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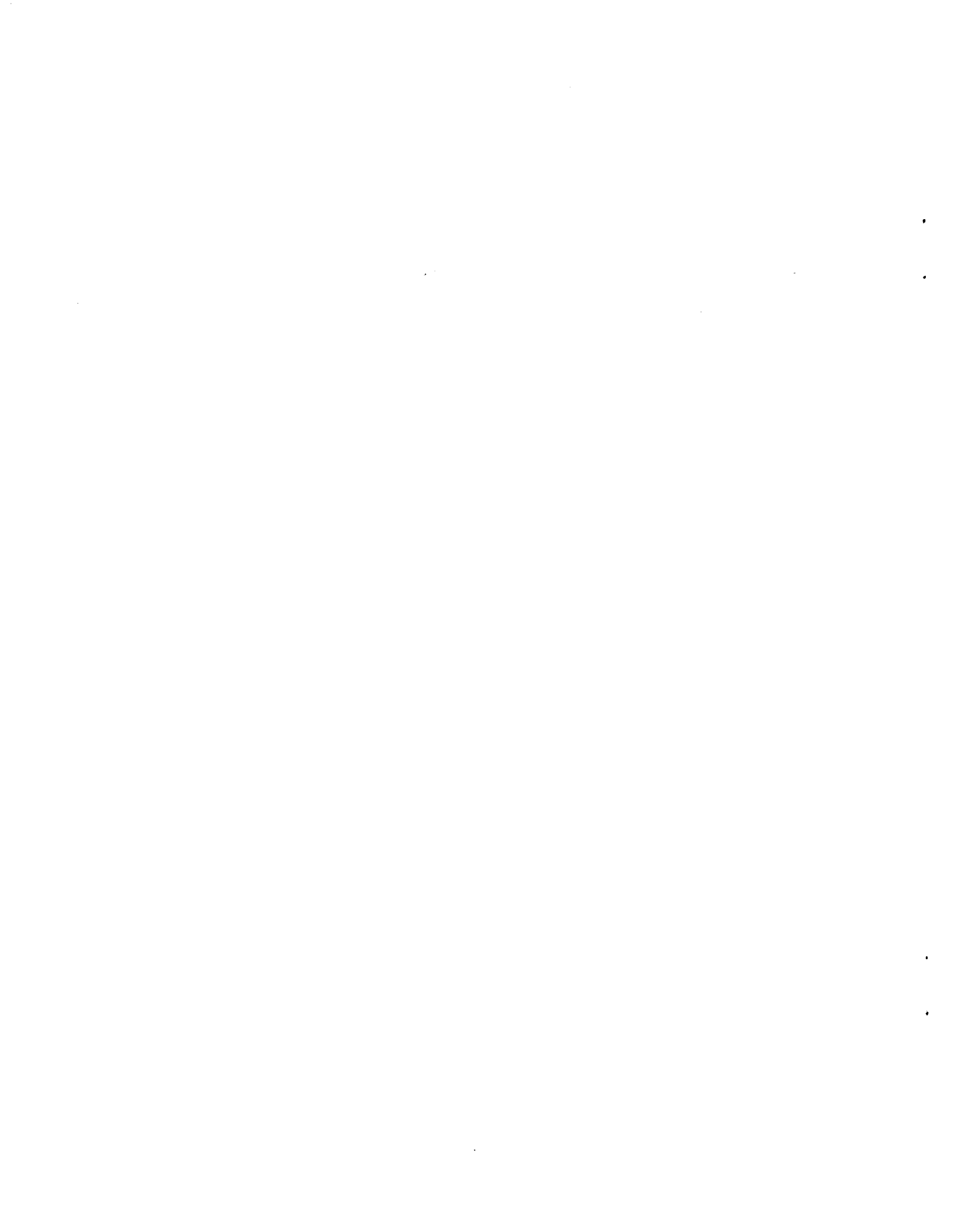
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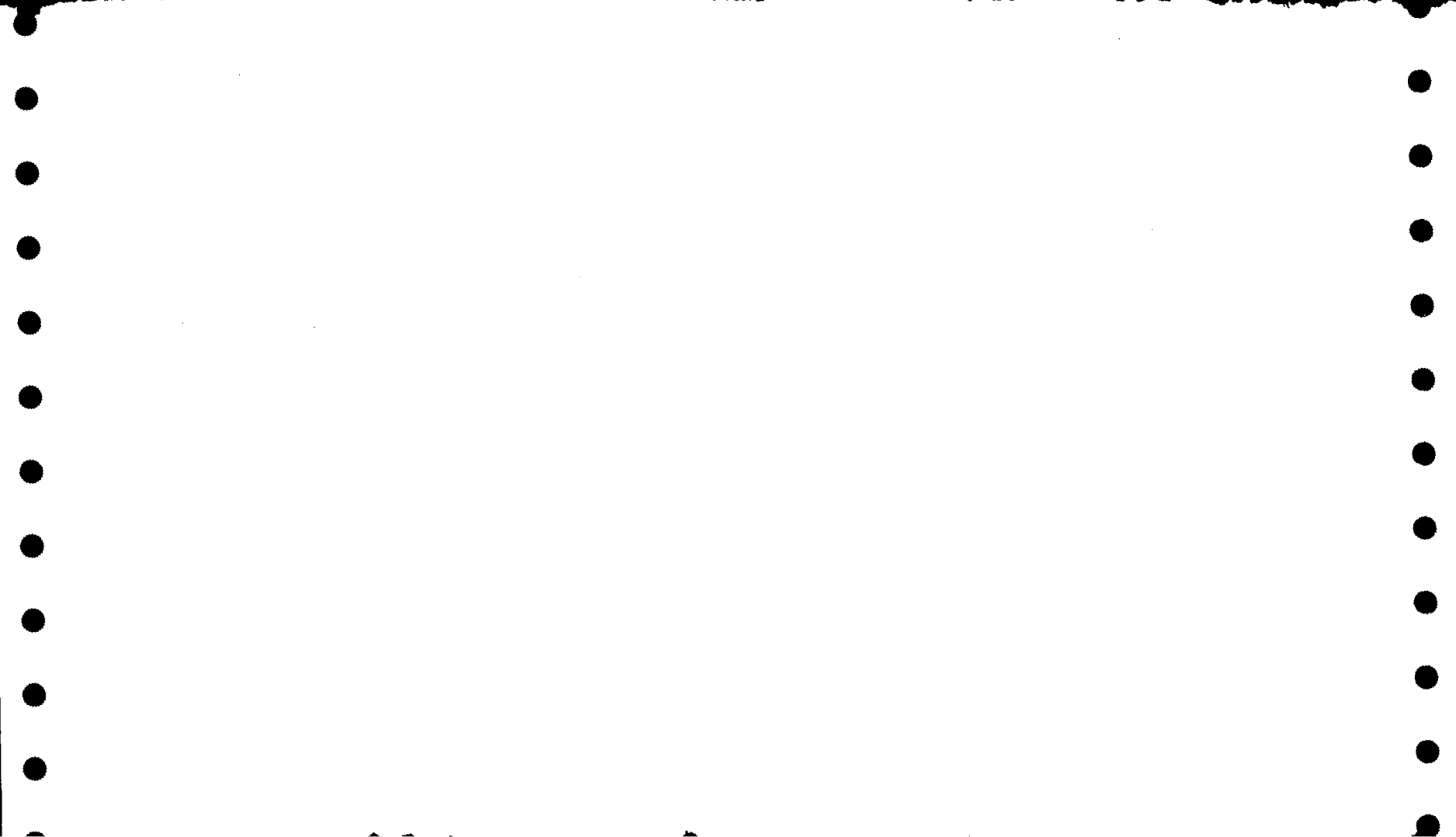
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THE MILLING OF PRISTINE AND BROMINATED P-100 GRAPHITE FIBERS

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SUMMARY

Techniques were developed for the ball milling of pristine and brominated P-100 graphite fibers. Because of the lubricative properties of graphite, large ball loads (50 percent by volume) were required. Use of 2-propanol as a milling medium enhanced the efficiency of the process. Milled brominated P-100 fibers had resistivities which were indistinguishable from milled pristine P-100 fibers. Apparent loss of bromine from the brominated fibers suggests that bromine would not be the intercalate of choice in applications where milled fibers of this type are required. Other intercalates which do not degas may be more appropriate for a milled fiber application. These same results, however, do provide evidence that bromine molecules leave the fiber surface when removed from overpressure of bromine. While exploring possible solvent media for milling purposes, it was found that brominated fibers are stable in a wide variety of organic solvents.

INTRODUCTION

Recent years have seen a vast increase in the use of carbon and graphite fibers in the aerospace industry. Due to their very high strength and low mass density, they have been used almost exclusively as structural components. But graphite is a moderately good electrical conductor, and there are many applications which could take advantage of this fact. The electrical conductivity of many products can be further enhanced by the process of intercalation, which is the insertion of guest molecules between graphene planes. While almost any strong oxidizing or strong reducing agent can act as an intercalate, most intercalation compounds decompose in the presence of oxygen or water vapor. However, several of the transition metal chlorides, and recently bromine, have been shown to have appreciable environmental stability when graphite fibers are used as the host material (ref. 1).

Many of the difficulties which arise when intercalation of graphite fibers is attempted could be eliminated if the fibers were used in a chopped or milled form. These include the spooling of the fibers on nonreactive (glass) mandrels and then respooling the brominated product onto a less fragile mandrel, increased reaction time because the intercalate must migrate through the spool, and limited reactor geometry. The high aspect ratio of the resultant chopped or milled fibers would have important advantages over graphite powders in the areas of electromagnetic shielding and reflection of radio waves.

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Perhaps the most immediate and obvious form of use for milled or chopped intercalated graphite fibers is the manufacture of conductive paints and inks. The potential applications for these kinds of products might include paint-on electromagnetic interference (EMI) shielding, radar and radio antenna reflector surfaces, and the enhancement of composite panel electrical contacts for improved lightning strike resistance in composite aircraft.

This study reports a successful set of milling techniques developed for high modulus graphite fibers. The effects of bromination upon the milling of the fibers was investigated, as well as the effect of milling upon the brominated fibers. In the process, the stability of brominated fibers in organic milling media was also revealed. Described below are various milling and analysis techniques developed along with the results for each case.

METHODS AND MATERIALS

The fibers used in this study were very high modulus pitch-based P-100 graphite fibers manufactured by Union Carbide. The fibers have 10 μm diameters and are sold in strands of 2000 filaments. Fibers were used directly off the roll as received from the manufacturer as control samples. Samples of approximately 100 gm were first spooled onto a glass mandrel and then heated to 350 $^{\circ}\text{C}$ in air overnight to remove sizing from the fiber surface. They were next brominated at room temperature using bulk fiber bromination techniques described elsewhere (ref. 2). To prepare for milling, the strands were cut into 5 cm long bundles. The bundles were found to have a mass of about 160 mg each.

The fibers were milled using a Norton ball (Model PC-1921-A01) mill using standard procedures (refs. 3 to 7). The ceramic mill bottle, which measured 12 cm in height and 9 cm in diameter, was weighed and tared. To this approximately 300 gm of milling balls was added, consuming about half of the bottle volume. The fiber bundles were then placed in the bottle. In the wet milled experiments this was followed by adding about 20 ml of the solvent. The bottle was then sealed and placed on the mill. The mill was activated and a plexiglass containment placed over the entire apparatus. Milling speed was controlled with a variable transformer to provide an optimum compromise between maximizing the speed while minimizing heat production.

The first sequence of fiber milling experiments tested the effects of various ball loads. The milling was performed dry using a constant fiber load of 10 strands of 2000 filaments (about 170 mg). Cylindrical ceramic balls of two sizes were used, the larger having a length of 21 mm and a diameter of 21 mm, and the smaller having a length of 13 mm and a diameter of 12 mm. The fibers were removed from the milling bottle using a laboratory spatula and transferred to small vials for storage. They were viewed and photographed under an optical microscope and a scanning electron microscope (ISI-Mini SEM). In this way the most efficient ball size and load was determined.

The search for a possible milling medium was complicated by the use of the brominated graphite fibers. Precautions had to be taken to assure that the medium did not cause significant desorption of the bromine from the fibers. To that end, the conductivity of brominated P-100 graphite fibers was monitored as a function of time as they were soaked in several organic solvents. The following solvents were used: acetone (Mallinckrodt), benzyl alcohol (Fisher), bromoform (Fisher), butyl acetate (Kodak), carbon tetrachloride (Fisher),

chloroform (Matheson Coleman and Co.), 95 percent ethanol (Fisher), 2-propanol (Midamercia Corp.), methanol (Fisher), trichloroethylene (Fisher), and toluene (Fisher). Fibers were mounted on four-point test chips (ref. 8) and submerged in the respective solvent. Four-point resistance measurements were made using a Keithely Model 220 constant current source and a Keithely Model 181 nanovoltmeter.

The next series of experiments was designed to determine the effect of a milling medium upon the optimum milling time. The fiber load was increased to 50 strands (about 850 mg), and 300 gm loads of the smaller balls were used while the duration of the milling period was varied. These experiments used about 20 ml of 2-propanol as a milling medium. The fibers were milled for 5 hr with a 1 ml sample of fiber/alcohol slurry withdrawn each hour for analysis. When the milling time had elapsed, the bottle was removed from the mill and slowly opened to vent any positive pressure buildup. The entire contents of the bottle were then transferred into a beaker. To the now empty bottle was added another 20 ml of the solvent. The bottle was agitated for a few moments, and then the liquid contents were poured into the beaker holding the slurry and balls. The graphite-solvent mixture was poured off of the milling balls into another beaker. The balls were rinsed with another 20 ml of alcohol which was then added to the fiber/alcohol slurry. The slurry was transferred to centrifuge tubes and centrifuged at about 4300 rpm for 20 to 30 min (Fisher Centrifuge). After centrifugation, the tubes were drained and kept in an inverted position for 2 days to allow the milled powder slug to dry. When dry, these slugs were easily removed and transferred to a separate container for storage.

The resistance of the milled fibers was measured using a four-point probe chip made of platinum leads sputtered onto a substrate made of aluminum oxide (fig. 1). After the chip was weighed, a template was made by placing cellophane tape over the entire chip and cutting out a rectangular shaped piece of the tape across the platinum contacts. With a Pasteur pipet, a small sample of the graphite slurry was transferred to the open area and allowed to dry at room temperature. After drying, the rest of the tape template was carefully removed and the plate weighed again. Using a constant current of 100 μ A, the voltage drop across the powder test area was recorded using the same equipment used for the solvent stability tests.

Assuming a P-100 fiber density of 2.0 g/cm³ and a brominated P-100 fiber density of 2.1 g/cm³ (ref. 9), and that the film is nonporous, the resistivity (ρ) of the milled graphite powder was determined from:

$$\rho = \frac{RM}{lDL}$$

where R is the resistance (in ohms), M is the mass of the powder in the sample (gm), l is the length of powder under current flow (cm), D is the density (gm/cm³), and L is the length of the test film (cm). While the film most likely is porous, it was thought that the porosity would be the same in all samples, so that the relative ρ , if not the absolute, would be valid.

The last series of experiments were performed in the 2-propanol solvent rather than on the fiber powder. NMR spectral data were collected using a Varian FT80-A in deuterated chloroform with 1 percent tetramethylsilane as a standard. Data were collected on the solvent separated from the graphite

slurry and on fresh alcohol that had bromine added to it directly. Silver nitrate turbidity tests were performed on the experimental solvent using a 10 percent aqueous solution (ref. 10). Quantifying bromine/alcohol color characteristics was performed by adding varying amounts of bromine to samples of 2-propanol. These samples were covered and allowed to stand for about 72 hr after which the sample color was compared to the experimental solvent extract.

RESULTS AND DISCUSSION

In developing a methodology for milling graphite fibers, several parameters were analyzed to optimize the operating conditions (refs. 3 to 7). These parameters included ball size, ball size combination, number of balls, milling duration, milling media, and mill rotation rate.

The first set of experiments was designed to test the milling capability of different ball sizes with varying ball load on a constant fiber load. It should be noted that graphite powder is an excellent lubricant and consequently caused a great deal of difficulty when ball loads were small (up to 20 small or 15 large balls). A typical distribution of fiber sizes after 1 hr of milling is shown in figure 2. It can be seen that a great deal of variation exists in the distribution of fiber lengths, from fibers about 0.5 mm in length, to fiber lengths too short to be resolved (1 μ m or less).

On several of these trials it was noted that after 1 hr several fiber strands had not broken down significantly. Inspection after milling often revealed fiber strands still intact and full length. With larger ball loads, the occurrence of fibers not breaking down became increasingly less frequent, and it was found that the greatest operating efficiency was achieved with a ball load of about 300 gm or about half the volume of the milling bottle. This rule applied to either size ball.

It became obvious early on that the safety and efficiency of the procedures could be enhanced if a liquid milling medium could be found. One important requirement of the medium is that it not cause debromination of the fibers. This was tested by monitoring the resistance of 1 cm long filaments of fibers submerged in various media under consideration. Table I shows the average resistance ratio (resistance, R /initial resistance, R_0) for 6 fibers in each of 12 solvents which were candidates for milling media. There was no change in resistance for any of the solvents after 5 days of exposure. This is far longer than any expected milling time. After 24 days two of the solvents dissolved the carbon paint used to affix the fibers to their holders. Beyond those, only methanol showed some gain in resistance (6 \pm 3 percent). After 9 months two more solvents dissolved the carbon paint, and there was some degradation of the fibers in acetone (3 \pm 3 percent) and toluene (2 \pm 1 percent). Overall the results of the solvent stability tests showed that brominated fibers are very stable in the entire range of chemicals tested. Isopropyl alcohol was chosen as the milling medium because of its relative safety, low toxicity, and low cost.

Use of a solvent medium with the fibers provided for ease in powder transfer and analysis, while at the same time caused no apparent hindrance to the milling procedure. In fact, the milling became more efficient with the resulting powder from these runs appearing to have a much more uniformly distributed particle size (compare fig. 2 with fig. 3). For a given milling

duration the average particle size was also much smaller. In contrast to the dry milling, wet milling broke down the fiber strands virtually every time.

The brominated fibers provided an unexpected result when milled in the 2-propanol milling media. After the subsequent separation of the fibers from their solvent, it was noted that the alcohol was a light yellow color, in contrast to colorless alcohol separated from the pristine P-100 fibers. The yellow color was originally believed to be due to solvated bromine. But studies have shown that the brominated fibers are about 18 percent bromine by weight (ref. 11), so even if all of the bromine in the fibers went into solution, the solution would only be about 0.06 percent bromine by weight. Attempts at coloring fresh alcohol by adding bromine directly showed that even at bromine concentrations much higher than that available to the fiber-solvent system, bromination of the alcohol, which yields a colorless product, is dominant over bromine solvation, which yields a colored product (table II). It is suspected that the color is due to high color impurities generated by bromination of the graphite lattice.

Silver nitrate turbidity tests, however, indicated the presence of some bromide ions in solution by giving a light yellow precipitate. The solubility product of silver bromide is 7.7×10^{-13} (ref. 12) so this test is sensitive to very low bromine concentrations (ppb). Propanol samples from the pristine fiber runs gave no precipitate when treated with the silver nitrate. Isopropyl alcohol blanks were used throughout the procedure.

NMR spectra were taken on concentrated solutions of the 2-propanol wash from both the pristine and brominated milled fibers. Figure 4(a) shows the spectra of 2-propanol as received from Mid-America Chemical Corp. Note the doublet about 1.2 ppm and multiple peaks about 3.9 ppm downfield of the tetramethylsilane standard. Figure 4(b) reveals that the NMR spectrum of the wash from the pristine P-100 fibers is little changed. The only shift is a slight upfield shift of the hydroxyl singlet from about 3.9 to about 3.5 pp. Hydroxyl peaks are notoriously sensitive to solvent effects.

NMR spectra of 2-propanol washed from the milled brominated P-100 fibers differed significantly from the other two (fig. 4(c)). The data showed a wide doublet, also about 1 ppm, indicating a large number of alkyl products present. The position of the multiple peak was no longer clear, although there are several broad peaks in the range of 2 to 3.5 ppm and another centered about 7 ppm. The implication is that the solvent washed from the brominated fibers contained a wide variety of lattice fragments, much more than in the pristine case. This is probably due to the bromine attacking the lattice as it was freed by the milling process.

Resistivity measurements on the milled fibers using the four-point probe chips were hampered by difficulties measuring the cross-sectional area of the sample. Nevertheless, the results indicated that, after milling, the relative difference in resistivity between the two types of milled fibers was not significantly different. The average resistivity value for 13 samples of the brominated powder was 59 ± 19 mohm-cm while that of 14 samples of the pristine powder had an average resistivity of 46 ± 18 mohm-cm. These values were shown to be not significantly different from each other using Student's t-test at $p \gg 0.05$ (ref. 13).

It was shown by Jaworske and Zinolabedini (ref. 14) that brominated fibers experience a loss of bromine from the perimeter of the fiber. The results of these tests and analyses support this view. When the fibers are milled, a large number of edges are created. Bromine is lost from each of these edges reducing the amount of bromine in the fiber. As the length of the fiber approaches some lower limit in size, the bromine depletion zones meet, and the result is an unbrominated fiber. According to Jaworske and Zinolabedini, the size should be about 4 μm for P-100 fibers. One could argue that the resistivity of such a particle may even be somewhat higher than the pristine value because of the disruption in the lattice caused by intercalation. This may be reflected in the above data.

CONCLUSIONS

It was shown that graphite fibers can be successfully milled to suit the needs of a variety of applications. The apparent loss of bromine from the brominated fibers suggests that bromine would not be the intercalate of choice in applications where milled powder of this type is required. These same results, however, do provide valuable evidence for the debromination phenomenon reported earlier. Other intercalates which do not exhibit this degassing behavior may be appropriate for milled fiber applications. While exploring possible solvent media for milling purposes, it was found that brominated fibers are stable in a wide variety of organic solvents.

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TABLE I. - THE RESISTANCE RATIO (RESISTANCE/
INITIAL RESISTANCE) OF BROMINATED P-100
GRAPHITE FIBERS STORED IN
SOLVENTS OVER TIME

Solvent	5 days	24 days	9 months	
Water	1.00	1.00	1.00	
Methanol	↓	1.06±0.03	1.04±0.03	
Ethanol		1.00	1.00	
2-propanol		↓	1.00	1.00
Benzyl alcohol			1.00	1.00
Acetone		↓	1.03±0.03	1.03±0.03
Chloroform			1.00	1.00
Bromoform			(a)	(a)
Carbontetrachloride		(a)	(a)	
Trichloroethane		1.00	(a)	
Butyl acetate		1.00	1.00	
Toluene		↓	1.00	1.02±0.01

^aCarbon paint used to affix the samples dissolved and fibers were lost.

TABLE II. - QUALITATIVE COLOR TEST OF BROMINE IN
2-PROPANOL

[+ = relative measure of shade/intensity.]

Sample	Br ₂ conc., percent	Color	Phases
Pristine	0	Colorless	1
P-100-Br	<0.06	Yellow (++)	1
2-propanol	5	Lighter yellow (+)	2
2-propanol	12	Darker yellow (+++)	2

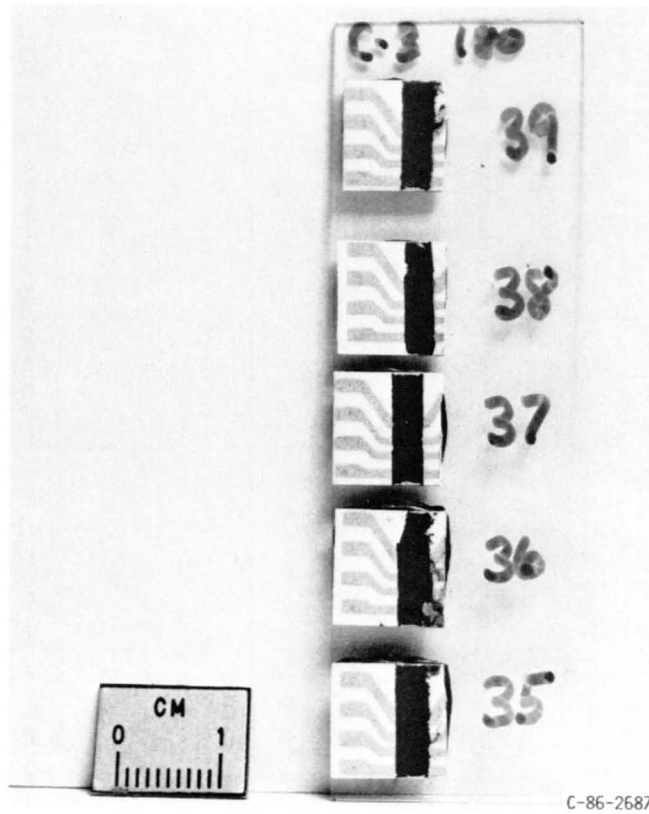


FIGURE 1. - FOUR-POINT RESISTANCE PROBE CHIPS USED TO MEASURE THE RESISTANCE OF MILLED FIBER SAMPLES.

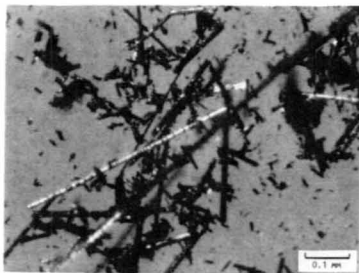


FIGURE 2. - PHOTOMICROGRAPH OF PRISTINE P-100 GRAPHITE FIBERS AFTER 1 HR IN A BALL MILL WITH NO MILLING MEDIUM.

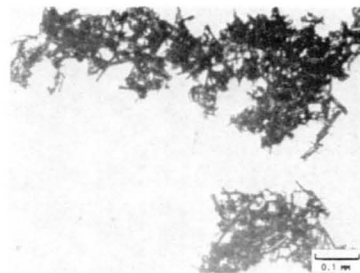


FIGURE 3. - PHOTOMICROGRAPH OF PRISTINE P-100 GRAPHITE FIBERS AFTER 1 HR IN A BALL MILL WITH 2-PROPANOL AS THE MILLING MEDIUM.

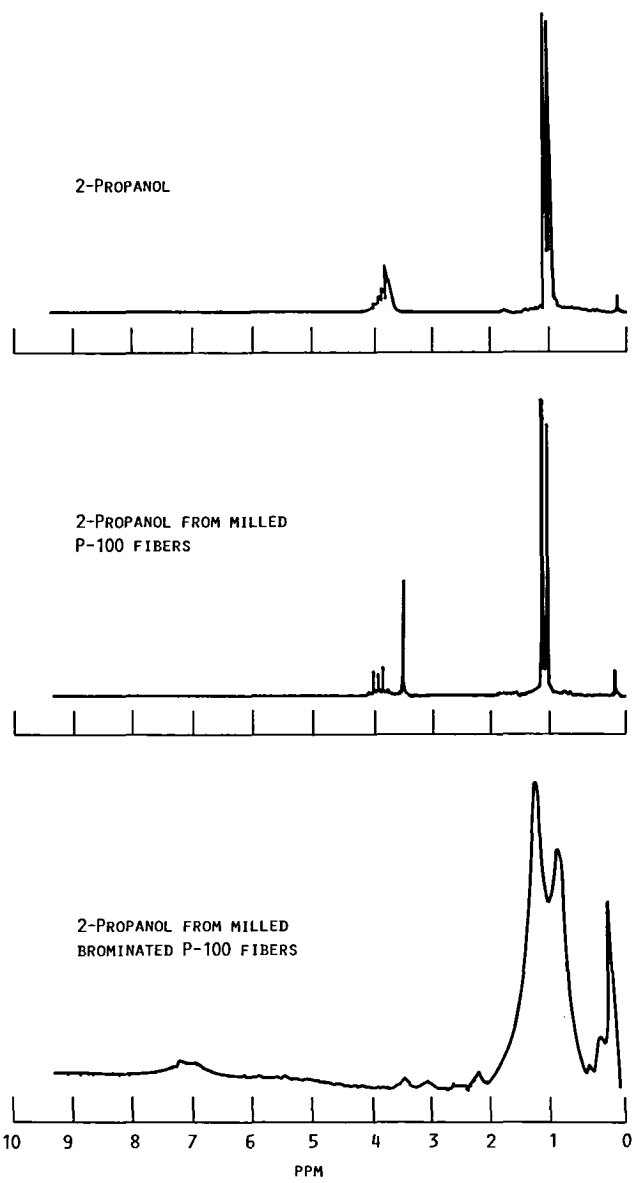
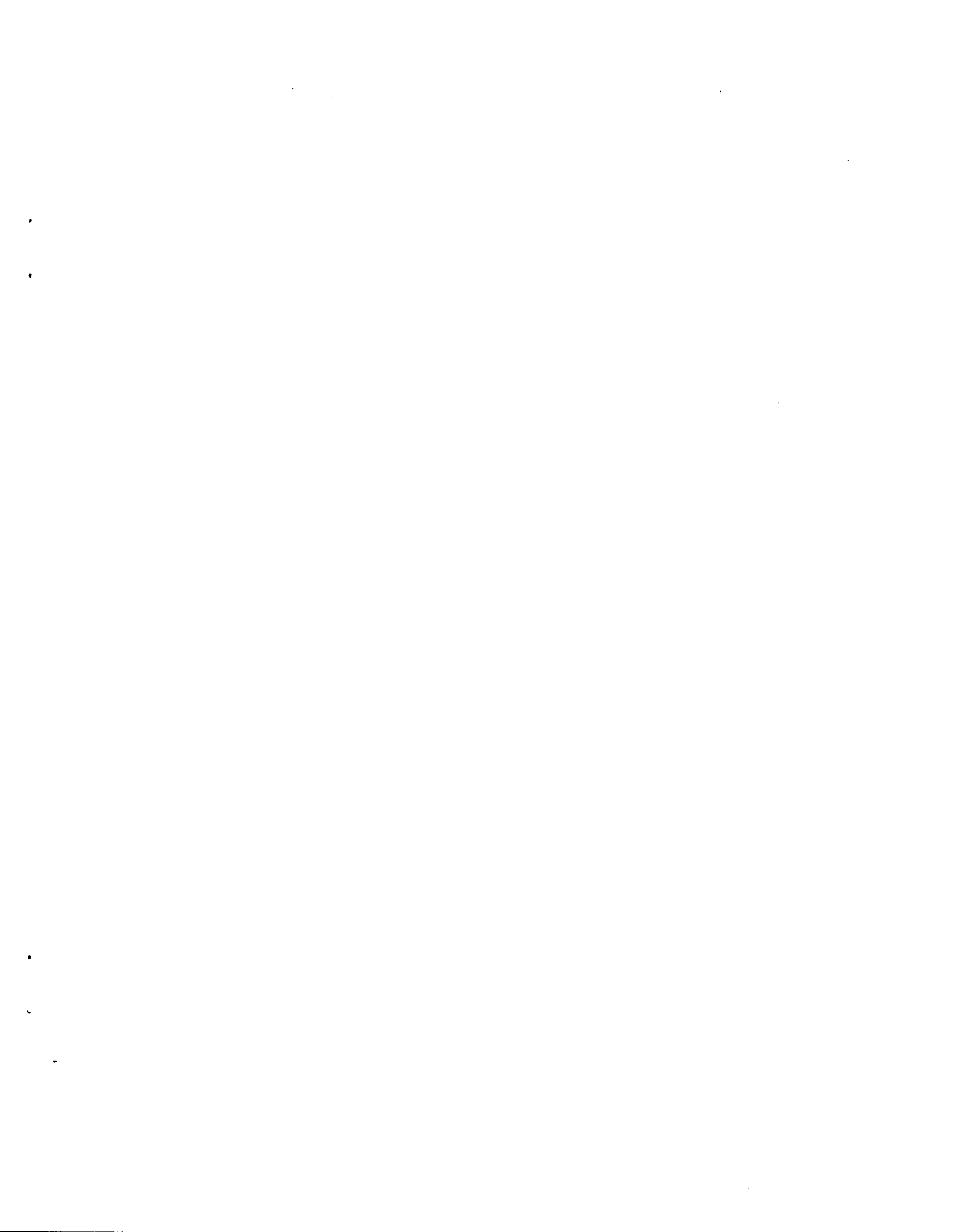


FIGURE 4. - NMR SPECTRUM OF 2-PROPANOL, 2-PROPANOL FROM MILLED P-100 FIBERS, AND 2-PROPANOL FROM MILLED BROMINATED P-100 FIBERS.



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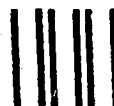
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