LA-4896-PR
A Progress Report
SPECIAL DISTRIBUTION
ISSUED: March 1972

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CMB-13 Research on Carbon and Graphite
Report No. 18
Summary of Progress from May 1 to July 31, 1971*

by

Morton C. Smith

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*Supported in part by the Office of Advanced Research and Technology of the National Aeronautics and Space Administration.

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I. INTRODUCTION

This is the eighteenth in a series of progress reports devoted to carbon and graphite research in LASL Group CMB-13, and summarizes work done during the months of May, June, and July, 1971. It should be understood that in such a progress report many of the data are preliminary, incomplete, and subject to correction, and many of the opinions and conclusions are tentative and subject to change. This report is intended only to provide up-to-date background information to those who are interested in the materials and programs described in it, and should not be quoted or used as a reference publicly or in print.

Research and development on carbon and graphite were undertaken by CMB-13 primarily to increase understanding of their properties and behavior as engineering materials, to improve the raw materials and processes used in their manufacture, and to learn how to produce them with consistent, predictable, useful combinations of properties. The approach taken is microstructural, based on study and characterization of natural, commercial, and experimental carbons and graphites by such techniques as x-ray diffraction, electron and optical microscopy, and porosimetry. Physical and mechanical properties are measured as functions of formulation, treatment, and environmental variables, and correlations are sought among properties and structures. Raw materials and manufacturing techniques are investigated, improved, and varied systematically in an effort to create specific internal structures believed to be responsible for desirable combinations of properties. Prompt feedback of information among these activities then makes possible progress in all of them toward their common goal of understanding and improving manufactured carbons and graphites.

Since its beginning, this research has been sponsored by the Division of Space Nuclear Systems of the United States Atomic Energy Commission, through the Space Nuclear Propulsion Office. More recently additional general support for it has been provided by the Office of Advanced Research and Technology of the National Aeronautics and Space Administration. Many of its facilities and services have been furnished by the Division of Military Application of AEC. The direct and indirect support and the guidance and encouragement of these agencies of the United States Government are gratefully acknowledged.

II. SANTA MARIA COKE

A. Previous Work

Santa Maria coke and the nearly isotropic graphites made from it have previously been discussed in Reports 9 through 17 in this series.

B. Santa Maria Fillers (H. D. Lewis)

Particle-size, surface-area, and helium-density measurements were completed on the four Santa Maria fillers listed in Table I, which are being used for the manufacture of molded graphites. Micromerograph particle-size data are plotted in Fig. 1, and have been corrected for material coarser than 50 mesh. As is

TABLE I

PARTICLE CHARACTERISTICS OF SANTA MARIA FILLERS

	Lot No.			
	G-36	G-37	G-38	G-39
Helium density, g/cm^3	1.934	2.191	2.196	2.134
Micromerograph sample statistics(a)				
$\bar{x}_3$	3.428	2.764	2.930	2.238
$s^2_{x_3}$	2.164	1.493	1.769	1.381
$\bar{x}$	-0.055	-0.061	-0.001	-0.017
s^2_x	0.225	0.281	0.271	0.240
$\bar{d}_3$, microns	70.124	28.031	37.189	16.756
$s^2_{d_3}$, (microns)^2	10,274	600.2	1571	264.7
$\bar{d}$, microns	1.103	1.135	1.196	1.153
s^2_d, (microns)^2	0.853	1.060	1.086	0.803
g_d	15.17	11.822	13.543	6.045
CV_d	0.837	0.906	0.871	0.778
S_W, m^2/g	0.3278	0.3774	0.3553	0.5737
BET Surface area				
S_W, m^2/g	15.53	7.55	8.38	38.28
d_s(b)	0.20	0.36	0.33	0.07
Fuzziness ratio, R_F(c)	47.37	20.00	23.59	66.72

(a) Internal model.

(b) $d_s = 6/\rho S_W$

(c) $R_F = S_W (\text{BET}) \div S_W (\text{Calc})$.

typical of Santa Maria fillers, these distributions tend to be bimodal and are poorly represented by the lognormal model.

Lot G-36 is a sample of Santa Maria LV coke received from the Y-12 Plant of Union Carbide Corporation and identified by them as Santa Maria "Blend 2" material. Although this was originally understood to be a graphitized filler, its high impurity content (e.g., 0.48% H_2O, 3.04% S) indicates that it is probably in its original, as-calcined, "LV" condition. This is also suggested by the relatively low particle density measured by helium pycnometry. Lot G-36 is a relatively coarse flour, containing 2.95 wt % of particles coarser than 297 μ (50 mesh), and a few particles as large as 750 μ. Its surface area is relatively large, probably because of surface-connected porosity in the coarser particles. This is reflected in a large "Fuzziness Ratio."

Lot G-39 is "low-fired" Santa Maria coke, also obtained from Y-12. Its impurity contents are much lower than those of Lot G-36, although still very appreciable (e.g., 0.10% H_2O, 0.27 % S), and it is a much finer flour. The very high "Fuzziness Ratio" of Lot G-39 may reflect poor resolution of a relatively large fraction of particles smaller than 1 μ.

TABLE II

COMPOSITIONS AND DENSITY DATA, HOT-MOLDED SANTA MARIA GRAPHITES

Specimen No.	Binder		Calculated Binder Optimum, pph	Binder Residue %		Density, g/cm^3				Dimensional Change, Baked to Graphitized, %		
						Packed Filler		Bulk				
	Type	Conc., pph		Baked	Graph.	Baked	Graph.	Baked	Graph.	Δl	Δd	Δv
72A-1	LAP(b)	26	---	---	---	---	---	1.724	1.685	+0.8	+0.2	+1.3
72B-1(a)	PR(c)	22	18.0	54.5	52.6	1.614	1.629	1.811	1.821	+0.1	-0.5	-0.9
72C-1	AB(d)	22	19.0	7.9	5.8	1.660	1.623	1.689	1.643	+1.5	+0.5	+2.3
63F-7	Varcum(e)	23	17.6	39.2	37.8	1.602	1.629	1.766	1.771	0.0	-0.3	-0.6
63H-8	Pitch(f)	27	20.4	43.8	42.0	1.622	1.607	1.813	1.790	+0.8	+0.03	+0.9

(a) Specimen developed one radial crack during molding.

(b) Levulinic acid polymer.

(c) Pot residue from the preparation of PFA Resin EMW 314, catalyzed with 2% maleic anhydride.

(d) Athabaska "Bottoms," a heavy residue from the Athabaska bitumen.

(e) Grade 8251, catalyzed with 2% maleic anhydride.

(f) Barrett grade 30MH.

Lots G-37 and G-38 are samples of Great Lakes 1078 graphite flour identified by them as "Run 1" and "Run 2," respectively. They were obtained through Westinghouse Astronuclear Laboratory, and are samples of Santa Maria LV coke purified and ground by Great Lakes Carbon Co. Both are relatively pure (e.g., 30-50 ppm H_2O, < 50 ppm S). The two lots are very similar in particle characteristics, and quite different from Lots G-36 and G-39. Lot G-38, the coarser of the two Great Lakes 1078 flours, contained 0.12 wt % of particles coarser than 297 μ (50 mesh).

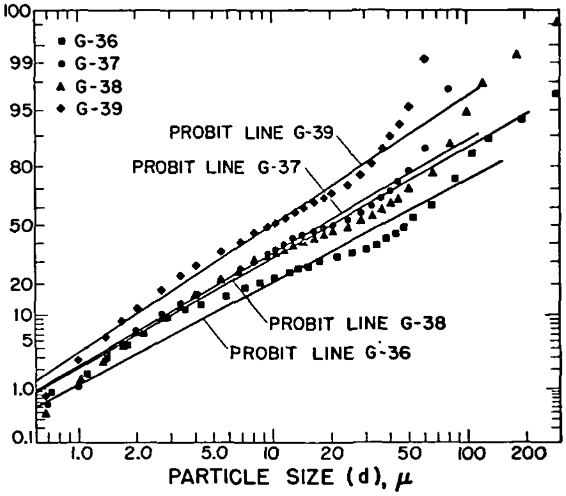

Fig. 1. Log-probability plots of Micromerograph particle-size data for four Santa Maria fillers.

C. Hot-Molded Graphites (R. J. Imprescia)

The five hot-molded graphites listed in Tables II and III were made from Lot G-26 Santa Maria graphite flour, the Y-12 "Blend 1" filler described in Report No. 16 in this series. Three different experimental binders were used to make the Series 72 graphites, and in the tables these graphites are compared with two Series 63 graphites which were made from the same filler using Varcum 8251 furfuryl alcohol resin and Barrett 30MH coal-tar pitch. With the exception of specimen 63F-7, which was molded using "Program B" (involving a lower heating rate), all graphites were made by "Program A," and all were graphitized to 2800°C in either flowing helium or flowing argon.

Of the three experimental binders, only the polyfurfuryl alcohol ("PFA") pot residue appears to merit further consideration. Specimen 72B-1 made from it contained one obvious radial crack after hot-molding, and had relatively high anisotropies of flexure strength and electrical resistivity, suggesting that it contained

TABLE III

PROPERTIES OF HOT-MOLDED SANTA MARIA GRAPHITES

SPECIMEN NO:	72 A-1	72 B-1	72 C-1	63 F-7	63 H-8
Binder Type (a)	LAP	PR	AB	Varcum	Pitch
Density, g/cm^3	1.685	1.821	1.643	1.771	1.790
Comp. Str., psi					
With-grain	4708	---	---	6829	9347
Across-grain	5956	---	---	8522	10,722
Flexure Str., psi					
With-grain	1517	2552	469	2622	3215
Across-grain	1016	751	306	1315	2572
CTE, x 10^{-6}/°C (b)					
With-grain	6.43	---	---	6.18	5.26
Across-grain	5.90	---	---	7.81	6.31
Resistivity, μ Ω cm					
With-grain	2005	1476	3135	1496	1548
Across-grain	2272	2120	---	1932	1707
Therm. Cond., W/cm°C					
With-grain	0.59	0.78	0.34	0.89	0.93
Across-grain	0.59	0.69	0.33	0.59	0.76
Young's Mod., 10^6 psi					
With-grain	0.86	---	---	1.33	1.12
Across-grain	0.66	---	---	0.73	0.93
Internal Friction (c)					
With-grain	---	---	---	8.4	---
Across-grain	---	---	---	7.7	---
Anisotropies					
BAF (d)	1.047	1.060	1.042	1.030	1.069
Compr. Str.	1.26	---	---	1.25	1.15
Flexure Str.	1.49	3.40	1.53	1.99	1.25
CTE	0.92	---	---	1.26	1.20
Resistivity	1.13	1.44	---	1.29	1.10
Therm. Cond.	1.00	1.13	1.03	1.51	1.22
Young's Mod.	1.30	---	---	1.82	1.21
Internal Friction	---	---	---	1.09	---

(a) See footnotes to Table II.

(b) Coefficient of Thermal Expansion, average, 25-645°C.

(c) Tan α x 10^3.

(d) Bacon Anisotropy Factor , σ_{oz}/σ_{ox}.

TABLE IV

HOT-MOLDED GRAPHITES MADE FROM NATURAL GRAPHITE FILLERS

Specimen No.	Mix Composition, parts by wt.					Fiber Condition[c]	Calc. Binder Optimum, pph	Binder Res. % Baked	Density, g/cm^3			Dimensional Change, Baked to Graphitized, %		
	Kynol	Rayon	Thermax	G-34[a]	Pitch[b]				Packed Filler Baked	Bulk Baked	Bulk Graph.	$\Delta \ell$	Δd	Δv
75B-1	0	0	0	100	14.0	---	10.0	42.3	1.939	2.054	1.903	+2.8	+0.3	+3.4
75H-1	4.2	0	26	74	15.6	as-rec	15.0	46.0	1.743	1.902	1.854	0	-0.4	-0.9
75D-5	0	0	25	75	14.6	---	14.9	70.0	1.746	1.917	1.855	+0.3	-0.3	-0.3
75C-1	4.2	0	0	100	14.6	as-rec	11.0	39.4	1.911	2.052	1.908	+2.4	+0.1	+2.6
75G-1	4.2	0	0	100	14.6	415°C	12.0	---	1.884	2.056	1.909	+3.1	+0.1	+3.4
75G-2	4.2	0	0	100	14.6	505°C	11.8	---	1.889	2.056	1.903	+3.1	+0.2	+3.6
75G-3	4.2	0	0	100	14.6	615°C	15.9	---	1.786	2.011	1.861	+2.8	+0.3	+3.3
75I-1	0	4.2	0	100	14.6	as-rec	10.8	39.9	1.917	2.060	1.902	+3.2	+0.2	+3.4
75I-2	0	4.2	0	100	14.6	300°C	15.5	---	1.795	2.020	1.875	+3.0	+0.1	+3.1
75I-3	0	4.2	0	100	14.6	400°C	13.8	---	1.837	2.066	1.904	+3.4	+0.1	+3.6
75I-4	0	4.2	0	100	14.6	500°C	17.5	---	1.747	2.000	1.860	+2.6	+0.1	+2.9
75I-5	0	4.2	0	100	14.6	600°C	14.9	---	1.808	2.020	1.876	+2.6	+0.2	+3.0

(a) Lot G-34 natural flake graphite.

(b) Barrett 30MH coal-tar pitch.

(c) Temperature of preliminary heat treatment of fiber.

numerous microcracks oriented in the with-grain direction. However, it had higher bulk density and carbon residue than either of the specimens made with standard binders, and its with-grain properties compared favorably with those of the Lot 63 graphites. If microcracking can be avoided, very good graphites can probably be made from this binder.

D. Ablation-Test Specimens

Santa Maria fillers were used in the manufacture of four of the graphites prepared for ablation-testing, discussed in Section IV of this report.

III. HIGHLY ORIENTED POLYCRYSTALLINE GRAPHITES

A. Previous Work

Highly anisotropic graphites made by intentionally producing a high degree of preferred orientation of filler particles have previously been discussed in Reports 7, 8, 10, 11, 12, 16 and 17 in this series.

B. Fiber and Carbon-Black Additions (R. J. Imprescia)

Manufacturing and properties data are summarized in Tables IV and V for three series of hot-molded graphites in which the principal filler material was a relatively coarse natural flake graphite (CMB-13 Lot G-34, described in Report No. 16). The first series, consisting of specimens 75B, 75C, 75D, and 75H, was made to investigate the effects of adding both Kynol phenolic fibers and Thermax carbon black to the same mix. The second series, specimens 75C and 75G, explored the effect of preheating the Kynol to pyrolyze it partially before it was added to the mix. The third series, specimens 75I, was similar to the second except that the fiber used was a chopped rayon flock, $5\,\mu$ dia and 0.1 in. long, obtained from J. M. Napier of the Y-12 Plant, Union Carbide Corporation. In all cases the binder was Barrett 30MH coal-tar pitch.

TABLE V

PROPERTIES OF HOT-MOLDED ANISOTROPIC GRAPHITES

	Kynol Fibers							Rayon Fibers				
SPECIMEN NO:	75B-1	75H-1	75D-5	75C-1	75G-1	75G-2	75G-3	75I-1	75I-2	75I-3	75I-4	75I-5
Fiber Condition	---	as-rec.	---	as-rec.	415°C	505°C	615°C	as-rec.	300°C	400°C	500°C	600°C
Density, g/cm^3	1.903	1.854	1.855	1.908	1.909	1.903	1.861	1.902	1.875	1.904	1.860	1.876
Flexure Str., psi												
With-grain	2044	2798	3143	3021	2413	2702	2393	2328	2622	3092	2259	2600
Across-grain	652 (a)	955	1118	678	703	701	691	655	692	843	677	746
Resistivity, $\mu\Omega$cm												
With-grain	631	711	743	447	484	451	487	443	457	434	478	469
Across-grain	1649	2928	2676	3561	2876	2729	3013	2807	3004	2720	3025	2719
Therm. Cond., W/cm°C												
With-grain	2.14	1.59	1.36	2.65	2.35	2.49	2.04	1.95	2.23	2.49	2.19	2.38
Across-grain	0.44	0.44	0.47	0.37	0.43	0.59	0.52	0.43	0.39	0.41	0.35	0.53
Anisotropies												
BAF (b)	2.78	2.39	2.10	3.57	3.85	3.58	3.26	3.30	3.54	3.68	3.47	3.21
M-Factor (c)	4.3	5.1	4.4	8.3	7.6	8.5	6.7	6.9	6.2	7.6	7.3	7.0
Flexure Str.	3.14	2.93	2.81	4.46	3.43	3.85	3.46	3.55	3.79	3.67	3.34	3.49
Resistivity	2.61	4.12	3.60	7.97	5.94	6.05	6.19	6.34	6.57	6.27	6.33	5.80
Therm. Cond.	4.86	3.64	2.89	7.16	5.52	4.24	3.94	4.56	5.78	6.11	6.27	4.51

(a) One test specimen only.

(b) Bacon Anisotropy Factor, σ_{oz}/σ_{ox}.

(c) Exponent of cosine in cosine function which best represents angular distribution of intensities of reflected x-rays.

Specimens 75B and 75D were prepared by standard solvent-blending and hot-chopping methods, molded using "Program A," and graphitized at approximately 2800°C in flowing helium. For all other specimens the same procedures were used except that the hot-chopping step was omitted in order to preserve the integrity of the fragile, heat-treated fibers.

On heating, the as-received Kynol and rayon fibers soften and flow under pressure, and typically have coking values of about 50%. Therefore, for the purpose of calculating binder residue, an as-received fiber was considered to be part of the binder, and the binder residues calculated in this way were relatively low. The heat-treated fibers used in other mixes were present in various conditions of carbonization, and could be considered neither binder nor filler; for these mixes, therefore, no binder-residue calculations were made. For specimen 75B, which contained no additive, binder residue was low. For specimen 75D, containing Thermax but no fiber, binder residue was anomalously high.

Packed filler densities and binder optima were calculated with the assumption that only the Lot G-34 natural graphite and the Thermax carbon black were filler materials. Where a fiber residue was also present, the calculated binder optimum listed in Table IV is probably higher than the correct value.

The data of Table V for specimens 75B-1 and 75C-1 indicate that the Kynol addition to a coarse natural graphite increased with-grain strength and thermal and electrical conductivity, with little effect on across-grain strength but with some reduction of across-grain conductivities. Comparison of specimens 75B-1 and 75D-5 indicates that the carbon-black addition interfered with filler-particle packing and reduced density, but significantly increased strength and electrical resistivity in both orientations. It reduced thermal conductivity considerably in the with-grain direction, but if anything increased it a little across-grain.

Specimen 75H-1 was made in an attempt to combine the effects of the Kynol and Thermax additions, and in particular to increase across-grain strength without sacrificing with-grain thermal conductivity. Comparison with the properties of specimen 75B-1 indicates that a significant strength increase was achieved, but still with considerable loss of with-grain thermal conductivity. However, the loss in conductivity was less than when Thermax was used alone (specimen 75D-5).

The effects of heat-treating the Kynol and rayon fibers before adding them to the mix are summarized in Figs. 2 and 3. Although density data for the rayon additions are erratic, the trend for both fibers is evidently a decrease in bulk density of the finished graphite as heat-treatment temperature of the fiber is increased. Flexure strengths and electrical resistivities are nearly the same for the two types of fibers, and are nearly independent of heat-treating temperature. Across-grain thermal conductivities are nearly constant, but with-grain thermal conductivity increases with heat-treatment temperature in the case of the rayon fiber and decreases for the Kynol. Anisotropies (Fig. 3) tend to decrease slightly with increasing heat-treatment temperature for the Kynol fiber, but are nearly independent of heat-treatment for the rayon.

For the production of fiber-reinforced, highly anisotropic graphites, there is evidently some advantage in heat-treating rayon fibers to a temperature in the vicinity of 400°C. However, green Kynol fibers have effects very similar to heat-treated rayon fibers, and heat-treating the Kynol fibers appears to reduce the properties of the finished graphite.

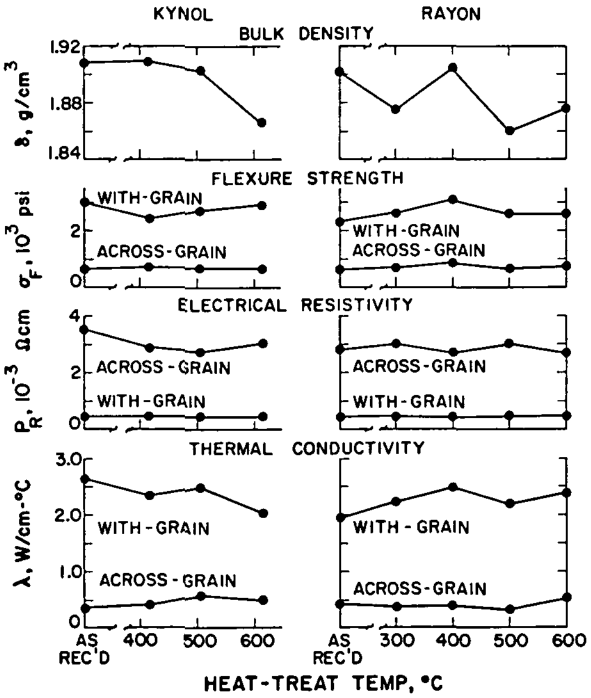

Fig. 2. Effects of prior heat-treatment of Kynol and rayon fibers on the properties of hot-molded anisotropic graphites containing fiber additions.

C. Needle-Coke Fillers (R. J. Imprescia)

The possibility of substituting finely ground needle coke for natural graphite in the manufacture of highly oriented graphites was discussed in Report No. 16 in this series. In preparation for experiments intended to explore this possibility, the fillers listed in Table VI were prepared from a commercial needle coke, CMB-13 Lot CNL-1, purchased from the Carbon Products Division of Union Carbide Corporation. Before grinding, the lump coke was graphitized to about 2510°C. In the preparation of filler GP-16, the graphitized lump coke was screened to separate material finer than 29/64 in. but coarser than 8 mesh. This sized material was ground by schedule S+T+I, involving two hammer-millings and one pass through a Trost fluid-energy mill. Filler GP-17 was

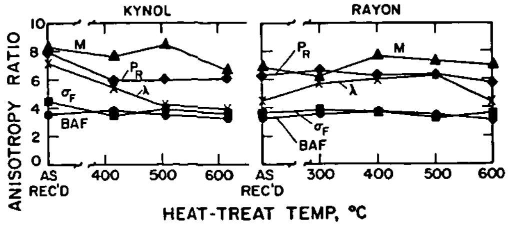

Fig. 3. Effects of prior heat-treatment of Kynol and rayon fibers on the anisotropies of hot-molded graphites containing fiber additions.

TABLE VI

SIEVE ANALYSES OF GROUND NEEDLE COKES

	Weight Percentage in Fraction					
	GP-16			GP-17		
Sieve Fraction	Schedule S	Schedule S+ T	Schedule S+ T+ I	Schedule S	Schedule S+ T	Schedule S+ T+ L
+ 16	5.0	0	0	2.5	0	0
-16 + 25	10.0	0.5	0	9.0	0.5	0
-25 + 45	32.5	12.0	trace	30.0	11.5	0.5
-45 + 80	18.0	26.0	0.5	30.5	31.5	1.0
-80 + 170	22.0	34.0	1.0	19.5	37.5	1.5
-170 + 325	10.0	17.5	2.5	5.5	12.5	7.5
-325	2.5	10.0	96.0	3.0	7.0	89.5

Grinding Conditions:

Schedule S --- Williams laboratory hammer mill, 1/8-in. hole, perforated-discharge screen, feed rate 90 g/min.

Schedule T --- Weber hammer mill, 0.040-in. hole, perforated-discharge screen, feed rate 30 g/min.

Schedule I --- Trost fluid energy mill, jet pressures (psi): feed/opposite = 100/100, feed rate 15 g/min.

Schedule L --- Trost fluid energy mill, jet pressures (psi): feed/opposite = 100/80, feed rate 15 g/min.

made from the unscreened lump material, and was ground by schedule S+ T+ L. This is very similar to the S+ T+ I schedule, differing only in the final fluid-energy milling conditions. In the "I" procedure used for Lot GP-16 the two opposing jets of the Trost mill were both maintained at 100 psi; in the "L" procedure used for Lot GP-17, the jet on the feed side was kept at 100 psi but the opposite jet was decreased to 80 psi. For both lots, screen analyses were very similar after two hammer millings ("Schedule S+ T"). However, the reduction in pressure of the opposing jet significantly reduced the proportion of -325 mesh fines produced in Trost milling, so that filler GP-17 is somewhat coarser than GP-16. Other particle characteristics of Lot GP-17 are discussed in Section V of this report.

Lot GP-16 was used as the principal filler to manufacture the graphites listed in Tables VII and VIII. The binder was Barrett 30 MH coal-tar pitch, and standard manufacturing procedures were used except that hot-chopping was omitted from the mixing process. In calculating binder residues, Kynol fiber was considered to be binder. The calculated binder optima are probably high in the case of graphites containing Kynol, since the calculation is based on packed filler density and does not account for space occupied by the Kynol residue.

In the 75J series of specimens, Kynol additions of 0, 1, 2, and 4.2 parts per hundred parts of needle-coke filler were made to the raw mix. (Larger Kynol additions, 10 pph or more, caused the dies to rupture during hot molding.) The effects of the additions are summarized in Fig. 4. The trend of bulk density with Kynol content was not consistent, and thermal conductivity, across-grain flexure strength, and with-grain electrical resistivity were little affected by it. However, both with-grain flexure strength and across-grain electrical resistivity increased with Kynol concentration. Anisotropies were not as high as when natural-graphite fillers were used, but were higher than those of most commercial graphites and increased slightly with Kynol content.

The 75K series of graphites was made to explore the effects of adding fine natural graphite (CMB-13 Lot G-21) to a needle-coke graphite containing a constant proportion (4.2 pph) of Kynol fiber. As is illustrated by Fig. 5, the effects were relatively small and somewhat inconsistent. However, flexure strength decreased in both with-grain and across-grain orientations as natural-graphite concentration increased. There is no evident advantage in adding natural graphite to the Kynol-reinforced needle-coke graphite except perhaps for increases in density and with-grain thermal conductivity when the additions are small.

D. Ablation-Test Specimens

Highly oriented graphites were also included in the group of materials prepared for ablation-testing, discussing in the next section of this report.

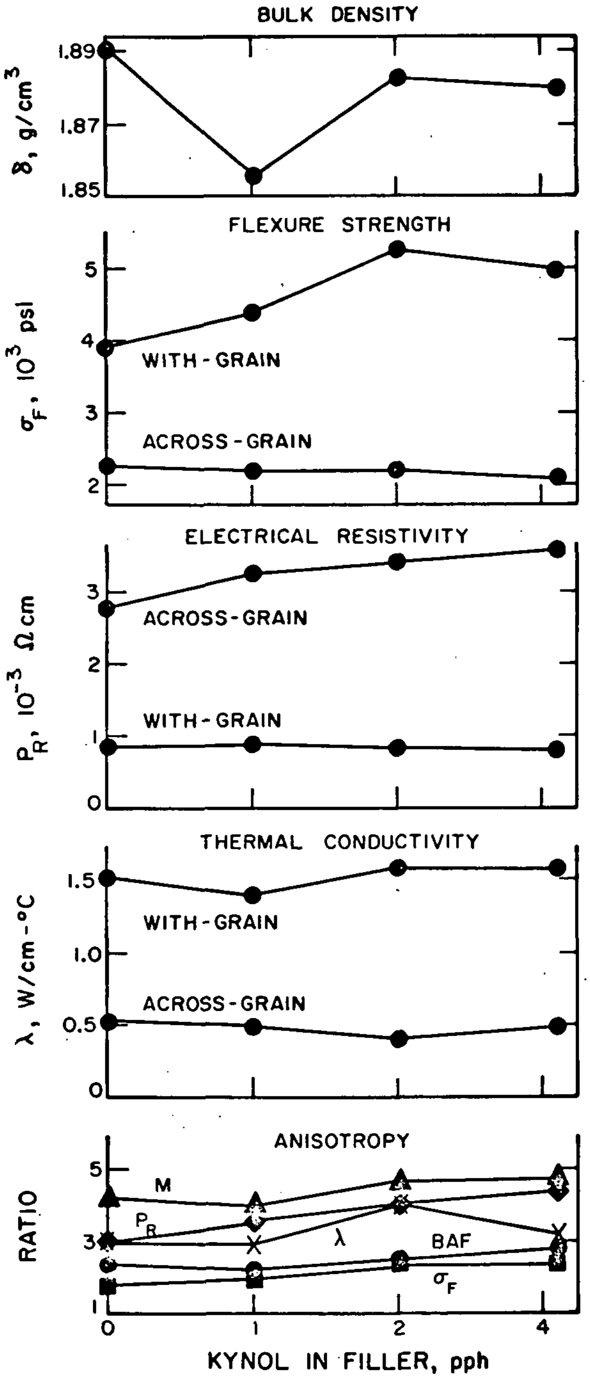

Fig. 4. Effects of Kynol additions on the properties of anisotropic graphites made from a needle-coke filler.

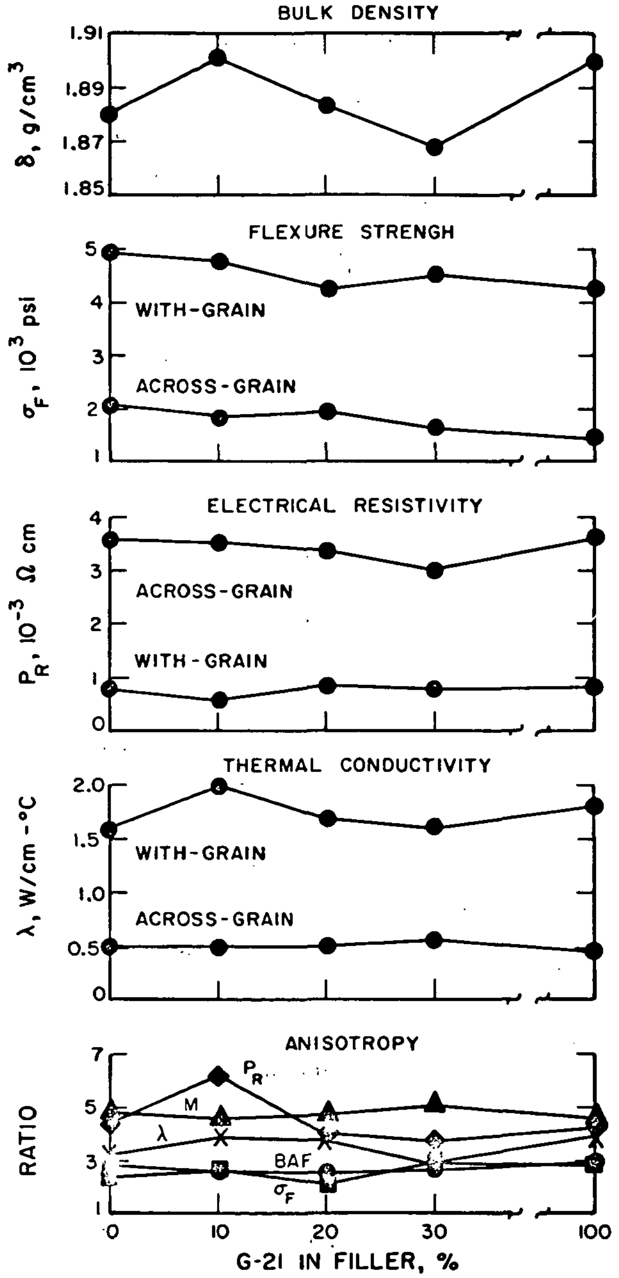

Fig. 5. Effects of natural-graphite additions on the properties of a needle-coke graphite containing 4.2 pph of Kynol fiber.

TABLE VII

HOT-MOLDED GRAPHITES MADE FROM NEEDLE-COKE FILLER GP-16

Specimen No.	Mix Composition, parts by wt.				Calc. Binder Optimum, pph	Binder Residue(c) %		Density, g/cm^3				Dimensional Change, Baked to Graphitized, %		
								Packed Filler		Bulk				
	GP-16(a)	G-21(b)	Kynol	Pitch		Baked	Graph.	Baked	Graph.	Baked	Graph.	$\Delta \ell$	Δd	Δv
75J-1	100	0	0	21.0	19.0	65.3	63.2	1.673	1.669	1.903	1.891	+0.1	+0.1	+0.3
75J-2	100	0	1	21.2	19.4	63.3	61.3	1.665	1.659	1.899	1.885	+0.4	0	+0.4
75J-3	100	0	2	21.4	18.9	55.6	53.7	1.675	1.672	1.894	1.883	+0.1	+0.0	+0.4
75J-4	100	0	4.2	21.9	21.6	65.4	62.7	1.620	1.616	1.893	1.880	+0.2	+0.1	+0.3
75K-1	90	10	4.2	22.0	20.4	63.6	60.4	1.650	1.641	1.925	1.901	+0.5	+0.0	+0.5
75K-2	80	20	4.2	21.0	20.8	62.8	58.2	1.643	1.634	1.913	1.883	+0.5	+0.0	+0.6
75K-3	70	30	4.2	20.0	20.6	65.4	59.0	1.651	1.635	1.912	1.868	+0.8	+0.1	+1.0
75A-5	0	100	4.2	18.8	18.3	68.4	53.1	1.729	1.697	1.999	1.904	+1.9	-0.0	+1.8

(a) Graphitized needle-coke flour.

(b) Fine natural flake graphite.

(c) Includes Kynol residue.

IV. MATERIALS FOR ABLATION-TESTING

A. General

Manufactured polycrystalline graphites have been shown to have important advantages over other refractory engineering materials in resistance to mass loss, surface recession, and aerodynamic shape change during atmospheric entry under severe conditions of velocity, temperature, and pressure. However, different types and grades of graphite are known to vary widely in ablation behavior, and large variations are often observed among different billets of the same grade or different pieces from the same billet. The reasons for these differences are not usually obvious, and are not generally understood.

The factors which control the ablation behavior of graphite are now being investigated actively by a large number of organizations and agencies. In general, however, these investigations -- no matter how intelligently conceived and carefully executed -- are fatally handicapped by lack of information concerning the materials being investigated, and by the unavailability of series of samples which represent systematic variations of one or a few parameters. There are several interrelated reasons why this general situation exists, and why it cannot be expected to change.

All true graphites are nearly pure crystalline carbon, representing one component and one phase. The broad range of properties observed among different graphites therefore cannot be explained by differences in composition or crystallographic nature, and must be explained by differences in internal structure. The structure of a graphite is established during its manufacture, by the individual characteristics and the interactions among the raw materials and manufacturing procedures used. It is a tradition of the graphite industry that information concerning these manufacturing variables is proprietary. Typically, an investigator outside of the industry works with materials which are identified to him only by grade designations, and he has no detailed information on how they were made, or from what. Even if he has the capability of observing the internal structures that control properties, he has no basis for understanding how the structures originate, for identifying or evaluating the parameters that affect them, for estimating the degrees of flexibility and control possible with regard to such parameters, or for discovering the degree to which the

TABLE VIII

PROPERTIES OF ANISOTROPIC GRAPHITES MADE FROM NEEDLE COKE

SPECIMEN NO:	75 J-1	75 J-2	75 J-3	75 J-4	75 K-1	75 K-2	75 K-3	75 A-5
Kynol Conc., pph	0	1	2	4.2	4.2	4.2	4.2	4.2
G-21 Conc., % of filler	0	0	0	0	10	20	30	100
Density, g/cm^3	1.891	1.855	1.883	1.880	1.901	1.883	1.868	1.904
Flexure Str., psi								
With-grain	3930	4399	5280	4951	4771	4267	4567	4309
Across-grain	2238	2190	2204	2102	1845	1955	1697	1484
Resistivity, $\mu\Omega$ cm								
With-grain	871	900	845	823	570	845	795	854
Across-grain	2791	3285	3424	3582	3535	3397	3010	3624
Therm. Cond., W/cm°C								
With-grain	1.53	1.41	1.60	1.59	1.95	1.68	1.61	1.82
Across-grain	0.52	0.48	0.40	0.48	0.49	0.49	0.54	0.45
Anisotropies								
BAF(a)	2.35	2.26	2.59	2.84	2.56	2.52	2.65	2.95
M-Factor(b)	4.2	4.0	4.7	4.8	4.6	4.7	5.0	4.6
Flexure Str.	1.76	2.01	2.40	2.36	2.59	2.18	2.69	2.90
Resistivity	3.02	3.65	4.05	4.35	6.20	4.02	3.79	4.24
Therm. Cond.	2.97	2.91	4.01	3.30	3.97	3.83	3.00	4.04

(a) Bacon Anisotropy Factor, σ_{oz}/σ_{ox}.

(b) Exponent of cosine in cosine function which best represents angular distribution of intensities of reflected x-rays.

controllable variables are in fact being exercised by the graphite manufacturer. In general, except for properties measurements which he makes himself, the investigator of graphites works in a vacuum. He can only buy various commercial grades of graphite, determine their properties and variability, and then buy other grades. This cannot result in a systematic or highly productive investigation of their behavior.

Any change in raw materials or manufacturing procedures results in a change in internal structure of the finished graphite. Any change in structure results in changes in properties, and affects different properties in different ways and to different degrees. Thus an increase in thermal conductivity might result from a change in type or particle-size distribution of the filler, a change in kind or concentration of binder, a change in the proportion of carbon black present, improved mixing or mix-conditioning, an increase in forming pressure, baking more slowly or under pressure, graphitizing to a higher temperature, or impregnating. Any of these production changes would probably also alter such other properties as Young's modulus, ultimate strength, strain to fracture, and thermal-expansion coefficient, each to a different degree. Straightforward correlations of ablation behavior with individual properties are generally impossible for commercial graphites, because so many properties change at once. Confusing incidental correlations occasionally appear: for example, a strong positive correlation between electrical conductivity and ablation resistance, which results from the fact that several structural factors which increase conductivity also interact, in different ways, to improve ablation behavior.

To identify and learn to control the structural factors that can improve ablation behavior will require systematic long-range programs involving the controlled variation of manufacturing parameters, characterization of the resulting structures, measurements a variety of properties, investigations of ablation behavior, and development of firm correlations among all of these variables and observations. Such programs require several iterations, and are very expensive in time, manpower, equipment, and money. The graphite industry cannot be expected to support or pursue them independently. It is a highly competitive industry, which survives on large volume and low unit cost. It cannot justify a large budget for development of special materials whose potential market is measured in pounds rather than tons, even if the final price per pound is high. Support for the development of improved ablators has been provided to the graphite industry intermittently by various government agencies, but in general on a short-term basis which has not permitted them to pursue the more productive long-range approaches that the ablation problem requires. There is no evidence that this general situation will change.

Over a period of several years, CMB-13 has developed some of the expertise that has normally existed only within commercial graphite companies, and has learned to synthesize and characterize raw materials, to adjust and control manufacturing procedures, and to produce a wide variety of high-quality graphites consistently and reproducibly. Some of these graphites have been developed through several generations to emphasize certain properties which are believed to be desirable for ablation resistance, such as high density, low connected porosity, high thermal conductivity, fine grain size, and the extremes either of isotropy or controlled anisotropy.

Recently a cooperative program has been undertaken with the NASA Ames Research Center in which well-characterized graphites manufactured by CMB-13 will be tested in the NASA-Ames ablation-testing facility, and the results of these tests will guide the development of improved second-generation materials by CMB-13. It is expected that, with a few iterations of this cycle, a considerable body of information will be collected with regard to the structures and properties which improve ablation behavior, and the raw materials and manufacturing procedures which are responsible for them. The details and progress of the program will be described in this series of reports, and also in NASA-Ames and other publications, and so will be available to other interested producers and users of graphite. It is hoped that this cooperative, NASA-supported effort will contribute to the development of significantly improved ablation-resistant graphites.

TABLE IX

MIX COMPOSITIONS FOR ABLATION-TEST SPECIMENS

Mix Code	Original Lot No.	Composition, parts by weight
A	75B-5	100 G-34, 4.2 Kynol, 14.6 PP-4
B	75A-5	100 G-21, 4.2 Kynol, 18.7 PP-4
C	75D-5	75 G-34, 25 TP-4, 14.0 PP-4
D	59K-5	85 G-21, 15 TP-4, 22.0 PP-4
E	75H-1	74 G-34, 26 TP-4, 4.2 Kynol, 15.6 PP-4
F	69D	100 CNL-1(1190), 32 PP-4
G	69I	100 CNL-1(2420), 21 PP-4
H	75K-1	90 GP-16, 10 G-21, 4.2 Kynol, 22 PP-4
I	77J	85 G-26, 15 TP-4, 25 EMW-321
J	65B-1	100 CP-17, 30 PP-4
K	73C	100 C-15(1090), 26 PP-4
L	73F	100 C-15(2170), 24 PP-4

G-34 --- Coarse natural-graphite filler.

G-21 --- Fine natural-graphite filler.

CNL-1(1190) --- Needle-coke filler heat-treated to approximately 1190°C.

CNL-1(2420) --- Needle-coke filler heat-treated to approximately 2420°C.

GP-16 --- Needle-coke filler heat-treated to approximately 2520°C.

G-26 --- Santa Maria coke heat-treated to approximately 2500°C.

CP-17 --- Santa Maria coke heat-treated to approximately 1090°C.

C-15(1090) --- Santa Maria coke heat-treated to approximately 1090°C.

C-15(2170) --- Santa Maria coke heat-treated to approximately 2170°C.

TP-4 --- Thermax carbon black.

Kynol --- Phenolic fibers.

PP-4 --- Coal tar pitch, Barrett grade 30MH.

EMW-321 --- Experimental furfuryl alcohol resin.

TABLE X

ABLATION TEST SPECIMENS: DENSITIES AND TYPICAL PROPERTIES

							Typical Properties[a]										
							Flexure Str. psi			Elect. Resist. μΩ cm			Therm. Cond. W/cm-°C			Crystalline Anisotropy	
Specimen No.	No. of Spec.	Mix Code	Filler Type[b]	Spec. Prep.[c]	Spec. Orien.[d]	Spec. Dens. g/cm^3	WG	AG	Ratio	WG	AG	Ratio	WG	AG	Ratio	BAF[e]	M[f]
77A-5	1	A	Nat.	MTS	AG	1.930	2678	673	3.98	492	3702	7.52	2.50	0.37	6.76	3.64	7.3
77A-7	1	A	Nat.	MTS	AG	1.915	2678	673	3.98	492	3702	7.52	2.50	0.37	6.76	3.64	7.3
77B-1	1	B	Nat.	MTS	AG	1.817	4309	1484	2.90	854	3624	4.24	1.82	0.45	4.04	2.95	4.6
77B-4	1	B	Nat.	MTS	AG	1.887	4309	1484	2.90	854	3624	4.24	1.82	0.45	4.04	2.95	4.6
75A-5B	2	B	Nat.	MB	AG	1.908	4309	1484	2.90	854	3624	4.24	1.82	0.45	4.04	2.95	4.6
77C-1	1	C	Nat.	MTS	AG	1.865	3143	1118	2.81	743	2676	3.60	1.36	0.47	2.89	2.10	4.4
77C-3	1	C	Nat.	MTS	AG	1.870	3143	1118	2.81	743	2676	3.60	1.36	0.47	2.89	2.10	4.4
75D-5B	2	C	Nat.	MB	AG	1.854	3143	1118	2.81	743	2676	3.60	1.36	0.47	2.89	2.10	4.4
77D-1	1	D	Nat.	MTS	AG	1.850	5140	1986	2.61	901	3470	3.85	1.50	0.43	3.49	2.78	5.3
77D-2	1	D	Nat.	MTS	AG	1.788	5140	1986	2.61	901	3470	3.85	1.50	0.43	3.49	2.78	5.3
59K-5	2	D	Nat.	MB	AG	1.819	5140	1986	2.61	901	3470	3.85	1.50	0.43	3.49	2.78	5.3
59K-5	2	D	Nat.	MB	WG	1.819	5140	1986	2.61	901	3470	3.85	1.50	0.43	3.49	2.78	5.3
77E-1	1	E	Nat.	MTS	AG	1.840	2798	955	2.93	711	2928	4.12	1.59	0.44	3.64	2.39	5.1
77E-3	1	E	Nat.	MTS	AG	1.866	2798	955	2.93	711	2928	4.12	1.59	0.44	3.64	2.39	5.1
75H-1B	2	E	Nat.	MB	AG	1.834	2798	955	2.93	711	2928	4.12	1.59	0.44	3.64	2.39	5.1
77F-2	1	F	NC	MTS	AG	1.752	4248	2472	1.72	1081	2449	2.27	1.19	0.59	2.01	1.805	2.64
77F-3	1	F	NC	MTS	AG	1.845	4248	2472	1.72	1081	2449	2.27	1.19	0.59	2.01	1.805	2.64
77G-1	1	G	NC	MTS	AG	1.904	6007	3038	1.98	834	3109	3.73	1.71	0.52	3.29	2.327	3.37
77G-3	1	G	NC	MTS	AG	1.915	6007	3038	1.98	834	3109	3.73	1.71	0.52	3.29	2.327	3.37
77L-1	1	H	NC	MTS	AG	1.883	4771	1845	2.59	570	3535	6.20	1.95	0.49	3.97	2.56	4.6
77L-2	1	H	NC	MTS	AG	1.923	4771	1845	2.59	570	3535	6.20	1.95	0.49	3.97	2.56	4.6
75K-1B	2	H	NC	MB	AG	1.890	4771	1845	2.59	570	3535	6.20	1.95	0.49	3.97	2.56	4.6
75K-1B	2	H	NC	MB	WG	1.890	4771	1845	2.59	570	3535	6.20	1.95	0.49	3.97	2.56	4.6
77J-1	1	I	Iso.	E	WG	1.896	---	---	---	1368	1884	1.38	0.91	0.62	1.47	1.382	0.48
77J-4	1	I	Iso.	E	WG	1.886	---	---	---	1368	1884	1.38	0.91	0.62	1.47	1.382	0.48
65B-1B	2	J	Iso.	MB	AG	1.755	5326	5302	1.00	1184	1221	1.03	1.12	0.96	1.17	1.027	0.18
73C-2	2	K	Iso.	MB	AG	1.765	6129	6391	0.96	1418	1564	1.10	0.94	0.90	1.04	1.049	0.25
73F-2	2	L	Iso.	MB	AG	1.799	4739	3966	1.23	1394	1542	1.11	0.91	0.86	1.06	1.050	0.23

(a) Based on tests from similar materials with identical mix compositions.

(b) Nat. = Natural graphite, NC = Needle coke, Iso. = Isotropic coke.

(c) MTS = molded to shape, finish-machined. MB = machined from molded billet. E = machined from extruded rod.

(d) Orientation of the cylindrical axis of the specimen with respect to the "grain." WG = With-grain, AG = Across-grain.

(e) Bacon Anisotropy factor.

(f) Exponent of cosine in cosine function which best represents angular distribution of intensities of reflected x-rays.

B. Initial Ablation-Test Specimens (R. J. Imprescia)

Thirty eight graphite ablation-test models, in the form of cylinders 0.60 in. dia and 1.25 in. long with a nose radius of 1.15 in. at one end, have been prepared and sent to NASA-Ames for ablation testing. These represent duplicate samples of each of seventeen CMB-13 state-of-the-art graphites, and include both with-grain and across-grain samples of two of the highly oriented types. The individual samples and their compositions, principal manufacturing conditions, and properties are listed in Tables IX and X.

The compositions of the mixes used to manufacture these graphites are listed in Table IX, together with code letters by which the individual mixes are identified in Table X. Most of these mixtures have also been used previously to make graphites whose properties have been listed in earlier reports in this series. Therefore the original lot number of each mix is also given in Table IX.

The four filler materials included in these mixes are: (1) A needle coke, Lot CNL-1, purchased from Carbon Products Division of Union Carbide Corporation, and heat-treated by CMB-13 to three different temperatures: 1190, 2420, and 2520°C. (2) Santa Maria isotropic coke, purchased from Collier Carbon and Chemical Co. and heat-treated by CMB-13 to three different temperatures: 1090, 2170, and 2500°C. (3) A relatively coarse natural graphite, Lot G-34, purchased from Southwestern Graphite Co. (4) A fine natural graphite, Lot G-21, from the same producer.

Two binders were used: Barrett coal-tar pitch, grade 30MH, and EMW-321, an experimental furfuryl alcohol resin synthesized by CMB-13.

Two additions were made to several of the graphites: Kynol phenolic fiber, and Thermax carbon black.

Sixteen of the anisotropic specimens were molded to essentially the model shape, in order to cause the preferred orientation of the filler particles to follow the contour of the nose radius, and then were machined to the final model dimensions. The molding was done in graphite dies which were heated at 50°C/hr to 900°C, with constant pressure on the specimen of 6000 psi. Twenty specimens were machined from larger, cylindrical billets, which were molded similarly to the model shapes except that the nose shape was not reproduced and the lower pressure of 4000 psi was maintained. From two of these billets, duplicate samples were machined in both the with-grain and the across-grain orientations. Two specimens were machined from extruded rods which were made with the experimental resin binder, extruded by standard methods, cured in air at 2.5°C/hr to 230°C, and baked in vacuum at heating rates of 2.5°C/hr to 450°C and then 25°C/hr to 900°C. All specimens were graphitized in flowing helium to 2800°C. None was impregnated or subjected to any other special treatment.

Table X identifies the individual specimens and lists their measured bulk densities. Typical properties are given from tests on similar materials previously made from identical mix compositions, which have been discussed in previous reports.

C. NASA-Langley Ablation Samples (R. D. Reiswig, L. S. Levinson)

In ablation tests made at the NASA Langley Research Center, it has been observed that the ablated surface of a glass-like carbon is sometimes very smooth and reflective, with a wave-like pattern of concentric rings that suggests melting and flow. Through Dr. H. G. Maahs of NASA-Langley, a series of tested glass-like carbon ablation models was obtained, some of which showed this unusual surface pattern while others did not. Three of these models were sectioned and examined by optical and electron microscopy. Two of them, a Beckwith Vitreous Carbon sample and a Lockheed glassy carbon sample, had the "melted" appearance on the ablated surface described above. The third was a Beckwith sample that, instead of maintaining a smooth surface, had developed deep oxidation pits.

Previous microscopic studies made here of carbons known to have melted and refrozen have indicated that, during freezing, the carbon forms easily identifiable dendrites of very well-crystallized graphite. Noda and Inagaki (quoted in DCIC Report 68-2, "A Review of Glass-like Carbons") report that apparent melting of glassy carbon produced a structure whose x-ray parameters were exactly those of natural graphite. This is the type of material observed microscopically in melted carbon examined here, and it is easy to identify by its optical anisotropy and lamellar microstructure. It was therefore expected that, if melting of the ablating surface had occurred, it could be detected microscopically.

Examination of the NASA-Langley specimens indicated that the glass-like carbon structure had not been significantly altered at any point in the sections examined. No graphitic material could be found even at very high magnification and very close to the smoothly ablated surfaces, in the rings of the surface structure or elsewhere. It is felt that, if melting had occurred, positive evidence of it would have been found in at least a thin surface layer. In the absence of such evidence it was concluded that melting had not occurred, and that the unusual appearance of some of the tested glass-like

TABLE XI

PARTICLE CHARACTERISTICS OF POCO FILLERS

	Sample	
	CMB-6 (Calcined)	PXB-5Q1S (Graphitized)
Helium density, g/cm^3	1.928	2.215
Micromerograph sample statistics(a)		
$\bar{x}_3$	2.683	2.467
$s^2_{x_3}$	1.362	1.235
$\bar{x}$	-0.067	0.033
s^2_x	0.220	0.220
$\bar{d}_3$, microns	24.26	19.40
$s^2_{d_3}$, (microns)^2	384.6	287.6
$\bar{d}$, microns	1.09	1.21
s^2_d, (microns)^2	0.90	1.04
g_d	10.1	9.91
CV_d	0.87	0.84
S_W, m^2/g	0.4521	0.4355
BET surface area		
S_W, m^2/g	21.92	5.50
d_s(b)	0.14	0.49
Fuzziness ratio, R_F(c)	48.48	12.63

(a) Interval model.

(b) $d_s = 6/\rho S_W$.

(c) $R_F = S_W\ (\text{BET}) \div S_W(\text{Calc.})$.

carbon models is the result of a remarkably uniform removal of carbon by normal ablation processes.

V. RAW MATERIALS

A. POCO Fillers

Two filler flours produced by POCO Graphite, Inc., have been examined. The first of these, identified as POCO TD PXB-5Q1S, is a sample of graphite flour sent by a POCO representative to P. E. Armstrong, CMB-13. The second, a coke flour which has been calcined at about 1100°C, was obtained from LASL Group CMB-6.

Both fillers consisted principally of substantially equiaxed particles with the fine, randomly oriented domain structure that is typical of POCO graphites. However, a better development of this structure by ion-bombardment etching reflected the higher heat-treating temperature to which the graphitized specimen had been subjected. This was also indicated by the crystalline parameters determined by x-ray diffraction, which were $L_c = 17.4$ Å and $d_{002} = 3.44$ Å for the CMB-6 sample and $L_c = 365$ Å, $d_{002} = 3.365$ Å for the graphitized material. Helium density of the calcined CMB-6 sample was 1.928 g/cm^3; that of the graphitized PXB-5Q1S sample was 2.215 g/cm^3.

Particle-size and surface-area data are summarized in Table XI, and Micromerograph particle-size data are plotted in Fig. 6. The two materials are very similar in particle-size distribution, and neither is well represented by the lognormal model. They differ widely in measured (BET) surface area, S_W, as would be expected from their heat-treatment history. The calcined CMB-6 sample was very difficult to outgas in preparation for the BET measurement, suggesting a relatively high content of residual volatile material.

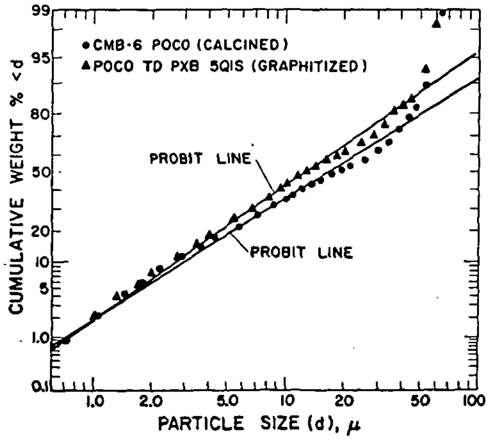

Fig. 6. Log-probability plots of Micromerograph particle-size data for two POCC fillers.

TABLE XII
PARTICLE CHARACTERISTICS
OF GRAPHITIZED NEEDLE-COKE FILLER, LOT GP-17

Helium density = $2.207\ \mathrm{g/cm^3}$

Micromerograph sample statistics:

Interval Model	Lognormal Model
$\bar{x}_3 = 2.533$	$\hat{\mu}_{x_3} = 2.55$
$s^2_{x_3} = 0.775$	$\hat{\sigma}^2_{x_3} = 0.808$
$\bar{x} = 0.193$	------
$s^2_x = 0.373$	------
$\bar{d}_3 = 17.717$ microns	$\hat{\mu}_{d_3} = 19.21$
$s^2_{d_3} = 206.5\ (\mathrm{microns})^2$	------
$\bar{d} = 1.558$ microns	$\hat{\mu}_d = 1.70$
$s^2_d = 2.598\ (\mathrm{microns})^2$	$\hat{\sigma}^2_d = 3.60$
$g_d = 25.487$	------
$CV_d = 1.035$	$CV_d = 1.12$
$S_W = 0.3276\ \mathrm{m^2/g}$	$S_W = 0.3170$

BET surface area: $S_W = 8.26\ \mathrm{m^2/g}$

$d_s{}^{(a)} = 0.33$

$R_F{}^{(b)} = 25.22$

(a) $d_s = 6/\rho S_W$.

(b) R_F = Fuzziness Ratio = $S_W(\mathrm{BET}) \div S_W$(Calc, Interval Model).

B. Mesophase Fillers (L. S. Levinson, R. D. Reiswig)

Samples of four particulate mesophase materials produced by Great Lakes Research Corporation were received from Westinghouse Astronuclear Laboratory, and have been examined by optical and electron microscopy.

A sample of "Low-Fired Coal-Tar Pitch Mesophase," which had been calcined at about 1000°C, consisted of solid-appearing, generally equiaxed particles, whose internal structures had not developed sufficiently to be clearly revealed by ion-bombardment etching. In an accompanying sample of "High-Fired Coal-Tar Pitch Mesophase," which had been graphitized to 2700°C, many of the particles contained fine carbon black, which had blocked the growth of lamellae. In black-free areas lamellar structures were well developed, and the optical domains were elongated and relatively large. Particularly in the finer sizes, particles which did not contain carbon black therefore tended to be acicular and to consist of a single domain or a few preferentially aligned domains. These particles would be expected to assume a preferred orientation during forming, which would also represent a preferred alignment of domains and would therefore produce some degree of anisotropy in a finished body. However, the larger proportion of particles contained carbon black and were blocky and substantially equiaxed, so that the degree of anisotropy would probably not be high.

A "High-Fired PR Resin," graphitized to 2700°C, contained Thermax carbon black, which was added intentionally to interfere with coalescence of mesophase particles and restrict development of lamellar structures. Where it was present it had done so, and the mesophase product ground to substantially equiaxed particles. However, the Thermax was not uniformly distributed, and where it was absent large, highly lamellar domains had formed. This fraction of the material ground to acicular, anisotropic particles, which would be expected to produce some degree of anisotropy in a graphite in which this material was the filler.

A "High-Fired PRR Resin" sample, graphitized to 2700°C, contained no carbon black and had a well-developed lamellar structure and a large optical domain size. Locally the lamellar pattern was contorted, and some relatively large particles with this type of structure were nearly equiaxed. However, most of the particles, in all sizes, had nearly planar structures, were acicular in shape, and often consisted of single domains. This filler would probably produce highly anisotropic graphites.

C. Needle-Coke Filler (H. D. Lewis)

The preparation of filler lot GP-17 is discussed above in connection with the manufacture of highly oriented graphites from needle-coke fillers, and its sieve analysis is given in Table VI. It was prepared by grinding a

TABLE XIII

CARBON YIELDS

OF EXPERIMENTAL FURFURYL ALCOHOL RESINS

Resin	Catalyst	Residue After 220°C, %	Carbon Yield After 2800°C, %
QX-261	MA[(a)]	86.9	48.8
QX-262	MA	63.6	42.4
QX-263	MA	86.3	51.0
QX-265	MA	85.2	48.3
EMW 302	MA	80.2	47.4
QX-261	QX 260	82.0	37.1
QX-262	QX 260	50.1	26.5
QX-263	QX 260	78.7	50.8
QX-265	QX-260	81.7	31.5
EMW 302	QX 260	79.9	52.2

(a) Maleic anhydride.

commercial, lump, needle coke which had been heat-treated to 2510°C. In addition to screen analysis, it has been examined by helium pycnometry and by Micromerograph and BET Surface-Area analysis, with the results listed in Table XII.

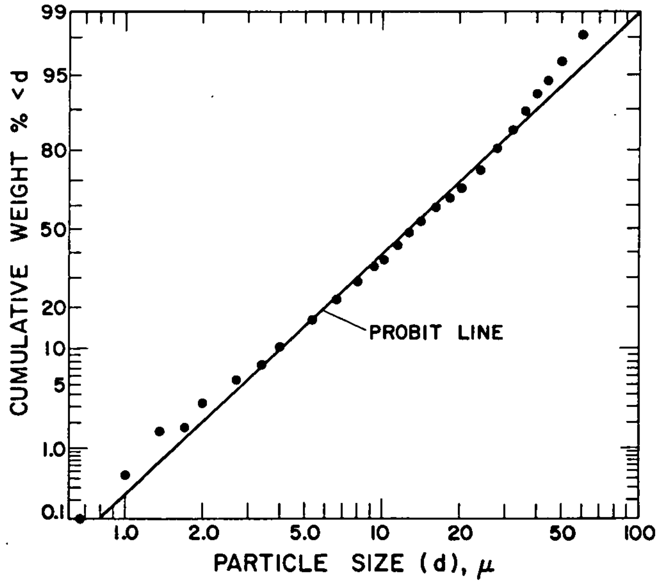

Fig. 7. Log-probability plot of Micromerograph particle-size data for a graphitized needle-coke filler, Lot GP-17.

The Micromerograph data plotted in Fig. 7 indicate that the particle-size distribution of Lot GP-17 is quite well approximated by the lognormal model. For this reason, sample statistics from both the lognormal and the finite interval model are listed in Table XII. In this case the two sets of statistical parameters agree quite well, which is frequently not the case for isotropic fillers.

D. Quaker Oats Co. Resins (E. M. Wewerka, J. A. O'Rourke)

A group of experimental furfuryl alcohol resins and a new curing catalyst, all produced by Quaker Oats Co. and identified as the "QX" series, were described in Report No. 17 in this series. These have been evaluated by adding 5 wt % of either maleic anhydride or QX 260, the experimental Quaker Oats Co. catalyst, to samples of each of the QX resins and to a standard LASL resin (EMW 302, viscosity 420 cp), curing to 220°C, then heat-treating to 2800°C. Carbon yields are listed in Table XIII, and x-ray parameters after high-temperature heat-treatment in Table XIV.

Carbon yields (Table XIII) were higher with maleic anhydride than with QX 260 curing catalyst. However, after curing, samples catalyzed with maleic anhydride were badly puffed, cracked, or broken, while those containing QX 260 were relatively compact, uncracked, and glassy looking. All samples cracked badly during subsequent baking at the rates normally used for graphite manufacture, which are evidently too high for unfilled carbon artifacts of any kind. With slower baking, QX 260 may be useful in producing carbon artifacts having increased strengths and fewer internal cracks. Further experiments with this catalyst are being conducted, among other things to determine whether carbon residue can be increased by adjusting the concentration used.

None of the QX resins yielded particularly large amounts of carbon compared with the standard LASL resin. However, it was not expected that the modifications undertaken by Quaker Oats would necessarily be reflected in high carbon yields.

With both catalysts, carbon yields from the QX 262 resin were quite low, probably because of its high

TABLE XIV

CRYSTALLINE PARAMETERS OF GRAPHITIZED BINDER RESIDUES

		Non-graphitizing C		Graphitizing Fraction		
Resin	Catalyst	L_c (Å)	d_{002} (Å)	L_c (Å)	d_{002} (Å)	~w/o
QX-261	MA[(a)]	25.9	3.44	---	---	Trace
QX-262	MA	25.8	3.44	---	---	Trace
QX-263	MA	22.5	3.44	---	---	Trace
QX-265	MA	28.5	3.45	170	3.37	5.5
EMW-302	MA	26.2	3.44	---	---	---
QX-261	QX-260	25.8	3.44	---	---	< 1
QX-262	QX-260	26.2	3.44	---	---	Trace
QX-263	QX-260	24.4	3.44	135	3.38	3
QX-265	QX-260	29.0	3.44	280	3.37	8
EMW-302	QX-260	26.5	3.44	140	3.38	3.5

(a) Maleic anhydride.

monomer content. Somewhat surprisingly, QX 261 -- a 1600 cp resin that is nearly free of monomer -- yielded only moderate amounts of carbon. As was discussed in Report No. 17, the QX 261 is also difficult to work with in extrusion due to problems associated with dryness of the green mix, and extruded rods made from it have a tendency to crack during heat treatment.

Resins QX 263 and QX 265 were purposely modified by their manufacturer with the intention of introducing material into them which would increase the degree of graphitization of the carbon residue during high-temperature heat-treatment. The x-ray parameters listed in Table XIV indicate that, in the case QX 263, this was not successful. A small increase in the proportion of graphitized material was accomplished with resin QX 265, although nongraphitizing material still constitutes the major proportion of its carbon residue.

E. Polyphenylene Carbon Precursors (E. M. Wewerka)

Several additional polyphenylenes have been synthesized in the continuing effort to develop this type of polymer into useful binders and carbon precursors.

Polyphenylene No. 7 was synthesized by the same procedure used to make polyphenylene No. 1 (described in Report No. 16), and was a linear, para-linked polymer of benzene. Infrared spectroscopy and x-ray diffraction measurements, both in the as-polymerized state and after heat-treating the carbon residue to 2800°C, indicate that No. 7 is nearly identical to No. 1. Thus, experimental reproducibility is evidently adequate for the purposes of this investigation. The x-ray parameters of the carbon residue from polyphenylene No. 7, after heating to 2800°C, were L_c = 147 Å and d_{002} = 3.378 Å .

Polyphenylenes No. 8 and 9 are copolymers of benzene and biphenyl, made respectively, from 3:1 and 6:1 mole ratios of benzene to biphenyl. The infrared spectra of the two polymers appear similar, showing a complex set of bands in the aromatic substitution region. Unfortunately, these bands cannot so far be assigned to the various substitution modes. Other than showing that the polymerization involves more than simple para-linking, infrared methods will probably not be useful in determining the structures of these more-complex polyphenylenes. Necessarily, their characterizations will be based primarily on x-ray diffraction data and empirical measurements of such things as softening points and carbon yields.

In the as-polymerized condition, polyphenylenes 8 and 9 both soften at 280°C, indicating that their molecular structures are quite highly disordered compared to the linear polymer of benzene. Only No. 8 has so far been examined by x-ray diffraction after heat-treatment to 2800°C. In that condition, its residue was found to consist mostly of disordered carbon (L_c = 30.3 Å, d_{002} = 3.43 Å), but to contain about 1% of relatively well-ordered graphite (L_c = 210 Å, d_{002} = 3.37 Å). It has not yet been firmly established whether or not a correlation exists between the degree of disorder in the polymer and that in its heat-treated carbon residue.

Attempts to produce polyphenylenes by a solvent polymerization route have continued to be unsuccessful, for reasons which are not clear. The solvents used (nitrobenzene, dichlorobenzene, etc) are usually good ones in which to conduct aromatic substitution reactions. An investigation of catalysts other than the $AlCl_3$-$CuCl_2$ system currently used has been undertaken.

F. Synthesis of γ-BL (E. M. Wewerka, R. J. Barreras)

The independent synthesis of 4-furfuryl-2-pentenoic acid-γ-lactone ("γ-BL"), which was first isolated from γ-alumina-polymerized furfuryl alcohol resins, is still being pursued. As has previously been reported, the first two steps of the synthesis have been well worked out, and are producing satisfactory yields of 2-furaldehyde and α-furylacetone. The third step involves ethynylating the α-furylacetone with lithium acetylide-ethylene diamine complex in an acetylene atmosphere. The reaction proceeds smoothly but yields are unsatisfactory ranging from 5% to a once-only high of 55%. Apparently there are several side reactions which use up the ketone, the major one probably being enolization of the ketone. (Upon neutralization, the ketone is regenerated.) Little enhancement of the yield has resulted from changing the rate of ketone addition or from running the reaction in benzene, a nonpolar solvent, or in tetrahydrofuran, a more highly polar solvent. Another source of product loss is residual material left in the distilling pot after purification of the yne-ol by a distillation in which the lower-boiling ketone (starting material) is separated from the higher-boiling yne-ol.

The next step in the synthesis involves carboxylation of the yne-ol by preparing the Grignard magnesium salt of the yne-ol and reacting it with carbon dioxide. All preparations so far attempted have yielded no appreciable product. The reaction is now being tried in a high-pressure reaction vessel, to insure the presence of CO_2 at all times.

VI. THE PARTICLE-PACKING PROBLEM

(H. D. Lewis, A. Goldman)

Theoretical and experimental investigations of the particle-packing problem have been discussed in several previous reports in this series. Briefly, the problem consists of demonstrating the mathematical validity and the applicability to real particle systems of the maximum variance-coefficient of variation model described by Lewis and Goldman in LASL Report No. LA-3656.

Two approaches are being taken in investigating the mathematical validity of the model. Both are based on the problem of maximizing the packing density of line segments on a line. One considers the analytical solution of the integral equation describing random sequential packing on the line, using various forms of probability-density functions to represent particle-size distributions. The other approach considers the Monte Carlo solution, with various restrictions on random position-selection of particles whose sizes are determined by random selection from a known distribution or combination of distributions.

Applications of the analytical method to the case of monosized particles and to uniform ("rectangular") distributions of particle sizes were discussed in Report No. 14 in this series. It was found that packing density indeed increased with increasing coefficient of variation (CV_d).

Recent developments, involving W. M. Visscher of LASL Group T-9, have been concerned with modifications to the analytical solution required to simulate the density functions which must be used to represent real data -- that is, experimentally determined particle-size distributions. At least two possibilities exist: using combinations of uniform probability densities,and using combinations of linear probability densities redefined over the size-range of interest, in either case to simulate a probability density representing the particle-size distribution.

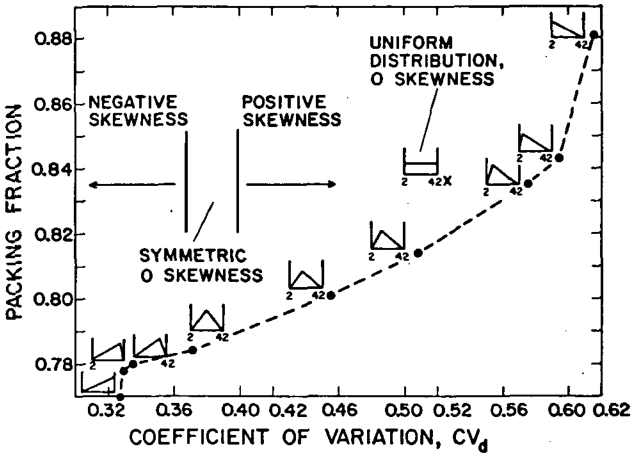

Fig. 8. Effect of coefficient of variation on packing density for a family of distributions represented by combinations of two linear functions.

Figure 8 illustrates important results obtained from recent computer runs in which combinations of two linear functions were used to simulate density functions that crudely represent the general shapes of real particle-size distributions. As is illustrated by the small diagrams set into the figure, the solution to the integral equation was obtained for several size-distribution functions having a constant size range of 2 to 42 and skewness values ranging from -474 to +474. The plot of packing fraction vs CV$_d$ again shows that packing fraction is an increasing function of coefficient of variation. Both CV$_d$ and packing fraction were found to increase only slightly as skewness increased from the most negative value to zero. However, both increased continuously and quite rapidly with increasing positive skewness. One point, indicated by an X, was plotted for a uniform distribution having approximately the maximum possible value of CV$_d$ -- which, for the uniform distribution, is $1/\sqrt{3}$. With positively skewed linear combinations, packing fractions significantly higher than this were achieved.

The simulation of real particle-size data by using combinations of up to 30 linear functions has been undertaken, but is considerably more complex than defining the distributions discussed above. Current work involves the preparation of computer programs for real-data simulation for use in both analytical and Monte Carlo solutions to the linear and pseudo two-dimensional packing problems.

VII. ANISOTROPIES OF CREEP-TESTED POCO GRAPHITES

(J. A. O'Rourke)

The tensile creep behavior of POCO grade HPD-1 graphite at 2200 to 2500°C was discussed in Report No. 17 in this series. During routine examination of tested specimens from the creep experiments described in that report, it was observed that, in the direction of elongation, Young's modulus increased rapidly with extent of tensile strain. To determine whether this change was an effect of progressive crystalline reorientation, measurements were made of the anisotropies of several tested bars representing different amounts of tensile deformation. The results of these measurements are listed in Table XV and plotted in Fig. 9. Samples 1284 and 1285 had been

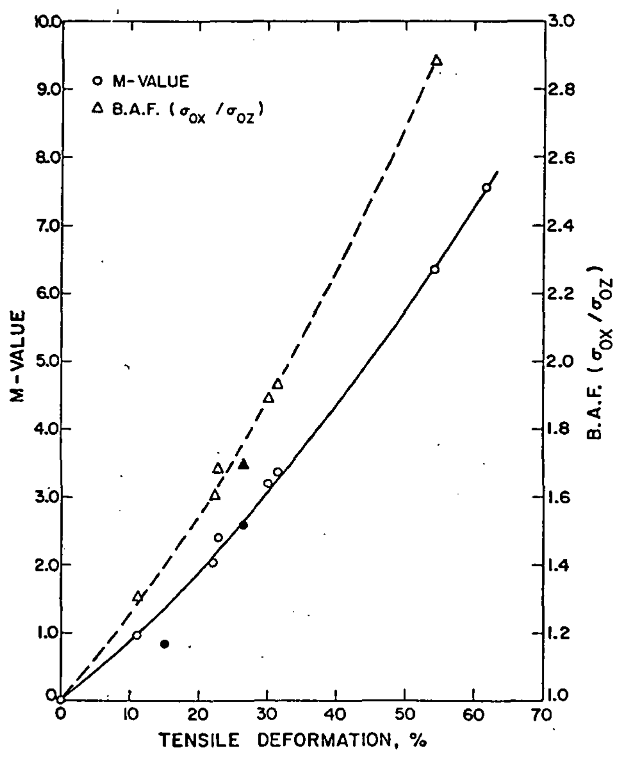

Fig. 9. Bacon Anisotropy Factors, σ_{ox}/σ_{oz}, and M-values for POCO Grade HPD-1 graphite extended in tensile creep. Filled symbols indicate specimens heat-treated to 2900°C before creep-testing.

TABLE XV

ANISOTROPIES OF CREEP-TESTED POCO GRAPHITE SAMPLES

CMB-13 Sample No.	Creep Elongation, %	Heat Treatment Prior to Creep Test	M Value	B.A.F., σ_{ox}/σ_{oz}
1308	0	As-Received	0.0	1.00
1307	11.1	As-Received	0.97	1.304
1285	15.0	1/2 hr @ 2900°C	0.84	---
1296	22.2	As-Received	2.04	1.602
1294	22.8	As-Received	2.40	1.682
1286	26.4	1/2 hr @ 2900°C	2.59	1.694
1297	30.1	As-Received	3.20	1.891
1292	31.5	As-Received	3.36	1.930
1305	54.3	As-Received	6.35	2.881
1284	61.7	As-Received	7.55	---

mounted in an epoxy resin in such ways that, for them, only M-values could be determined. Samples 1285 and 1286 had been heat-treated to 2900°C prior to creep-testing. The anisotropy measurements are believed to be at least as accurate as the elongation measurements.

From these data it is evident that a preferred orientation indeed begins to develop in the POCO graphite essentially at the onset of high-temperature tensile deformation, and that it continues to develop at an accelerating rate with increasing deformation. Both the amount of tensile strain possible and the degree of preferred orientation finally produced are surprisingly high.

To determine whether this change in anisotropy was accompanied by a change in crystalline perfection, x-ray measurements of the crystalline parameters L_c and d_{002} were made on two of the creep-tested samples. For sample 1307, which had been extended 11.1%, these values were $L_c = 256\,Å$ and $d_{002} = 3.379\,Å$. For sample 1305, extended 54.3%, they were $L_c = 310\,Å$ and $d_{002} = 3.372\,Å$. While these differences are not great, it does appear that tensile deformation at 2500°C increases the degree of graphitization of a POCO graphite.

VIII. PUBLICATIONS RELATING TO CARBONS AND GRAPHITES

Smith, M. C., "CMB-13 Research on Carbon and Graphite, Report No. 17, Summary of Progress from February 1 to April 30, 1971," LA-4770-MS, September, 1971.

Kelly, B. T., Whittaker, A., Tobin, D., and Wagner, P., "The Effect of Doping on the Thermal Conductivity of Polycrystalline Graphite," Carbon, Vol. 9, No. 4, pp. 447-455, 1971.

Imprescia, R. J., Lewis, H. D., and O'Rourke, J. A., "Grindability of Petroleum Cokes," Bull. Am. Ceram. Soc., Vol. 50, pp. 792-793, 1971.

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