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Effects of Graphitization on the Environmental Stability of Brominated Pitch-Based Fibers

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EFFECTS OF GRAPHITIZATION ON THE ENVIRONMENTAL STABILITY OF BROMINATED PITCH-BASED FIBERS

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SUMMARY

The residual bromine graphite intercalation compounds of high modulus pitch-based fibers (Amoco P-55, P-75, P-100, and P-120) were formed and their resistances were monitored under a variety of environmental conditions. A threshold graphitization was observed below which the bromination reaction does not occur to an appreciable extent. The graphitization of the P-55 fibers falls below that threshold, precluding an extensive reaction. The P-75, P-100, and P-120 fibers all form bromination compounds which are stable at ambient conditions, under vacuum, and under high humidity (100 percent humidity at 60 °C). The thermal stability of the resistivity increased with decreasing graphitization, with the stable temperature for P-120 being 100 °C; for P-100, 200 °C; and for P-75, 250 °C. When cost is a consideration, bromination of pitch-based fibers is an economical way to achieve low resistivities.

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INTRODUCTION

Graphite fibers are an attractive material for the aerospace industry. Their high strength and low density make them ideal as a replacement for many metal components. It is not surprising, therefore, that graphite/epoxy and graphite/polyimide composites are being used in increasingly larger percentages of modern aircraft and spacecraft.

There are some structural components which heretofore have remained metallic because graphite fiber composites lack the necessary electrical conductivity. One of the most promising approaches to improving the composite conductivities is by improving the graphite fiber conductivity prior to composite fabrication through the process of intercalation. It has been shown recently that bromine forms a compound with highly graphitic pitch-based fibers which is indefinitely stable in air, vacuum, high humidity, and temperatures up to 200 °C (ref. 1).

These particular fibers (Amoco P-100), while suitable for bromination, are limited in their application because of their high cost, and unique mechanical properties (ref. 2). While useful for stiffness-critical applications, their strain to failure ratio is too low to be used for large aircraft structural components. These large structures could have improved lightning-strike resistance and electromagnetic shielding characteristics if their conductivity could

be improved. Other, less graphitic pitch-based fibers can also have their conductivities improved significantly by the process of bromination provided they are sufficiently graphitic (ref. 3).

An important property of any intercalation compound which hopes to gain widespread use is its environmental stability. In this study, the effect of graphitization on the environmental stability of the residual bromine compounds of various graphite fibers is examined. This will be done by comparing the stability of the resistance of the residual bromine compound of four different grades of graphite fiber, each exposed to four different environments: ambient, high vacuum (10^{-6} torr), high humidity (100 percent at 60 °C) and high temperature (up to 400 °C in air). Finally, other considerations in the application of these fibers as engineering materials will be discussed.

METHODS AND MATERIALS

All fibers used in this study were pitch-based fibers commercially available from Amoco (formerly Union Carbide). The P-55, P-75, and P-120 brominated fiber data are compared with P-100 fiber data reported previously (ref. 1). While there are differences in precursors, process parameters, and heat treatment temperatures among these various grades of fiber, they are differentiated primarily by their final degree of graphitization, which increases with designation number.

The fibers were brominated at room temperature in the vapor phase using standard techniques described elsewhere (ref. 1). After the fibers were removed from the bromine they were allowed to equilibrate for several days in ambient laboratory air. It is this final residual bromine compound whose stability will be discussed.

The property that was used to measure the stability of the bromine compound was the resistivity. In addition to being a property that is easy to monitor, nondestructive, and sensitive to changes in bromine concentration, it is the property of interest for our intended applications. It should be noted, however, that resistivity is not a direct measure of bromine concentration in the fiber.

Individual filaments were mounted on sample holders which contained four-point electrical contacts (fig. 1) using carbon paint (Structure Probe Inc.). Those fibers subjected to the high temperature tests were mounted on holders made of aluminum oxide with sputtered platinum contacts. Other fibers were mounted on holders made from printed circuit board material. A Keithley model 225 constant current source supplied 100 μA of direct current along the fiber through the outer contacts, while a Keithley model 181 nanovoltmeter measured the voltage drop between the inner contacts. Voltages were measured at both polarities, and averaged to cancel out electrochemical and electrothermal effects. The relative uncertainty in the voltage measurements was about 0.2 percent. The length (about 1 cm) and diameter (about 10 μm) of the fibers was assumed to be invariant throughout the tests.

The fibers were first exposed to ambient laboratory conditions for long periods of time. Their resistances were measured first hourly, then daily, then weekly, then monthly, and compared to their initial values. No special precautions were taken to keep them in a dry or isothermal environment.

A second group of the brominated fibers was stored in a bell jar at a vacuum of at least 10^{-6} torr (10^{-4} Pa) at ambient temperature. The fibers were removed from the bell jar to measure their resistances and then promptly returned. Effort was made to expose them to the ambient pressure for as short a time as possible.

A third group of fibers was subjected to a high humidity environment. The adverse effects of humidity on transition metal chloride intercalated fibers is well documented (see for example, refs. 4 and 5) and, although humidity effects were not observed in P-100 fiber (ref. 1), they remain a major concern. Groups of fibers were sealed with parafilm in beakers containing a large reservoir of water. These were then stored in 60 °C isothermal chambers. The resulting humidity (nearly 400 torr of water vapor) is about five times that encountered at room temperature. The fibers were removed to ambient conditions and allowed to cool before their resistances were measured. After their resistances were measured they were quickly returned to the humidity chamber.

A group of each of the brominated fiber types was placed in an air filled, large thermal mass oven set at 100 °C. They were removed at intervals and placed on an aluminum block to cool to room temperature before their resistances were measured. Similar tests were conducted on fibers at 150, 200, 250, 300, 350, 400, and 450 °C. The large oven and aluminum block minimize the heat-up and cool-down times. Even at 450 °C there was less than 1 min transition time each way. The reported time is that actually spent at the test temperature.

RESULTS AND DISCUSSION

The reaction of bromine with the P-55 fibers was qualitatively different from the other fibers. The resistivity of P-120, P-100, and P-75 fibers all decreased by about a factor of five upon bromination, but the P-55 fiber resistivity only decreased by a few percent. This may be evidence for a threshold graphitization below which bromination, at least under our reaction conditions, will not occur. The bromination reaction is more fully discussed elsewhere (ref. 3), but the stability of the brominated P-55 fiber also has qualitatively different features which will be discussed below.

The resistance of all four brominated fiber types proved to be invariant at ambient temperature and humidity for at least 8 months. The largest changes in resistance over this time were of the order of a few tenths of a percent, and showed no trend. This is undoubtedly a measure of the noise of our measuring methods.

The high humidity environment had no effect on the brominated fiber resistivities for at least 7 months. Once again any changes over this period of time were less than 1 percent. Unlike many of the transition metal chlorides graphite intercalation compounds which are very hygroscopic, brominated graphite does not draw water from the air (ref. 4). It is the reaction of the compound with water that leads to increased resistivity (ref. 5).

The resistances of the brominated P-75, P-100, and P-120 fibers were unchanged after at least 2 months exposure to the vacuum environment. Brominated P-55 fibers, however, experienced a decrease in resistivity when exposed to the vacuum. This is consistent with in situ behavior which shows a decrease

when the fibers are removed from the bromine (ref. 3). Vacuum continues to draw out the bromine which further lowers the resistivity of the fiber. Why loss of bromine results in a decrease in the resistivity of P-55 fibers remains unclear at this time.

There were marked differences in the thermal stability of the residual bromine compound of each of the four fiber types. It should be noted that the resistance ratio (resistance, R/initial resistance, R_0) for pristine P-55, P-75, P-100, and P-120 fibers shows no significant increases at temperatures as high as 400 °C.

The resistance ratio of brominated P-55 fibers as a function of time exposed to high temperatures in air (fig. 2) shows different behavior. At temperatures of 300 °C and below the resistance of the fibers drops about 4 percent within the first 30 min. It remains at this value for at least 24 more hours and probably indefinitely. This is consistent with the explanation given above for the behavior under vacuum; that is, bromine is being driven from the surface which lowers the resistivity of the fibers. At higher temperatures the resistance behavior begins the same way, but then oxidation of the fiber causes the resistance to increase further.

When the thermal stability of P-75 fibers is examined (fig. 3), the functional form more closely resembles that reported earlier (ref. 4) for brominated P-100 fibers (fig. 4). When the thermal stability of P-120 fibers (fig. 5) is added to the analysis, the trends become clear. For fibers more graphitic than a certain threshold value (somewhere between P-55 and P-75), the thermal stability of the bromine compound decreases with increasing graphitization. This can be illustrated by comparing the relative thermal stabilities of the fibers at a given temperature such as 350 °C (fig. 6).

Another way to visualize the effects of graphitization is to compare the resistance ratio of the brominated compounds of the four fiber types as a function of temperature after a given exposure time (fig. 7). It is obvious from this plot that increased graphitization results in lower temperature stability. An important property is the temperature above which high temperature exposure in air results in a degradation of the electrical properties. For P-120 that temperature is between 100 and 150 °C, for P-100 it is between 200 and 250 °C, and for P-75 it is between 250 and 300 °C.

It is important to keep in perspective that the resistance ratio characterizes the change in resistance from the stable residual bromine compound. It should be noted that the initial resistivities of the various grades of fibers are different. Perhaps for the applications engineer a more useful plot would be of mean resistivity as a function of temperature after a given exposure time (fig. 8). This plot reveals that even relatively large resistance ratio changes actually represent rather small resistivity changes. Pristine fiber resistivities are included for comparison.

Perhaps the greatest impediment to the utilization of these fibers by industry is their relatively high price. A plot of current retail price (1986) as a function of resistivity is revealing (fig. 9). Note that a premium is paid for small increments in resistivity improvement below the 1000 $\mu\Omega$-cm level. Bromination can significantly enhance the price per resistivity level at projected value added costs, but only for highly graphitic fibers.

CONCLUSIONS

The residual bromine compounds can be formed with high modulus pitch-based fibers. There seems to be a threshold graphitization for bromine compounds that falls between that of P-55 fibers and P-75 fibers, that is, fibers with a graphitization of P-75 fibers and better readily brominate, whereas those with a graphitization below that do not. The P-75, P-100, and P-120 fibers all form bromination compounds which are stable at ambient conditions, under vacuum, and under high humidity (100 percent humidity at 60 °C). The thermal stability of the resistivity increases with decreasing graphitization, with the stable temperature for P-120 being 100 °C; for P-100, 200 °C; and for P-75, 250 °C. Although the resistance ratios appear large in some of the high temperature tests, the actual change in resistivity is often relatively small. When cost is a consideration, bromination of pitch-based fibers is an economical way to achieve low resistivities.

P-55 fibers did not form a residual bromine compound that resulted in a large decrease in fiber resistivity. The P-55 bromine compound resistance was unaffected by humidity, but actually decreased slightly in vacuum and when heated in air.

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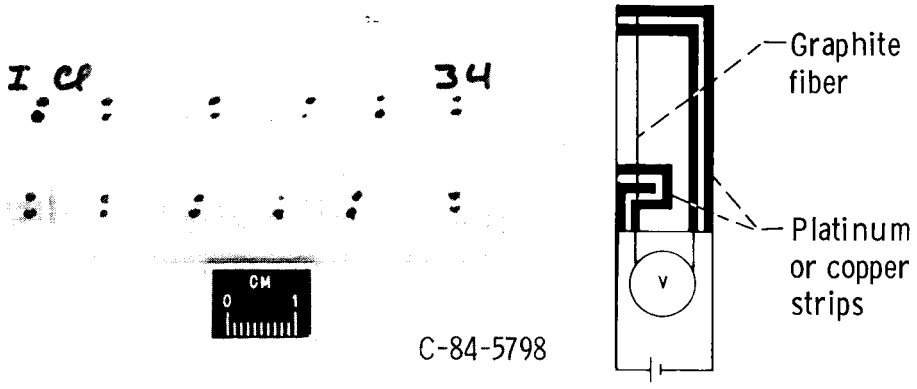

Figure 1. - Four point measurement sample holder of the type used in the stability studies.

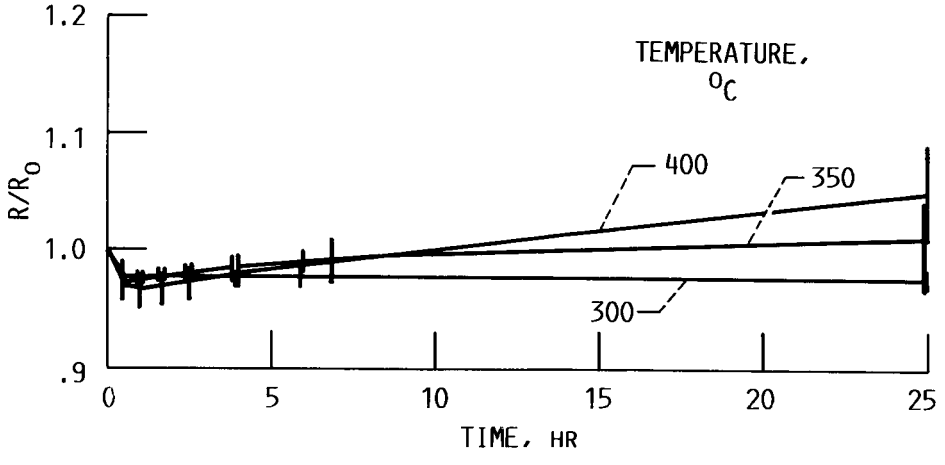

FIGURE 2.- AVERAGE CHANGE IN RESISTANCE RATIO (R/R_0) WITH TIME FOR BROMINATED P-55 FIBERS EXPOSED TO INDICATED TEMPERATURES. VERTICAL LINES INDICATE THE SAMPLE STANDARD DEVIATION.

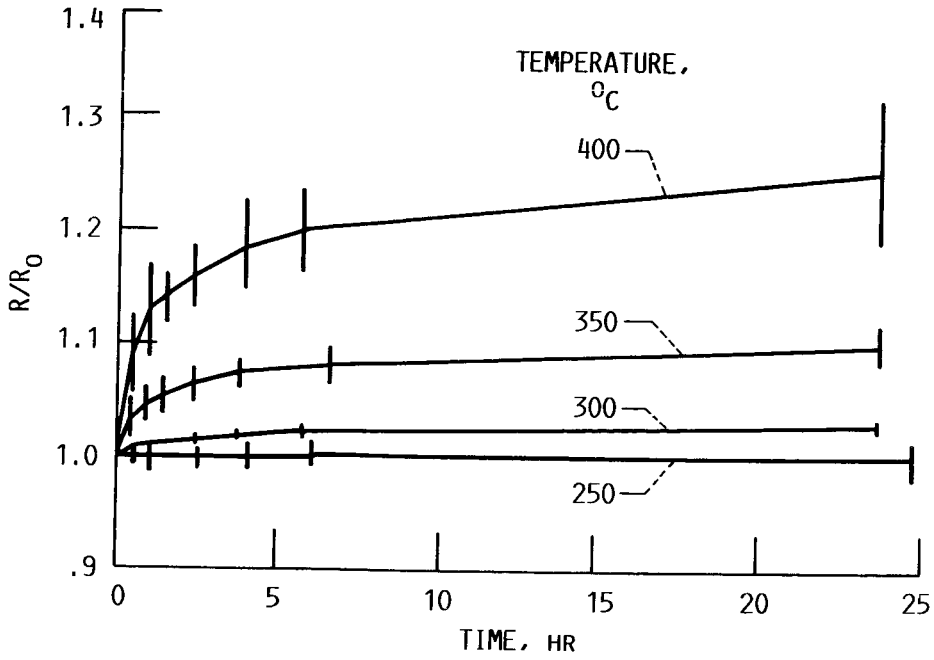

FIGURE 3.- AVERAGE CHANGE IN RESISTANCE RATIO (R/R_0) WITH TIME FOR BROMINATED P-75 FIBERS EXPOSED TO INDICATED TEMPERATURES. VERTICAL LINES INDICATE THE SAMPLE STANDARD DEVIATION.

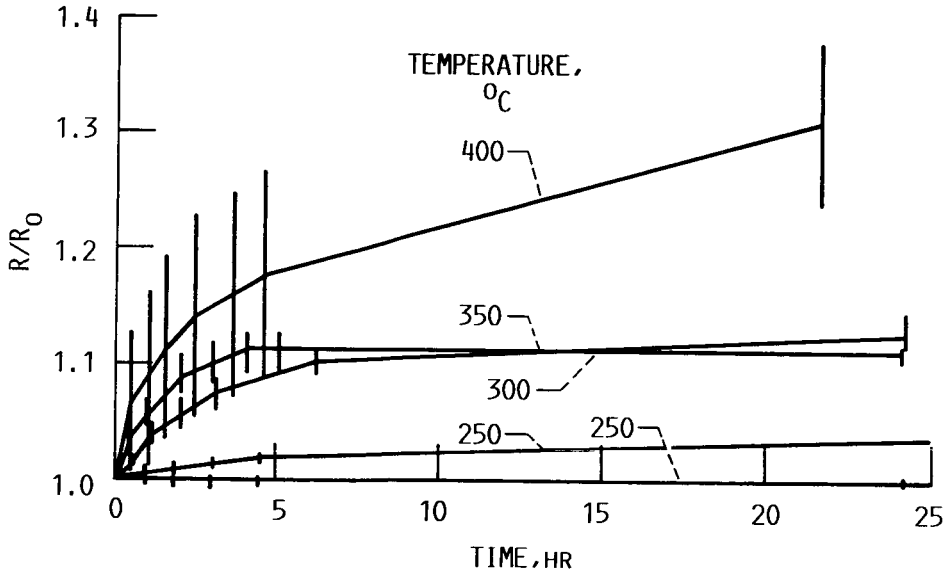

FIGURE 4.- AVERAGE CHANGE IN RESISTANCE RATIO (R/R_0) WITH TIME FOR BROMINATED P-100 FIBERS EXPOSED TO INDICATED TEMPERATURES. VERTICAL LINES INDICATE THE SAMPLE STANDARD DEVIATION.

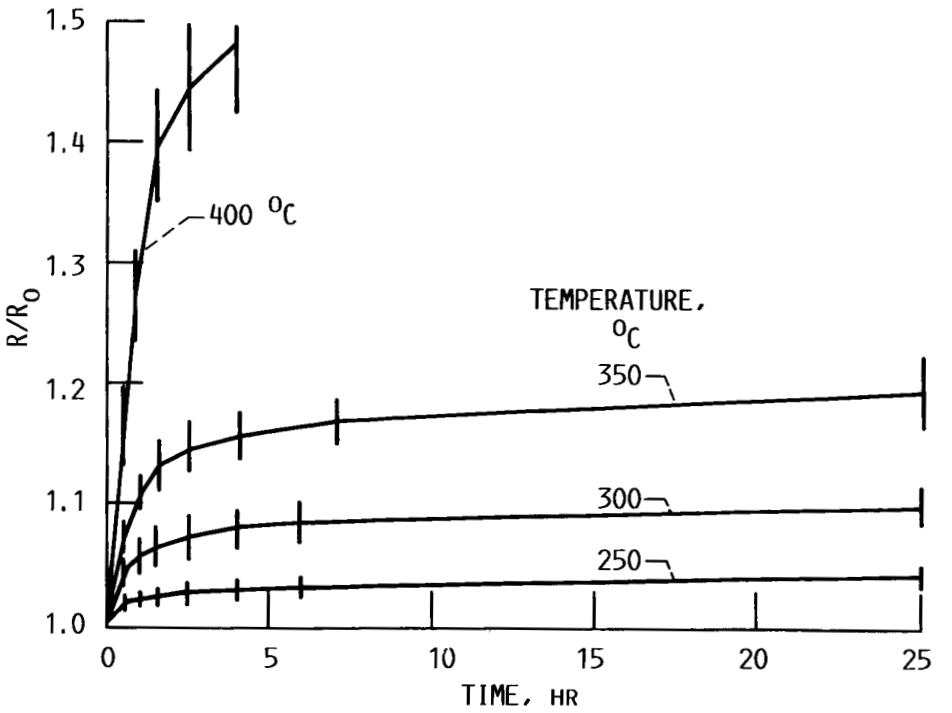

FIGURE 5.- AVERAGE CHANGE IN RESISTANCE RATIO (R/R_0) WITH TIME FOR BROMINATED P-120 FIBERS EXPOSED TO INDICATED TEMPERATURES. VERTICAL LINES INDICATE THE SAMPLE STANDARD DEVIATION.

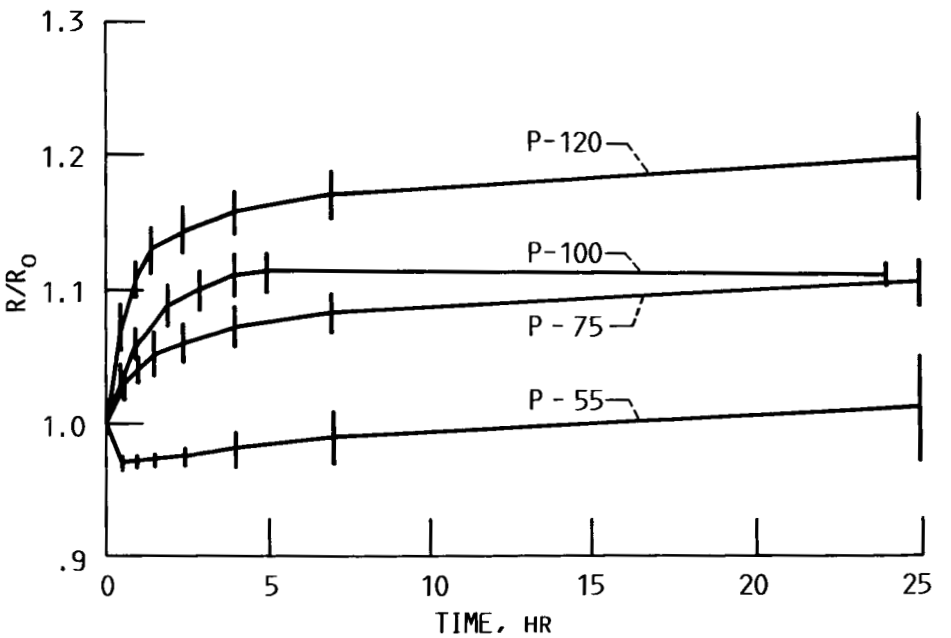

FIGURE 6.- AVERAGE CHANGE IN RESISTANCE RATIO (R/R_0) WITH TIME FOR BROMINATED P-55, P-75, P-100, AND P-120 GRAPHITE FIBERS AT 350 °C. VERTICAL LINES INDICATE THE SAMPLE STANDARD DEVIATION.

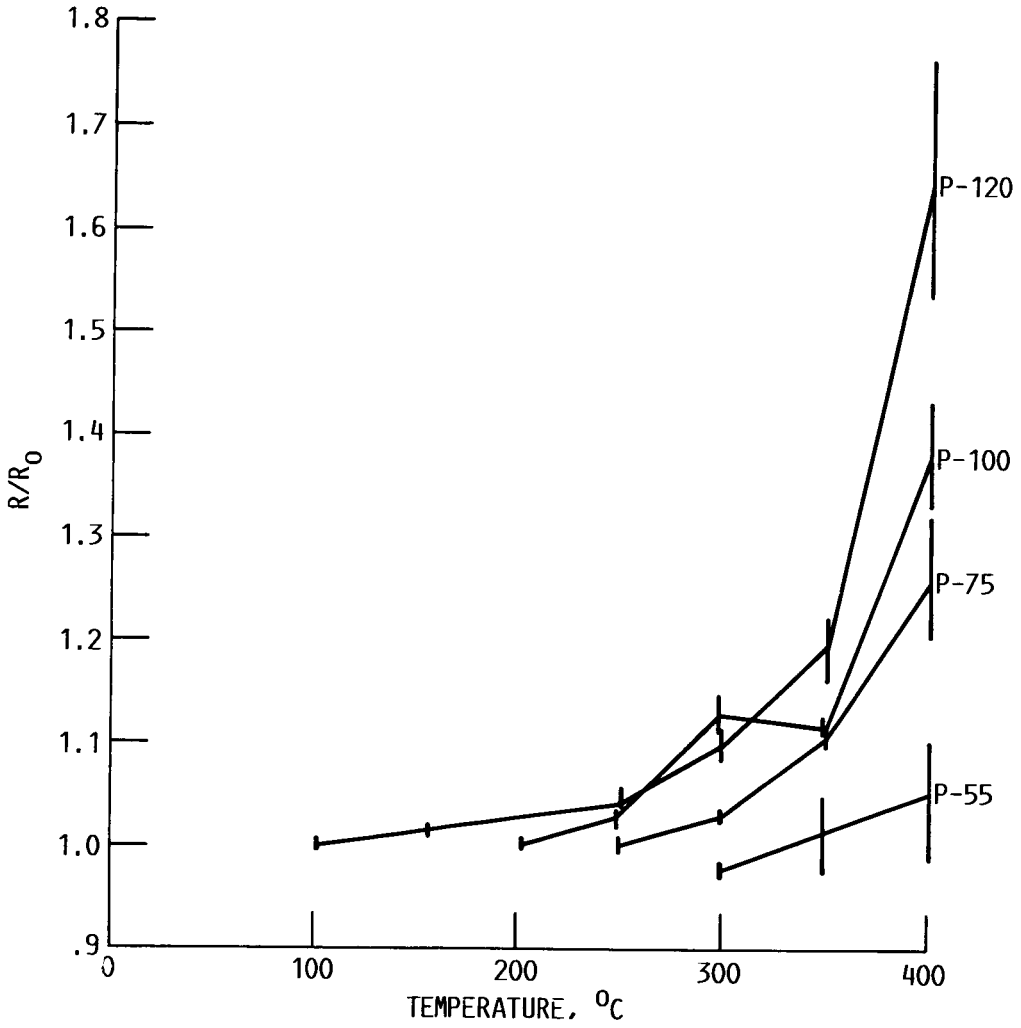

FIGURE 7. - AVERAGE CHANGE IN RESISTANCE RATIO (R/R_0) WITH TEMPERATURE FOR BROMINATED P-55, P-75, P-100, AND P-120 GRAPHITE AFTER 24 HOURS EXPOSURE TO TEMPERATURE IN AIR. VERTICAL LINES INDICATE SAMPLE STANDARD DEVIATION.

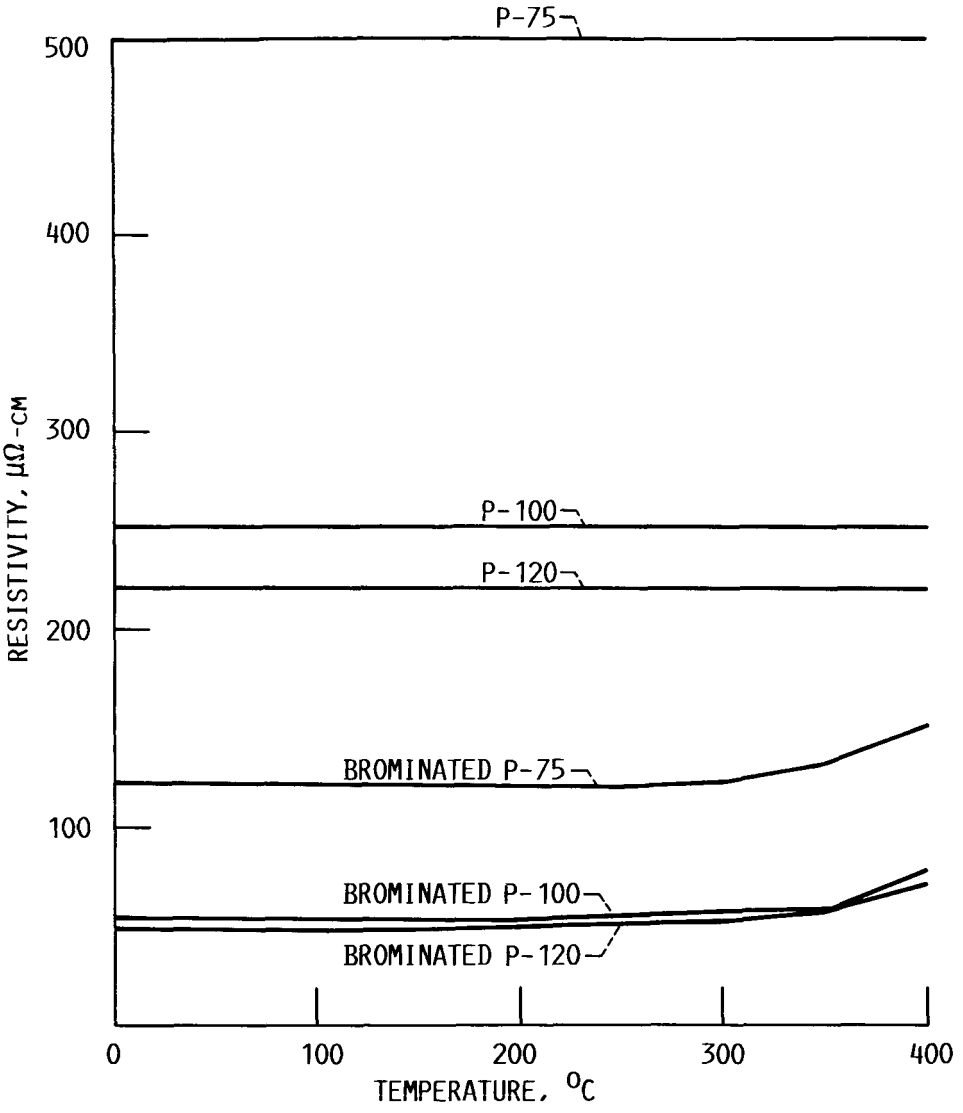

FIGURE 8.- AVARAGE CHANGE IN RESISTIVITY WITH TEMPERATURE FOR PRISTINE AND BROMINATED P-75, P-100, AND P-120 GRAPHITE AFTER 24 HOURS EXPOSURE TO TEMPERATURE IN AIR.

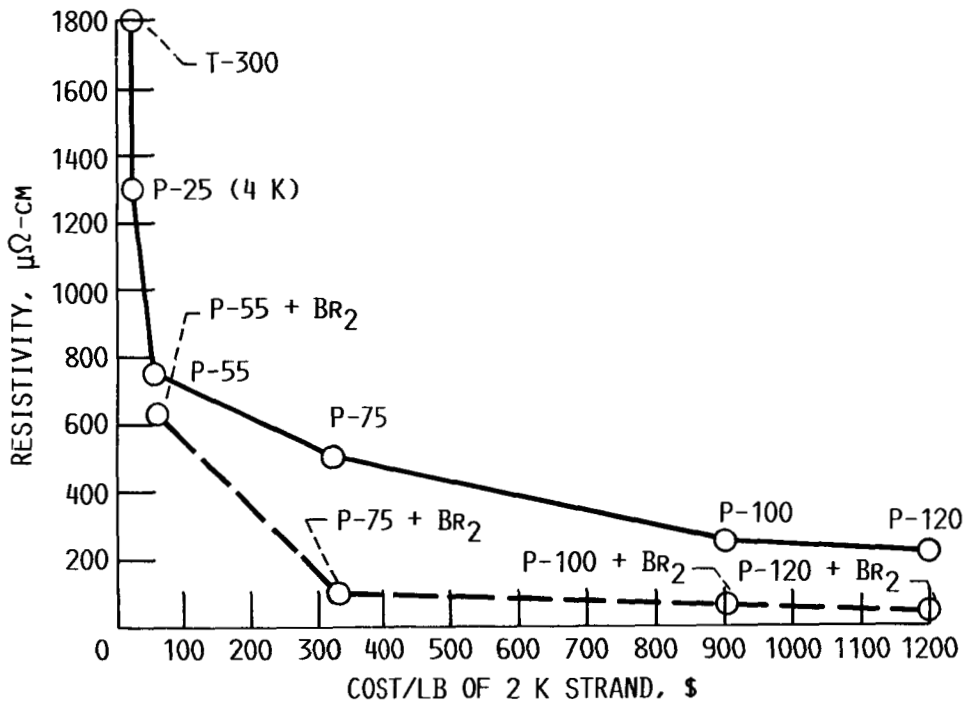

FIGURE 9. - RESISTIVITY OF SEVERAL GRADES OF PRISTINE AND BROMINATED CARBON AND GRAPHITE FIBERS AS A FUNCTION OF COST (1986).

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15. Supplementary Notes

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16. Abstract

The residual bromine graphite intercalation compounds of high modulus pitch-based fibers (Amoco P-55, P-75, P-100, and P-120) were formed and their resistances were monitored under a variety of environmental conditions. A threshold graphitization was observed below which the bromination reaction does not occur to an appreciable extent. The graphitization of the P-55 fibers falls below that threshold, precluding an extensive reaction. The P-75, P-100, and P-120 fibers all form bromination compounds which are stable at ambient conditions, under vacuum, and under high humidity (100 percent humidity at 60 °C). The thermal stability of the resistivity increased with decreasing graphitization, with the stable temperature for P-120 being 100 °C; for P-100, 200 °C; and for P-75, 250 °C. When cost is a consideration, bromination of pitch-based fibers is an economical way to achieve low resistivities.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
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