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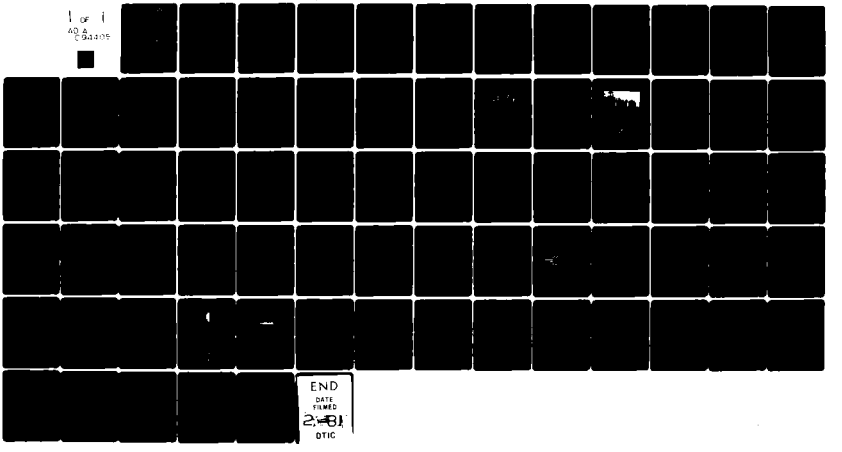

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TECHNICAL REPORT

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INTERCALATED GRAPHITE FIBER CONDUCTOR

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December 1980

Final Report for Period 26 September 1979 - 15 December 1980

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Electrical Conductance	

20 ABSTRACT (Continue on reverse side if necessary and identify by block number)

Lightweight electrical conductors were developed from graphitic fibers intercalated with highly electrophilic intercalants. Conductance increases of 30-36 times over the unintercalated fibers were observed. This corresponds to about 45% of the specific conductivity of copper at room temperature. Unlike copper, the intercalated graphite fibers exhibit a nearly zero temperature coefficient of conductance. The intercalated yarn did not change its resistance during 100 hours of passage of current at 1 watt power dissipation and current densities of 25-35 A/mm^2. Four graphite "wires," equivalent in size to 17-20

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AWG copper wire were delivered.

SUMMARY

This report describes the exploratory development, fabrication, testing and evaluation of lightweight electrical conductor "wires" comprised of graphitic fibers intercalated with highly electrophilic molecules ("intercalants") to enhance their electrical conductivity. Evaluation of the electrical resistance of two representative high modulus graphite fibers housed in special glass containers during their intercalation with various state-of-the-art intercalants (arsenic pentafluoride, antimony pentafluoride, fluorosulfonic acid) indicated that certain mixtures of these intercalants as well as elevated temperatures provide sufficiently fast intercalation rates and permitted selection of the preferred intercalant compositions.

Conductance increases of 30-36 times were observed on the fully intercalated graphite fibers, corresponding to specific conductivity (conductivity/density) increases of up to 20 times, or 45% of the specific conductivity of copper at room temperature. In addition: (1) the temperature coefficient of the conductance (or resistance) was found to be at or very close to zero over the 20°-90°C range tested; (2) the intercalated yarn did not change its resistance during passage of current at 1 watt power dissipation level for >100 hours and current densities of 25-35 A/mm^2; and (3) the resistance values were stable and reproducible after repeated exposure of the encapsulated intercalated fibers to -100°C.

Four graphite "wire" samples, comprised of multifilament bundles equivalent in size to 17-20 AWG copper wire and having the above mentioned electrical and thermal characteristics were provided with high temperature low resistance contacts, and

encapsulated in an air-tight Teflon-metal assembly. After being intercalated with arsenic pentafluoride, the "wires" were tested and delivered to MERADCOM.

PREFACE

This report was prepared by Ilmar L. Kalnin, Research Associate, Celanese Research Company. The work reported herein, which was performed under Contract DAAK70-79-C-0182, was sponsored by MERADCOM, Electrical Power Laboratory, Electrical Equipment Division, Ft. Belyoir, VA 22060. W. David Lee was the MERADCOM Project Engineer. The time period covered by the effort was 26 September 1979 to 15 December 1980.

Besides Ilmar Kalnin as the Principal Investigator, the many discussions and consultations with Harris Goldberg and Arnold J. Rosenthal are noted. The expert technical support of George Breckinridge is acknowledged. Joseph R. Leal served as Contract Administrator.

This is the Final Technical Report issued under Contract DAAK70-79-C-0182. It was submitted by the author in December 1980.

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I. INTRODUCTION

Recent academic research has demonstrated that the electrical conductance of synthetic or natural graphite crystals is greatly enhanced upon their intercalation* with strong electron acceptor molecules[1-3]. In optimal cases, such as when a synthetic graphite of high structural perfection (e.g., HOPG** graphite) is intercalated with a strong electron acceptor (e.g., AsF_5 or SbF_5), the original conductivity increases about 20 times, approaching that of copper, the most widely used electrical conductor material. The combination of high conductivity and low density has attracted attention to the intercalated graphite as a possible lightweight conductor, because for weight critical conductors the appropriate measure of performance is not the conductivity by itself but rather the ratio: conductivity/density. This ratio is also called the specific conductivity, and is in correspondence with the analogous terms, specific strength and specific modulus (strength/density and modulus/density, respectively) employed as efficiency indicators for advanced fiber reinforced composites.

On this basis, the specific conductivity of the acceptor intercalated graphite is at least twice as high as that of copper, because of the low density of the former (2.3-2.5 kg/dm^3) relative to that of copper (9 kg/dm^3). Also, theoretical calculations indicate that higher specific conductivities, say several times that of copper, may be achievable when a perfect graphite structure is intercalated with low-scattering acceptor molecules[4]. Thus, in principle, the replacement of copper by

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* Intercalation is defined as the insertion of atoms or molecules between the planes of a layered material, such as graphite, without affecting the intraplanar structure.

** HOPG is the acronym for High Oriented Pyrolytic Graphite, available from Union Carbide Company.

intercalated graphite could provide considerable weight savings in electrical conductor systems used in heavy vehicles and missiles. Also, a lightweight electrical conductor for redeployable power cable systems might facilitate the delivery of electrical power in the field.

In contrast to copper or any other ductile metal that is readily processable to form continuous electroconductive wire, the intercalated graphite crystals, although highly conductive by themselves, so far have not been consolidated into a wire by any mechanical means[5]. Because of their inherent brittleness, it is very doubtful that a satisfactory consolidation can be achieved. An obvious way of avoiding this problem is to intercalate a graphite multifilament yarn so as to raise its electrical conductance while maintaining continuity and sufficient mechanical strength.

Early exploratory studies on intercalation of commercially available carbon/graphite fibers have shown that the so-called "graphite" fibers i.e., fibers having relatively high Young's moduli, >400 Gigapascals (GPa) , can be intercalated, whereas the lower modulus "carbon" fibers (Young's moduli <250 GPa) will intercalate little, if at all [6,7]. This difference in intercalatability has been explained by attributing the driving force for the intercalation to electrical charge transfer between the graphite crystal lattice and the intercalant molecules. The extent of this charge transfer increases with the lattice perfection; greatest for the HOPG and natural graphite, less so for the high modulus "graphite" fiber, and still much less for the lower modulus "carbon" fibers that are commonly used as the reinforcement in high performance structural composites. The first reported resistance measurements on some commercial graphite filaments intercalated with HNO_3 indicated that intercalation had the largest conductance-increasing effect, approximately 12

times, on an ex-rayon fiber with the highest modulus (Thornel 75)[6]. For similar high modulus ex-PAN filaments (Celion® GY-70), conductance gains of up to 30 times have been reported upon electrochemical intercalation with fluorosulfonic acid[8].

Recent exploratory work at Celanese resulted in the fabrication of experimental graphitic fibers having a more perfect lattice structure and orientation than the heretofore commercially available ones. These fibers showed not only a substantial conductance enhancement upon intercalation, but also a higher intrinsic conductivity before the intercalation. Typically, while the conductivity of the reinforcing carbon fibers is only about 1/40 that of the HOPG, and that of a high modulus commercial graphite fiber (Celion® GY-70) is about 1/16, experimental graphite fiber having conductivities to about 1/8 that of HOPG have been prepared here. Resistance measurements on the single filaments of the latter intercalated with certain state-of-the-art intercalants, indicated conductance enhancements of up to 50 times the original conductance[9]. The enhancement of conductivity value is different because the calculation of the conductivity also requires knowledge of the intercalated filament density and cross-sectional area, none of which is adequately measurable on the micron size filaments. At the time this project was initiated, no published information concerning the intercalation behavior and the conductivity enhancements of larger assemblies of graphite filaments, corresponding in cross-section to typical metal wires, was available.

II. PROJECT OBJECTIVE AND DEVELOPMENTAL PROGRAM

The objective of the project was to develop, fabricate, test and deliver evaluation samples of short length conductor "wire" made from intercalated graphite fibers. These samples

were to have certain chemical, physical and electrical characteristics and meet certain environmental requirements,* as follows:

Sample Composition. The samples were to be composed of continuous highly graphitic fiber "wires" intercalated with a state-of-the-art intercalant, reported to yield large conductance enhancements on graphite, such as antimony pentafluoride, SbF_5, or arsenic pentafluoride, AsF_5, alone or together with other intercalating agents and accelerators. Efforts to obtain stable optimized graphite/intercalant ratios or "stages"** should be made.

Physical Characteristics. The to be developed graphite wire samples should be 10-30 cm in length and contain enough intercalated fibers to correspond in cross-sections to standard conductor wires in the range of #36 to #16 AWG (American Wire Gauge), or 0.0127 to 1.31 mm^2, respectively.

Electrical Connections. Electrical termination to the multifilament connectors are to be provided for the evaluation of the overall conductivity by the conventional (four-terminal) method and as a current carrying conductor.

Protective Coating or Cover. The samples are to be protected from the degrading effects of ambient air, primarily its moisture content, and damage by handling. Similarly, the

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* Interim samples lacking one or more of these requirements may be available to MERADCOM upon request during the course of the development.

** Stage may be defined as the number of graphite basal planes between the nearest neighbor lattice planes of the intercalant. E.g., in Stage IV - four graphite basal planes are present between the two adjacent intercalant lattice planes.

environment shall be protected from possible contamination by the conductor materials.

To meet the objective and the requirements, the following technical tasks and the time period allotted for each task were set as follows:

1. Select and characterize representative experimental graphite yarns* having graphitic structures and meeting the cross-sectional wire size requirements.
   September - October, 1979 (1 month)
2. Develop a simple non-corrosive air-tight enclosure to assess the response of the graphite yarns to different intercalants. Measure the conductance change during the intercalation.
   November 1979 - March, 1980 (5 months)
3. Evaluate the electrical and thermal properties of the intercalated yarns. Identify and select the preferred intercalants and intercalation procedures for application to the graphite fiber wires.
   January - May, 1980 (5 months)
4. Develop techniques for electrically contacting and for encapsulating graphite fiber wires.
   February - June, 1980 (5 months)
5. Fabricate prototype wire samples. Evaluate their electrical and thermal properties.
   April - December, 1980 (8 months)
6. Deliver samples meeting the contract requirements to MERADCOM.
   August - December, 1980 (5 months)

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* Yarn is defined here as a continuous multifilament bundle and is used interchangeably with the term "multistrand wire."

III. TECHNICAL DISCUSSION

A. Selection and Properties of Graphite Yarns. Two one-meter lengths of two kinds of tow bundle, each comprised of graphite yarn, were selected as the starting material for the preparation and initial screening of intercalated graphite "wire." Each yarn contains 384 bean-shaped filaments with an equivalent circular cross-section in the range of 0.018-0.021 mm^2. This cross-section corresponds to that of 35-34 AWG conductor wire. Both kinds of fiber were made from the same polyacrylonitrile (PAN) precursor and heat treated at 2900-3000°C.

The yarns of each bundle were characterized by measurement of the filament tensile strength, Young's modulus, breaking elongation, linear density (denier), bulk density, and d.c. resistance. The measurements were made on five filaments each taken from 3-4 randomly selected yarn samples. The denier and the mechanical properties were measured by standard Celanese test methods used for the characterization of graphite filament yarns. The density was determined by the density gradient tube method, ASTM D1505, and the resistance was measured by the four terminal method using an L&N Kelvin bridge.

The average mechanical properties of the yarn are listed in Table 1. Densities, electrical d.c. resistances per unit length, and the calculated resistivities are shown in Table 2. The observed variability is typical of graphite yarns made from commercially available precursor material.

TABLE 1. MECHANICAL PROPERTIES OF GRAPHITE YARNS

YARN SPECIMEN	TENSILE STRENGTH (10^3 psi)	(MPa)	YOUNG'S MODULUS (10^6 psi)	(GPa)	BREAKING STRAIN (%)	YARN DENIER (g/9000m)
Lot 3-157-11						
A	290	2.00	76.3	526	0.37	375
B	313	2.16	77.8	537	0.40	383
C	354	2.44	89.7	619	0.39	371
D	267	1.84	87.0	600	0.30	371
Average	305	2.10	82.7	570	0.37	375
Lot GR-02						
A	212	1.46	102.0	704	0.20	344
B	344	2.37	97.8	673	0.34	357
C	312	2.08	95.0	655	0.33	357
Average	285	1.97	98.3	678	0.29	353

TABLE 2. RESISTANCE AND RESISTIVITY OF GRAPHITE YARNS

YARN SPECIMEN	DENSITY (g/cm^3)	UNIT RESISTANCE (ohm/cm)	RESISTIVITY (ohm/cm)
Lot 3-157-11			
A	2.040	2.455	513×10^{-6}
B	2.045	2.458	505 "
C	2.030	2.616	560 "
D	2.040	2.617	548 "
E	2.025	2.379	520 "
Average	2.036	2.505	529×10^{-6}
Lot GR-02			
A	2.090	2.004	371×10^{-6}
B	2.093	2.017	385 "
C	2.091	1.920	373 "
D	2.087	2.118	393 "
E	2.083	2.075	392 "
Average	2.090	2.027	383×10^{-6}

B. Enclosure for the Testing of Intercalants. Since the literature data indicate that graphite intercalated with AsF_5 or SbF_5 are affected by moisture, dry air-tight enclosures for the intercalated yarns are needed. The enclosure developed for the exploratory intercalation was made of borosilicate glass and was designed to contain two graphite yarns and the intercalant. Briefly, this container consists of a small glass bulb supporting a central filling tube and two pairs of curved tubular sidearms, each pair accommodating one piece of graphite yarn at right angles to each other. A dimensioned sketch of the container is given in Figure 1.

The electrical connections are made in the following manner. After the graphite yarn pieces, 20-25 cm long, have been inserted into the respective sidearms, portions of the tubing near the ends are collapsed around the yarns to provide a snug fit. Electrical contacts to the yarn are than made by pouring molten low-melting alloy ("Cerro® eutectic Bi-Pb or Bi-Sn alloys) into each tube end around the yarn and inserting a piece of copper wire into the alloy before solidification. The most suitable alloy for this purpose was one having the lowest thermal expansivity - Cerrotru® (eutectic temp. 138°C), since several container sidearms cracked during cooling of the molten solder because of excessive thermal stresses, while several others failed later as these tubes were heated, cooled or handled during the equilibration at elevated temperatures. The occurrence of the failures is shown in the respective tables.

The surviving containers, however, remained air-tight during the course of the exploratory work. Prior to starting the intercalation, several of the containers were tested on the vacuum line and found to be leak free after 18 hours under

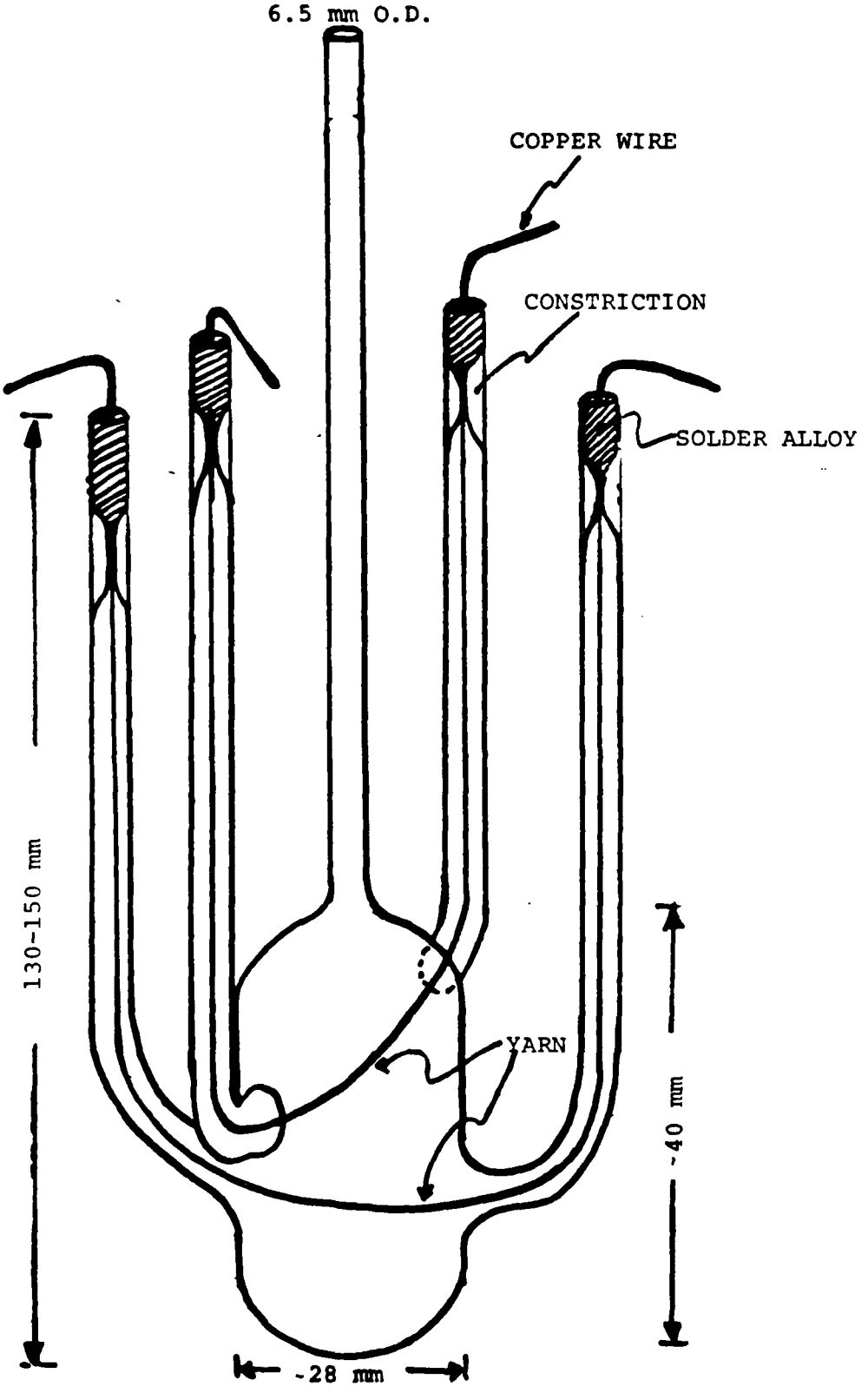


FIGURE 1. GLASS CONTAINER FIXTURE FOR THE INTERCALATION AND TESTING OF GRAPHITE YARNS

mechanical pump vacuum (<100 millitorr). Figure 2 is a photograph of the glass container ready for intercalation.

C. Exploratory Intercalation

1. Intercalation With Single Intercalants (AsF_5, SbF_5, HSO_3F). Two containers of the encapsulated yarn were intercalated with gaseous arsenic pentafluoride, AsF_5; two with liquid antimony pentafluoride, SbF_5; and one with liquid fluorosulfonic acid, HSO_3F. The intercalation with AsF_5 was carried out by attaching the glass fixture through the center stem to a Monel manifold and backfilling the evacuated manifold to atmospheric pressure with AsF_5 from a commercial gas bottle (Ozark-Mahoning Co., Lot KS-20-259). Prior to contacting the yarn, the AsF_5 was degassed by repeated condensation/evaporation via a liquid nitrogen trap.

Since the intercalation with AsF_5 proceeded rather slowly, the fixture was kept on the manifold in contact with excess AsF_5 for about 18 hours (overnight) before being sealed off at the stem. SbF_5 (about 0.3 cm^3, from Ozark-Mahoning Co., Lot JP-2-45) and HSO_3F (about 1 cm^3, redistilled from 99% pure material, lot S-03, supplied by ROC/RIC Co.) were syringed directly into the fixture through the center stem, which was then sealed off immediately.

The containers containing the intercalating yarns were then set aside at room temperature and the decrease in the electrical resistance was measured and recorded at various time intervals. The results are listed in Tables 3 and 4. The data indicate that the AsF_5 intercalates very slowly, the SbF_5 much faster, but the HSO_3F, hardly at all. However, the sealed-in yarns must have been mixed up and mislabeled by the glassblower, since those showing a 60-65 ohm resistance obviously

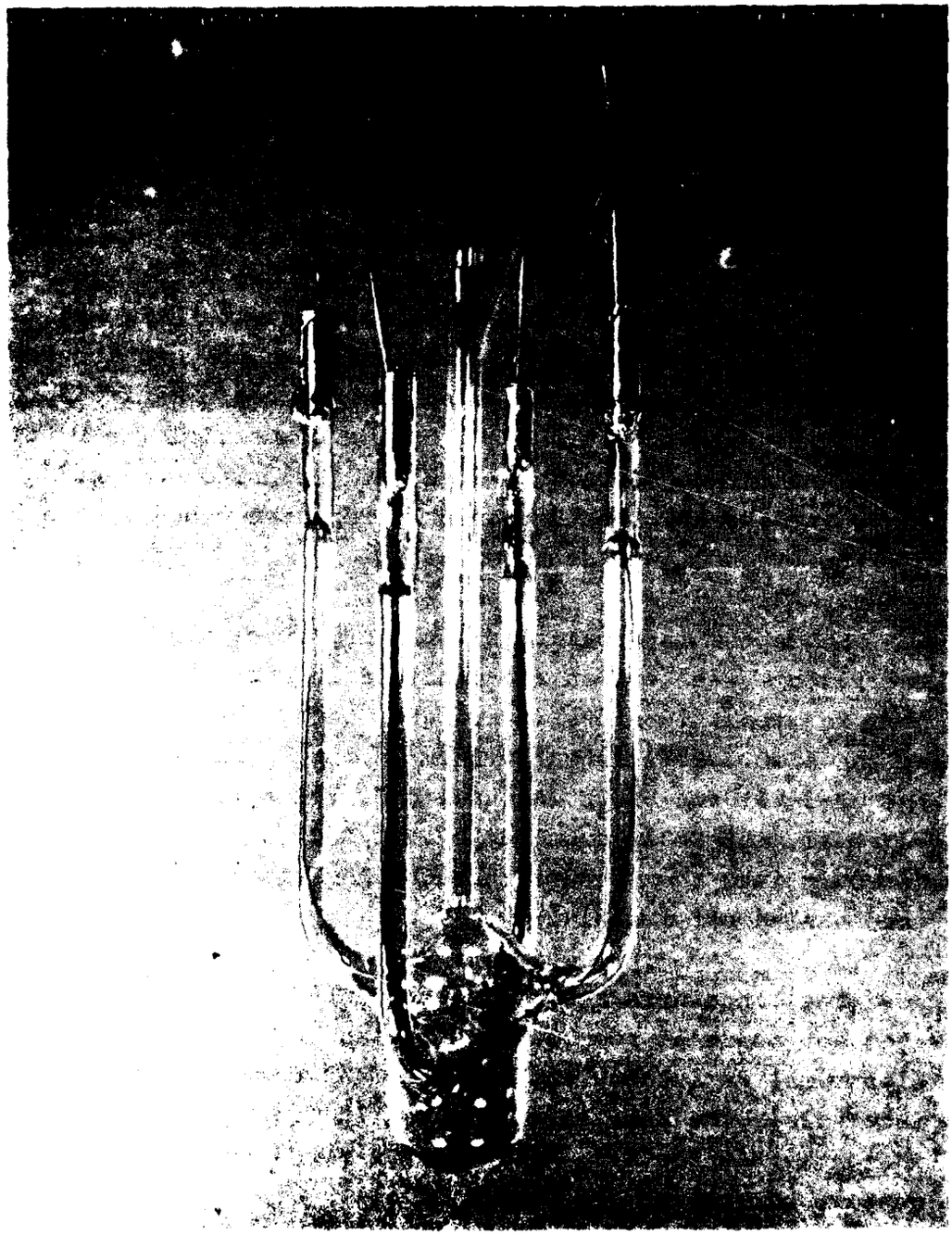


TABLE 3. ELECTRICAL RESISTANCE CHANGE OF CONTAINED GRAPHITE YARN SAMPLES DURING INTERCALATION WITH AsF_5 AT ROOM TEMPERATURE

CONTAINER NO.	1		5	
YARN[1]	ST	GR[2]	ST[2]	GR
EXPOSURE TIME (Hours) (Days)				
0	65.8	64.3	43.5	42.8
0.3	63.4	62.2	42.8	42.5
0.7	61.8	60.2	42.7	42.2
1.0	60.5	59.0	42.6	41.9
1.3	59.8	58.0	-	-
18	45.4	45.9	35.3	34.3
25	43.2	43.8	-	-
42	39.6	40.7	-	-
2	38.5	39.8	-	-
7	29.5	32.3	19.4	20.6
9	27.2	30.4	18.5	19.1
11	25.7	29.1	17.8	17.8
21	17.9	21.5		
25	16.1	19.7		
31	14.1	17.0		
36	12.8	15.1		
51	5.0	5.7		30
58	4.9	5.5		

(1) ST denotes Lot ST3-157-11; GR denotes Lot GR-02.
(2) Mislabelled (?). Results suggest that yarn GR in container No. 1 is really yarn ST in container No. 5.

TABLE 4. ELECTRICAL RESISTANCE CHANGE OF CONTAINED GRAPHITE YARN SAMPLES DURING INTERCALATION WITH SbF_5 or HSO_3F AT ROOM TEMPERATURE

INTERCALANTS:	SbF_5		SbF_5		HSO_3F	
CONTAINER NO.	2		6		7	
YARN(1)	ST	GR	ST	GR	ST	GR
EXPOSURE TIME (Hours) (Days)						
0	60.3	44.3	45.9	49.8	42.8	46.3
4	22.6	22.3	-	-	-	-
8	7.0	4.6	-	-	-	-
2	6.6	3.5	6.2	7.3	41.6	46.0
7	6.4	2.8	5.0	6.8	41.9	45.7
14	6.15	2.6	4.7	6.9	41.9	46.0
20	6.1	2.6	4.7	6.6	-	-
35	6.1	7.5			41.9	46.1
50	6.1	open			-	-

(1) ST denotes Lot ST3-157-11; GR denotes Lot GR-02.

belong to the ST3-157-11 lot, while those in the 40-50 ohm range are those of GR02. Nevertheless, the data on both AsF_5 and SbF_5 intercalations indicate the conductivity of the higher modulus graphite fibers (Lot GR02) increases substantially faster during the intercalation relative to the other lot. Furthermore, since the AsF_5 intercalates very slowly at room temperature (the resistance dropping to about half its original value in 5 days), intercalation at elevated temperatures may be required in this case. Fibers intercalated with the SbF_5, on the other hand, attain >95% of their ultimate conductance within 2 days. The continuing slow drift upward may be due to progressive intercalation of these yarn segments contained in the glass capillary construction next to the contacts. The relatively large SbF_5 molecules produce substantial swelling of the graphite yarn at the end of the intercalation. As a result, one of the yarns present in container No. 2 started to fracture progressively after some three weeks of intercalation and finally broke altogether at one of the constrictions; the other yarns remaining intact at room temperature. The yarns exposed to HSO_3F alone, showed virtually no change in the electrical resistance while at room temperature.

2. Intercalation With Binary Mixtures (SbF_5-HSO_3F; AsF_5-HSO_3F; HSO_3F-SO_3). Since there are reports that mixtures of intercalants are more effective than single intercalating agents, two sets of graphite yarn, housed in the glass containers (Figure 1) were intercalated each with: (1) a mixture of antimony pentafluoride and fluorosulfonic acid in a 1.7:1 weight ratio (containers No. 9 and 10); or (2) a mixture of arsenic pentafluoride and fluorosulfonic acid in a weight ratio of 1:2 (containers No. 14 and 20). In addition, one container was intercalated with a fluorosulfonic acid-sulfur trioxide mixture (container No. 16, 8:1 weight ratio). In all these cases there is

more than enough intercalant present for attaining the lowest possible intercalation stage (Stage I). The decreases in electrical resistance during the intercalation are listed in Table 5. Again, the higher modulus (GR) yarns intercalate more rapidly than the lower modulus (ST) ones. Assuming that the observed resistance drop is proportional to the extent of intercalation, the mixture AsF_5-HSO_3F intercalates much faster than the AsF_5 alone. The intercalation of the HSO_3F-SO_3 is quite fast also, but within a month the SO_3 had penetrated through the glass constriction and was degrading the low melting solder which turned black on the outside and cracked the surrounding glass tubing. The addition of HSO_3F to the SbF_5 decreased the rate of resistance drop in comparison to that of neat SbF_5, but eliminated the yarn fracture.

3. Ternary Mixtures (SbF_5-HSO_3F-SO_3; AsF_5-HSO_3F-SO_3). To determine whether the addition of a third component (SO_3) confers additional advantages, four more sets of graphite yarn were intercalated - two with a mixture of SbF_5-HSO_3F-SO_3 (weight ratio 2:10:1) and two with AsF_5-HSO_3F-SO_3 (weight ratio 5:10:1). The corresponding electrical resistance data are given in Table 6, showing that the AsF_5-HSO_3F-SO_3 mixture may intercalate somewhat more effectively at room temperature relative to the binary mixture. For the SbF_5-containing mixture, however, no significant difference was observed.

4. Intercalation at Elevated Temperatures. In order to determine the completeness of the room temperature equilibration and possibly assess the effect of temperature on the intercalation kinetics, most of the filled containers, after an extended intercalation at room temperature, were also exposed to elevated temperatures up to 90°C by immersion in a heated oil bath.

TABLE 5. ELECTRICAL d.c. RESISTANCE (ohms) OF GRAPHITE YARNS DURING INTERCALATION WITH SbF_5-HSO_3F, AsF_5-HSO_3F AND HSO_3F-SO_3 AT ROOM TEMPERATURE

INTERCALANTS:	SbF_5-HSO_3F		SbF_5-HSO_3F		AsF_5-HSO_3F		AsF_5-HSO_3F		HSO_3F-SO_3	
CONTAINER NO.	9		10		14		20		16	
YARN[1]	ST	GR	ST	GR	ST	GR	ST	GR	ST	GR
EXPOSURE TIME (Hours) (Days)										
0	59.1	52.2	56.2	49.3	65.0	42.6	61.3	47.8	55.2	47.1
0.2	37.6	29.6	34.1	28.4						
0.5					27.5	5.5				
1							16.1	12.1	17.5	13.1
1					22.6	4.5	13.7	9.8	14.1	3.4
2					12.4	7.3	12.7	12.2	12.7	2.7
7								open at constriction		
16	13.6	8.5	17.8	8.9						
23	10.8	6.9	9.7	7.3			10.5			
30									6.3[2]	1.6[2]

(1) ST denotes Lot ST3-157-11; GR denotes Lot GR-02.
(2) The glass tubing surrounding the solder was cracked due to corrosive attack on the solder.

TABLE 6. ELECTRICAL d.c. RESISTANCE (ohms) OF GRAPHITE YARNS DURING INTERCALATION WITH SbF_5-HSO_3F-SO_3 AND AsF_5-HSO_3F AT ROOM TEMPERATURE

INTERCALANT:	SbF_5-HSO_3F-SO_3				AsF_5-HSO_3F-SO_3			
CONTAINER NO.	13		18		15		19	
YARN(1)	ST	GR	ST	GR	ST	GR	ST	GR
EXPOSURE TIME (Hours) (Days)								
0	56.2	43.2	62.6	47.0	58.0	47.0	55.5	47.2
0.2					15.5	13.9		
0.8	34.5	30.7						
1							3.5	8.1
2			41.5	13.5				
1	10.5	15.8			5.2	13.2	3.2	5.9
2	10.5	15.2			3.1	12.0	3.0	4.2
7			33.0	12.0			3.6	3.0

(1) ST denotes Lot ST3-157-11; GR denotes Lot GR-02.

a. Single Intercalants. Containers housing the graphite yarns intercalated with AsF_5, SbF_5, or HSO_3F were first heated at 60°C for 24 hours, cooled to room temperature for the resistance measurement, then reheated to 90°, held for 24 hours, then cooled down for the second room temperature measurements. The data indicating the presence or absence of intercalation equilibria are listed in Table 7. Comparison of the samples intercalated for different lengths of time shows that intercalation times of over 50 days are needed to achieve equilibration at or near room temperature in single intercalant systems. Surprisingly, the graphite yarn in the HSO_3F container began to intercalate at 90°C, as indicated by the irreversible resistance drop which, however, is too small to be explored further.

b. Binary Intercalant Mixtures. Since the HSO_3F-SO_3 containing ampoule failed earlier by solder corrosion, there were only two types of binary mixtures to be tested: AsF_5-HSO_3F and SbF_5-HSO_3F. The respective containers were first held at 60°C for one day (24 hours) or longer, and afterward at 90°C for another 24 hours. The resistance data shown in Table 8 indicate that both the intercalated higher modulus yarns became open circuited, having broken at one of the glass constrictions. Of the remaining two yarns, one was increasing in resistance during the heating at 60°C, and only the remaining one (No. 20, ST) appeared to be close to equilibrium. Further efforts were, therefore, directed toward completing the intercalation of the yarns intercalated with SbF_5-HSO_3 (containers No. 9 and 10), all of which survived the heating, but had not yet attained equilibrium. Inexplicably, the approach to equilibration in this system was relatively slow, since even after two heating cycles, between room temperature and 90°C, the resistance values continued to decrease (cf Table 9). Finally, after heating at 60°C for

TABLE 7. ELECTRICAL d.c. RESISTANCE (ohms) OF INTERCALATED GRAPHITE YARN AFTER EXPOSURE TO ELEVATED TEMPERATURES

INTERCALANT:	AsF_5		AsF_5		SbF_5		SbF_5		HSO_3F	
CONTAINER NO.	1		5		2		6		7	
YARN[1]	ST	GR	ST	GR	ST	GR	ST	GR	ST	GR
BEFORE HEATING[2]	4.9	5.5	14.9	13.5	6.1	open	4.8	6.7	41.9	46.1
AFTER 24 HOURS AT 60°C[3]	4.8	5.3	11.2	7.4	6.1	open	4.8	6.7	41.3	46.1
AFTER 24 HOURS AT 90°C[3]	4.9	5.3	9.0	5.6	6.2	open	(4)		34.4	37.0

(1) ST denotes Lot ST3-157-11; GR denotes Lot GR-02.
(2) Prior equilibration times at room temperature: container No. 1, 58 days; No. 5, 23 days; No. 2 and 6, 50 days; No. 7, 36 days.
(3) Resistance measured at room temperature, ca. 20°C.
(4) Container cracked at the sidearm upon removal from the hot bath.

TABLE 8. ELECTRICAL d.c. RESISTANCE (ohms) OF GRAPHITE YARNS INTERCALATED WITH BINARY INTERCALANTS AFTER EXPOSURE TO ELEVATED TEMPERATURES

INTERCALANT:	AsF_5-HSO_3F				SbF_5-HSO_3F			
CONTAINER NO.	14		20		9		10	
YARN[1]	ST	GR	ST	GR	ST	GR	ST	GR
BEFORE HEATING[2]	12.4	7.3	10.5	open	10.8		8.7	7.3
Days @ 60°C[3]								
1	4.3	open			6.8	4.3	3.4	5.0
2	3.9	open	10.3	open				
5	10.9	open						
Days @ 90°C[3]								
1.5			8.6	open	5.7	3.9	2.5	4.7
After 10 days @ 22°C[3]			8.3	open				

(1) ST denotes Lot ST3-157-11; GR denotes Lot GR-02.
(2) Prior equilibration times at room temperautre: container No. 14, 3 days; No. 20, 25 days; No. 9 and 10, 23 days.
(3) The resistances are measured at the respective temperatures.

TABLE 9. ELECTRICAL RESISTANCE (ohms) @ 22°, 60° and 90°C OF GRAPHITE YARNS BEING INTERCALATED WITH SbF_5-HSO_3F

INTERCALANT:		SbF_5-HSO_3F			
CONTAINER NO.		9		10	
YARN[1]		ST	GR	ST	GR
FIRST HEATING CYCLE[2]					
Temperature (C):	22°	5.64	4.04	2.00	4.28
	60°	5.63	4.01	2.03	4.28
	90°	5.64	4.04	2.05	4.26
	22°	5.62	3.90	1.99	4.25
SECOND HEATING CYCLE[2]					
Temperature (C):	22°	5.61	3.83	1.98	4.20
	60°	5.60	3.86	2.00	4.22
	90°	5.60	3.88	2.03	4.23
	60°	5.58	3.77	2.00	4.19
	22°	5.54	3.67	1.97	4.16
HEATING TIME @ 60°C					
(Days)	0	5.58	3.77	2.00	4.19
	3	5.28	3.46	1.98	4.11
	7	5.01	3.35	1.96	3.93
	11	4.91	3.19	1.945	3.74
	14	4.37	3.22	1.93	3.42

(1) ST denotes Lot ST3-157-11; GR denotes Lot GR-02.
(2) Initial temperature @ 22°C; up to 60° in ~2 hours; up to 90° in ~2 hours; cooling to 60° in ~3 hours; cooling to final temperature in ~16-17 hours.

14 days, the resistances became practically constant, indicating presence of equilibrium.

c. Ternary Intercalant Mixtures. Two containers (Nos. 13 and 15) of the above mentioned ternary intercalant mixtures were heated at 60°C for 5 days, with its resistance being monitored while two others (containers No. 18 and 19) were heated at 60° for only 5 hours, followed by raising the temperature to 90° and holding it there for 36 hours (1.5 days) in order to ensure equilibration. The resistance values at these temperatures are given in Table 10. The data show that two of the intercalated yarns (one in container No. 18, the other in No. 15) exhibit unstable resistance contact characteristics, apparently caused by corrosion of the solder materials by the SO_3. In addition, one of the yarns became open because of thermal stress cracking of the container (No. 19). The residual resistance data indicate that, on the average, there is no significant difference between the graphite yarns intercalated with the binary mixture and those with the ternary one, except for a faster intercalation rate in cases where SbF_5 is one of the components. This, however, is probably due to the very low vapor pressure (<1 torr) at room temperature and may be improved by carrying out all the intercalations involving SbF_5 at elevated temperatures, >60°C.

D. Temperature Dependence of the Conductance (Resistance). After the intercalated yarns had been fully equilibrated, if necessary by heating at 90°C, the temperature dependence of the resistance of the yarns intercalated with AsF_5 (containers No. 1 and 5), with SbF_5 (No. 2), and with the SbF_5-HSO_3F mixture (Nos. 9 and 10) was determined at 22°, 60° and 90°C by slowly heating the oil bath up or down and holding at the respective temperatures. The data for the single intercalants AsF_5 and SbF_5, given in Table 11, indicate that the relative

TABLE 10. ELECTRICAL d.c. RESISTANCE (OHMS) OF GRAPHITE YARNS INTERCALATED WITH TERNARY INTERCALANTS AFTER EXPOSURE TO ELEVATED TEMPERATURES

INTERCALANTS:	SbF_5-HSO_3F-SO_3				AsF_5-HSO_3F-SO_3			
CONTAINER NO.	13		18		15		19	
YARN[1]	ST	GR	ST	GR	ST	GR	ST	GR
INITIAL RESISTANCE	10.3	14.7	57.7	11.5	3.1	12.0	3.4	3.5
DAYS AT 60°C								
1 day	9.4	11.2			2.0	15.5	σ	
2 days	9.4	9.1	57.3	11.2	1.8	~39	open[3]	5.1
5 days	9.2	6.5			1.9	~58[4]		
DAYS AT 90°C								
1.5 days			~55.3	10.8			open[3]	3.6
22°C								
AFTER 10 DAYS	6.6	3.1	~62[4]	11.5		(5)	open[3]	4.5

(1) ST denotes Lot ST3-157-11; GR denotes Lot GR-02.
(2) Prior equilibration times at room temperature; containers No. 13 and 15; 3 days, Nos. 18 and 19; 25 days. The resistances are measured at the given temperatures.
(3) The glass sidearm cracked at the capillary constriction/solder interface, but was quickly repaired with plastic shrink tubing.
(4) The resistance fluctuates around the given values in an unstable fashion.

change in the resistance (conductance) over the temperature range measured is quite small, ranging from near zero to 3 percent. The same is also the case for the yarns intercalated with the binary SbF_5-HSO_3F and AsF_5-HSO_3F (Table 12). Since the measured resistance also includes the resistance change due to warming up of the solder contacts, the true intercalated yarn resistance is likely to be even smaller and may well be zero or even negative. Even so, with the contact resistance included, the highest observed conductance (resistance) change with temperature in the intercalated graphite fiber is only 4.4% per 100°C - about 9 times less than that of copper (~40% increase per 100°C). Based on these observations, the development of intercalated graphite fiber conductors having zero temperature coefficients of resistance over their thermal stability range is feasible, once improved electrical terminals having the desired thermal characteristics are developed and introduced.

F. The Current-carrying Characteristics of the Intercalated Graphite Yarns. A potentially useful graphite wire conductor should possess a reasonable current carrying capability. This is usually expressed in terms of maximum current rating or, in other words, the maximum current which can be passed continuously through a unit cross-sectional area (usually cm^2 or mm^2) of the conductor without any long term degradation. Since no published information concerning the possible current rating levels or power dissipating ability of the intercalated graphite yarns was available, some experiments to assess this capability were carried out on yarns intercalated with a single intercalant (AsF_5) as well as a mixture of intercalants (SbF_5-HSO_3F-SO_3) intercalated previously in glass containers Nos. 5, 13, and 18, respectively.

The equipment used consisted of a d.c. power supply (Deltron, Inc.) and two Keithley digital multimeters that were connected in

TABLE 11. ELECTRICAL RESISTANCE (ohms) @ 22°, 60°, AND 90°C OF GRAPHITE YARNS, FULLY INTERCALATED WITH AsF_5 and SbF_5

INTERCALANT:	AsF_5				AsF_5				SbF_5	
CONTAINER NO.	1				5				2	
GRAPHITE YARN[1]	ST		GR[4]		ST[4]		GR		ST[3]	
HEATING CYCLE[2]	UP	Down	Up	Down	Up	Down	Up	Down	Up	Down
TEMPERATURE (°C)										
22°	4.89	4.89	4.86	4.86	8.80	8.80	5.88	5.87	6.39	6.40
60°	4.93	4.92	4.89	4.88	8.88	8.90	5.96	5.96	6.38	6.39
90°	4.95		4.93		8.96		6.05		6.39	
% INCREASE IN RESISTANCE (90°-22°C)	1.2		1.4		1.8		3.0		0	

(1) ST denotes the yarn lot ST3-157-11; GR denotes the lot GR-02.
(2) Initial temperature @ 22°; up to 60° in ~2 hours; up to 90° in ~2 hours, cooling to 60° in ~3 hours; cooling to final temperature in ~16-17 hours.
(3) The GR yarn of this container broke during the room temperature intercalation.
(4) Mislabelled (?). Results suggest that yarn GR in container No. 1 is really yarn ST in container No. 5.

TABLE 12. ELECTRICAL RESISTANCE (OHMS) AT 22°, 60° and 90°C OF GRAPHITE YARNS INTERCALATED WITH $SbF-HSO_3F$ and AsF_5-HSO_3F

INTERCALANT:		$SbF5-HSO_3F$								AsF_5-HSO_3F
CONTAINER NO.		9				10				20
GRAPHITE YARN[1]		ST		GR		ST		GR		GR
HEATING CYCLE[2]		Up	Down	Up	Down	Up	Down	Up	Down	Down
TEMPERATURE	22°C	4.35	4.34	3.20	3.26	1.91	1.91	3.39	3.38	8.40
	60°C	4.34	4.34	3.23	3.26	1.94	1.94	3.40	3.40	
	90°C	4.33		3.26		1.96		3.40		8.60
% RESISTANCE INCREASE (90°-22°C)		0		0		2.6		0.6		2.4

(1) ST denotes Lot ST3-157-11; GR denotes Lot GR-02.
(2) Initial temperature at 22°; up to 60° in 2 hours; up to 90° in 2 hours; cooling to 60° in 3 hours; cooling to final temperature in 16-17 hours.

series and in parallel to the terminals of the encapsulated yarn to measure the applied current and the voltage, respectively. In the first examination, the current was set and maintained at progressively higher levels, starting with a few milliamperes, and the current and voltage were read and/or recorded on a two-pen recorder (Hewlett-Packard 7132A). If the readings remained stable for at least 15 minutes, the current was raised to the next higher level; and so on, until the potential began to drift upward, indicating the onset of deintercalation or, alternately, degradation of the contacts. The pertinent data are listed in Table 13. It is seen that the resistance begins to increase at a current input of about 0.45A, corresponding to a current density of about 23A/mm^2 (mean yarn cross-section $\approx$0.02mm) and a power dissipation of about 1.5 watts. At higher inputs (>4 watts), an increase in the resistance, indicative of deintercalation, takes place. The observed maximum current density compares favorably with the current rating given in the literature for a copper wire of comparable cross-section - 12 A/mm^2.

For the other yarns intercalated with the ternary intercalant mixture, the current was increased stepwise to the level required to dissipate 1 watt of power. At that point the current was passed through the yarn continuously for at least 100 hours in order to determine the stability of the resistance at that power level. As seen in Table 14, under the 1 watt input conditions, estimated to raise the specimen temperature to 80-90°C, the resistance decreased very slightly - from 2.12 to 1.88 ohms for the GR yarn and from 4.91 to 4.89 ohms for the ST one. Upon discontinuing the current, there was hardly any resistance change, thus confirming the small temperature dependence of the intercalated yarn resistance.

The same type of Joule heating was then applied to another graphite yarn intercalated with the same intercalants at a later

TABLE 13. D.C. CURRENT CARRYING CHARACTERISTICS OF GRAPHITE YARNS INTERCALATED WITH AsF_5 (Container No. 5)

GRAPHITE YARN[1]	ST			GR			
Applied Current, I (mA)	Potential Drop, V (mV)	Resistance V/I (ohms)	Power Dissipation (Watts)	Applied Current, I (mA)	Potential Drop, V (mV)	Resistance V/I (ohms)	Power Dissipation (W)
4.20	37	8.8		10.31	61	5.92	
15.63	138	8.8		20.47	121	5.91	
30.43	267	8.77		87.73	517	5.89	
52.25	459	8.78		148.64	879	5.91	
				190.78	1131	5.93	
128.4	1128	8.79		266.8	1590	5.96	
				311.3	1864	5.99	
237.2	2090	8.81		378.7	2240	6.04	0.85
				479.1	2960	6.17	1.4
357.8	3160	8.83	1.13	562.2	3550	6.31	
425.7	3770	8.86		639.5	4150	6.48	2.65
482.5	4300	8.91		683.2	4520	6.61	
525.8	4700	8.94	2.5	720.1	4860	6.74	3.5
583.5	5270	9.03		768.3	5320	6.92	
604.1	5480	9.07	3.3	830.5	8440↑[2]	10.1↑[2]	7.0
668.9	6150	9.19		--	--	--	
700.0	6500↑[2]	9.28↑[2]	4.7	43.8	880	20.1	
--	--	--					
14.49	129	8.9					

(1) ST denotes Lot ST3-157-11 GR denotes Lot GR-02.
(2) ↑ indicates unstable, progressively increasing potential readings at the given input current.

TABLE 14. D.C. CURRENT CARRYING CHARACTERISTICS OF GRAPHITE YARNS INTERCALATED WITH SbF_5-HSO_3F-SO_3 (Container No. 13)

GR-02 Yarn

Cumulative Time Of Exposure (Hours)	Applied Current, I (mA)	Potential Drop, V (mV)	Resistance V/I (ohms)	Power Dissipation (W)
	100	213	2.13	
	200	423	2.11	
	300	622	2.07	
	400	817	2.04	
	500	1067	2.13	
	600	1272	2.12	
0	700(1)	1485	2.12	1.04
27	700	1493	2.13	1.05
96	700	1344	1.92	0.94
100	700	1320	1.88	0.92
After cooling to room temperature.			1.87	

ST3-157-11 Yarn

	100	0.5060	5.06	
	200	1.026	5.12	
	300	1.520	5.07	
	400	2.023	5.08	
0	460(2)	2.26	4.91	1.04
24	460	2.26	4.91	
48	460	2.25	4.89	
115	460	2.25	4.89	1.04
After cooling to room temperature.			4.92	

(1) Corresponds to current density ~35 A/mm^2.
(2) Corresponds to current density ~23 A/mm^2.

date (container No. 18). In this case, shown in Table 15, however, the resistance continued to decrease during the heating until a constant value was finally achieved after about 100 hours. It appears that in this case the intercalation equilibrium was not complete at room temperature at the time the Joule heating was initiated. This direct heating technique, then, can be utilized advantageously in the future to increase the intercalation rate and achieve faster equilibration.

F. Contact Resistance. The measured resistance of the encapsulated intercalated yarn is actually the sum of: (a) the contact resistance between the solder and the yarn; and (b) the resistance of the yarn which is intercalated to or near equilibrium composition. As a result, the yarn resistance cannot be evaluated to the desired degree of accuracy, unless the contact resistance values are known or can be estimated. In the past, electrical contacts were made to graphite single filaments by means of commercially available precious metal pastes that were put on the filament and subsequently baked at elevated temperatures to evaporate and/or decompose the organic binder base, leaving a sintered metal powder behind as the electrical contact. The electrical resistance of such contact was not important, because the electrical properties of the filaments could be measured by null techniques, such as the four-terminal method, not requiring low contact resistances. For graphite yarn conductors, however, this may not often be the case, and the contact resistance included in the circuit may well exceed the resistance of the intercalated yarn. Unfortunately, there is no useful information on the subject of electrical contacts to graphite fiber bundles or yarns in the literature. A great deal of exploratory work was, therefore, done by Celanese with its own funds and at no direct cost to the Government to develop materials and techniques of application that would provide

TABLE 15. D.C. CURRENT CARRYING CHARACTERISTICS OF ANOTHER GRAPHITE YARN INTERCALATED WITH SbF_5-HSO_3F-SO_2 (Container No. 18)

Cumulative Time Of Exposure (Hrs.)	Applied Current, I (mA)	Potential Drop, V (mV)	Resistance V/I (ohms)	Power Dissipation (W)
		GR02 Yarn		
	100	1.125	11.25	
	200	2.225	11.12	
	300	3.072	10.24	
	350	2.911	8.32	
0	400	2.776	6.94	1.11
24	400	2.290	5.73	0.92
	425	2.419	5.69	1.03
72	450	2.060	4.57	0.97
	475	2.163	4.55	1.03
100	475	2.050	4.32	
101	500 (1)	2.158	4.32	1.08
After cooling to room temperature - 4.56				

(1) Corresponds to current density ~25 A/mm^2.

contacts having a satisfactory corrosion resistance and low contact resistance on the graphite yarns or yarn bundles. The low melting solders, used as electrical contacts as well as sealants for the glass containers described earlier, and high temperature gold varnish, used on the prototype wires to be described later, are two of the most conspicuous developments arising from this work. The efforts of this project were focused solely on determining the contact resistance of the low melting solders providing the electrical connections to the glass-encapsulated intercalated graphite yarns.

In the first approach tried, the terminal portions of the four glass sidearms of the encapsulating ampoule were cut to about 1-2 cm. below the constriction in a dry box. An electrical contact to the yarn protruding through the constriction was then made by filling the cut tubing end with liquid mercury. Assuming the resistance of the mercury/intercalated yarn interface to be negligibly small, the measured resistance would be essentially the sum of that of the short segment (which can be corrected for) and that of the solder-fiber contact. Containers Nos. 2 and 6, containing yarns intercalated with SbF_5, were employed initially. Unfortunately, the above mentioned mercury/yarn interface was unstable. As soon as the mercury contacted the intercalated yarn, the circuit resistance increased rapidly. The minimum resistance readings at the moment of contact ranged from 2.2 to 2.7 ohms, but there is no assurance that these really represent the resistance of the terminal.

The next approach involved measuring the intercalated yarn resistance directly by the four-terminal method. After the top portions of the ampoule sidearms containing the solder were broken off in the dry box, the yarn was pulled out and placed in a 4-terminal holding fixture in which the resistance per unit

length was measured by a Keithley 191 multimeter. The measured resistance per unit length, multiplied by the previously measured reference length (length of the unsupported yarn) gives the true intercalated yarn resistance, which upon subtraction from the total experimental resistance (as measured prior to the opening of the ampoule and corrected to the same reference length) would yield the electrical contact resistance of the Bi-Sn solder/intercalated yarn interfaces. The initial contact resistance between the unintercalated (pristine) yarn and the solder is known to be small (<0.1 ohms) and was disregarded. The data and the resistance calculations made on yarns intercalated with SbF_5-HSO_3F(containers 9 and 10), shown in Table 16, indicate that conductance increases up to 37 times are obtainable as the result of intercalation. The contact resistances, however, vary rather widely from near zero to 3 ohms in an irregular fashion.

Further attempts were made to determine the contact resistance of yarns intercalated with AsF_5-HSO_3F, AsF_5-HSO_3F-SO_3, and HSO_3F-SO_3 (containers No. 14, 15, and 16, respectively). Most of these containers had cracked near the solder joints during the prior heating in the oil bath. The pertinent data and calculations are listed in Table 16. It is seen that the resistances (row 5) calculated from the measured 4 point resistance of the intercalated yarns are substantially higher than the ones measured directly with the yarn in the sealed ampoule. This increase is probably due to deintercalation and/or hydrolysis of the intercalated yarns following the cracking of the ampoule, even though the ampoules were later stored in a dry box until the yarn withdrawal. Consequently, the true conductance increases cannot be reliably determined, even though they will be greater than the 6 to 30X range given by the ratio of the resistances before and after the intercalation. Consequently, the contact

TABLE 16. INTERCALATED GRAPHITE YARN RESISTANCE AND CONTACT RESISTANCE BETWEEN THE YARN AND THE SOLDER CONTACTS

INTERCALANT:	SbF_5-HSO_3F				HSO_3F-AsF_5		HSO_3F-AsF_5-SO_3		HSO_3F-SO_3	
CONTAINER NO.	9		10		14		15		16	
YARN[1]	ST	GR	ST	GR	ST	GR	ST	GR	ST	GR
Pristine Yarn Resistance (ohms)	59.1	52.2	56.2	49.2	65.03	42.6	58.0	47.0	55.2	47.1
Corrected Pristine Resistance (ohms)	54.1	48.2	51.2	45.2	56.6	37.4	51.0	41.4	51.2	41.9
Yarn Length[2] (cm)	20.6	22.7	19.5	21.3	20.2	18.7	20.4	20.7	21.3	21.0
4 Point Resistance (ohms/cm)	0.0737	0.0576	0.10	0.007	0.393	0.376	0.55	0.173	0.178	0.416
Calculated Intercalated Yarn Resistance (ohms)	1.5	1.3	1.95	1.65	7.94	7.0	11.2	3.6	3.8	8.7
Experimental Yarn Resistance (ohms)[3]	4.5	3.3	1.9	3.25	3.74	(6.4)[4]	2.34	(10.6)[4]	5.9	1.4
Conductance Enhancement	36X	37X	27X	27X	15X	6X	22X	-	13.5X	30X
Contact Resistance	3.0	2.0	0	1.6	Neg.	Neg.	Neg.	-	2.1	Neg.

(1) ST denotes the yarn lot ST3-157-11; GR denotes the lot GR-02.
(2) Refers to yarn length between the two glass constrictions in the sidearms.
(3) Corrected to the reference length.
(4) Last reading before losing electrical continuity.

resistances were calculated as negative in most cases. Since this is physically impossible, more reliable techniques for determining the interfacial contact resistance need to be developed.

G. Encapsulation in Leak-tight Flexible Enclosures. Numerous plastic materials have been evaluated with respect to acid corrosion resistance and moisture permeability under a Celanese funded project. Of these, Teflon®, grades FEP and TFE, was by far the most corrosion resistant to fluorine containing chemicals. Since the moisture permeability of the TFE is much less than that of the FEP, attempts were made to utilize the TFE in the form of a suitably sized shrink-tubing as the protective enclosure for the prototype intercalated graphite fiber (IGF) wires.

H. Fabrication of Prototype Wires

1. Contacting and Encapsulation of Yarn Bundles. The initial scale-up efforts were directed toward providing corrosion resistant electrical contacts to the ends of graphite yarn bundles and encapsulating this assembly in a flexible Teflon sheath provided with access openings for subsequent intercalation. The alternate approach, fiber intercalation followed by contacting and encapsulation, is less feasible on a batch scale because of the greater likelihood of the state-of-the-art intercalants reacting with the surrounding materials. The bundles consisted of 60 ends of graphite yarn (Lot ST3-157-11; total number of filaments, ~23,000), about 20 cm. long and having an initial resistance of 0.047 ohms/cm. The electrical contacts to the bundle were made by inserting each bundle end into a sleeve of copper tubing (6.5 mm OD, 4mm ID, 4-4.5 cm. long) and bonding the bundle and sleeve together by conductive gold paste. The contact resistance was derived by measuring the electrical resistance of the whole assembly and subtracting the resistance

of the bundle length between the sleeves.

The initial attempts to make contacts with a gold-filled paste curable at 150°C (Engelhard Industries A-2709) were not successful, since even after repeated curing, the total resistance would not go below about 60 ohms. This level of resistance indicates excessive contact resistance. Subsequent replacement of the Engelhard paste with another commercial paste (Cermalloy Co., No. 4350 L), produced much lower contact resistances. This paste, however, requires a two-step bonding procedure; a partial cure at 140°C for 5 minutes, followed by baking in air at 525°C for 8 minutes. Three sleeve-bundle assemblies, bonded with the Cermalloy high temperature paste, all had resistances of about 0.9 ohms, which, after subtracting the 0.6 ohm bundle resistance, gives a contact resistance of 0.3 ohms or about 0.15 ohm/end. For protection against environmental effects, especially degradation by moisture, the sleeved bundle is inserted in a shrinkable Teflon TFE tubing, which is shrunk tightly onto the sleeves by heating the assembly in an air circulating oven at 350°C for 5 minutes.

There is at least one other consideration associated with the intercalation of the encapsulated bundle in situ. First, before the intercalation, at least one of the sleeves has to remain partly open to allow access of intercalant to the encapsulated bundle. After the intercalation, however, the opening has to be closed so as to prevent moisture penetration. In the present design, the intercalant is to be admitted through either a thin S.S. tube (1.5 mm OD, 0.75 mm ID), or a hollow needle of about the same size inserted into the fiber bundle and through the sleeve and bonded in place with the gold-filled high temperature paste. After the intercalation, the tube would be soldered or welded shut. Although the gold paste did

not provide a sufficiently strong and secure bond, a low melting solder (Indalloy 136, Indium Corporation of America) appears to be satisfactory.

The final procedure for contacting and encapsulating a flexible cable-like graphite yarn bundle consists of the following steps:

a. Precoat both ends of the bundle with the gold paste, insert them into the likewise precoated copper sleeves and tack them together by curing at 140°C for 5 minutes.

b. Place the sleeve-bundle assembly into the expanded Teflon TFE tubing, put the whole unit in an air oven and shrink at 350°C for 5 minutes. Take out and cool.

c. Heat the sleeve and the bundle with a small torch quickly to above 500°C for a few minutes to bake out the gold paste.

d. Put the hollow S.S. tubing into the sleeve next to the bundle and fill the residual space of the sleeve with the molten solder and cool.

e. Measure the total resistance of the assembly and estimate the contact resistance.

A sketch of an encapsulated and contacted bundle end is given in Figure 3.

Three such 60 end bundles were prepared for evaluation of the leak-tightness of the seal and the intercalatability of the present configuration. Two of these showed reasonably low

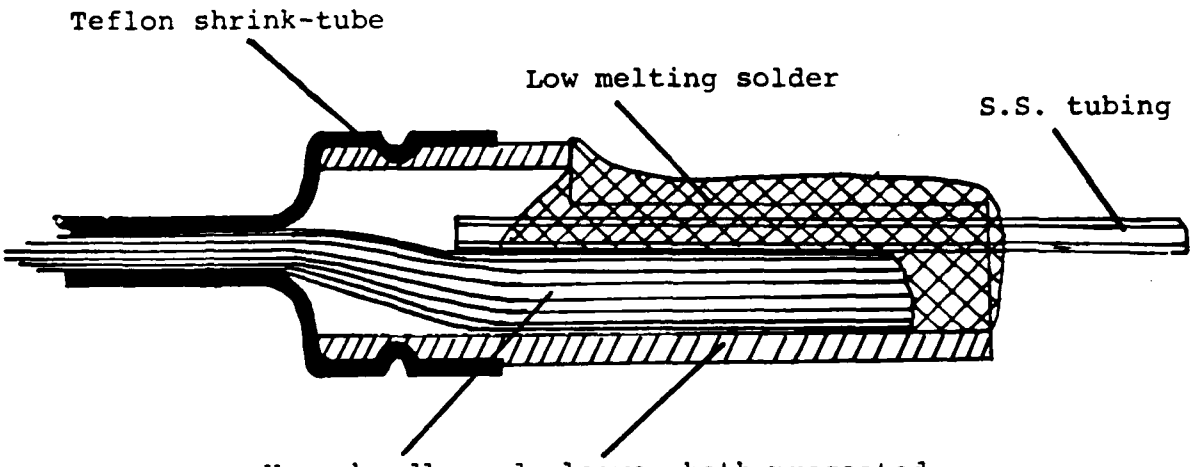


FIGURE 3. DIAGRAM OF ONE END OF AN ENCAPSULATED AND CONTACTED GRAPHITE FIBER BUNDLE

contact resistances, 0.14 ohms/bundle or 0.07 ohms/end and are also suitable for subsequent evaluation of intercalation of yarn bundles.

To evaluate the leak tightness of the contacts and the enclosure, the above assemblies were attached one at a time by means of a vacuum fitting to a vacuum manifold, which was then pumped by a mechanical pump to a pressure of about 27 Pa (200 millitorr) or less, then left under this pressure overnight (approximately 16 hours). A pressure increase to less than 267 Pa (2 torr) by the next day was indicative of a sufficient leak tightness. The assemblies tested differed by: (a) sleeve geometry - a straight vs. notched sleeve; and (b) sleeve material - copper vs. monel, since some initial experiments indicated that copper may adhere less well to the shrink-tube than other metals. The solder used to cap off the sleeves was Cerrolow 136, which had been used previously for making air-tight solder seals to graphite yarn encapsulated in Pyrex ampoules.

The results indicated that the TFE shrink tubing does not provide sufficiently tight joints to any of the metal sleeves. Further experimentation showed, however, that an additional application of a short length of FEP shrink tubing over the edge of the TFE one makes the joint sufficiently tight. This step is now included in the current yarn encapsulation procedure. Furthermore, it became evident that the Cerrolow 136 solder bond to the metal is not sufficiently air-tight either. Several other corrosion resistant solders reported to bond well to copper are currently under test. In the interim, the soldered areas are being overlaid with the FEP shrink tube in order to stop any leakage through the solder joint.

Subsequently, several other specialty solders, supplied by the Indium Corporation of America and listed in Table 17 were examined. Initial wettability studies of these solders, applied together with one of the recommended Indalloy fluxes, No. 2 or 3 (composition not disclosed), showed that both copper and porous gold are wetted quite adequately. Since the corrosion resistance to fluoride is reportedly better for indium than for tin or lead, the indium-rich solders, Nos. 3 and 7, were chosen for further assessment of the leak tightness. This was done using the customary Teflon-encapsulated 60 end graphite yarn bundle, one end of which was provided with the copper-sleeved electrical terminal, made as described above, while the other terminal was 6.4 mm O.D. copper tubing attached to the vacuum line. Two such assemblies were prepared, the terminal of the first one having been soldered shut with Indalloy No. 3; that of the second, with the No. 7 solder, with No. 3 flux being used in both cases. It was found that after 3 days' exposure under rough vacuum, the ampoule soldered with the No. 3 solder gave a very slight pressure increase (from ~40 Pa to 400 Pa - ~300 to 3000 millitorr), while the one soldered with No. 7 increased from 40 to 200 Pa (300 to 1500 millitorr). Consequently, both of these ampoules were considered to be practically air-tight and both solders appear useable for the closure of the terminal sleeves.

2. Encapsulated "Wire" Intercalation. The intercalation was to be accomplished by exposing the encapsulated wire to the gaseous intercalant or, in the case of liquid intercalant, by introducing the latter dropwise into the assembly through a tubular insert incorporated in the terminal sleeve for that purpose. After the intercalation, these tubes would be permanently closed off. To explore the feasibility of these approaches, four encapsulated bundles were intercalated, two each, with the preferred

TABLE 17. COMPOSITION AND MELTING RANGE OF CANDIDATE SOLDERS FOR AN AIRTIGHT CLOSURE

Indalloy® No.	Composition (Weight %)				Melting Range (°C)
	Sn	Pb	In	Ag	
2		15	80	5	142-149
3			90	10	141-237
7		50	50		180-209
9	70	18	12		162
10		75	25		250-264

state-of-the-art intercalants, i.e., gaseous AsF_5 or liquid SbF_5-HSO_3F (50-50 vol.%), while monitoring the progress of intercalation by electrical resistance measurements across the terminals during the intercalation.

The first graphite yarn bundle to be intercalated was bent into a U-shape and placed in a Pyrex vacuum vessel containing four platinum wire feedthroughs. Electrical connections to carry out the monitoring were made with fine copper lead wires soldered to the terminal sleeves on one end and butt welded to the Pt wire on the other end. The vessel containing the "wire" was then put on the vacuum line, evacuated and backfilled to approximately atmospheric pressure with AsF_5. The AsF_5 was replenished several times as it intercalated.

The initial 4 point resistance, R, of the assembly was 0.57 ohms, composed of about 0.43 ohms of yarn resistance and 0.14 ohms of contact resistance. After an hour of intercalation, as the R had decreased to 0.17 ohms, the butt weld contacts gradually came loose and reliable resistance readings could not be obtained. Some 24 hours later the unreacted AsF_5 was removed by vacuum (~50 Pa, ~400 millitorr) at about 40°C for 2 hours, after which the intercalated wire was taken out and stored in a dry box. Its 4 point resistance measured in the dry box was 0.030 ohms, which again is composed of the intercalated yarn and the contact resistance components, neither of which could be determined separately.

To avoid the inherently weak butt welds and eventually to intercalate longer assemblies, the second intercalation run was set up by attaching the assembly directly to the AsF_5 transfer line through one of the copper sleeves and a suitable vacuum fitting. This eliminates excessive bending of the wire and the

use of butt welds, but does not allow a four point resistance measurement without a substantial modification of the terminal fabrication procedure to provide leak tight feedthroughs for the lead wires. The initial 2 point resistance, R, of the assembly was 1.24 ohms, composed of the estimated yarn resistance of 0.41 ohms and contact resistance of 0.78 ohms (by difference). The intercalated R dropped to 0.87 ohms after 60 minutes, to 0.79 after 24 hours and to 0.63 ohms after 100 hours of exposure, indicating a decrease in both the yarn and the contact resistances as a result of the intercalation. Again, the lack of a suitable method prevents separation of the two resistances.

The liquid phase intercalation with SbF_5-HSO_3F was carried out in the dry box by introducing the intercalant dropwise into the assembly through a syringe needle soldered in the sleeve terminal. In the first run, a total of 8 drops (about 1.3 g) of intercalant was added over 60 minutes. The leads for the 4 point resistance measurement were clipped directly on the terminals. Surprisingly, the resistance increased during the intercalation - from 1.20 ohms initially, to 1.56 ohms after 60 minutes, and 1.74 ohms after 24 hours. The reason for this may have been that the gold paste contacts, baked out at 350°C rather than the 500°C, were being corroded by the intercalant. A second specimen was, therefore, prepared by a fabrication procedure modified to bake the gold paste at 500°C. The electrical resistance of this 60 end bundle assembly, intercalated as above (except for more intercalant to assure complete intercalation), behaved as expected, decreasing from the original 0.41 ohms, (0.31 ohms yarn resistance + 0.10 ohms contact resistance) to 0.38 ohms after 60 minutes of intercalation, 0.24 ohms after 24 hours, and 0.20 ohms after 50 hours. This decrease is substantially less than observed previously on the first assembly intercalated from the gas phase.

Two additional graphite fiber assemblies, composed of 60 ends of yarn (60 x 384 = 23,040 filaments), were encapsulated to the point at which the terminals were still open, then placed in a closed vessel next to a few grams of liquid SbF_5 for about 24 hours. The next day the vessel was heated at 75°C for 3.5 hours, while a slow stream of dry nitrogen was passed through the vessel to increase the vaporization rate of the SbF_5. After cooling and removal of the wires, their electrical resistance was virtually unchanged, indicating that under these conditions no intercalation of the wires had occurred. On the basis of these trials, it was decided to intercalate the prototype graphite wire specimens with gaseous AsF_5, which provided more consistent conductance enhancements than the liquid SbF_5-HSO_3F intercalant.

3. Fabrication of Graphite Fiber Prototype Wires - First Set

a. Contacting and Encapsulation. In the meantime, additional minor improvements were made on the electrical terminals of these fiber assemblies in order to decrease further the contact resistance and to facilitate the intercalation. As a result, the final fabrication procedure of the assemblies consisted of the following steps:

Fabricate terminal sleeves by cutting off 4 cm sections from standard 6.4 mm O.D. copper tubing, provide them with a square cutout ("window") on one side, round off all edges, and precoat the inside wall with gold-filled paste (Cermalloy 4350 L). Cut and debur 2.5 cm. long lengths of 3.2 mm O.D. copper tubing to serve as inserts in the sleeves facilitating the admission of the intercalant.

Impregnate both ends of the graphite yarn bundle with the gold-filled paste and let dry. Place the ends into the sleeves, putting the tubular insert onto each end. Push two short pieces of 20 gauge copper wire into the bundle from each end (to serve as the current leads), and two pieces of 30 gauge

nickel wire into the bundle from the side to serve as the voltage leads for subsequent resistance measurements. Bake out the whole assembly - first at 140°C for 10 minutes, then at 500°C for 10 minutes in an air oven.

Insert the assembly in the TFE shrink tubing and shrink down at 350°C for 7 minutes in an air oven. Cool down, put short FEP shrink tube pieces over the copper sleeve/TFE junctions and shrink these with a heat gun to make the underlying joints leak tight.

Reheat the assembly and fill the windows with No. 3 solder making them leak tight.

Put the assembly on the vacuum/gas supply manifold and intercalate.

After the intercalation, collapse the ends of the sleeves with a suitable pair of pliers and solder them shut with No. 3 or 7 solder.

Five graphite yarn "wire" assemblies were prepared in this manner and intercalated with AsF_5. The first of these (GR01-30-TSF/CU-ASF-1) contained 30 yarn ends. The second one (GR01-40-TSF/CU-ASF-2) had 40 ends, but the last three (GR01-60-TSF/CU-ASF-3, 4, 5) had 60 ends. The cross-sectional areas of the three sizes before the intercalation are ~0.57, 0.76, and 1.14 mm^2, respectively, roughly corresponding to 20, 18, and 17 gauge copper wire. An encapsulated prototype is shown schematically in Figure 4 and photographically in Figure 5.

b. Intercalation. The previously reported experiments indicated that intercalation of the graphite wires from the gas

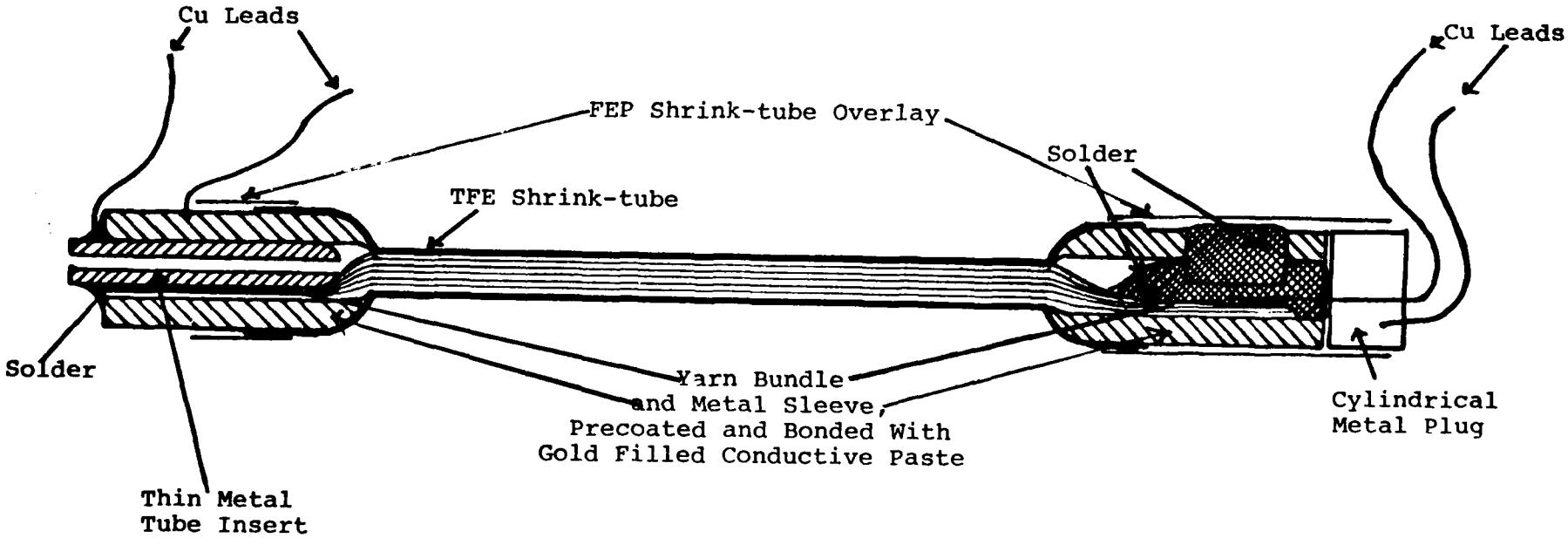
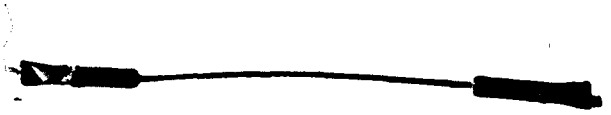


FIGURE 4. DIAGRAM OF AN ENCAPSULATED GRAPHITE WIRE PROTOTYPE



phase (AsF_5) is preferable to that from the liquid phase (SbF_5-HSO_3F), since a gaseous intercalant penetrates a compacted yarn bundle much more readily than a liquid one. Several additional room temperature intercalations of GR01 yarn with AsF_5 were carried out in order to pinpoint the conditions under which the intercalated yarn would show enhanced conductance as well as promising thermal stability.

The final procedure used for the intercalation of the above prototype wires was as follows: the samples were placed in a Pyrex vessel which was attached to a vacuum/AsF_5 supply manifold, evacuated and kept under vacuum for 2-3 hours to check for leak tightness. The vessel was then back filled with 67-80 kPa (500-600 torr) of AsF_5 that was previously freed from non-condensable gases by vacuum pumping. The samples were retained at room temperature under AsF_5 for about 24 hours, after which the vessel was heated to 65°C, the AsF_5 flushed out with N_2, and the intercalated samples held in rough vacuum (13-40 Pa, 100-300 millitorr) for 2 hours in order to remove any free or weakly bound AsF_5. The vessel was then transferred to a dry box, and the samples stored therein until their sleeve ends were crimped and dip soldered in the No. 7 solder.

Two of the prototype samples - the 30 and 60 end ones (GR01-30-TSF/CU-ASF-1 and -3) were sent to MERADCOM, while the others were retained for further testing of their thermal and environmental stability at the Celanese Research Center.

4. Fabrication of Graphite Fiber Prototype Wires - Second Set

After having gained some fabricating experience, a second set, employing longer wire - at least 24 cm in length - was prepared. These wires, composed of 40 and 60 yarns ends, respectively, were fabricated and encapsulated by the procedures described above, except that only Ni wire was used as the lead-in

wire for external connections.

Four of these wires (two composed of 40 and two of 60 yarn ends) were intercalated with AsF_5 by the same technique described above, except that, after a 24 hour intercalation at room temperature, the cables were retained for 6 more hours at 80° ±2°C at 60-67 kPa (450-500 torr) AsF_5 pressure in order to assure a more complete intercalation. It was followed by a stabilizing heat treatment at 65°C for 2 hours in rough vacuum.

Two of the second set of prototype samples - the 60 and the 40 end ones (GR01-60-TSF/CU-ASF-11 and -14) - were also sent to MERADCOM, the others being retained for further testing.

5. Testing and Evaluation.

a. Electrical d.c. Resistance. The d.c. 4 point resistances were measured with a Keithley 191 multimeter before and after the intercalation as well as after the complete encapsulation, i.e., soldering the pinched-off copper end sleeves. The pertinent data and the nominal conductance enhancements, obtained by dividing the resistance of the pristine yarn bundle by that measured after the intercalation, are given in Table 18. The nominal conductance enhancements, in the range of 30 to 36 times, were obtained in nearly all cases, with the exception of one sample subjected earlier to unsuccessful intercalation with SbF_5. Knowing that the given intercalation procedure with AsF_5 results in fiber weight gains of about 80%[9], and assuming that the fiber density does not change significantly after the intercalation, the conductivity gains resulting from intercalation are in the range of 16 to 20, i.e., not far from the conductivity gains observed on the more perfect bulk graphites, such as HOPG. These are encouragingly high values, especially since the nominal conductance of the assembly still includes a small but unknown

TABLE 18. D.C. RESISTANCE OF ENCAPSULATED GRAPHITE FIBER WIRES BEFORE AND AFTER INTERCALATION WITH AsF_5

First Set

Designation (1)	No.	Effective Length (cm)	Wire Resistance A Before (2) (ohms)	Wire Resistance B After (2) (ohms)	Wire Resistance C After (3) (ohms)	Nominal Conductance Enhancement (4)
GR01-30-TSF/CU-ASF-1	A	14.0	0.817	0.019	0.025	33X
GR01-40-TSF/CU-ASF-2	B	13.5	0.588	0.010	0.018	33X
GR01-60-TSF/CU-ASF-3	C	13.3	0.387	0.004	0.012	32X
GR01-60-TSF/CU-ASF-4	D (5)	13.5	0.379	0.017	0.017	22X
GR01-60-TSF/CU-ASF-5	E (5)	13.8	0.392	0.015	0.013	30X

Second Set

GR01-60-TSF/CU-ASF-11		29.1	0.861	0.028	0.035	31X
GR01-60-TSF/CU-ASF-12		29.0	0.864	0.025	0.030	35X
GR01-40-TSF/CU-ASF-13		28.9	1.279	0.035	0.049 (6)	36X
GR01-40-TSF/CU-ASF-14		28.9	1.289	0.037	0.041	35X

(1) GR01 = Fiber lot. 30, 40, 60 = No. yarns in the wire. TSF = Teflon sleeves: (TFE grade under FEP). CU = copper terminals. ASF = Arsenic pentafluoride intercalant. 1, 2, ... = Sequential sample number.
(2) Intercalation.
(3) Complete encapsulation.
(4) (Column A ÷ B.)
(5) These specimens were intercalated with AsF_5, after an unsuccessful attempt to intercalate them with SbF_5.
(6) Both of the outer (current) leads broke off during the final soldering.

contribution from the contact resistance at the terminals, which, because of the existing sample geometry, cannot be fully eliminated by the 4 point measuring technique. Consequently, the true conductivity enhancements all will be at the high end of the observed conductivity range, i.e., around 20X.

The effective wire lengths listed in Table 18 were calculated by dividing the measured resistance by the known linear resistance of the GR-01 single yarn (1.75 ohms/cm). Also, it should be noted from the Table that the resistance of a specimen becomes appreciably higher when the lead-in wires fail (sample GR01-40-TSF/CU-ASF-13).

6. Thermal Response. The resistance change with temperature of some of the encapsulated samples was determined by placing the sample to be tested in an air oven that was equipped with a feed-through fitting to accommodate the 4 leads to the Keithley 191 multimeter. These leads were electrically welded to the four terminal wires of the cable. The temperature was determined by means of a chromel-alumel thermocouple mounted next to the specimen. The temperature of the oven was raised slowly for from about 23° to 100°C, and held at 50°, 75° and 100°C, for 15-30 minutes until the corresponding resistance readings stabilized. The results on the first specimen of the Set 1 (Code No. D), Table 19 indicated an irreversible resistance increase with time. Subsequently, this sample turned out to have lost its leak-tightness so that the intercalate was being slowly degraded by ambient moisture.

The second sample (No. E) of Set 1 did not show such irreversibility (Table 20). However, the first and the second heating cycles, indicated a rather irregular temperature dependence, possibly due to loss of intercalation equilibrium. The third heating cycle, on the other hand, carried out about a week later

TABLE 19. THE D.C. RESISTANCE CHANGE WITH TEMPERATURE OF THE GRAPHITE FIBER WIRE "D" (GR01-60-TSF/CU-ASF-4) (1)

Time (Min.)	Temperature (°C)	Average (2) Resistance (ohms)
0	23.0	0.029
26	52.3	0.034
52	75.3	0.035
75	90.1	0.037
85	99.5	0.038
145	101.8	0.038
Oven turned off to cool overnight.		
After 24 hrs.	23	0.045
" 48 hrs.	23	0.057
" 55 hrs.	50	0.061
" 96 hrs.	23	0.070
" 300 hrs.	23	0.098

(1) GR01 = Fiber lot. 30, 40, 60 = No. yarns in the wire. TSF = Teflon sleeves: (TFE grade under FEP). CU = copper terminals. ASF = Arsenic pentafluoride intercalant. 1, 2, ... = Sequential sample number.
(2) The resistances are averages of two readings taken with the current flow in opposite directions.

TABLE 20. THE D.C. RESISTANCE CHANGE WITH TEMPERATURE OF THE GRAPHITE FIBER WIRE "E" (GR01-60-TSF/CU-ASF-5)[1]

Elapsed Time (Min.)	Temperature (°C)	Average[2] Resistance (ohms)
	Cycle 1	
0	27.5	0.015
50	52.3	0.032
90	76.0	0.040
110	90.0	0.065
140	100.7	0.040
160	100.0	0.039
	Oven turned off to cool.	
After 16 hours.	23	0.013
	Cycle 2	
0	23	0.013
35	51	0.040
105	97.8	0.038
135	100.5	0.058
230	101.1	0.024
280	80	0.015
350	59	0.015
400	47	0.013
	Oven turned off to cool.	
After 16 hours.	23	0.013
	Cycle 3	
0	25.5	0.012
20	51.7	0.015
80	75.0	0.015
120	99.5	0.015
180	102.2	0.016
After 24 hours.	23	0.014
After 100 hours.	23	0.014

(1) GR01 = Fiber lot. 30, 40, 60 = No. yarns in the wire. TSF = Teflon sleeves: (TFE grade under FEP). CU = copper terminals. ASF = Arsenic pentafluoride intercalant. 1, 2, ... = Sequential sample number.
(2) Averages of two readings, current flow in opposite directions.

gave reproducible resistance values that changed only slightly with temperature. The resistance readings are averaged, because they differed somewhat upon reversing the polarity. This difference is probably due to contact potential differences at the graphite-gold-copper or nickel contacts. To avoid a possibly detrimental effect of oxidized copper, only nickel wire was used as the lead material during the fabrication of the second set of wires.

In order to assure equilibration, all four samples of the second set were cycled twice between room temperature and 100°C, before any resistance readings were taken. Each up and down cycle lasted approximately 4 hours. The resistances were then obtained using a variable power supply to provide a 100 mA current through the samples and 2 Keithley multimeters to read the current and voltage, respectively, during the continuous change of temperature, because the previously used Keithley 191 was not sufficiently accurate for the low resistance levels of the cables. The resistance data taken during the third cycle are listed in Table 21.

The data show that, after completion of the third thermal cycle, the resistance readings are slightly higher than at the beginning. Also, the resistance increase upon heating to 100°C is about 10-20%, which is significantly higher than the near-zero change seen many times on the neat, unencapsulated intercalated graphite samples. This is due to the fact that the 4 point measurement as applied to the encapsulated cable contacts does not give the true resistance of the intercalated graphite bundle, because of the terminal geometry that includes some contact resistance in the 4 point measurement.

TABLE 21. THE ELECTRICAL RESISTANCE CHANGE WITH TEMPERATURE OF THE SECOND SET OF INTERCALATED GRAPHITE FIBER WIRES

Sample Number

*GR01-60-TSF/CU-ASF-11			GR01-60-TSF/CU-AsF-12			GR01-40-TSF/CU-ASF-13			GR01-40-TSF/CU-ASF-14		
Elapsed Time (min.)	Temp. (°C)	d.c.Ω (ohms)	Elapsed Time (min.)	Temp. (°C)	d.c.Ω (ohms)	Elapsed Time (min.)	Temp. (°C)	d.c.Ω (ohms)	Elapsed Time (min.)	Temp. (°C)	d.c.Ω (ohms)
0	25	0.040	0	24	0.038	0	24	0.079	0	24	0.042
20	57	0.042	15	50	0.039	15	50	0.084	10	50	0.047
30	70	0.043	35	70	0.040	35	70	0.090	30	70	0.049
35	80	0.044	55	90	0.043	60	90	0.101	45	90	0.052
40	90	0.045	60	100	0.045	70	100	0.114	70	100	0.055
50	100	0.046	125	99	0.051	130	102	0.125	130	100	0.055
60	102	0.046	155	85	0.051	170	85	0.119	160	85	0.053
105	102	0.047	190	70	0.051	200	70	0.107	220	60	0.049
135	102	0.048	250	50	0.050	265	55	0.100	260	40	0.047
						335	42	0.097			
Oven turned off to cool.											
After 16 hrs.	24	0.042	After 16 hors.	24	0.047	After 16 hrs.	24	0.096	After 16 hrs.	24	0.046

* GR01 = Fiber lot. 30, 40, 60 = No. yarns in the wire. TSF = Teflon sleeves: (TFE grade under FEP). CU = copper terminals. ASF = Arsenic pentafluoride intercalant. 1, 2, ... = Sequential sample number.

In principle, an improved assessment of the contribution of the metal contact materials to the temperature dependence of resistance could be made from the shape of the resistance versus the temperature curve. An alternate approach would be the redesigning of the test sample terminals to provide a configuration permitting an accurate 4 point measurement of only the intercalated graphite resistance.

IV. CONCLUSIONS AND RECOMMENDATIONS

The electrical conductance of high modulus ex-PAN graphite fibers, having pristine electrical conductivities of 1900-3150 ohm^{-1} cm^{-1}, can be increased 30-36 times, upon intercalation with strong state-of-the-art electron acceptor molecules such as AsF_5, and SbF_5. The final intercalated conductance level increases roughly in proportion to the pristine conductance.

The intercalation with a single intercalant at room temperature is not feasible because of too slow or detrimentally fast intercalation rates. Binary intercalant mixtures, such as AsF_5-HSO_3F or SbF_5-HSO_3F, or ternary mixtures, such as the above with SO_3 added, can be intercalated at an acceptably fast rate (within 2-24 hours) at room or at elevated temperatures (60-90°C) in nearly all cases. An additional equilibration heat treatment at about 90°C for several hours appears to be desirable in order to attain stable and reproducible electrical characteristics. Under the present conditions the intercalants which provide both a satisfactory intercalatability and reproducibility are AsF_5-HSO_3F, SbF_5-HSO_3F, or AsF_5 alone.

The contact materials - commercially available binary or ternary alloys of Bi-Sn-Pb-In - used to make contacts to the graphite yarn for the intercalation testing, showed a high contact resistance, 1-2 ohms per terminal, in many cases. No contact corrosion was observable during the intercalation unless SO_3 was present in the intercalant. The porous gold-base contacts baked onto the graphite prototype "wire," however, were estimated to have a satisfactory contact resistance (a small fraction of an ohm), in addition to being corrosion resistant and stable at elevated temperatures.

The thermal and mechanical shock resistance of the glass containers serving as protective enclosures during the exploratory screening and evaluation of intercalants were barely adequate because the containers had a tendency to crack during heating or cooling. The Teflon shrink enclosure, however, used on the prototype wire appears to provide adequate moisture protection in air and allows heating to well above 100°C.

Enhancement of the electrical conductivity upon intercalation in the glass container was difficult to assess because the contact resistance, which could not be measured accurately, was often comparable to or higher than the resistance of the intercalated yarn. In those cases in which the contact resistance was lowest, conductance enhancements of about 30 times were observed, the conductance increasing monotonically and smoothly with increasing intercalation at a given temperature to reach a maximum value. This is in contrast to the staged intercalation behavior observed on the bulk graphites.

The intercalated prototype wires, having a much lower contact resistance, showed very consistent conductance enhancements of 30-36 times the pristine conductance. From previous knowledge of the weight gain of these intercalates (+80%), the respective conductivity enhancement is 16-20X. Assuming no change in the fiber density upon the intercalation, the same value would also hold for the specific conductivity enhancement. The absolute specific conductivity of the best AsF_5-intercalated prototype wires would then correspond to about 45% of the specific conductivity of copper metal at room temperature, and about 60% at 100°C.

The temperature coefficient of the intercalated fiber conductance, as derived from resistance measurements over 20°-90°C temperature range is quite small - <3% over the 68°C range, i.e.,

<4.5% over 100°C excursion. This value, observed on graphite fibers intercalated with single as well as multiple intercalants, is much less than the corresponding temperature coefficient for copper (approximately 45% over a 100°C range) and may be utilizable in applications in which a temperature independent conductance is required.

For the graphite prototype wire, the observed resistance change with the temperature is much higher, 10-20%, because it includes a contribution from the relatively large temperature dependence of the contact materials, the porous gold and the low melting solder.

A brief exploration of the current-carrying characteristics of the intercalated 384-filament yarns (equivalent to size 34 AWG wire) shows that currents providing some 1 watt power dissipation and corresponding to current densities of 25-35 A/mm^2 can be passed through the yarn for at least 100 hours without a change in conductance. This current density compares favorably with the rating given for copper - 12 A/mm^2 in high performance plastic enclosures. At power inputs above 4 watts, a gradual conductance decrease, indicative of deintercalation, was observed.

Short lengths, 20-30 cm, of graphite fiber "wire," equivalent in size to No. 17-20 AWG metal wire, that are air-tight for at least several weeks, thermally stable to at least 100°C, and provide conductivity enhancements to about 20 times as well as nearly temperature independent conductance can be fabricated.

In light of the progress being made to date, it is recommended that additional effort be applied to increase the conductivity enhancement. To do this, it may be necessary to identify graphite

fibers with higher pristine conductivities. Such fibers may not be commercially available yet, but the technology to achieve the higher moduli (and thus higher conductivity) is known. It is also recommended that the search continue for improved intercalants, especially those that will yield thermally stable intercalated yarns with a zero temperature coefficient of resistance.

Along with enchanced conductivities, a concurrent thrust should be made to decrease contact resistance and corrosion. This will require a more intensive search for contact materials. It will also involve optimization of the lead wire placement and terminal design.

Finally, it is recommended that reliable techniques be developed for the measurement of small contact resistances.

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