LA-4171-MS

8/1/69

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

CMF-13 Research on Carbon and Graphite

Report No. 9

Summary of Progress from February 1 to April 30, 1969

MASTER

P2145

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

This LA...MS report presents the summary of progress of CMF-13 research on carbon and graphite at LASL. Previous summary of progress reports in this series, all unclassified, are:

LA-3693-MS
LA-3758-MS
LA-3821-MS
LA-3872-MS
LA-3932-MS
LA-3989-MS
LA-4057-MS
LA-4128-MS

This report, like other special-purpose documents in the LA...MS series, has not been reviewed or verified for accuracy in the interest of prompt distribution.

Distributed: May 13, 1969

LA-4171-MS
SPECIAL DISTRIBUTION

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

CMF-13 Research on Carbon and Graphite

Report No. 9

Summary of Progress from February 1 to April 30, 1969*

by

Morton C. Smith

*Supported in part by funds transferred by NASA through the joint AEC-NASA Space Nuclear Propulsion Office, and directly from the NASA Office of Advanced Research and Technology.

flg

CMF-13 RESEARCH ON CARBON AND GRAPHITE

REPORT NO. 9: SUMMARY OF PROGRESS FROM FEBRUARY 1 TO APRIL 30, 1969

I. INTRODUCTION

This is the ninth in a series of progress reports devoted to carbon and graphite research in LASL Group CMF-13, and summarizes work done during the months of February, March and April, 1969. 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 CMF-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 material 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 jointly by the Division of Space Nuclear Systems of the United States Atomic Energy Commission and by the National Aeronautics and Space Administration, 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 NASA. Many of its facilities and services have been furnished by the Division of Military Applications 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. General

Santa Maria coke is an unusual petroleum coke which offers great promise for use as the principal filler material in the manufacture of isotropic, high-expansion carbons and graphites in general, including a wide variety of molded, pressed, and extruded grades for nuclear, aerospace, and other special uses. It is commercially available as either green or calcined coke of uniform structure and quality, in large tonnages and at moderate prices, and it has an assured, stable, continuing source of supply.

The major peculiarity of Santa Maria coke is an internal structure which causes it, during grinding, to break principally into compact particles that are substantially equiaxed and inherently isotropic. Only in the very finest sizes (e.g., $< 2\mu$ dia) do the particles produced by grinding tend to become acicular or tabular in shape and anisotropic in internal structure and properties. Unless the filler used contains an exceptionally large proportion of these extreme fines, a sound graphite produced from a Santa Maria filler will be very nearly isotropic in both crystallite orientation and properties. Because of the internal structures of the filler particles, it will also necessarily have high coefficients of thermal expansion and relatively high electrical resistivity.

Using Santa Maria fillers, LASL Group CMF-13 has produced essentially isotropic graphites by both hot-molding and extrusion, with both pitch and resin binders, and both with and without carbon-black filler additions. Particle-size distributions, mix formulations, and manufacturing procedures have not yet been optimized. Typically, however, in addition to isotropy and high thermal expansion, these graphites have had moderate to high bulk density, high strength and electrical resistivity, moderate thermal conductivity and elastic moduli, and low connected porosity. They have graphitized well, to apparent crystallite sizes (L_c values) of the order of 300 Å.

Unless they can be modified substantially by filler additions, graphites made from Santa Maria fillers will probably not be useful where very high electrical conductance is essential -- e.g., in furnace electrodes. Their resistance to thermal stress and thermal shock may be limited by their high thermal expansion coefficients, but is at least moderately high. Their thermal expansion behavior will be useful in reducing expansion mismatches wherever coatings are required and in assemblies involving metals, carbides, and other materials. Their isotropies, graphitizing characteristics, densities, and porosity distributions make them appear promising for a wide variety of nuclear reactor applications. Their resistance to erosion and ablation has not been investigated, but is expected to be relatively high.

In several respects the Santa Maria fillers resemble those used in the manufacture of the Poco graphites, and graphites made from them resemble the Poco grades both in structure and in properties. Santa Maria coke also resembles the experimental Robinson coke produced by the Carbon Products Division of Union Carbide Corporation, but has larger optical domain size, coarser and more highly developed radial structures, and much less sensitivity to thermal stress. It differs widely in structure from the Gilsocarbons, but has some of their properties and can probably be substituted for them to advantage in many cases -- particularly for the production of fine-grained isotropic graphites.

B. Source, Availability and Price

Santa Maria coke is a delayed coke produced at the Santa Maria (California) Refinery of the Union Oil Co. of California. It is calcined and marketed exclusively by Collier Carbon and Chemical Corporation, which is a wholly owned subsidiary of Union Oil Co. of California.

The Santa Maria oil field is in Santa Barbara County, California. It was discovered in 1934, and now has approximately 600 producing wells. Its production is a very heavy (15°API) crude oil which goes entirely to the modern, 33,000 bbl/day Santa Maria Refinery. This refinery treats only the Santa Maria crude, using established procedures which can be expected to yield consistent residues and, from these, a consistent coke. Its coke production is 330,000 tons/year, much of which goes eventually to the phosphorus industry.

This coke is marketed in two standard lump forms, both nominally minus 3/8-in. dia: Santa Maria Green Petroleum Coke, and Santa Maria LV Coke -- which is the same coke, calcined by the Collier Corporation at about 1800°F. Analytical data supplied by the Collier Corporation for the Green and LV cokes are listed in Table I, together with LASL analyses representing a 500-lb sample of the LV coke purchased by CMF-13 in January, 1969, and a part of that sample which was subsequently graphitized by CMF-13 at 2800°C. The sulfur content of Santa Maria coke is higher than that of many other cokes, although it is not exceptional in this regard, and its content of other impurities is not unusual.

In bulk carload lots (50 to 70 tons/carload, F.O.B. Callendar, California), Santa Maria coke in standard lump form was quoted by the Collier Corporation in April, 1969, at \$9.64/ton for the Green coke and \$12.50/ton for the LV coke. Collier Corporation's screening system is such

TABLE I

CHEMICAL ANALYSES, SANTA MARIA COKE

	Santa Maria Green Coke, Collier Co. Data			Santa Maria LV Coke				
				Collier Co. Data			CMF-13 Sample	
	Typical	Range	Specification	Typical	Range	Specification	As Received	Graphitized 2800°C
Proximate Analysis:								
Moisture	7.0%	6.0-12.0	8% ave.	0.20%	0.01-1.5	1.5% max.	0.17%	Nil
Ash (dry basis)	0.4%	0.3-0.7	1.0% max.	0.70%	0.5-1.0	1.0% max.	0.45%	0.033%
VCM (dry basis)	11.8%	10-14	14.0% max.	0.80%	0.2-1.5	1.5% max.	---	---
Fixed C (dry basis)	87.8%	85.3-89.6	85.0% min.	98.5%	98-99	97.5% min.	---	---
Elemental Analysis (dry basis):								
S	4.0%	3.7-5.5	5.5% max.	4.0%	3.5-5.5	5.5% max.	3.40%	0.01%
Fe	0.03%	0.01-0.05	0.05% max.				0.013%	0.001%
V	0.11%	0.09-0.15	0.15% max.				0.05%	0.015%
Si	0.02%	0.01-0.04	0.04% max.				0.03%	<0.0003%
Ni	0.068%	0.035-0.075	0.075% max.				0.03%	<0.001%
P	Nil	---	0.001% max.				---	---
Na							200 ppm	<5 ppm
Mg							50 ppm	<1 ppm
Ca							200 ppm	<3 ppm
K							100 ppm	<50 ppm
Al							100 ppm	<10 ppm
Ti							30 ppm	< 5 ppm
Zr							100 ppm	20 ppm
Nb							300 ppm	<10 ppm
Cr							10 ppm	<10 ppm
Mn							1 ppm	<1 ppm
Cu							5 ppm	<3 ppm
Pb							20 ppm	<10 ppm
B							5 ppm	2 ppm

that they have some flexibility with regard to the size range of their products, although they claim not to have crushing or grinding equipment.

C. Santa Maria Green Coke

According to its supplier, Santa Maria Green Petroleum Coke has been coked at approximately 900°F and has a typical bulk density of 45 lb/ft^3, a range of bulk densities of 43 to 48 lb/ft^3, a calorific value of 14,500 Btu/lb, and the chemical analysis given in Table I. The screen analysis of as-received lump material taken from a 500-lb sample purchased by CMF-13 in December, 1968, is given in Table II.

Green Santa Maria coke has an apparent crystallite thickness (L_c) of 24.3 Å and apparent interlayer spacing (d_{002}) of 3.43 Å. It contains about 44% amorphous carbon, plus at least two crystalline components. (The overlapping, unresolved diffraction peaks representing the crystalline species are undoubtedly misleading with regard to the actual average value of d_{002}, which is probably greater than the measured 3.43 Å.)

TABLE II
SCREEN ANALYSES OF SANTA MARIA COKES
AS-RECEIVED

Screen Fraction (U.S. Std. Sieves)	Weight Percent in Fraction Green Coke	LV Coke
+ 1/4	4.4	16.3[(b)]
-1/4 + 4	10.7	33.9
-4 + 8	24.5	45.1
-8 + 16	14.9	4.5
-16 + 25	10.1	0.1
-25 + 45	11.4	trace
-45 + 80	8.3	0
-80 + 170	5.8	0
-170 + 325	3.4	trace
- 325[(a)]	6.5	trace

(a) Determined by difference.

(b) Very little coarser than 3/8 in.

Under polarized light the microstructure of the green coke is seen to consist of approximately equixed, randomly oriented optical domains, largely in the size range below 10μ dia. Some coke lumps contain cracks and smooth-walled blowholes. However, their internal porosity consists principally of lenticular or crescent-shaped voids usually less than 10μ long. (These appear to be cleavage cracks resulting from the volume shrinkage that occurred during coking.) The long dimensions of these voids are parallel to the layer planes of adjacent material.

An unusual structural feature common in Santa Maria coke is a spheroidal unit, commonly 30μ or less in diameter, within which several lenticular voids, the optical domains revealed by polarized light, the layer planes of the graphite structure, and any lamellar markings developed by etching, are arranged in a rosette pattern radiating from a common center. This is illustrated by Fig. 1. Among other cokes so far examined by CMF-13, similar radial patterns have been observed only in the Robinson coke produced by Carbon Products Division of Union Carbide Corporation, in which the rosettes are smaller, less well developed, and relatively infrequent. Another similarity between Santa Maria and Robinson cokes is in the fine, randomly oriented optical domain structure. However, the individual domains are very much smaller in the Robinson coke.

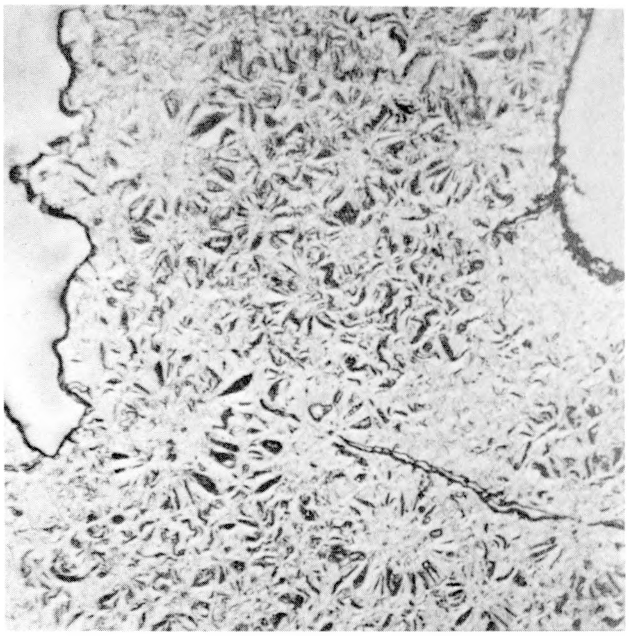

Fig. 1. Cracks, blowholes and radial structures in Santa Maria coke. Hydrogen-ion etch, 500X.

These radial patterns suggest the presence in the refinery residue from which the coke was made of a dispersed nucleating agent from which the structures have grown. Their centers appear to be more dense than is the material around them, but nothing which can be identified as a nucleus has so far been found. The radial arrangement of lamellae which develops within these spheroidal units should be contrasted with the concentric, onion-skin arrangement observed in carbon blacks, fluid cokes, and the Gilsocarbons. Both arrangements produce particles which are inherently isotropic. However, grinding to particle sizes significantly smaller than the original spheroids destroys both the onion-skin pattern and the isotropy derived from it. The intergrown radial arrangement in Santa Maria coke and its random optical domain structure preserve particle anisotropy to particle sizes distinctly smaller than the spheroidal units observed in the lump material. Particularly for the production of fine-grained isotropic graphites, the Santa Maria coke therefore has an obvious advantage in this regard.

When they exist in the interiors of relatively large

TABLE III

CRYSTALLINE PARAMETERS OF HEAT-TREATED SANTA MARIA COKE

CMF-13 Lot No.[(a)]	Heat Treatment	Bulk Density, g/cm^3	L_c, Å	d_{002}, Å	Remarks
CP-4	None; green coke	0.625	24.3	3.43	44 % amorphous carbon
CP-4	Calcined to 900°C	0.872	15.7	3.43	15% amorphous C. Metallic contamination.
CP-4	Calcined to 900°C	0.930	16.2	3.42	19% amorphous C.
CP-6	Calcined to 900°C	0.936	15.3	3.43	26% amorphous C.
CP-7	Calcined to 900°C	0.631	16.0	3.42	25% amorphous C.
CP-8	Calcined to 900°C	0.995	16.8	3.43	19% amorphous C.
CP-4	1 hr at 1300°C	1.085	29.7	3.44	
CP-4	1 hr at 1500°C	1.038	36.2	3.44	Metallic contamination.
CP-4	1/2 hr at 2800°C	---	353	3.37	
CP-6	1/2 hr at 2800°C	---	380	3.368	
CP-7	1/2 hr at 2800°C	---	400	3.369	
CP-8	1/2 hr at 2800°C	---	350	3.369	

(a) Grinding conditions for each lot are described below.

particles, the lenticular voids characteristic of Santa Maria coke are not usually penetrated by the epoxy resin used to mount the coke for microscopic examination, indicating that in general they are not surface-connected. In smaller particles these voids tend to be accessible to the resin, and in very small particles (<10 μ dia) there are usually no voids present. Apparently during comminution the paths of cracking and fracture tend to pass preferentially through the lenticular voids, opening them to the external surface or making them part of a new surface. This is also indicated by a continuous increase in helium pycnometer density as the coke is ground to progressively smaller average particle sizes. In well-bonded graphites made from Santa Maria fillers, strength would be expected to increase as filler-particle size diminished simply because of progressive elimination of intraparticle defects of this type. A limit should be reached at a particle diameter near 10 μ, at which essentially all such voids will have been eliminated, after which -- if particle packing is good -- the principal effect of a further reduction in filler particle size will be an increase in anisotropy.

D. Heat Treating the Green Coke

Samples of the ground green coke were calcined in vacuum at 900°C, after which some of the samples were further calcined in helium at either 1300°C or 1500°C or graphitized in helium at 2800°C. Crystalline parameters of the green and heat-treated materials are listed in Table III. Calcining at 900°C reduced the amorphous carbon content of the coke to about one-half its original value, and calcination at 1300°C essentially eliminated the amorphous carbon. Reorganization of this carbon produced very small graphite crystallites which, in effect, diluted the more coarsely crystalline material initially present, so that calcination at 900°C actually reduced the apparent average crystallite size of the coke from about 24 Å to about 16 Å. Heat treatment at 1300°C caused further reorganization of amorphous carbon but also produced growth of crystallites already formed, so that L_c was increased to about 30 Å. Calcining at 1500°C caused further growth, to about 36 Å, and graphitization at 2800°C produced relatively large crystallites, in the range 350 to 400 Å. Apparent interlayer spacing was not significantly changed by calcining to at least 1500°C, but was reduced to 3.369 Å by graphitization at 2800°C. The Santa Maria coke graphitizes quite well, and the high-temperature graphitizing heat-treatment reduces its impurity content to very low levels -- as is indicated by the last column of Table I.

None of these heat treatments appeared to affect the optical domain size of the coke. The intensity of polarized light effects increased with heat-treating temperature, and fine lamellar structures not evident in the etched green or calcined coke were developed by etching after graphitizing. Helium pycnometer density increased with heat-treating temperature, indicating progressive opening of internal voids to the particle surfaces as calcination and then graphitization occurred. Under the microscope it appeared that calcination had increased the internal porosity of the larger coke particles and produced some small, narrow cracks which might represent connections between internal voids and particle surfaces. After graphitization it appeared that both the number and the width of the internal voids had increased further, with perhaps an increase also in the number of small, narrow cracks within the larger particles.

E. Santa Maria LV Coke

According to the Collier Company, Santa Maria LV (low-volatiles) coke has been calcined in a rotary kiln at about 1800°F and has a typical bulk density of 50 lb/ft^3, with an expected range of bulk densities of 48 to 51 lb/ft^3. Analysis of material from the 500 lb sample of LV coke purchased by CMF-13 (Table I) showed that its impurity content was relatively low, and well within the chemical specification published by the supplier. The screen analysis of the CMF-13 sample is given in Table II. Obviously it had been carefully sized by the supplier.

As received from the Collier Company, the LV coke has an internal structure which cannot be distinguished microscopically from that of the green coke. The rosette pattern described above may be slightly more pronounced in the LV coke, and small narrow cracks of the type observed in coke calcined by CMF-13 are present, sometimes in a radial pattern. As with the green coke, the x-ray diffraction pattern of the LV coke showed the presence in it of at least two crystalline components, which probably affected the measured value of d_{002}. Its apparent x-ray parameters (L_c = 19.7 Å, d_{002} = 3.42 Å), its helium pycnometer density (1.889 g/cm^3), and its grinding behavior (discussed below) suggest that it was calcined at some temperature between the 900°C and 1300°C temperatures used by CMF-13 in heat-treating the green coke.

During grinding of the LV coke a strong odor of hydrogen sulfide was evident, which was not noticed when material vacuum-calcined by CMF-13 was ground. During graphitization of the LV coke, much fume was produced together with heavy layers of condensation products in cool regions of the furnace. These observations and the fabrication behavior described below suggest that the Santa Maria LV coke should be calcined to a somewhat higher temperature than that used by the supplier before it is either used as a coke filler or graphitized to produce a graphite filler.

F. Grinding Experiments

Grinding experiments have been performed on the Santa Maria green coke as-received and in several conditions of heat treatment, and also on the Santa Maria LV coke as-received and after graphitizing at 2800°C. The laboratory mills and grinding conditions used are listed in Table IV, where each grinding procedure is identified by a letter which will be used in later tables to describe series of grinding operations.

Screen analyses of the products of grinding these materials in a variety of ways are listed in Table V, and Micromerograph sample statistics for some of them are listed in Table VI. In all cases the initial mill feed was the lump coke either as-received or after heat-treatment to the temperature indicated in Column 3 of Table V. The sequence of grinding passes is indicated in Column 4 of Table V, where each letter indicates one pass under the conditions listed opposite that letter in Table IV. From the screen analyses listed in Table II, it is evident that the CMF-13 sample of LV coke had been carefully sized by the supplier. It contained almost no fines, while the CMF-13 sample of green coke contained normal proportions of all size fractions down to minus 325 mesh. Direct comparisons of the grinding behavior of these two

TABLE IV

GRINDING MILLS, CONDITIONS AND PROCEDURES

Grinding Procedure	Type of Mill	Discharge	Pressure, psi, Pusher/Opposite	Feed Rate, g/min(d)
A	Williams hammer mill(a)	Screen, 0.0625-in. dia holes	---	87
B	Weber hammer mill(b)	Screen, 0.050-in. wide slots	---	38
C	Weber hammer mill	Screen, 0.010-in. wide slots	---	20
D	Williams hammer mill	Screen, 0.0313-in. dia holes	---	50
E	Weber hammer mill	Screen, 0.024-in. dia holes	---	50
F	Williams hammer mill	Screen, 0.0313-in. dia holes	---	38
G	Weber hammer mill	Screen, 0.008-in. wide slots	---	28
H	Weber hammer mill	Screen, 0.024-in. dia holes	---	28
I	Trost fluid-energy mill(c)	Orifice, 1.25-in. dia	100/100	15
J	Trost fluid-energy mill	Orifice, 1.25-in. dia	100/100	74
K	Trost fluid-energy mill	Orifice, 1.25-in. dia	100/100	38
L	Trost fluid-energy mill	Orifice, 1.25-in. dia	100/80	14
M	Trost fluid-energy mill	Orifice, 1.25-in. dia	100/60	15
N	Trost fluid-energy mill	Orifice, 1.25-in. dia	100/40	15

(a) "Lab" Hammer Mill, Williams Patent Crusher and Pulverizer Co.

(b) Model S500 Laboratory Pulverizing Mill, Weber Bros. and White Metal Works, Inc.

(c) Trost Model GEMTX Laboratory Mill, Trost Jet Mill Division, George W. Helme Co., Inc.

(d) Accurate to about ±5%.

feeds are of course complicated by this difference in particle-size distribution of the initial mill feeds.

Because of its unusual internal structure, Santa Maria coke tends during grinding to break into somewhat angular but substantially equiaxed particles, as is illustrated by Fig. 2, 3 and 4. Particles larger than about 30μ dia -- approximately the size of the spheroidal structural units described above -- still consist of groups of randomly oriented optical domains, often in a radial pattern, and so are inherently isotropic. At smaller particle sizes there is an increasing tendency toward internal structures consisting of nearly parallel lamellae, but even somewhat below 10μ dia (approximately the maximum dimension of the lenticular voids) most of the particles remain substantially equiaxed. In this size range, therefore, many of the particles are probably anisotropic, but in general their shapes are such that they would have little tendency to assume preferred orientations during

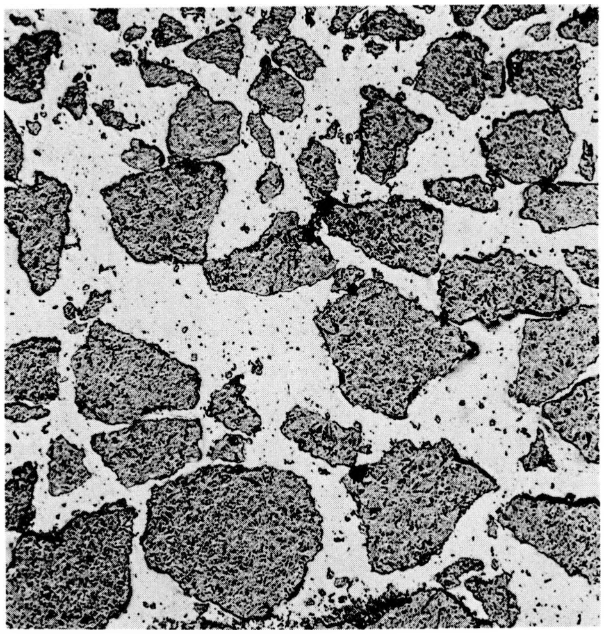

Fig. 2. Typical particle shapes of ground Santa Maria coke. Clear areas are epoxy mounting resin. Hydrogen-ion etch, 500X.

TABLE V

SCREEN ANALYSES OF GROUND SANTA MARIA COKE

CMF-13 Lot No.	Coke Used	Ht-Treating Temp, °C	Grinding Schedule[(a)]	Weight Percent in Screen Fraction (U.S. Std. Sieves)						
				+16	-16+25	-25+45	-45+80	-80+170	-170+325	-325[(b)]
---	Green	None	A	0	0	0.2	5.4	32.0	58.6	3.8
CP-6	Green	None	A+B	0	0	trace	2.6	7.0	34.6	55.8
CP-4	Green	None	A+B+C	0	0	trace	trace	2.0	50.7	47.3
CP-5	Green	None	A+B+C+L	0	0	0	0	0	0	100[(d)]
CP-7	Green	None	A+B+L	0	0	0	0	0	0	100[(e)]
---	Green	900	A	trace	1.2	18.4	33.6	19.4	13.8	13.6
CP-8	Green	900	A+B	0	trace	4.4	25.0	28.4	21.6	20.6
---	Green	900	A+B+B	0	trace	1.3	18.8	34.8	22.2	22.9
---	Green	900	A+B+C	0	0	0.2	5.0	27.4	31.8	35.6
---	Green	900	D	0	trace	6.2	36.3	26.6	13.8	17.1
---	Green	900	D+E	0	trace	0.6	16.2	35.4	22.2	25.6
---	Green	900	F	0	trace	9.8	37.8	25.2	12.4	14.8
---	Green	900	F+C	0	0	1.4	14.3	31.8	26.0	26.5
---	Green	900	F+G	0	0	1.4	15.8	33.2	25.4	24.2
---	LV	Mfr.[(c)]	A	0	3.8	23.8	30.6	21.6	9.8	10.4
CP-9	LV	Mfr.	A	0	2	19	30	24	12	13
---	LV	Mfr.	A+B	0	0.2	6.6	25.2	37.4	18.2	12.4
---	LV	Mfr.	H	0	trace	1.2	10.6	36.3	30.0	22.0
---	LV	Mfr.	A+H	0	trace	0.4	7.8	35.2	33.4	23.2
CP-10	LV	Mfr.	A+H	0	trace	2	13	33	22	29
---	LV	Mfr.	A+H+I	0	0	trace	10	15	10	65
---	LV	Mfr.	A+H+L	0	0	trace	15	20	20	45
---	LV	Mfr.	A+H+M	0	0	trace	15	25	20	40
---	LV	Mfr.	A+H+N	0	0	trace	20	30	20	30
CP-11	LV	Mfr.	A+J	0	trace	20	25	25	10	20
CP-12	LV	Mfr.	A+K	0	trace	15	15	20	15	35
CP-13	LV	2800	A+B	0	trace	25	20	30	10	15
CP-14	LV	2800	A+B+I	0	trace	15	20	25	15	25

(a) Letters refer to grinding procedures listed in Table IV.

(b) Determined by difference.

(c) Calcined by manufacturer to ~1800°F.

(d) 0.1% > 10 μ, 74.6% >5 μ.

(e) 1.3% > 10 μ, 95.5% >5 μ.

Fig. 3. Typical particle shapes of ground Santa Maria coke. Rough gray areas between particles are epoxy mounting resin. Xenon-ion etch, 3200X.

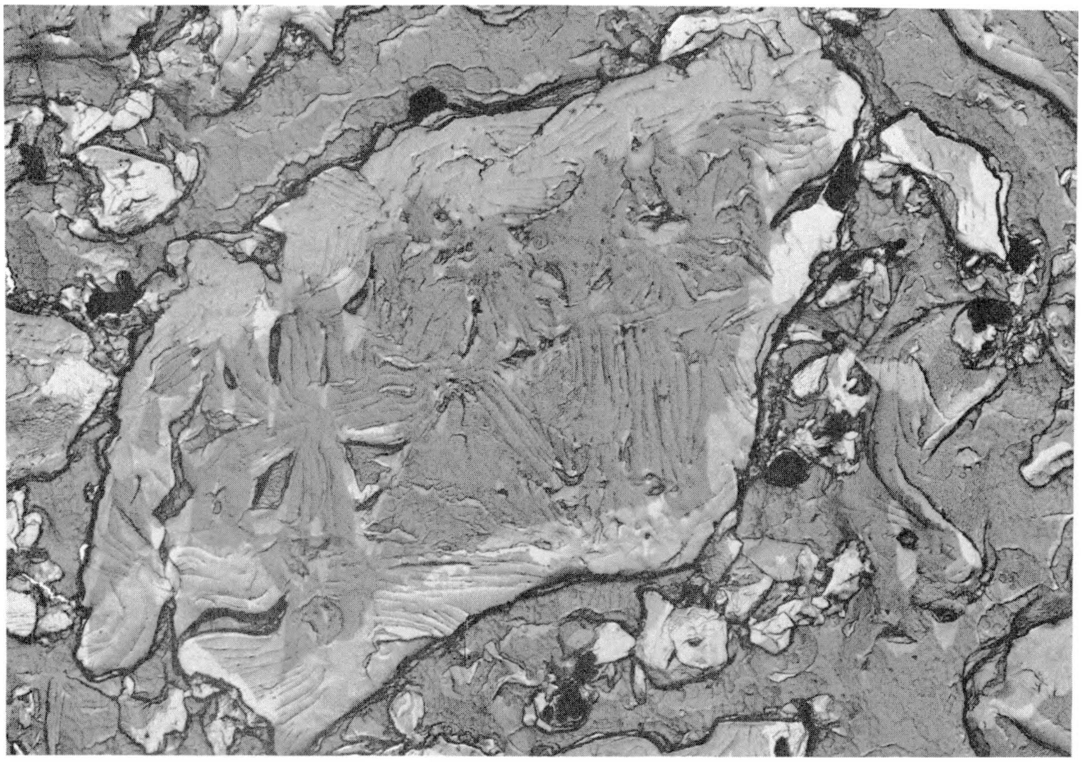

Fig. 4. Internal structures of Santa Maria coke particles graphitized at 2800°C. Rough gray areas are epoxy mounting resin. Xenon-ion etch, 3200X.

TABLE VI

PARTICLE CHARACTERISTICS OF GROUND AND HEAT-TREATED SANTA MARIA COKE

			Micromerograph Sample Statistics[b]								BET Surface Area		
Lot No.	Heat Trt. °C[a]	Helium Density, g/cm^3	$\hat{\mu}_{x3}$	$\hat{\sigma}_x^2$	$\hat{\mu}_x$	$\bar{d}_3$ microns	$\bar{d}$ microns	s_d^2 microns	S_W cm^2/g	CV_d	$\bar{S}_W$ cm^2/g	d_s[c] microns	Fuzziness Ratio[d]
CP-4	1300	2.049											
CP-5	900	1.947											
CP-6	110	1.368											
CP-6	900	1.899[e]	3.3643	1.8220	-2.1014	71.900	0.304	0.479	2715	2.277	20,400	1.50	7.50
CP-6	2800	2.047	3.4033	1.7385	-1.8123	71.707	0.389	0.711	2322	2.165	18,800	1.56	8.10
CP-7	900	1.954	1.4126	0.3891	0.2453	4.989	1.552	1.146	9101	0.690	46,400	0.66	5.09
CP-7	2800	2.214	1.3000	0.3868	0.1397	4.452	1.395	0.919	8977	0.687	45,200	0.60	5.03
CP-8	900	1.888	4.4513	2.6674	-3.5509	325.39	0.181	0.159	1405	3.661	44,700	0.71	31.7
CP-8	2800	1.989	4.7840	3.4940	-5.6978	686.22	0.019	5.650	1446	5.650	16,200	1.86	11.2
CP-13	None	2.145	5.2176	3.6637	-5.774	1152.	0.194	0.014	945	6.16	64,800	0.43	68.6
CP-14	None	2.157	4.5147	3.6263	-6.364	559.9	0.011	0.004	1864	6.05	78,600	0.35	42.2

(a) Heat-treatment after grinding.

(b) Lognormal assumption.

(c) Diameter of smooth-shelled sphere having equal specific surface area.

(d) Ratio of specific surface area measured by BET method to that calculated from Micromerograph sample statistics assuming smooth-shelled spheres.

(e) With 10 min. (instead of 20 sec.) equilibration time, this became 1.966 g/cm^3.

forming and so, when used as a filler, they will produce a nearly isotropic product. At still smaller sizes the particles tend to become increasingly acicular in section, and particles whose maximum dimensions are less than about 2 μ often have aspect ratios of two or three to one, with relatively well-ordered internal structures composed usually of single optical domains. In the very fine size range, then, the particles tend to become inherently anisotropic and so shaped that they will tend to assume preferred orientations during forming. A carbon or graphite made from a Santa Maria filler can therefore be expected to develop anisotropy in some proportion to the fraction of the filler present as extremely fine particles. However, as is demonstrated below, the proportion of extreme fines must become very high before anisotropy becomes significant.

Heat treatment of the lump coke did affect grindability, the particle-size distribution produced by a given grinding operation, and the abrasiveness of the coke. However it did not noticeably affect the shapes or general internal structures of the particles produced by grinding. These particle characteristics appeared to be the same whether the coke was ground green, after calcining, or after graphitizing to 2800°C.

Green Santa Maria coke grinds easily to very fine particle sizes. As is shown by Table V, one pass through a hammer mill (Schedule A) reduced the lump green coke to a size distribution such that more than 90% of it by weight was finer than 80 mesh (177 μ), but produced very few extreme fines. A second hammer-milling (Lot CP-6, Schedule A + B) then reduced it to about 90% minus 170 mesh (88 μ), with about half of the material finer than 325 mesh (44 μ). Results from a third hammer-milling (Lot CP-4, Schedule A + B + C) were anomalous, but indicated that under the grinding conditions used very little further reduction occurred in the third pass. Fluid-energy grinding after either two hammer-mill passes (Lot CP-7) or three hammer-mill passes (Lot CP-5) reduced the green coke to 100% minus 325 mesh. Micromerograph analysis of Lot CP-5 showed an extremely narrow distribution of particle sizes, in which almost three-fourths of the material by weight existed as particles between 5 and 10μ dia and essentially none of it was finer than 0.8μ dia or coarser than 16μ dia. Lot CP-7 had an even narrower particle-size distribution, in which more than 90% of the weight of material was present as particles between 5μ and 10μ dia. At least in fluid-energy grinding, the green Santa Maria coke breaks naturally to particle sizes approximating the optical domain sizes observed in the lump material. Not all of the fine particles produced represent single optical domains, but most of them do.

Lump green coke which had been vacuum-calcined by CMF-13 at 900°C had lower grindability than the as-received material, and was distinctly more abrasive to the grinding equipment. However, calcination greatly reduced the tendency of the coke to break into extremely fine (<10μ dia) particles, and increased the degree of control possible over particle-size distribution in size ranges coarser than this. The first hammer-milling pass (Schedule A) produced only about half as much minus 80 mesh material as in the case of the green coke, although -- unexpectedly -- it did produce more minus 325 mesh fines. Subsequent hammer-millings shifted the size distribution toward finer particle sizes, but increased the proportion of minus 325 mesh material quite slowly. Three stages of hammer-milling (the A + B + C sequence) produced a particle-size distribution approximating that of Great Lakes Grade 1008-S graphite flour, which has been used very successfully at LASL for a variety of purposes.

The grinding behavior of the as-received Santa Maria LV coke was quite similar to that of coke calcined by CMF-13 at 900°C. However, the LV coke showed slightly lower grindability and, in a given grinding procedure, yielded less minus 325 mesh fines, suggesting that it had been calcined somewhat above 900°C. By adjusting grinding variables, a great deal of flexibility was developed with regard to the particle-size distribution produced by grinding the LV coke.

Lump coke graphitized by CMF-13 at 2800°C was ground in two stages of hammer-milling (Schedule A + B) to produce Lot CP-13. Part of this ground material was further reduced in one pass through the fluid-energy mill (Schedule A + B + I) to produce Lot CP-14. Although the graphitized material is quite soft, its grindability is actually somewhat less than that of the calcined coke and distinctly less than that of the green coke -- perhaps because the graphitized particles are somewhat resilient. However it grinds easily and under good control, and with little apparent mill wear. Fluid-energy grinding of the graphitized Santa Maria material (Lot CP-14) produced an unusually flat particle-size distribution, with only a normal proportion of minus 325 mesh fines.

Several of the ground products listed in Table V have been heat-treated for use as fillers, and then investigated with regard to helium pycnometer density, Micromerograph particle-size distribution, and BET specific surface area. Results are listed in Table VI. In a given condition of heat treatment, helium density increased as the material was more finely ground, suggesting again that fracture during grinding occurs preferentially through enclosed voids. The equilibration period of 20 sec usually used in helium pycnometry was satisfactory for all of these materials except a sample of Lot CP-6 which, after grinding, was calcined at 900°C. This sample required about 10 min to reach pressure equilibrium, which is believed to indicate the presence of internal voids connected to external surfaces by passages so fine that the voids were not completely evacuated by the normal (20 min) outgassing treatment. These passages may be the small, narrow cracks observed microscopically in the calcined coke.

The data of Table VI also indicate that, for a given grinding product, helium density increases with the temperature to which the material is subsequently heat-treated. Again this suggests that shrinkage of the coke progressively opens its internal porosity to particle surfaces. However, BET measurements of specific surface area

TABLE VII

MANUFACTURING CONDITIONS, HOT-MOLDED GRAPHITES MADE FROM SANTA MARIA FILLERS

Graphite Lot No.	Raw Mix		Molding Conditions		Binder Residue, %(d)	Appearance
	Filler(a)	Binder, pph(b)	Pressure, psi	Heating Cycle, °C(c)		
56 A-1	CP-4(Green)	30	2000	5 hr to 900°, 1 hr hold	---	Many cracks
56 F-1	CP-5(Green)	None	4000	5 hr to 900°, 1 hr hold	---	Many cracks
56 G-1	50 CP-5(Green), 50 CP-4(2800)	None	4000	5 hr to 900°, 1 hr hold	---	Many cracks
56 H-1	25 CP-5(Green), 75 CP-4(2800)	None	4000	5 hr to 900°, 1 hr hold	---	Soft and weak
56 R-2	30 CP-7(Green), 70 CP-4(900)	None	4000	5 hr to 900°(e)	---	Soft and weak
56 I-1	37 CP-7(Green), 63 CP-4(900)	None	4000	5 hr to 900°, 1 hr hold	---	Stronger than 56 H-1
56 W-1	37 CP-7(Green), 63 CP-4(900)	4	4000	5.5 hr to 970°(e)	---	Many cracks
56 U-1	44 CP-7(Green), 56 CP-4(900)	None	4000	5 hr to 1000°(e)	---	Cracks
56 B-1	CP-4(900)	30	4000	5 hr to 900°, 1 hr hold	45.6	Cracks
56 J-1	CP-5(900)	18	4000	5 hr to 900°, 1 hr hold	67.6	Many cracks
56 P-1	CP-6(900)	25	4000	18 hr to 840°	46.1	Good
56 O-1	CP-7(900)	35	4000	18 hr to 840°	56.6	Cracks
56 S-1	CP-8(900)	30	4000	18 hr to 840°	46.7	Very good
56 L-1	70 CP-7(900), 30 CP-5(1300)	30	4000	5 hr to 900°, 1 hr hold	56.3	Many cracks
56 E-1	CP-4(1300)	17	4000	5 hr to 900°, 1 hr hold	58.6	One delamination
56 K-1	CP-5(1300)	30	4000	5 hr to 900°, 1 hr hold	49.8	Many cracks
56 C-1	CP-4(1500)	30	4000	5 hr to 900°, 1 hr hold	35.6	Fine edge cracks
56 M-1	CP-7(2600)	22.2	4000	5 hr to 900°, 1 hr hold	~27.2	Cracks
56 N-1	CP-7(2600)	20	4000	18 hr to 840°	---	Good but stuck to punches
56 D-1	CP-4(2800)	30	4000	5 hr to 900°, 1 hr hold	29.1	Good
56 T-1	CP-6(2800)	20	4000	18 hr to 840°	42.2	Very good
56 Q-1	CP-7(2800)	20	4000	18 hr to 840°	49.9	Very good
56 V-1	CP-8(2800)	20	4000	18 hr to 840°	43.7	Very good
56 Y-1	CP-9(LV)	35	4000	18 hr to 900°	44.7	Good
56 Z-1	CP-10(LV)	30	4000	18 hr to 900°	45.8	Good
5A6-1	CP-11(LV)	25	4000	18 hr to 900°	55.	Good
5B6-1	CP-13(2800)	35	4000	18 hr to 900°	44.7	Good
5C6-1	CP-14(2800)	30	4000	18 hr to 900°	45.3	Good
56 X-1	85.3 CP-8(2800), 14.7 Thermax	24.9(f)	10,000(g)	8 hr to 200°	---	Very good
56 X-2	85.3 CP-8(2800), 14.7 Thermax	24.9(f)	5300	8 hr to 200°(h)	36.8	Very good
57 B-1	CP-6(900)	27(i)	4000	18 hr to 900°	---	Good
57 C-1	CP-6(900)	27(i)	4000	18 hr to 900°	---	Good
57 D	CP-6(900)	27(i)	4000	18 hr to 900°	---	Broken
57 E-1	CP-10(LV)	27(i)	4000	18 hr to 900°	---	Good
57 F-1	CP-10(LV)	27(i)	4000	18 hr to 900°	---	Good

TABLE VII (Continued)

(a) Fillers are described in Tables V and VI. Parenthetical number indicates maximum temperature, in °C, to which filler was heat treated. "Thermax" is Thermax carbon black.

(b) Barrett 30MH pitch unless otherwise noted.

(c) Constant heating rate unless otherwise noted.

(d) Determined for hot-molded or baked condition.

(e) Manual control.

(f) Varcum 8251 resin containing 4 wt % maleic anhydride.

(g) Steel die.

(h) 8 hr to 200°, 6 hr to 420°, 3 hr to 900°, 1 hr hold.

(i) Solvent blended.

---

and the calculated "fuzziness ratios" -- which compare measured specific surface area with that calculated from Micromerograph data, assuming all particles to be smooth-shelled spheres -- are not consistent with this. The anomalous surface-area measurements for Lot CP-8, in particular, are not understood.

Use of the lognormal model -- on which the Micromerograph statistics of Table VI are based -- for large-variance particle-size distributions can be very misleading when $\bar{d}$ and s_d^2 values are deduced from weight-fraction data. However, the $\hat{\mu}_{x3}$ and $\hat{\sigma}_x^2$ values listed in Table VI can be used at least qualitatively for comparisons among these filler materials.

As is evident from the x-ray data of Table III, the grinding procedures used had no significant effects on the crystalline parameters of the Santa Maria coke. It made no apparent difference in either crystal structure or microstructure whether the coke was ground and then heat-treated or heat-treated and then ground. Among the samples examined by x-ray diffraction (Table III), Lot CP-7 -- which had been fluid-energy milled to a very fine particle size -- was unusually fluffy and packed only to very low bulk density in the sample holder. As is described below, it also produced quite anisotropic graphites.

G. Hot-Molded Graphites

Much of the initial investigation of the usefulness of Santa Maria coke as a filler for graphite manufacture has been by hot-molding, principally because -- since a long baking cycle is avoided -- it produces finished experimental graphites in relatively short times. With the exceptions noted below, the binder used for hot-molding was Barrett No. 30MH pitch, which in all early experiments was ground to about 50% minus 200 mesh and mixed dry with the filler in a 2-qt twin-shell blender. In general molding was at 4000 psi in 2.5-in. dia graphite dies, and temperature was increased at a constant rate to about 900°C. The hot-molded specimens were cooled in the die under atmospheric pressure only, ejected from the die, and graphitized in flowing helium to about 2800°C.

Manufacturing conditions for the individual hot-molded graphites are listed in Table VII, where the filler used is identified by the "Lot No." used in Tables V and VI plus a parenthetical number indicating the temperature in Centigrade degrees to which it was heat-treated prior to use as a filler. Properties of the finished graphites were not determined in all cases, usually because the hot-molded compact produced was so badly cracked that sound specimens for testing could not be machined from it. Properties which have been measured are listed in Table VIII.

1. Green Coke Fillers:

Two attempts were made to produce hot-molded graphites from hammer-milled Santa Maria green coke fillers. In the case of Lot 56A-1 (Table VII), 30 pph of pitch was used as the binder. For Lot 56F-1 no binder was used, in the hope that residual hydrocarbons in the green coke would bond filler particles to-

TABLE VIII

PROPERTIES OF HOT-MOLDED GRAPHITES MADE FROM SANTA MARIA FILLERS[a]

Graphite Lot. No.	Density, g/cm^3	Electrical Resistivity $\mu\,\Omega$ cm		Thermal Expansion[c] x 10^{-6}/°C		Crystalline Anisotropies[d]		Anisotropy Ratios		Crystallite Parameters Å	
		WG[b]	AG	WG	AG	BAF	M	Electrical Resistivity	Thermal Expansion	L_c	d_{002}
56 B-1	1.655	2452	2484	5.39	5.74			1.01	1.07		
56 P-1	1.658	2151	1999	4.76	5.38	1.02	0.1	0.93	1.13		
56 S-1	1.591	2140	2221	5.72	5.79	1.02	0.2	1.04	1.01		
56 E-1	1.628	3644	4289	5.56	5.75	~1.00	~0.0	1.18	1.03	290	3.369
56 C-1	1.625	3226	3667	3.97	5.48	1.04	0.2	1.14	1.38	340	3.370
56 D-1	1.690	2960	3762	5.84	7.77	1.08	0.4	1.27	1.33	370	3.370
56 T-1	1.667	2991	3942	5.74	6.94	1.06	0.6	1.32	1.21		
56 Q-1	1.722	3659	5268	4.80	7.19	1.40	1.5	1.44	1.50		
56 V-1	1.582	2854	---	4.84	7.28	1.03	0.2	---	1.50		
56 Y-1	1.496	2150	2025	5.66	6.29	1.037	0.20	0.94	1.11		
56 Z-1	1.591	1825	1710	5.06	5.02	~1.00	<0.1	0.94	0.99		
5A6-1	1.623	1805	1825	5.45	5.32	~1.00	<0.1	1.01	0.98		
5B6-1	1.734										
5C6-1	1.725										
56 X-1	1.823	1707	2521	4.65	5.39	1.02	0.2	1.48	1.16		
56 X-2	1.770	---	1759	5.19	5.58	1.02	0.2	---	1.08		
57 A-1	---	1910	1975	6.36	6.06	1.029	0.32	1.03	0.95		
57 B-1	1.706	1920	1990	5.08	5.81	1.029	0.23	1.04	1.14		
57 C-1	1.683	2200	2210	5.50	5.45	1.017	0.20	1.00	0.99		
57 E-1	1.781										
57 F-1	1.761										

(a) All specimens graphitized in flowing helium at about 2800°C.

(b) WG = With-grain, AG = Across-grain.

(c) Average, 25-645°C.

(d) BAF = Bacon anisotropy factor, M = exponent of cosine in cosine function which best represents angular distribution of intensities of reflected x-rays.

gether. In both cases the hot-molded compacts were badly cracked as they were ejected from the die and contained many large blowholes, which often appeared to be totally enclosed. Between the cracks and blowholes the structure was very dense, containing only lenticular voids of the type initially present in the coke. The boundaries between filler particles had disappeared. Particularly when no binder was used, a high degree of crystalline anisotropy had developed. Apparently the green coke becomes plastic at elevated temperatures, and capable of deforming under pressure to fill the interstices between filler particles. In doing so, it develops a high degree of preferred orientation of crystallites, and a highly anisotropic graphite is produced. Presumably the pitch addition reduced anisotropy by filling interstices so that there was less plastic flow of the coke into them, and therefore less preferred orientation of crystallites within the coke.

In the case of the green coke filler, closing of voids by material flow and internal evolution of a large volume of gas during heating developed pressures sufficient to form large blowholes, and probably to fragment the body within the mold. A large volume shrinkage of the coke as a result of pyrolysis and the high thermal contraction coefficient of the filler undoubtedly contributed to the fragmentation. Very slow heating and cooling during the molding cycle would probably at least reduce the damage.

Six hot-molded compacts were made in which, to reduce gas evolution during molding, the green Santa Maria coke was mixed with coke which had been calcined at 900°C or graphitized at 2800°C. Of these, Lots 56G-1, 56W-1, and 56U-1 were badly cracked as they were ejected from the die. Lots 56H-1, 56R-2, and 56I-1, were all made without binder additions and were all intact but were soft, weak, and poorly bonded. Microscopic examination of graphite 56G-1 revealed narrow, contorted voids, and large cracks -- usually parallel to the molding direction -- with smaller cracks approximately normal to the large ones. In graphite 56I-1, most of the filler particles were surrounded by narrow voids, most of the porosity was accessible to the mounting resin, and a few cracks parallel to the molding direction were observed.

Some modification of particle-size distribution, mix formulation, and molding procedure can probably produce dense, highly anisotropic, hot-molded graphites from the green Santa Maria coke. However, any development of such graphites by CMF-13 has been postponed until the more conventional manufacturing procedures have been more fully explored.

2. Fillers Vacuum-Calcined at 900°C: Graphite Lots 56B-1 and 56J-1 were hot-molded using fillers which had been vacuum-calcined by CMF-13 at 900°C and a "Standard" molding procedure in which the compact was heated under pressure from room temperature to 900°C at a constant rate of about 180°C/hr. Both compacts were seriously cracked as they were ejected from the die. The same was true of Lot 56L-1 in which, to reduce gas evolution during molding, the 900°C-calcined filler was diluted with coke which had been calcined at 1300°C. Microscopic examination of graphites 56B-1 and 56J-1 showed evidence of poor mixing in the form of lenticular volumes of binder residue not containing filler particles. Both contained fine, rather uniformly distributed pore networks which were quite well penetrated by the mounting resin. In 56B-1 there were a few stringers of voids, but in general the voids followed the boundaries of filler particles. In 56J-1 most of the cracks were approximately parallel to the molding axis.

In producing Lots 56P-1 and 56S-1, the heating rate during hot-molding was reduced to about 45°C/hr. Both graphites were sound, although both contained regions of unmixed binder residue, often accompanied by coarse pores, and also regions where the filler particles had not been wet by binder. The properties of both are listed in Table VIII. Lot 56O-1 was made under the same conditions but from a very finely ground filler. It was cracked on ejection from the die, apparently because the connected porosity in it was too restricted to permit free evolution of gases evolved, even at the relatively low heating rate used.

These results, and others cited below, suggest that to avoid damage during hot-molding it would be desirable to heat-treat the Santa Maria filler to a relatively high temperature, in order to reduce the volume of gas evolved from it, and also to heat slowly during molding in order to permit the gas which is evolved to escape without damaging the structure.

3. Fillers Calcined at 1300°C and 1500°C: Lots 56E-1 and 56K-1 were made from Santa Maria coke calcined in helium at 1300°C, and Lot 56C-1 from coke calcined in helium at 1500°C. Unfortunately, all three were hot-molded using the "standard", relatively high heating rate of 180°C/hr, and all showed some cracking. Lots 56E-1 and 56K-1 were poorly mixed, containing undistributed volumes of binder residue. 56E-1 contained many long narrow voids and void stringers. In 56K-1 the voids were generally fine, well-distributed, and quite accessible to

the mounting resin. Many fine cracks were observed in 56 K-1, frequently associated with concentrations of binder residue. Lot 56 C-1 appeared to contain more voids outlining filler particles and somewhat larger voids than did Lot 56 B-1, made from the same filler calcined at only 900°C, but was not as badly cracked as 56 B-1.

4. Fillers Graphitized at 2600°C: Two compacts were hot-molded from a very finely ground Santa Maria filler (Lot CP-7) which had been graphitized at 2600°C. Lot 56 M-1, molded using the "standard" (180°C/hr) heating rate was cracked as ejected from the die, although it is not obvious that this would have occurred with a less finely ground filler. It contained lenticular bodies of unmixed pitch residue, often associated with a locally high degree of porosity, and many small voids. Its cracks were of all sizes, and were largely normal to the molding direction.

Lot 56 N-1 was molded using the lower (45°C/hr) heating rate, and was sound as ejected from the die. However, it stuck to the graphite punches and was broken in the attempt to separate it, so that no properties were measured on it. The microstructure of 56 N-1 was distinctly better than that of 56 M-1, but it did contain regions of segregated pitch, often associated locally with blowholes and small cracks.

5. Fillers Graphitized at 2800°C: Graphites 56 D-1, 56 T-1, 56 Q-1, and 56 V-1 were hot-molded from Santa Maria fillers graphitized at 2800°C, one of which (used in Lot 56 Q-1) was the very finely ground filler which had consistently given trouble when it had been heat-treated at lower temperatures. All of these graphites were sound, although all showed evidence of poor mixing. Lot 56 D-1 had an unusually nonuniform pore structure, including many large voids, void stringers, and long narrow voids surrounding the larger filler particles. Lot 56 T-1 had generally fine porosity, quite accessible to the mounting resin, but contained some pore stringers normal to the molding axis and a few fine cracks and regions of coarse porosity, usually associated with binder segregates. Many filler particles were not wet by the binder. Lot 56 Q-1 contained a few cracks and blowholes associated with lenticular binder segregates, but most of its porosity was fine, somewhat angular, and uniformly distributed. Lot 56 V-1 was more porous than other graphites in this group.

The properties of these four graphites are listed in Table VIII.

6. LV Coke Filler: In order to determine whether Santa Maria LV coke, calcined by the supplier, differed significantly in behavior from Santa Maria coke calcined by CMF-13, three hot-molded graphites were made using as fillers the LV coke ground by three different procedures. The filler for Lot 56 Y-1 was hammer-milled once, that for Lot 56 Z-1 was hammer-milled twice, and that for Lot 5A6-1 was hammer-milled once and then fluid-energy milled. All three graphites were sound. Because of differences in filler-particle size distribution, their properties -- listed in Table VIII -- cannot be compared directly with those of graphites similarly made from cokes calcined by CMF-13. They appeared, however, to be quite similar in behavior and properties to Lots 56 P-1 and 56 S-1, discussed above, which were made from coke calcined at 900°C by CMF-13. The microstructures of all three of these graphites showed evidence of poor mixing in the form of segregated regions of binder residue not containing filler particles and also of filler particles not wet by binder. No cracks were observed, but all three graphites were very porous.

7. Resin-Bonded Graphites: Hot-molded graphites 56 X-1 and 56 X-2 were made from the residue of a resin-bonded mix prepared for an extrusion experiment described below. The raw mix contained, by weight, 85.3 parts of hammer-milled Santa Maria flour which had been graphitized at 2800°C, 14.7 parts of Thermax carbon black, and 24.9 parts of Varcum 8251 (a commercial furfuryl alcohol resin) catalyzed by the addition of 4 wt % maleic anhydride. Lot 56 X-1 was compacted at 10,000 psi in a steel die, heated in the die under pressure to 200°C, cooled under atmospheric pressure only, and ejected from the die, then cured, baked, and graphitized in cycles normally used by CMF-13 for extruded, resin-bonded graphites. Lot 56 X-2 was compacted at 5300 psi in a graphite die, heated in the

die under pressure to 900°C in a cycle intended to allow for thermal activity in the resin as it polymerized and pyrolyzed, cooled under atmospheric pressure and ejected from the die, and then graphitized. Both graphites appeared sound and well mixed, although both were found to contain many microscopic cracks, chiefly at interfaces between filler particles and binder residue in the case of 56X-1 and distributed between interfaces and binder residue in the case of 56X-2. Their properties are given in Table VIII.

8. Solvent Blending: The structural deficiency common to most of the pitch-bonded, hot-molded graphites described above has been segregated areas of binder residue unmixed with filler particles, and commonly associated with cracks and large blowholes. Obviously this results from poor mixing, which is difficult to avoid in a dry particulate system. In an attempt to avoid it a series of solvent-blending experiments was undertaken in which an organic liquid was used to dissolve as much as possible of the binder, the solution was mixed with a Santa Maria filler, and the solvent was then removed by evaporation. The ideal result would be filler particles completely coated with pitch or with the soluble fraction of the pitch.

In the first experiment of this type tetrahydrofuran ("THF") was used as the solvent for Barrett 30MH pitch, in the proportion 1.5 ml THF to 1 gram of pitch. (Dissolution of the pitch was not complete, but its insoluble components were at least finely dispersed in the solution, as was indicated by a very low sedimentation rate.) The solution was poured onto the dry filler and mixed by hand-spatulation, which was continued in a warm-air stream until the odor of the solvent could no longer be detected. Graphite Lot 57A-1 was produced from the mix by hot-molding. It was compared with Lot 56P-1, similarly made from a similar mix but with dry blending of the filler and ground pitch binder. Lot 56P-1 contained relatively large pores, usually associated with bodies of unmixed binder residue. There were many pore colonies and stringers of pores, and many filler particles not wet by the binder. Lot 57A-1 had a very fine, uniform, moderately accessible pore network with only a few void stringers, and was essentially free of cracks, blowholes, and segregated binder residue. It contained a small number of cavities much larger than the filler particle size, apparently representing poor compaction in the die. However, a relatively crude solvent-blending procedure had improved the graphite structure markedly.

Lot 57B-1 was made similarly, using THF solvent and hand-spatulation. However, mixing was continued by passing the mix repeatedly through a food chopper until essentially all of the solvent had evaporated. Properties of the hot-molded product are listed in Table VIII and represent a distinct improvement over those of Lot 56P-1, a similar graphite which was prepared by dry mixing. In microstructure, Lot 57B-1 was much like Lot 57A-1, but with some indications of binder segregation in a few regions and a slightly coarse pore structure.

In preparing Lot 57C-1, acetone was used as the solvent instead of THF, in the proportion of 3.75 ml acetone per gram of pitch. (The solubility of 30MH pitch in acetone is relatively low.) The pitch was added to the solvent with mechanical stirring which was continued for 1 hr, after which the dry filler was stirred in. Again repeated passes through the food chopper were used to complete mixing and evaporate the solvent. The hot-molded product appeared to represent some improvement over the similar dry-mixed graphite, Lot 56P-1, but to be inferior to Lot 57B-1, in the preparation of which the solvent used was THF. In particular, it contained slightly more visible porosity and more colonies of voids. Accordingly, all subsequent solvent-blended lots in this series were prepared using THF.

In producing Lot 57D-1 -- again using THF -- it was found that additional passes through the food chopper after all of the solvent had been driven off produced a significant temperature rise in the mix. Chopping was therefore continued until mix temperature reached 90°C. (Previous attempts to hot-chop dry-blended, pitch-bonded mixes had been unsuccessful.) The hot-molded compact produced was broken into two pieces as it was ejected from the die. In a repeat run, Lot 57D-2, the compact was again broken into two pieces. In a third run, Lot 57D-3, heating rate during molding was reduced to 13°C/hr, and the compact broke into five pieces. All three specimens had relatively high bulk densities as hot-molded, with little visible porosity and this porosity in general not accessible to the mounting resin. In this case the damage may not have resulted from gas evolution. It may instead be related either to large thermal contractions or to particle packing intimate enough so that unusual restraints were imposed on the shrinkage accompanying binder pyrolysis. No evidence of binder segregation was found, and the few fine cracks observed were near external surfaces and perpendicular to the molding axis.

Graphite Lots 57 E-1 and 57 F-1 were made using THF solvent and with the chamber of the food chopper heated externally by an electrical tape. For Lot 57 E-1 the chamber was heated initially to 100°C and chopping was repeated until the mix temperature reached 140°C. For Lot 57 F-1 initial chamber temperature was 90°C, final mix temperature was 145°C, and a small addition of extrusion oil (5% of the weight of pitch) was made to the raw mix as a lubricant. Bulk densities as-molded were 1.644 g/cm^3 for Lot 57 E-1, 1.684 g/cm^3 for Lot 57 F-1, and only 1.563 g/cm^3 for Lot 56 Z-1, a comparable material produced by dry-blending.

It is apparent that significant improvements in density and other properties of hot-molded, pitch-bonded graphites produced from the Santa Maria coke can be achieved by improved mixing of the component raw materials, and that solvent-blending is one available method to improve mixing. Further improvements are possible by mixing hot instead of at room temperature, and by addition of a lubricant to the mix.

The experimental hot-molded graphites described above are obviously not the best that can be made by this method from the Santa Maria fillers. They were not optimized with regard to filler-particle size distribution, binder content, or mix additions, in general they were poorly mixed, and many of them were heated too rapidly during molding. Typically they were quite porous, and many were cracked. However, a number of useful conclusions can be drawn from this set of hot-molding experiments.

1. As would be expected from the shapes and internal structures of the filler particles, graphites produced from Santa Maria fillers are in general essentially isotropic with regard to crystallite orientation. Bacon anisotropy factors are normally less than 1.1 and frequently less than 1.05. Two exceptions to this are possible. One occurs when green coke is used as the filler and, in hot molding, plastic flow of filler particles reorients crystallites within them and creates a highly anisotropic structure. The other occurs when the filler is ground so finely that inherently anisotropic particles are created with acicular or tabular shapes which assume preferred orientations during forming. (The first of these cases is typified by Lots 56 A-1 and 56 F-1, the second by Lot 56 Q-1.) With rigid (calcined or graphitized) filler particles and a normal particle-size distribution, a relatively large proportion of extreme fines can be tolerated without producing a significant degree of crystalline anisotropy.

2. In spite of their crystalline isotropies, several of these hot-molded graphites were distinctly anisotropic in their properties. Since this was evidently not a result of preferred orientation of crystallites, it must be explained in terms of a preferred orientation of structural defects -- such as voids, cracks, binder segregates, and binder-deficient regions. It probably originates largely in lateral material flow during molding, and in particular in lateral flow of excess binder. It is evident from the properties of such graphites as 56 S-1 and 56 B-1 (Table VIII) that this type of anisotropy is not inherent in these graphites and that, by improved manufacturing procedures, it can be reduced to the same low level as the crystalline anisotropy.

3. Because of the randomness of crystallite orientation demonstrated by their optical domain structures and Bacon anisotropy factors, graphites made from Santa Maria fillers typically have relatively high coefficients of thermal expansion. This will reduce their usefulness in some applications, and probably limit their resistance to thermal stress and thermal shock. However, it will also reduce the thermal expansion mismatch between the graphite and the corrosion- and erosion-resistant coatings com-

monly used on graphite, and also between graphite and the various metals, carbides, ceramics, etc., with which it may be assembled in machines and structures. In many cases this will simplify designs and increase service life.

The high thermal contraction coefficients of the filler particles undoubtedly contributed to some of the structural damage described above, in particular to the formation of small cracks and narrow voids around filler particles. This represents a manufacturing difficulty that will be difficult to avoid completely when any high-expansion filler is used.

4. Again because of randomness of their internal structures, these graphites -- although they graphitize to moderately large crystallite sizes -- have relatively high electrical resistivities. Unless they can be modified significantly in this regard, for example by addition of a second filler component of much lower resistivity, they will probably not be attractive for applications such as furnace electrodes where low resistivity is essential. They may, however, be useful in resistively heated furnace elements. Their isotropy, graphitizability, potentially high density and low connected porosity make them interesting for a variety of nuclear reactor applications. Their structure suggests that they may have good resistance to wear, erosion, and ablation, although this and their thermal stress resistance require experimental investigation.

H. Extruded Graphites

Because of the limited capacity of the CMF-13 extrusion press, no attempt has been made to extrude pitch-bonded mixes involving Santa Maria fillers. All extrusions so far made from these fillers have been resin-bonded and have included a filler addition of 15 parts Thermax carbon black to 85 parts of the principal filler. The binder has been Varcum 8251 furfuryl alcohol resin containing 4 wt % maleic anhydride as a curing catalyst, diluted with 7.5% acetone to facilitate mixing. Standard CMF-13 mixing and blending procedures have been used, involving hand-stirring of the mix components for 10 min followed by twin-shell blending using an intensifier bar, and then nine passes through a food chopper and triple extrusion to complete mixing and mix-compaction. (In order, the chopping and extrusion sequence consisted of: 5 passes through the food-chopper; ram-extrusion as 0.5-in. dia rod; 2 passes through the food-chopper; ram-extrusion as 0.5-in. dia rod; 2 passes through the food-chopper; final ram-extrusion as 0.5-in. dia rod. The acetone binder-diluent is believed to have been removed completely by evaporation during chopping and pre-extrusion.) The 0.5-in. dia extruded rods were cured and baked in normal cycles and finally graphitized in flowing helium to about 2800°C.

Two attempts (Lots ABS3 and ABS4, listed in Table IX) were made to extrude mixes in which the principal filler was hammer-milled green Santa Maria coke. Neither mix could be extruded at the maximum capacity of the press (40 tons). If a serious effort were to be made to produce green-flour extrusions, the use of extrusion lubricants would probably be investigated.

Extrusion Lots ABS7, ABS11, and ABS14 were produced from Santa Maria coke which had been hammer-milled in the green condition and then vacuum-calcined by CMF-13 at 900°C. This type of mix was found to be very sensitive to binder concentration. Apparently the optimum proportion of binder is the minimum which makes extrusion possible. In all cases the green extruded rod was quite flexible and rubbery, with a tendency to sag between support points. The rods of Lot ABS11 were coiled in the green state and cured, but were not subsequently baked or graphitized. The rods of Lots ABS7 and ABS14 lost large amounts of surface material as exfoliated chips during graphitization. Apparently this was the joint result of internal gas evolution from use of an incompletely calcined coke and poorly interconnected porosity in the surface layers of the extruded rods. It could probably be prevented by calcining the coke to a higher temperature or by increasing the permeability of the graphite structure to gases -- probably by removing some fraction of the extreme fines from the filler. (The filler used in Poco graphites, for example, appears to have been closely sized, perhaps for this reason.) A few rods from each of these

TABLE IX

MANUFACTURING CONDITIONS, EXTRUDED GRAPHITES MADE FROM SANTA MARIA FILLERS

Graphite	Raw Mix			Extrusion Conditions			Green	
Lot No.	Filler Used(a)	Carbon Black(b)	Binder, pph(c)	Pressure, psi	Speed, in./min	Mix Temp. °C	Rod Dia., in.	Appearance after Graphitization
ABS 3	CP-6(Green)	15 pph	36.4 Varc.	> 26,000(d)	---	Room	---	
ABS 4	CP-6(Green)	15 pph	26.7 Varc.(e)	> 26,000(d)	---	54	---	
ABS 7	CP-6(900)	15 pph	21 Varc.(f)	19,350	138	54	0.504	Small chips exfoliated from ~50% of surface.
ABS 11	CP-6(900)	15 pph	23.8 Varc.(g)	1,575	145	43	---(h)	(Not baked or graphitized.)
ABS 14	CP-6(900)	15 pph	22 Varc.(g)	4,500	171	37	---(h)	Moderate number of large exfoliated chips.
ABS 10	CP-8(900)	15 pph	19.8 Varc.(i)	7,200	150	50	0.501	Medium-sized chips from almost entire surface.
ABS 9	CP-9(LV)	15 pph	22.5 Varc.	13,950	167	53	0.502	Satisfactory.
ABS 12	CP-9(LV)	15 pph	24 Varc.(g)	<1,500	---	35	---	Rough surface with network of fine cracks.
ABS 8	CP-10(LV)	15 pph	20 Varc.(f)	20,250	89	41	0.502	Satisfactory.
ABS 13	CP-10(LV)	15 pph	21.7 Varc.	9,000	157	43	0.502	A few small exfoliated chips.
ABS 1	CP-4(1300)	15 pph	21.3 Varc.	7,200	171	34	0.500	Moderate number of chips.
ABS 2	CP-7(2600)	15 pph	29.9 Varc.	11,250	157	54	0.502	
ABS 5	CP-8(2800)	14.7 pph	24.9 Varc.	5,040	171	50	0.501	
ABS 6	CP-6(2800)	15 pph	23.7 Varc.	9,360	171	42	0.502	

(a) Fillers described in Tables V and VI. Parenthetical number indicates temperature to which filler was calcined.

(b) Thermax carbon black.

(c) Varcum 8251 resin containing 4 wt % maleic anhydride.

(d) Stalled press; run aborted.

(e) Uncatalyzed.

(f) Mix too dry.

(g) Mix too wet.

(h) Too soft to measure.

(i) Complex mixing procedure.

lots showed fine end-cracks after curing. In general these cracks were neither numerous nor extensive. However, microscopic examination of sections through a rod from Lot ABS7 revealed one severe radial crack and several short axial cracks. The graphite appeared to be slightly deficient in binder. A rod from Lot ABS14 contained several serious cracks which were visible microscopically. Between these cracks there was little visible porosity in either graphite, and most of the pores were not accessible to the mounting resin.

Lot ABS10 was made from Santa Maria coke which had been vacuum-calcined at 900°C and then hammer-milled. It was quite similar in its behavior to lots made from coke which was ground and then calcined. Some of the rods produced showed fine end cracks after curing, and all rods exfoliated badly during graphitization. Because of a different filler-particle size distribution, the properties of this graphite were somewhat different from those of Lots ABS7 and ABS14, but the differences appeared to be small. Sections through rods of Lot ABS10 showed the presence of numerous long, thin pores, usually parallel to the edges of the larger filler particles, and with a tendency to link up to form cracks parallel to the extrusion axis. Their appearance suggested that they had formed while the binder was plastic and slightly tacky, probably during curing.

Santa Maria LV coke, which had been calcined by the supplier, was used as the principal filler in Lots ABS9, ABS12, ABS8, and ABS13. Although sulfur-containing gases are evolved from this coke during grinding and large quantities of volatile materials are expelled from it during graphitization, the LV coke has apparently been calcined at some temperature higher than the 900°C used by CMF-13 to calcine the green coke. As a result, extruded graphites made from LV coke were much less subject to exfoliation and surface damage during graphitization than were those made from 900°C-calcined coke. They could probably be further improved in this regard by calcining the coke to a still higher temperature. Again, at least a few of the rods from each lot made using the LV coke showed some fine end cracks after curing. Lot ABS9 contained many elongated pores, usually along filler-binder interfaces, and ranging in length up to about three times the diameters of adjacent, relatively large filler particles. A few appeared to pass entirely through binder residue, in a pattern unrelated to nearby particles. A few spongy regions were observed, and some short cracks. The filler used apparently was deficient in fines. Lot ABS12 was similar to this in microstructure, but with a tendency for the long, thin voids to link together and form cracks parallel to the extrusion direction. In this graphite a few of the larger filler particles appeared to have been pulled apart either by contraction of the binder residue around them or by the large thermal contraction of the filler particles themselves as the body cooled. The voids and cracks in general were not surface-connected, and were not entered by the mounting resin. Lot ABS8, made from a more finely ground filler, was similar in internal structure to ABS9, but with finer pores. It still appeared to be deficient in fine filler particles. Lot ABS13, with a slightly higher binder content than ABS8, was quite similar to it in microstructure but contained many fine, longitudinal cracks. These appeared to have formed while the binder was slightly tacky, probably during curing. Fewer short cracks were observed, and more large filler particles were outlined by narrow voids.

Extruded Lot ABS1 was made from hammer-milled coke calcined by CMF-13 at 1300°C. In spite of the relatively high calcining temperature, exfoliation of chips from rod surfaces occurred during graphitization. Microstructural examination showed the presence of a system of internal cracks -- including central, radial, and longitudinal types -- parallel to the extrusion axis, plus a few cracks normal to that axis. Most of the cracks were at filler-binder interfaces, although some were within the binder residue, and many were associated with void colonies accessible to the mounting resin. Some of the larger filler particles were entirely surrounded by voids. Mixing was good, so that these deficiencies must be attributed to some combination of particle-size distribution, mix formulation, and differential thermal contraction of filler particles and binder residue. Properties of this graphite are listed in Table X.

The filler for Lot ABS2 was a very fine, fluid-energy-milled flour which had been graphitized at 2600°C. Binder requirement was high, and the rods produced varied considerably in green diameter, density, and other properties along their lengths. In general, density increased with distance from the leading end of the extrusion, and the change in green diameter was sufficient to account for only about 30% of the density change. The properties listed in Table X are averages of quite widely scattered measurements at several points on several rods. Like the hot-molded graphite made from this same filler (Lot 56 Q-1, Table VIII), Lot ABS2 was highly anisotropic in both crystallite arrangement and properties. Its microstructure, illustrated by Fig. 5, demonstrated good mixing and was very fine and uniform, with no significant defects visible even at electron-microscope magnifications. There was very little visible porosity, and essentially no penetration of the sample by the epoxy mounting resin. An axial region about 80 μ dia appeared to be slightly deficient in filler

TABLE X

PROPERTIES OF EXTRUDED GRAPHITES MADE FROM SANTA MARIA FILLERS(a)

Graphite Lot No.	Density, g/cm^3	Young's Modulus WG(b) 10^6 psi	Compressive Str. WG psi	Electrical Resistivity μΩcm		Thermal Conductivity W/cm-°K		Thermal Expansion(c) x10^{-6}/°C		Crystalline Anisotropies(d)		Anisotropy Ratios			
				WG	AG	WG	AG	WG	AG	BAF	M	Bulk Sound Velocity	Electrical Resistivity	Thermal Conductivity	Thermal Expansion
ABS 9	1.786	1.33								~1.00	<0.1				
ABS 12	1.764	1.27								~1.00	<0.1				
ABS 8	1.797	1.43								1.040	0.16				
ABS 1(e)	1.877	---		1969	2349	0.65	0.58	4.58	4.92	~1.00	~0.0	---	1.19	1.12	1.07
ABS 2	1.91	2.19	14,700	2007	2980	0.53	0.36	---	---	1.43	1.9	1.21	1.48	1.47	---
ABS 5	1.84	1.60	11,900	1659	1754	0.81	0.74	4.5	5.2	1.04	0.2	1.019	1.06	1.09	1.16
ABS 6	1.88	1.63	15,200	1915	1898	0.77	0.73	4.4	4.9	~1.00	~0.0	0.996	0.99	1.05	1.11
ABS 13										~1.00	<0.1				
ABS 14										~1.00	<0.1				

(a) All specimens graphitized in flowing helium at about 2800°C.

(b) WG = With-grain, AG = Across-grain.

(c) Average, 25-645°C.

(d) BAF = Bacon anisotropy factor, M = exponent of sine in sine function which represents angular distribution of intensities of reflected x-rays.

(e) L_c = 270 Å, d_{002} = 3.372 Å.

particles, apparently reflecting a peculiarity in material flow through the extrusion die.

Graphite Lots ABS5 and ABS6 were made from Santa Maria fillers which had been graphitized at 2800°C. That used for Lot ABS6 had been hammer-milled in the green condition and contained a much higher proportion of minus 325 mesh fines than did the filler used for Lot ABS5, which was hammer-milled after calcination at 900°C. The green mix used to make Lot ABS5 showed an unusual "drying-out" behavior during chopping and pre-extrusion, apparently representing slow absorption of a relatively large amount of resin binder by the filler particles. (This filler, grinding lot CP-8 in Table V, also gave anomalous BET surface-area measurements, noted above in connection with Table VI. Its behavior is not understood. Part of this mix, left over from extrusion, was used to make hot-molded Lots 56X-1 and 56X-2, described above.) The mixing behavior of Lot ABS6 was normal. The microstructures of both graphites suggested slight binder deficiencies. Graphite ABS5 contained some large pores, a few stringers of pores, and many small cracks at or adjacent to interfaces between the larger filler particles and the binder residues -- whose lengths were usually the same as those of the adjacent particles. Lot ABS6 was similar in microstructure but was finer grained, so that its pores were generally smaller and its microcracks shorter.

Properties so far collected on these extruded graphites are listed in Table X and mercury porosimetry data are summarized in Table XI. Accessible porosities are low, especially for the baked condition of one lot investigated before it was graphitized. Undoubtedly this contributed to the exfoliation problem described above. Densities of graphites made from calcined cokes were affected by loss of volatile matter from the filler during graphitization, and were unspectacular. Densities of graphites made from graphitized fillers were moderately high and can probably be increased further by improving filler-

Fig. 5. Typical microstructure of extruded, resin-bonded graphite made from Santa Maria graphite flour, Lot ABS2. Xenon-ion etch, 5000X.

TABLE XI

MERCURY POROSIMETRY DATA, EXTRUDED GRAPHITES MADE FROM SANTA MARIA FILLERS

Graphite Lot No.	Condition	Total Porosity %	Porosity Accessible to Mercury at 2600 psi %	Porosimeter Sample Statistics[(a)]				
				$\bar{x}_3$	s^2_{x3}	g_{x3}	S_W m^2/g	CV_d
ABS1	Baked 900°C	20.0	1.4	-0.68	1.4	3.1	16.9	0.54
ABS1	Graphitized 2800°C	16.9	2.5	-0.59	2.0	3.9	18.7	0.56
ABS2	Graphitized 2600°C	15.5	3.4	-1.51	0.19	0.4	28.2	0.30
ABS5	Graphitized 2800°C	18.8	3.1	0.22	1.03	-0.65	8.6	0.77
ABS6	Graphitized 2800°C	16.9	2.0	-0.96	1.2	0.67	24.	0.43
ABS8	Graphitized 2800°C	20.5	3.5	-0.12	1.2	1.9	11.5	0.71
ABS9	Graphitized 2800°C	20.8	3.7	0.19	1.2	2.1	9.6	0.71
ABS12	Graphitized 2800°C	21.8	4.5	1.12	2.4	8.6	6.5	0.63

(a) Non-functional model

particle size-distribution and mix formulation. Manufacturing procedures were simplified and exfoliation damage during graphitization eliminated when graphitized fillers were used.

Only when the filler used was ground entirely to an extremely fine particle size (Lot ABS2) did the extruded graphite produced have an appreciable crystalline anisotropy. Otherwise, even a filler which was more than 55% minus 325 mesh yielded a graphite (Lot ABS6) that was essentially isotropic in crystallite orientation and only slightly anisotropic in properties. In general the extruded graphites were nearly isotropic, strong, and had moderate to high densities. Their electrical resistivities and thermal expansion coefficients were high, and their Young's moduli and thermal conductivities were normal. A short series of thermal-shock tests was made in the CMF-13 electron-beam apparatus on thin discs machined from Lots ABS5 and ABS6. Results indicated a moderate degree of thermal-shock resistance, somewhat inferior to that of CMF-13 Lot AAQ1 -- a very similar graphite in which the principal filler was Great Lakes Grade 1008-S graphite flour. Obviously these graphites can be improved, in particular by optimizing particle-size distributions and mix formulation. However, simply as isotropic extruded graphites they are unusual and interesting, and their properties indicate a wide range of potential usefulness.

It should perhaps be noted that in the above descripttions the emphasis has been on the deficiencies of the graphites produced, because these are potentially correctable. If the basis of comparison had been a real graphite instead of a hypothetical flaw-free one, it would be evident that the better experimental graphites already made from Santa Maria fillers are in fact at least equal in quality to most of the currently available commercial premium grades of graphite.

III. GRAPHITE FILLER MATERIALS

A. Grinding Research (R. J. Imprescia)

1. Effect of Grinding on Crystalline Parameters

In a few of the experiments on graphite described in previous reports in this series, small decreases in crystallite size (L_c) have been observed to result from grinding. Data from a recent experiment involving fluid-energy grinding of a pyrolytic graphite suggested that a large decrease in crystallite size had occurred, and that it was accompanied by a rather large increase in interplanar spacing (d_{002}). Significant changes in d_{002} as a result of grinding had not previously been observed. The experiment was therefore repeated using hammer-milled pyrolytic graphite, Lot GP(Py-7), as the feed to a Trost fluid-energy mill. In this case values of d_{002} were 3.424 Å before fluid-energy grinding and 3.418 Å after grinding, and the value of L_c remained constant at 193 Å. The change in d_{002} is not considered significant, and it is believed that the previous data were incorrect -- probably because of a mixup in samples submitted for x-ray analysis.

The conclusion previously reached concerning the effect of grinding on the crystalline parameters of graphite is therefore still maintained. Either hammer-milling or fluid-energy grinding of a graphite may produce a small decrease in its apparent crystallite size, but in general neither grinding method significantly changes the apparent interplanar spacing of the graphite.

2. Fluid-Energy Grinding Conditions

The manufacturers of the Trost fluid-energy mill recommend that it be operated with maximum air pressure (100 psi) on both the pusher jet, which feeds material into the mill, and the opposing jet. Because of blow-back problems with some mill feeds, it has occasionally been necessary to decrease pressure on the opposing jet of the CMF-13 mill. The effect of this change in grinding conditions was investigated in four grinding runs made on hammer-milled, calcined Santa Maria coke, Lot CP-10. Air pressure on the pusher jet was held constant at 100 psi, and air pressure on the opposing jet was decreased from 100 psi in 20 psi increments. (These are grinding conditions I, L, M and N in Table IV.) Screen analyses of the four grinding products are given in Table V. Using the same discharge orifice and essentially the same rate of feed to the mill, successive reductions in pressure on the opposing jet progressively reduced the grinding efficiency of the mill. The largest change was in the proportion of minus 325 mesh fines in the grinding product, which decreased from 65% when the opposing jet was operated at 100 psi to only 30% when it was at 40 psi. In general such a reduction in mill efficiency is undesirable. However, it may in some cases be desirable in order to limit the proportion of extreme fines produced in a given fluid-energy grinding pass, in which case this type of control will be useful.

Attempts to hold the opposing jet at a constant pressure of 100 psi while reducing pressure on the pusher jet to below 100 psi were unsuccessful. In all cases severe blow-back of the mill feed occurred when the pusher jet was at lower pressure than the opposing jet.

IV. GRAPHITE BINDERS

A. Molecular Composition of Furfuryl Alcohol Resins (E. M. Wewerka)

The low-molecular-weight fractions of three furfuryl alcohol resins have been separated from the bulk by vacuum distillation, further separated into individual molecular components by gas chromatography, and the components tentatively identified. One of the resins was a standard acid-polymerized resin, the second had been polymerized using γ-alumina, and the third was a furfuryl alcohol-formaldehyde resin. The low-molecular-weight portions of all three were found to contain in common, but in different proportions, five components tentatively identified as: furfuryl alcohol,difurfuryl methane, difurfuryl ether, furfuryl alcohol dimer, and furfuryl alcohol trimer. Only the copolymer resin contained in more than minor amounts a component, not yet identified, which was not common to all three types of resin.

Because the samples used degraded to some extent between separation from the bulk resin and identification, the identities and proportions of these resin components must be verified by further studies.

B. Initiation of Polymerization Reactions (E. M. Wewerka)

Some progress has been made in the study of charge-transfer initiation of polymerizations. The basic reaction used in the study is that between an alkyl vinyl ether (RO-C=C, where R represents n-butyl, isobutyl, etc) and tetracyanoethylene, "TCNE", $(CN)_2\text{-}C=C\text{-}(CN)_2$. These reactants form a donor-acceptor complex which, upon transfer of an electron from donor to acceptor, is believed to yield a polymerization-initiation complex which produces the first cationic polymerization step. The behavior of the proposed polymerization-initiation intermediate appears to be critical in determining whether polymerization of the alkyl vinyl ether will eventually occur. Researchers at duPont have shown that under certain conditions an ionic coupling may occur giving a cyclobutane product.

An attempt to synthesize and purify a cyclobutane product with R=n-butyl, isobutyl, or t-butyl, was not entirely successful. Isolation of pure crystalline products was difficult, and the materials isolated were highly unstable. In solution in acetonitrile, these compounds decompose to highly colored species having many absorption bands in the visible and ultraviolet regions. None of the observed bands represented the starting materials, but because of their positions they could well have represented either the charge-transfer complex, the polymerization-initiation complex, a cyclobutane, or all of them.

An attempt to cause polymerization according to the proposed reaction scheme was at least partially successful in one instance. The polymerization was carried out at 65°C in a sealed tube with dry-purified reactants from which oxygen had been removed by freeze-thaw cycling before the tube was sealed. By this method, isobutyl vinyl ether was polymerized with 1% TCNE in acetonitrile. However, in the absence of a solvent the identical reactants did not polymerize. The synthesis of cyclobutanes described above was conducted in tetrahydrofuran. Thus, existence of a solvent effect is indicated.

The liquid isobutyl vinyl ether polymer made by the charge-transfer method had an infrared spectrum identical with that of a sample of the amorphous commercial polymer. Molecular size distributions of the two were similar escept that the charge-transfer polymer exhibited a tail at the lower end of the distribution.

C. Phenolic and Epoxy Binders (J. M. Dickinson, E. M. Wewerka)

Three experimental resins obtained from the Reichold Chemical Co. are being investigated for possible use as binders for graphite manufacture. The resins are: Plyophen 23-039, a furane-modified phenolic; Plyophen 23-239, a temperature-resistant phenolic; and Epotuf 37-140, a general-purpose epoxy resin. Each has been hand-mixed with a graphite flour and pressed at room temperature and 15,000 psi into discs 1.5 in. dia and about 0.5 in. high. Of two specimens made from the epoxy resin, one cracked during curing and the other, after graphitizing, showed only about 25% yield of binder carbon. The temperature-resistant phenolic gave about 55% carbon yield with low shrinkage, and the modified phenolic about 50% carbon yield with somewhat higher shrinkage. The phenolic resins, at least, will be investigated further.

D. Furfuryl Alcohol-Formaldehyde Resins (E. M. Wewerka, J. M. Dickinson, J. A. O'Rourke)

It has previously been reported (LA-4128-MS) that anomalous results were obtained from experiments intended to elucidate the graphitizing behavior of furfuryl alcohol-formaldehyde copolymer resins. In particular, a strong but so far unexplained dependence of graphitizing behavior on the type of filler used was observed. As a first step in investigating this behavior, a furfuryl alcohol resin and a group of furfuryl alcohol-formaldehyde resins were cast, cured, baked and graphitized with no filler particles present.

X-ray diffraction examinations revealed no significant differences in the degree of graphitization of the various resins. After graphitizing all contained both nearly amorphous carbon and at least two crystalline components. The major component was a turbostratic, "non-graphitizing" carbon with a small crystallite size. Most samples also contained two distinct crystalline components, one of which was well ordered and the other nearly turbostratic. Analysis of the composite diffractometer peaks was very difficult, and the measurements made were correspondingly uncertain.

Graphitizing at 2800°C instead of 2500°C produced a small improvement in the crystallinity of the major, turbostratic component. It had no detectable effect on the two crystalline components except apparently to increase the proportion of the well-ordered one.

This study has not revealed the difference in inherent graphitizability of the carbon residue which was expected when formaldehyde was added to a furfuryl alcohol resin. It is possible that for some reason the formaldehyde was not actually present in the copolymer, as has been presumed. Therefore a series of extruded graphites is being prepared in which paraformaldehyde has been added in various proportions to a standard furfuryl alcohol resin. Paraformaldehyde is an oligimer which yields formaldehyde as it is heated, and this formaldehyde will be available during curing of the extruded rods. If it has an effect on graphitizability of the resin binder, the effect should be detectable in the properties of these rods after they have been graphitized.

V. HIGH-TEMPERATURE MECHANICAL PROPERTIES

(W. V. Green, E. G. Zukas)

A. Compressive Creep of Hot-Isostatically-Compacted Graphites

A series of compressive creep tests has been made on the hot-isostatically-compacted ATJ and ZTA graphites described in LA-4128-MS. Several of the specimens used were examined by scanning electron microscopy after 2% compressive strain and again after an additional 2% compressive strain. Each sample was tested in a complicated cycle involving changes both in temperature and in stress and also including strain-recovery experiments. Specimens of normal (uncompacted) ATJ and ZTA graphites were subjected to the same cycles for purposes of comparison. Conclusions from these experiments were similar to those previously stated for tensile creep (LA-4128-MS), and were:

1. Hot isostatic compaction of ATJ and ZTA graphites does not significantly change their compressive creep strengths. At a given bulk cross-sectional area, load, and temperature the hot-compacted material, in spite of its higher density, has essentially the same creep rate as normal ATJ or ZTA graphite.

2. The stress-dependence and temperature-dependence of creep rate and the strain-recovery behavior of these graphites were also not significantly affected by hot isostatic compaction.

3. Hot-isostatically-compacted ZTA graphite is slightly less anisotropic than was the same graphite before compaction. Its compressive creep rate varied by a factor of two between the with-grain and the across-grain orientations, compared with a factor of about ten for as-received ZTA graphite.

No evidence of new deformation modes was found in structural studies of strained specimens of the hot-isostatically-compacted graphites. Aside from a reduction of preferred orientation in the case of ZTA graphite, the effect of hot isostatic compaction appears to have been simply an increase in density, with no accompanying change in deformation behavior or high-temperature strength.

B. Evaluation of Back-Stresses Created by Creep Strain

In load-cycling experiments, it has been observed that a large decrease in unit load is frequently followed immediately by negative creep -- i.e., by recovery of some of the strain produced by the higher load. This suggests that, under the higher load, an internal "back-stress" has developed in the material, whose magnitude exceeds that of the external unit load remaining after the load reduction. In the presence of such a back-stress, it is probable that -- in producing positive creep -- only that part of the applied unit load is effective which is in excess of the back stress. If so, a relation should exist between creep rate and effective unit load (i.e., applied unit load minus back-stress).

Preliminary experiments intended to evaluate the back-stress developed in tensile creep have been made by straining specimens of ZTA graphite to about 10% elongation under a given unit load, and then reducing the load. If the load reduction is small, positive strain continues at a reduced rate. If it is large, negative creep occurs. Presumably, if unit load is reduced to just the magnitude of the back-stress, the subsequent creep rate will be zero.

Tests of this type are continuing, to determine whether the back-stress so measured is a function of either initial creep stress or prior creep strain or both, and how creep rate is related to the difference between the back-stress and the applied unit load.

VI. MATERIALS CHARACTERIZATIONS

A. Solid Raw Materials

1. Gilsocarbon (R. D. Reiswig, L. S. Levinson)

Under polarized light, samples of lump Gilsocarbon which had been graphitized at 2860°C showed essentially the same structure described in LA-4128-MS for the as-received material. Upon ion-bombardment etching, however, the heat-treated material developed the lamellar relief effects which delineate the orientations of basal planes in graphitic structures. The outer layers of the onion-skin patterns of individual nodules and the material cementing lumps together had well-developed lamellar structures. The cores of the nodules retained mottled structures resembling high thermal-expansion cokes. Cracks between layers of the onion-skin structure were common, suggesting that grinding of this material would break it up into curved flakes mixed with some blocky particles representing the kernels of the spheroidal particles.

2. Oleum Green Petroleum Coke (R. D. Reiswig, L. S. Levinson)

Aside from cracks, the Oleum green coke showed little structure except under polarized light, which revealed large optical domains in a streamer-like arrangement. The numerous cracks showed no particular arrangement relative to the streamers or to basal-plane orientations within the streamers.

After graphitization at 2800°C, the Oleum coke had a well-developed lamellar internal structure, similar to those of many other graphitized petroleum cokes. Many particles were plucked out of the surface of the specimen during replication for electron microscopy, suggesting relatively easy interlamellar cleavage of the graphitized material.

B. Polycrystalline Graphites

1. CMF-13 Lot AAQ1 (D. T. Eash)

Lot AAQ1 is an extruded, resin-bonded graphite whose manufacture and properties were described in detail in Report No. LA-3981. Recently eight with-grain specimens from two rods (No. 56 and 63) of AAQ1 graphite have been tested in compression using a new testing jig and a testing machine different from that previously used. Average ultimate compressive strength from these tests was 10,655 psi with standard deviation of 403 psi. This compares with an average of 10,916 psi and standard deviation of 357 psi reported in LA-3981 for eight with-grain specimens from four other rods of Lot AAQ1. Agreement is good enough to increase confidence in both testing procedures, and to suggest that aging the graphite for about one year has not significantly affected its strength properties.

2. X-Ray Parameters of ATJS Graphite (J. A. O'Rourke)

A single specimen of commercial Grade ATJS graphite was evaluated by x-ray diffraction and had the following crystalline parameters: apparent crystallite thickness, $L_c = 295$ Å; apparent interplanar spacing, $d_{002} = 3.361$ Å; Bacon anisotropy factor, $\sigma_{oz}/\sigma_{ox} = 1.20$; M-value (another indication of preferred orientation) 1.03.

3. Compressive Strengths of Commercial Graphites (D. T. Eash)

Using the new compression-testing system described above, ultimate compressive strengths have been measured on samples of the nine commercial graphites listed in Table XII. All were purchased as small-diameter rods and tested in the with-grain orientation. The correlation of compressive strength with density is not exact but is relatively good. An exception is the AAQ1 graphite described above, which, at a density of 1.901 g/cm^3, had a with-grain compressive strength of about 10,800 psi. AAQ1, however, is a resin-bonded graphite while all of the commercial graphites listed in Table XII were pitch-bonded.

4. Thermal Expansion of AXM-5Q1 Graphite

In a cooperative set of measurements, the thermal expansion of Poco Grade AXM-5Q1 graphite has been measured over the temperature range ambient to 2000°C by P. Wagner, CMF-13, P. E. Armstrong, CMF-13, and P. Gaal, Westinghouse Astronuclear Laboratory. Results are plotted in Fig. 6. Agreement is good, and it appears

TABLE XII

COMPRESSIVE ULTIMATE STRENGTHS OF COMMERCIAL GRAPHITES

Graphite Grade	No. of Specimens Tested	Average Density, g/cm^3	Compressive Strength, psi	
			Average	σ
580	12	1.750	11,873	461
886S	12	1.720	9,470	127
HLM-85	12	1.774	9,187	152
HPC	12	1.692	8,700	136
HLM	12	1.739	8,132	322
CS	12	1.690	6,596	326
AGSX	11	1.650	5,754	225
AGSR	12	1.619	5,486	202
HC	12	1.442	2,114	194

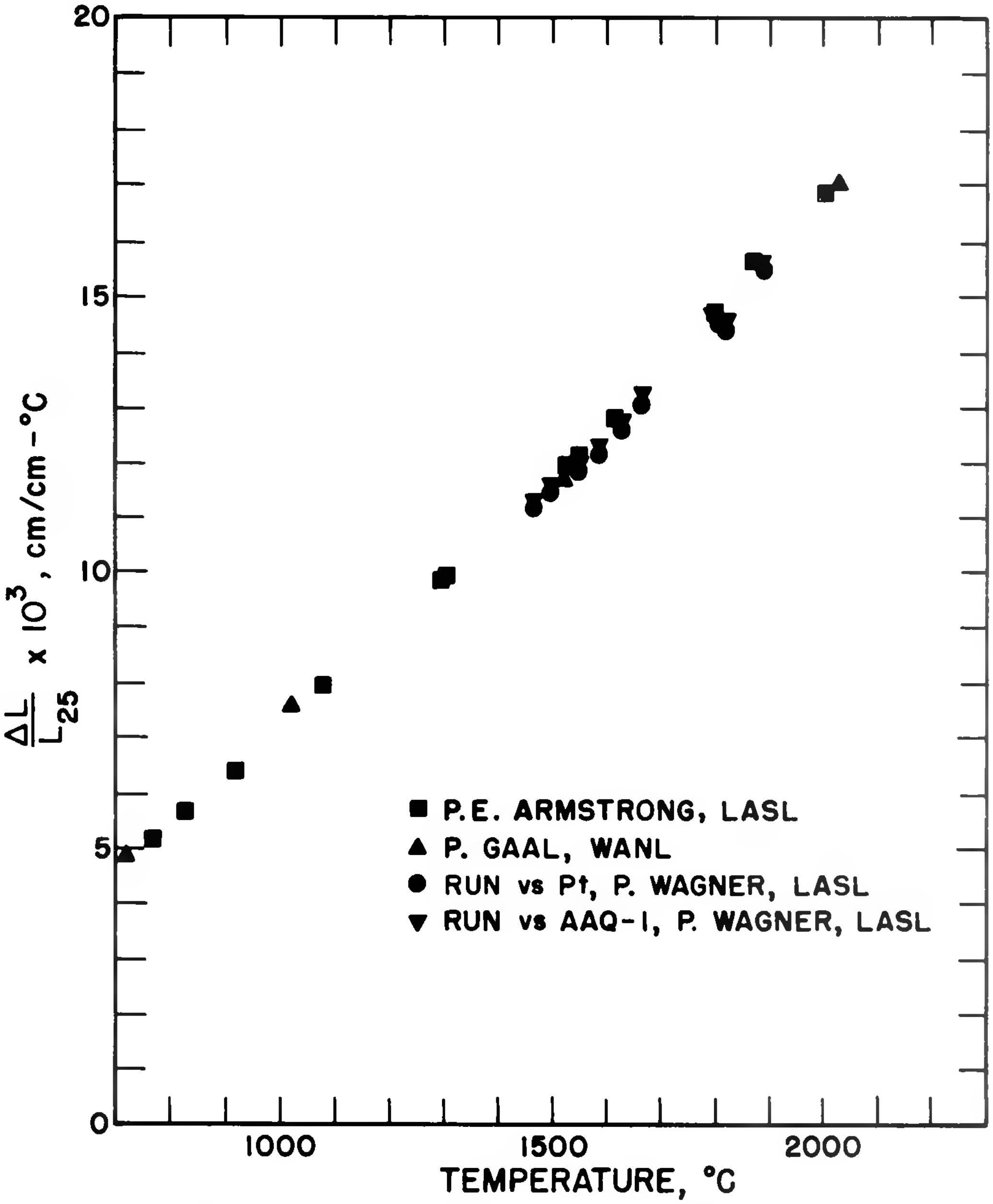

Fig. 6. Thermal expansion of Poco Grade AXM-5Q1 graphite.

that the minor discrepancies which previously existed among dilatometric measurements made in these three laboratories have now been resolved.

VII. PUBLICATIONS RELATING TO CARBONS AND GRAPHITES

Smith, M. C., "CMF-13 Research on Carbon and Graphite, Report No. 8, Summary of Progress from November 1, 1968, to January 31, 1969", LASL Report No. LA-4128-MS, March, 1969.

Wagner, P., "On the Technique of Measuring the High-Temperature Thermal Conductivity of a Rod", Brit. J. Appl. Phys. (J. Phys. D), Ser. 2, Vol. 2, 1969.

Wewerka, E. M., Walters, K. L., and Moore, R. H., "Differential Thermal Analysis of Furfuryl Alcohol Resin Binders", Carbon, Vol. 7, No. 1, pp. 129-141, 1969.