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PRELIMINARY INVESTIGATIONS INTO THE
PREPARATION OF EXTRUDED GRAPHITE

by

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For The Atomic Energy Commission

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ABSTRACT

It is possible, by proper selection of the starting materials and extrusion temperature, to control the density of hydraulically extruded graphite between the limits of 1.40 and 1.90 grams/cc.

Densities may be increased somewhat by means of impregnation with pitch or a thermosetting resin.

INTRODUCTION

Early in 1956, Group CMB-6 was requested to examine the usefulness of graphite as a fuel element.

This report will concern itself with the fabrication of graphite rods and tubular shapes.

At the outset of the program, the personnel of CMB-6 did not have an extensive knowledge of graphite manufacture. A review of the literature and discussions with representatives of companies producing graphite revealed that the industrial process for the manufacture of graphite consists of the following steps:

1. Mixing:

Crushed coke and recycled graphite are blended with a carbon black at about 140-150°C. Pitch is added to provide bonding, and finally lubricant is added.

2. Extrusion:

The hot mass, mostly in the form of soft pea-sized pellets, is extruded at 95°C to 110°C. The rod (or tube) is extruded directly into cold water to chill it and "set" its shape. This is the so-called "green" stock.

3. Baking:

The "green" extruded stock is placed in an upright position in the baking furnaces and the furnaces filled with a carbonized

foundry sand, to support the stock when the pitch softens and melts. The temperature is slowly raised (over a period of several days) to 850°C to 1000°C, then slowly cooled.

4. Graphitizing:

The baked stock is heated to 2300°C to 2800°C to convert the amorphous carbon (coke) to graphite.

Most of the data reported herein were gathered by deviating from these "standard" methods.

Equipment:

Mixing took place on a one gallon, electrically heated Baker-Perkins mixer equipped with dispersion blades (see Figure 1).

All extrusions were performed in a "home-made" hydraulically operated press, (see Figure 2). Tanks of compressed nitrogen were used to pressurize the oil system. Die nozzles and cylinders were electrically heated. Material leaving the die nozzle passed immediately into a tube filled with running water to chill the piece and preserve its straightness (see Figure 3).

All pressures reported were on a three-inch ram (7.07 square inches), with die orifice diameters of 5/8 and 3/4 inch.

Unless otherwise specified, the green stock was baked in loosely packed carbonized foundry sand in a stainless steel can. The can fitted into a vertical tube resistance furnace 8 inches in diameter and 26 inches high. The charge was heated to 950°C in the course of 72 to 84 hours. Figure 4 shows the Baker-Perkins mixer with coking furnaces in the background.

Graphitization was accomplished by induction heating in a graphite crucible to 2700°C for five minutes.

^{Parkins}
Fig. 1. Baker-Peters mixer showing mixing chamber and blocks.

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Fig. 2. Hydraulic extrusion equipment showing hydraulic cylinders and extrusion ram. Coking cans and furnaces in background.

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Fig. 3. Extrusion apparatus showing nitrogen tanks, hydraulic cylinders with extrusion ram, and quench tube for cooling the tubes immediately after extrusion.

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Fig. 4. Baker-Perkins mixer (foreground) with cooling cans and furnaces in the background.

I. Temperature as a Variable:

The extrusion material, with its relatively high pitch content, is more or less thermoplastic, with viscosities ranging over orders of magnitude. This is due to the fact that the pitch has no sharply defined melting point, but first softens, then melts to a sluggish semi-liquid, and finally becomes a thin, almost watery fluid.

This behavior would indicate that a most obvious variable to study would be the effect of temperature.

A. Graphite Density and Tensile Strength as a Function of Die Nozzle

Temperature:

Green Mix: 136 grams Thermax carbon black (a subsieve product of the Thermax Carbon Co. average particle size about 0.5 microns).

998 grams #1008 graphite flour (Typical sieve analysis)
98% through 100 mesh
95% through 150 mesh
55% through 200 mesh
40% through 240 mesh
35% through 325 mesh

437 grams medium vacuum pitch (Barrett #30)

47 grams Prowax 80 lubricant (Texaco)

Mixed at 145°C, loaded as rapidly as possible and extruded from 0.637 inch rod die whose cross-section was based on Schiele's Anti-friction Curve. This die will hereafter be called a 5/8 inch Tractrix die.

Die cylinder temperature = 115°C ±3°C.

<u>Nozzle Temperature °C</u>	<u>Tons on 3" Ram</u>	<u>Graphitized Density, gm/cc</u>	<u>Tensile Strength lbs/in.² (2500°C)</u>
82	13	1.40	1170
85	12	1.37	1290
87	12	1.47	1450
95	9	1.52	1220
105	8	1.57	1070
110	8	1.56	1190
115	6	1.57	----
122	9	1.60	----

B. Graphite Density and Tensile Strength as a Function of Die Cylinder

Temperature:

Green Mix: Same as in A.

Die: 5/8 inch Tractrix.

Die Nozzle Temperature = 105°C ±3°C.

<u>Cylinder Temperature °C</u>	<u>Tons on 3" Ram</u>	<u>Graphitized Density, gm/cc</u>	<u>Tensile Strength lbs/in.² (2500°C)</u>
87	13	1.58	910
110	9	1.55	990
115	8	1.57	1070
130*	10	1.47	1150

*Some cracking of extruded material.

In as-much-as cylinder temperatures between 85°C and 115°C do not seem to significantly affect the density of the finished product, such temperatures will not be reported if they lie within this range.

II. Technique Variables

A. Mixing:

The most commonly practiced method of mixing green materials for graphite manufacture consists of mixing and heating the dry ingredients (lampblack, ground coke, ground graphite) and adding pitch to this mixture. Heating and mixing is then continued until the experience of the operator tells him that the batch is ready to be loaded into the die.

It was found, however, that extrusion pressures could be approximately halved by first melting the pitch in the mixer, adding the Thermax black to the molten pitch, and after this is thoroughly wetted, adding the coke or graphite flour and mixing until thoroughly blended. This method insures complete wetting of the finer particles of Thermax, providing better lubrication in the die. This method of mixing has been called "reverse" mixing, as compared to the industrial procedure of "direct" mixing.

A typical comparison is shown below:

Green Mix: 440 grams pitch (med vac)
400 grams Thermax
735 grams #1008 graphite flour
47 grams Prowax 80

5/8 inch Tractrix Die

<u>Nozzle Temperature °C</u>	<u>Mixing Method</u>	<u>Tons on 3rd Ram</u>	<u>Graphitized Density, gm/cc</u>
107	Direct	15	1.75
108	Reverse	7	1.76

No significant advantage was found in mixing with solvents, and then evaporating before extrusion.

B. Re-extrusion

In an effort to increase densities and strengths by removal of entrapped air, extruded green material was crushed as it hardened on cooling, and fed directly back into the die for re-extrusion.

Green Mix: 136 grams Thermax

998 grams #1008 flour

437 grams medium vac pitch

47 grams Prowax 80

5/8 inch Tractrix die

Nozzle Temperature °C	Extruded, Once			Re-extruded		
	Tons on 3 rd Ram	Graphitized Density gm/cc	Tensile Strength lbs/in. ² (2500°C)	Tons on 3 rd Ram	Graphitized Density gm/cc	Tensile Strength lbs/in. ² (2500°C)
90	9	1.49	1020	22	1.57	910
105	8	1.57	1070	12	1.66	1630

C. Vacuum Extrusion

Removal of entrapped air was also attempted by vacuum extrusion. The die was sealed by means of a plug in the orifice and a gasket arrangement on the ram. Vacuum was then applied to the loaded die cylinder with a Hyper vac pump. The application of vacuum appeared to have no effect other than removal of lubricant through volatilization, thus increasing extrusion pressures.

Vacuum extrusion has therefore been abandoned.

D. Breaker Plate

In view of the success of re-extrusion as a means of increasing density, it was hoped that the same result could be attained merely by

inserting a breaker, or pre-extrusion, plate in the die, and extruding only once.

Accordingly, two plates were made, with rows of 1/4 inch holes, one plate having a total cross-sectional area of the holes about twice the area of the die orifice. The second plate had holes of a total cross-section approximately 25% greater than the die orifice.

A plate was inserted between the die and die cylinder, and the material extruded through the plate, into the die, and through the orifice.

The overall effect of this treatment was to reduce the density of the finished piece by about 0.05 gm/cc. Presumably, this is due to the smaller pressure drop through the orifice.

Accordingly, the breaker plate is not in use at present.

III. The Green Mix

The manufacture of graphite is essentially the process of compacting an incompressible powder and binding the particles with a "glue", such as pitch, which when baked and graphitized, does not completely fill the voids between particles. In such a process, the density and strength of the body formed must depend to a large extent upon the shape and size of the individual particles, the amount and character of the "glue" or pitch residue, and the physical changes undergone by the particles during processing.

Any study of graphite manufacture must then include a study of particle distribution and binder material.

A. Coke-Thermax Mixes

480 grams medium vacuum pitch

1135 grams Thermax plus Texas "95" coke (a petroleum residue coke, crushed, 95% through 100 mesh)

47 grams Prowax 80

5/8 inch Tractrix die.

<u>Nozzle Temperature C</u>	<u>Percent of Solids</u>		<u>Tons on 3" Ram</u>	<u>Graphitized Density gm/cc</u>
	<u>Thermax</u>	<u>Coke</u>		
85	12	88	7	1.51
80	20	80	5	1.56
90	30	70	3	1.68
90	35	65	4	1.68
90	40	60	3	1.72
90	50	50	5	1.75

In addition to the above, a pelletized mix consisting of 36 parts Thermax, 64 parts Texas "95" coke, 30 parts pitch and 7 parts erucic acid per 100 parts pitch was extruded. This material attained a graphitized density of 1.72 gm/cc, extruded at 90°C and 95°C both with and without breaker plate.

B. Graphite-Thermax Mixes

480 grams medium vacuum pitch

1135 grams Thermax plus #1008 graphite flour

47 grams Prowax 80

5/8 inch Tractrix Die.

<u>Nozzle Temperature °C</u>	<u>Percent of Solids</u>		<u>Tons on 3" Ram</u>	<u>Graphitized Density gm/cc</u>
	<u>Thermax</u>	<u>Graphite</u>		
105	12	88	8	1.57
103	20	80	3	1.65
105	30	70	4	1.79
103	40	60	12	1.81
87	50	50	8	1.81
85	60	40	5	1.83
110	100	0	21	1.92

At Thermax concentrations above 50% of total solids, the product became progressively harder and more brittle, with pronounced tendency to fracture during graphitization.

C. Coke-Graphite-Thermax Mixes

440 grams medium vacuum pitch

400 grams Thermax

735 grams Texas "95" coke plus #1008 graphite flour

47 grams Prowax 80

5/8 inch Tractrix die with breaker plate.

<u>Nozzle Temperature °C</u>	<u>Percent of Carbon Solids</u>			<u>Tons on 3" Ram</u>	<u>Graphitized Density gm/cc</u>
	<u>Coke</u>	<u>Graphite</u>	<u>Thermax</u>		
99	0	65	35	7	1.76
93	16	49	35	6	1.77
93	32.5	32.5	35	2	1.79
95	45	20	35	13	1.81

<u>Nozzle Temperature °C</u>	<u>Percent of Carbon Solids</u>			<u>Tons on 3rd Ram</u>	<u>Graphitized Density gm/cc</u>
	<u>Coke</u>	<u>Graphite</u>	<u>Thermax</u>		
90	49	16	35	2	1.80
95	52	13	35	12	1.82
95	55	10	35	12	1.81
90	65	0	35	3	1.72

The drop in density occurring with a reduction in graphite content from 10 to 0% was probably due to a particle size distribution phenomenon, rather than any real difference between a little bit of graphite per se, and no graphite at all.

D. Effect of Pitch Content

400 grams Thermax

735 grams #1008 graphite flour

47 grams Prowax

5/8 inch Tractrix die with breaker plate.

<u>Nozzle Temperature °C</u>	<u>Pitch, Percent of Solids</u>	<u>Tons on 3rd Ram</u>	<u>Graphitized Density gm/cc</u>	<u>Graphitized Diameter (Inches)</u>
101	31	25	1.66	0.629
97	33	15	1.67	0.622
95	35	13	1.72	0.612
95	37	11	1.74	0.606
95	40	9	1.77	0.604
90	42	6	1.76	0.598
90	44	3	1.73	0.595
87	46	5	1.80	0.587

With the rather notable exception of the last item, the density appeared to reach a maximum at about 40% of the total solids.

Pitch concentrations outside the above range were difficult to extrude successfully.

E. Effect of Lubricant

440 grams medium vacuum pitch

400 grams Thermax

735 grams #1008 graphite flour
lubricant

5/8 inch Tractrix die with breaker plate.

<u>Nozzle Temperature °C</u>	<u>Lubricant</u>	<u>Percent of Total Mix</u>	<u>Tons on 3rd Ram</u>	<u>Graphitized Density gm/cc</u>
99	Prowax 80	3	7	1.76
100	Prowax 80	2	9	1.76
98	Prowax 80	1	12	1.78
100	-----	0	13	1.81
95	Stearic Acid	1/2	12	1.76
93	Stearic Acid	1	14	1.79
86	Stearic Acid	1-1/2	9	1.79
86	Stearic Acid	2	8	1.79

F. Pitch Additives

According to patent literature, certain aromatic nitro and halogen compounds significantly increase densities by increasing the carbon residue deposited by the baked pitch. The most effective compound was alpha-nitronaphthalene.

1. Nitro Napthalene

Green Mix: 440 grams medium vacuum pitch

400 grams Thermax

735 grams #1008 graphite flour

5/8 inch Tractrix die with breaker plate.

<u>Nozzle Temperature °C</u>	<u>Nitro Napthalene (grams)</u>	<u>Tons on 3" Ram</u>	<u>Graphitized Density gm/cc</u>
99	0	7	1.76
98	5	8	1.76
88	15	6	1.78
80	25	7	1.80
60	35	15	1.81

The 25 gram run was repeated without the breaker plate, at 56°C and 22 tons. Density 1.83 gm/cc.

At greater than 35 grams nitronapthalene, temperatures had to be lowered so much, to hold the piece together, that extrusion was impossible with the available press. (i.e., pressures required exceeded 30 tons).

Nitrobenzene was also tried as an additive, but appeared to have little or no effect on the graphitized product.

2. Sulfur

Sulfur was added to the pitch, on the theory that the pitch hydrocarbons would decompose on baking, driving off H₂S and leaving the carbon residue. This should produce higher coking values, and thus possibly

higher densities. To a certain extent, this contention was borne out. There was certainly no doubt about the evolution of hydrogen sulfide.

Green Mix: 400 grams medium vacuum pitch

400 grams Thermax

735 grams #1008 flour

30 grams Stearic Acid

5/8 inch Tractrix die.

<u>Mould Temperature</u> <u>°C</u>	<u>Grams Sulfur</u>	<u>Tons on</u> <u>3" Ram</u>	<u>Graphitised</u> <u>Density</u> <u>gm/cc</u>
130	120	2	1.86
107	80	4	1.79
102	40	8	1.77

This material was extremely hard, but in spite of the high density of the 120 grams sulfur material, it contained many voids, and the strength was quite poor.

G. Miscellaneous Mixes

1. Binders

a. Resin "C", a standard industrial impregnant, was used as a binder, but was discarded when several runs yielded low densities and failed to hold their shape on extrusion.

b. "High Melting" Pitch; Attempts to raise densities led to the use of Koppers and Barrett pitches of 305° - 310°F "melting point". These two pitches gave essentially identical results.

Green Mix: Barrett or Koppers 305 - 310°F M. P. pitch

400 grams Thermax

735 grams #1008 graphite flour

25 grams Prowax 80

3/4 inch Conical Tapered die.

<u>Nozzle Temperature °C</u>	<u>Grams Pitch</u>	<u>Tons on 3" Ram</u>	<u>Graphitized Density gm/cc</u>
140	440	15	1.86
140	480	--	1.85
155	520	4	1.84
	560	Unable to extrude smoothly	

Above materials "atmosphere baked" - see section on baking.

c. Thermosetting Resins: Three thermosetting resins have been used as binders for room temperature extrusions. These were Varcum, Resinox and Plaspreg (trade names).

Plaspreg, a furfuryl alcohol monomer, catalyzed with maleic anhydride, seemed to yield superior densities. All three resins performed well in extrusion, however, the optimum mix attaining graphitized densities in excess of 1.65 gm/cc in every case.

Plaspreg-bonded extrusions, with 28% binder, containing methocel, were graphitized to densities of 1.75 to 1.80 gm/cc and took readily to impregnation with both Resin C and Plaspreg impregnant.

Tensile strengths at 2500°C were between 2000 and 3000 psi.

2. Maximum Density Mix

The maximum density achieved to date was derived from a green mix consisting of: 440 parts high melting (305 - 310°F) pitch

400 parts Thermax

551 parts Texas "95" coke flour

184 parts #1008 graphite flour

47 parts Prowax 80

This material, extruded at 135 - 140°C, attained a graphitized density of 1.90 gm/cc in a 5/8-inch rod, and 1.87 gm/cc in a one-inch rod after baking in packed sand. Transverse strength was found to be 4500 pounds per square inch and tensile strength (along the axis of extrusion) was 3800 psi.

IV. Treatment Subsequent to Extrusion

A. Baking

Finished densities and strengths of graphite pieces are largely dependent upon the baking process to which they have been exposed.

The standard industrial procedure of baking in carbonized foundry sand is not particularly conducive to high density.

The industrial laboratory practice of baking in vibrated, tightly packed sand is certainly superior to loose sand packing. This is apparently due to the physical restraint placed on the body during the period when the pitch is expanding. This method of packing seems to increase graphitized densities by approximately 0.02 to 0.03 gm/cc.

Even greater density increases are possible by a so-called "atmosphere bake". This consists of placing the green material in a loosely capped container, with no packing material. The vapors evolved from the heated pitch then decompose on the carbon, depositing still more carbon, and accomplishing

a sort of vapor phase impregnation. This can easily be shown by baking a previously baked or graphitized piece in the presence of green material. The weight (or density) gained by doing this is about one-third to one-half the weight gain experienced in a Resin C impregnation.

This method, however, suffers from the disadvantage of causing most (but not all) high density (greater than about 1.8 gm/cc) materials to warp, spall or blister in pieces much thicker than 0.1 inch.

The so-called "atmosphere baking" is definitely a superior method for treating impregnated pieces, which already have their basic shape and strength before impregnating and rebaking.

B. Impregnation

The standard method of increasing density in carbons is pitch impregnation. This process not only increases density, but yields a more uniform product, producing greater improvement in low density pieces than in high.

Impregnation has also been performed using Plaspreg resin as an impregnant. The first treatment with the resin results in a greater density increase than would be accomplished with Resin C pitch, but subsequent impregnations yield very little increase, possibly due to pore closure. Pitch impregnations, on the other hand, yield smaller, but reasonably uniform, increases through several impregnations. Thus the overall effect of a series of impregnations is about the same, using either Resin C or Plaspreg.

At low densities (below 1.7 gm/cc) densities can be increased by as much as 0.08 to 0.10 gm/cc by one Resin C impregnation. However, at densities above 1.9 gm/cc, a single impregnation will usually increase the density by about 0.02 to 0.03 gm/cc. These figures apply to the so-called "atmosphere baking" process. If the impregnated pieces are baked in sand, density increases are roughly one-half as great.

V. Miscellaneous Observations

Extrusion of tubing (1/4-inch I.D. by 5/8-inch or 3/4-inch O.D.) usually yielded slightly higher densities (0.02 to 0.03 gm/cc) than rod of the same diameter, under the same extrusion conditions. This observation led to the quest of a "skin effect" or density gradient.

A cylindrical piece was turned down in a series of cuts on a lathe, the density of the remaining core determined, and the density of the removed layer calculated with the following results:

<u>Diameter (Inches)</u>	<u>Core Density (gm/cc)</u>	<u>Density of Removed Layer (gm/cc)</u>
0.589 (original)	1.790	----
0.561	1.785	1.83
0.513	1.780	1.81
0.422	1.770	1.79

From the above, one would predict that extruded shapes of thin cross-section would have higher densities than massive pieces, but corroborative data is as yet too sketchy to be conclusive.

The observed phenomenon is, in all probability, due to the increased orientation of the particles in sliding contact with the die.

An observation that may be worthy of note is that there seems to be little, if any, correlation between density, transverse breaking strength, and tensile strength. In general, high density produces high strength, but every combination of high and low density, transverse strength, and tensile strength have been observed.

All tensile strengths reported in the earlier part of this report were

determined at 2500°C. These strengths have been found to be from one and one-half to two times as great as room temperature strengths.

Some generalized statements may be made about extrusion conditions. If the temperature is too low, the extruded material is prone to cracking, or "cold-checking". Too high temperatures will produce a "feathered" extrusion, and when extrusion rates are too great, splitting is apt to occur. However, no limits can be arbitrarily set. Only experience with a given mix can determine the optimum extrusion conditions.

Conclusion

Graphite has been prepared by means of hydraulic extrusion, with densities as high as 1.90 gm/cc, in rods of up to 3/4-inch in diameter. Densities higher than 1.90 gm/cc can be obtained by impregnating the graphite. It may be possible, by properly controlling the particle size distribution in the feed material, to achieve higher densities without impregnation.

Variables studied included die temperature, mixing technique, binder material, baking procedures, some lubricants and additives, and preliminary work on the investigation of the effect of particle size.