Toho-Beston (Japan) PAN, 6000 filaments
GY 70 SE	8.4	8.7±0.8■	55	59±11	1.96	—	75	60±11	270	190± 80	1.18	1.2 ±0.4	650	795±270	PAN, processed at T>3000°C, 386 filaments
Hercules															
HTS2	8	7.7±0.1	—	47± 4	1.66	—	39	—	420	—	—	3.0 ±0.2	—	1400±140	
HMS	8	8.2±0.3	—	53± 2	1.83	—	53	—	320	—	—	2.0 ±0.1	—	1030± 70	
ASI	8	8.3±0.4	—	55± 2	1.80	—	34	—	450	—	—	3.3 ±0.1	—	1820±100	
AS4	7-9	7.0±0.1	40	38± 4	1.77	—	30-32	—	430-450	—	—	3.7 ±0.2	—	1410±160	

*E = Young's modulus.

†TS = Tensile strength.

‡R_ℓ = Resistance per unit length.

§ρ = Resistivity

■Equivalent circular diameter.

1. Reaction with $TiCl_4$

Graphite is known to react with $TiCl_4$ in the presence of Cl_2 (Freeman and Lonergan, 1979). However, we were unable to measure any weight change after reacting C-6000 carbon fibers with 1.7 atmospheres of $TiCl_4$ and 1.0 atmospheres of Cl_2 at 250°C for 6 days. Room temperature reactions in liquid $TiCl_4$ and a 250°C reaction in 2 atmospheres of the vapor also produced no detectable reaction after 24 hours.

2. Reaction with $FeCl_3$

The product of the reaction between ferric chloride and graphite, first studied by Thiele (1932), is one of the most carefully studied metal-chloride graphite compounds (Stumpp, 1977). The procedure we followed for the reaction of C-6000 carbon fibers with $FeCl_3$ was essentially that detailed by Hooley and Bartlett (1967). Anhydrous $FeCl_3$ was reacted with the fibers near 315°C where the vapor pressure is 1 atmosphere. Under these conditions, earlier experiments with graphite had produced a nearly saturated compound. The resulting product with the C-6000 fiber was very hydroscopic and mechanically unstable. Table 2 shows the resulting percentage weight uptakes and resistivities. There had been some concern as to the need for Cl_2 to produce the desired reaction, but the data clearly show that a similar uptake is achieved with or without chlorine gas. In the case of pristine graphite, the reaction with $FeCl_3$ usually produces a reduction in resistivity. With the fibers we observed an increase in resistivity, typically by an order of 10 percent. Since these resistivity measurements were made in the ambient, moist air, it is possible that they reflect the effect of surface hydration. As a result of the minimal weight uptake, we decided not to pursue this reaction.

3. Reactions with $AlCl_3$

The initial carbon fiber-$AlCl_3$ reaction was carried out at 210°C in the presence of chlorine gas. Under these conditions the reaction with synthetic graphite produces a saturated compound (Rudorff and Zeller, 1955; Dzurus and Hennig, 1957). Three different fibers and highly

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Freeman, A.G. and J. Lonergan, 1979: Carbon, 17, p. 371.

Thiele, H., 1932: Z. Anorg. Allg. Chem., 207, p. 340.

Stumpp, E., 1977: Mat. Sci. Eng., 31, p. 53.

Hooley, J.G. and M. Bartlett, 1967: Carbon, 5, p. 417.

Rudorff, W. and R. Zeller, 1955: Z. Anorg. Allg. Chem., 279, p. 182.

Dzurus, M.L. and G.R. Hennig, 1957: J. Am. Chem. Soc., 79, p. 1051.

Table 2

EFFECT OF REACTING C-6000 WITH $FeCl_3$

Material	Percent Weight Uptake $(\Delta\omega/\omega_o) \times 100$	Dilatation $\Delta d/d_o$	Resistivity Ratio ρ/ρ_o
C-6000 No Cl_2	3.4 to 4.7	~0.0	1.0 to 1.1
C-6000 With Cl_2	5.1	~0.0	1.1

oriented pyrolytic graphite (HOPG) chips were reacted with the $AlCl_3$-Cl_2 mixture for 24 hours or more. The HOPG chips and the pitch fibers reacted in a similar manner as indicated by weight uptakes of over 100 percent, as shown in Table 3. The medium modulus PAN fibers showed 10 percent weight uptakes (varying from 1 to 25 percent) with a slight increase in resistivity. The pitch fibers underwent a marked decrease in resistivity, in a manner similar to graphite. Since the resultant materials were unstable in moist air, they were given an oxidative heat treatment at 320°C for at least 16 hours. This treatment produced a reduction in the fiber weight and a slight increase in the resistivity as seen in Table 3. The 10 to 20 percent resistivity increase resulting from these treatments on PAN fibers were insignificant solutions to the overall problem and the approach was abandoned. It was interesting, however, to observe how differently PAN fibers and pitch fibers react. The pitch fibers (which received higher heat-treatment temperatures) were more similar to the graphite chips in their weight uptake, and they exhibited resistivity changes characteristic of graphite.

4. Reactions with HNO_3/H_2SO_4 Mixtures

A patent[*] and a technical report[†] to the Air Force Materials Laboratory, both from the Celanese Corporation, describe a method for reducing the electrical conductivity of carbon fibers using a mixture of HNO_3 and H_2SO_4. Table 4, reproduced from the latter report, indicates that the resistivity of T-300 can be increased by at least a factor of 700 by such a treatment. This result led us to try the reaction with 10 different fiber types under a variety of conditions. The fibers were treated with the same reagent prescribed in the AFML report: a mixture of 1 part 90 percent HNO_3 and 3 parts (by weight) of H_2SO_4 (containing 30 percent

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[*] U.S. Patent No. 4,073,869, 14 Feb. 1978.

[†] AFML-TR-73-191, Part II, September, 1974.

Table 3

WEIGHT UPTAKES, DILATATION, AND RESISTIVITIES AFTER REACTIONS WITH $AlCl_3$ AND Cl_2 AND SUBSEQUENT OXIDATION IN AIR

Material	After $AlCl_3$ (Cl_2) Reaction			After Oxidation		
	ω_1/ω_o	$\Delta d/d_o$	ρ_1/ρ_o	ω_2/ω_o	$\Delta d/d_o$	ρ_2/ρ_o
T-300	1.01 to 1.25	0.1	.9 to 1.2	0.97 to 1.03	0.05	1.0 to 1.2
C-6000	1.03 to 1.12	0.05	1.0 to 1.1	0.97 to 1.04	0.05	1.0 to 1.3
Pitch, VSA-11	1.7 to 2.2	0.6	0.2 to 0.3	1.3 to 1.4	0.2	0.2 to 0.6
HOPG chips	2.0 to 2.4	--	--	1.7	--	--

SO_3). After the acid treatment, the fibers were rinsed in distilled H_2O, then acetone, and finally vacuum dried at 110°C for 15 minutes at approximately 0.5 torr. This is the same washing and drying treatment described in the AFML report. The resulting weight uptakes and resistivity changes for different reaction times and temperatures are presented in Table 5.

It is clear from Table 5 that we were not able to produce the large resistitivty increases indicated in the AFML report. For the PAN-based carbon fibers (e.g. T-300), the largest resistivity increases were less than 50 percent. The largest weight uptakes for the PAN fibers resulted with a 60-minute treatment time at 80°C. After this the fibers began to decompose.

The HOPG chips were included in the reaction vessels along with the fibers to monitor the acid strength and reaction rate. The most saturated graphite-HNO_3 compound corresponds to a weight uptake of 88 percent (C_6HNO_3). From Table 5 it is clear that the HOPG chips retained a large portion of the reactant even after the washing and drying procedure. The chips reacted immediately with the acid, expanding rapidly and turning blue in less than a minute.

The pitch fibers reacted much faster than the PAN fibers and partially decomposed within 10 minutes, as indicated by a blackening of the acid. The maximum resistivity change was found for pitch fibers which had been

Table 4

EFFECT OF CHEMICAL TREATMENT ON COMMERCIAL CARBON FIBERS AS REPORTED BY CELANESE CORPORATION TO THE AIR FORCE (AFML-TR-73-191, Part II, September 1974)

Table Reproduced Directly from Celanese Report

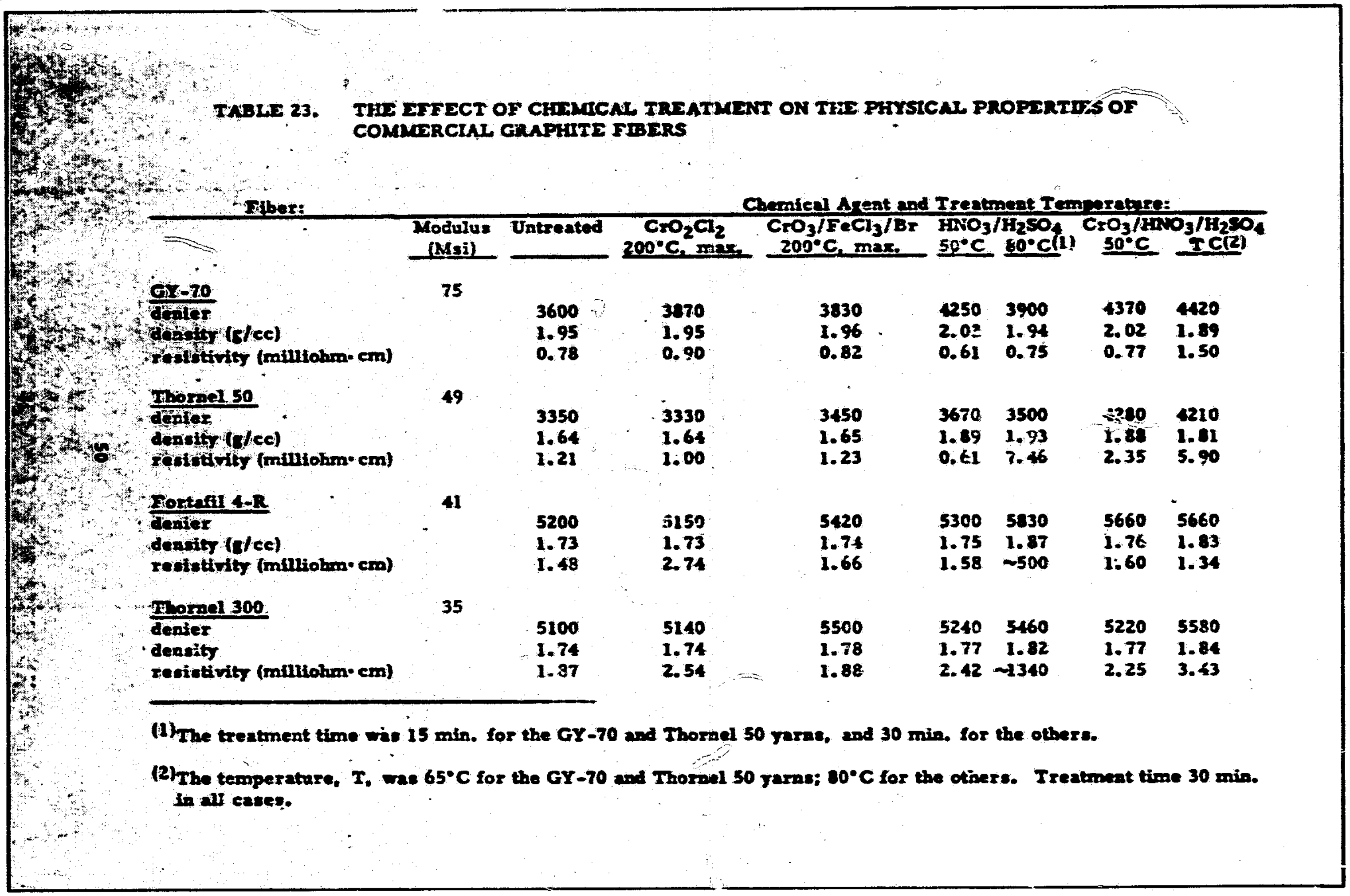

TABLE 23. THE EFFECT OF CHEMICAL TREATMENT ON THE PHYSICAL PROPERTIES OF COMMERCIAL GRAPHITE FIBERS

Fiber:			Chemical Agent and Treatment Temperature:					
	Modulus (Msi)	Untreated	CrO_2Cl_2 200°C, max.	$CrO_3/FeCl_3/Br$ 200°C, max.	HNO_3/H_2SO_4 50°C	HNO_3/H_2SO_4 80°C[1]	$CrO_3/HNO_3/H_2SO_4$ 50°C	$CrO_3/HNO_3/H_2SO_4$ T C[2]
GY-70	75							
denier		3600	3870	3830	4250	3900	4370	4420
density (g/cc)		1.95	1.95	1.96	2.02	1.94	2.02	1.89
resistivity (milliohm·cm)		0.78	0.90	0.82	0.61	0.75	0.77	1.50
Thornel 50	49							
denier		3350	3330	3450	3670	3500	4280	4210
density (g/cc)		1.64	1.64	1.65	1.89	1.93	1.88	1.81
resistivity (milliohm·cm)		1.21	1.00	1.23	0.61	7.46	2.35	5.90
Fortafil 4-R	41							
denier		5200	5150	5420	5300	5830	5660	5660
density (g/cc)		1.73	1.73	1.74	1.75	1.87	1.76	1.83
resistivity (milliohm·cm)		1.48	2.74	1.66	1.58	~500	1.60	1.34
Thornel 300	35							
denier		5100	5140	5500	5240	5460	5220	5580
density		1.74	1.74	1.78	1.77	1.82	1.77	1.84
resistivity (milliohm·cm)		1.37	2.54	1.88	2.42	~1340	2.25	3.43

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[1] The treatment time was 15 min. for the GY-70 and Thornel 50 yarns, and 30 min. for the others.

[2] The temperature, T, was 65°C for the GY-70 and Thornel 50 yarns; 80°C for the others. Treatment time 30 min. in all cases.

Table 5

WEIGHT UPTAKES, DILATATIONS, AND RESISTIVITY CHANGES PRODUCED BY TREATING CARBON FIBERS WITH AN HNO_3/H_2SO_4 MIXTURE

Material and Conditions	Percent Weight Uptake $(\Delta w/w) \times 100$	Dilatation $\Delta d/d_0$	Resistivity Ratio (ρ/ρ_0)
15 min @ 80°C			
C-6000	5	0.05	1.14
T-300	5	0.04	1.22
Pitch, VSA-11	6 to 11, Partial decomposition	0.03	1.8 to 2.5
HOPG	52 to 56		Exfoliated
15 min @ 90°C			
C-6000	7	--	1.0*
T-300	5	--	1.5*
Pitch, VSA-11	Partial decomposition	--	16±5*
HOPG	64 to 72		Exfoliated
30 min @ 80°C			
C-6000	1	~0.0	1.0 to 1.1
T-300	5 to 17	0.0	1.0 to 1.2
Pitch, VSA-11	Partial decomposition	--	--
HTS-2	4	0.0	1.0
HMS	13	0.04	0.7 (!)
AS-1	22	-0.02	0.8 (!)
AS-4	4	0.06	1.1
HOPG	68 to 89	--	Exfoliated
60 min @ 80°C			
C-6000	28	--	1.3*
T-300	24	--	1.3*
Pitch, VSA-11	Decomposed	--	--
HOPG	46 to 70	--	Exfoliated
18 hrs @ 80°C			
C-6000	Decomposed	--	--
HOPG	59	--	Exfoliated
24 hrs @ Room Temp.			
C-6000	12	0.0	1.2
T-300	19	--	1.4*
Pitch, VSA-11	16	.08	0.5 (!)
HOPG	53 to 84	--	Exfoliated

*Assuming no dilatation

reacted for 15 minutes at 90°C. Unfortunately, these fibers retained very little of their original strength.

The fact that we were unable to reproduce the factor-of-700 increase in resistivity that was reported by the Celanese group was obviously of major concern to us. We took great care to reproduce their experimental conditions and discussed the experiments directly with their technical people. The only significant difference that we were able to find between their work and ours was the method used for the resistivity determination. They measured the resistance of a bundle of fibers (T-300 comes in bundles containing 6,000 fibers) and we measured the resistance of many single fibers. If there were to be any measurement problem associated with contact resistance, it would be greatly magnified with a bundle of 6,000 fibers and would result in an apparent high resistivity value. We believe this to be the main source of the difference between their results and ours. A table in their patent indicates that the treated fibers which had resistivity increases of greater than a factor of 10 also had tensile strengths and Young's moduli reduced by more than a factor of 2. One could interpret this to indicate the onset of decomposition of their fibers. If this were the case, surface contact problems would also have been present. The Celanese researchers indicated that their resistance measurements had considerable variation and that the values they obtained varied with electrode pressure. Such variations are characteristic of contact problems. By measuring the resistance along various lengths of the same single fiber, we were able to eliminate any problems which might have arisen from contact resistance.

Another possibility for the difference between our results and those of the Celanese researchers is a difference in the fibers themselves. The Thornel 600 fibers which they studied were produced almost five years before the ones we purchased. Over that period of time production techniques could have changed in a way that would crucially alter the results of the same chemical treatments. At that time they found a variation in chemical reactivities from fiber lot to fiber lot. They found that a particular narrow range of temperatures and reaction times were needed to produce the large resistivity changes desired. They also were unable to produce similar resistivity changes with similar PAN fibers.

Unfortunately, our researches show that large increases in resistivity cannot be routinely produced by treating PAN carbon fibers with a mixture of 1 part 90 percent HNO_3 and 3 parts of H_2SO_4 containing 30 percent SO_3.

5. Strength of Treated Fibers

Table 6 displays the results of mechanical tests on various reacted fibers. Except for the case of the pitch fibers, no serious degradation of the mechanical properties was observed. In one case, T-300 in the HNO_3/H_2SO_4 mixture, the tensile strength may even have increased. However, the statistics were not good enough for a definitive statement to be made.

The pitch fibers that had the largest resistivity increases were too weak to be mounted for testing in the Instron mechanical testing machine.

Table 6

RESULTS OF MECHANICAL TESTS ON CHEMICALLY REACTED FIBERS

Fiber and Reaction	Percentage Weight Uptake $(\Delta\omega/\omega_0) \times 100$	Young's Modulus (Msi)	Tensile Strength (ksi)
C-6000			
Unreacted	0	32±4	400±160
$(AlCl_3 + Cl_2)$ Oxidized	4	33±3	458± 91
HNO_3/H_2SO_4, 30 min, 80°C	1	29±5	356± 95
HNO_3/H_2SO_4, 16 hr, Room Temp.	-?-	34±3	362± 86
T-300			
Unreacted	0	32±3	300±100
$(AlCl_3 + Cl_2)$ Oxidized	2.7	34±8	311±114
HNO_3/H_2SO_4, 30 min, 80°C	17	32±4	472±112
HNO_3/H_2SO_4, 16 hr, Room Temp.	-?-	34±5	403± 89
Pitch, VSA-11			
Unreacted	0	36±5	186± 20
$(AlCl_3 + Cl_2)$ Oxidized	39	34±5	115± 35
HNO_3/H_2SO_4, 15 min, 80°C	10	10±3	37± 13
HNO_3/H_2SO_4, 16 hr, Room Temp.	-?-	27±5	121± 11

III SUMMARY AND CONCLUSIONS

The object of this research was to investigate the effect of several chemical treatments on the electrical and mechanical properties of carbon fibers, with an optimum goal of increasing the electrical resistivity by a factor of 1000 without appreciably changing the mechanical properties.

We were able to effect resistivity increases from 10 to 50 percent without adversely affecting the tensile strength or Young's modulus for T-300 and C-6000 PAN fibers by treatments with either $AlCl_3$ or nitric acid mixtures. Larger increases in the resistivity ($\rho/\rho_0 \approx 16$) were produced with pitch fibers treated with nitric acid mixtures. However, this treatment also produced a partial decomposition of the pitch fiber and substantial deterioration of the mechanical properties.

A significant aspect of our investigations has been our inability to reproduce the large resistivity changes which were reported by researchers at the Celanese Corp. for certain carbon fibers treated with an HNO_3/H_2SO_4 mixture. Under the conditions in which they reportedly produced a factor-of-700 resistivity increase for T-300 fibers, we found a maximum increase of only 20 percent. We believe that their high resistivity values could possibly be due to contact resistances associated with their measuring techniques.

The rationale behind our approach was to immobilize the conductivity producing π-electrons in the microscopic aromatic structure of the carbon fibers without destroying the strength-producing σ-bonds. Our investigations indicate that certain moderate chemical treatments can produce such results, but the total reduction in the electrical conductivity which we have achieved has not been large enough to impact on any problems which might arise from the high conductivities of the fibers.

From our limited research we have not been able to ascertain any trends in the resistivity changes associated with the chemical treatments which we have applied. Also, we have certainly not determined any limitation to the possible resistivity changes that could be produced by chemical treatments. Such determinations can only come from further investigations.