NASA CR-72799

DEVELOPMENT OF SEAL RING CARBON-GRAPHITE MATERIALS
(TASKS I and II)

by

N.J. Fechter and P.S. Petrunich

UNION CARBIDE CORPORATION
Carbon Products Division
12900 Snow Road
Parma, Ohio 44130

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center
Contract NAS 3-13211
Lawrence P. Ludwig, Project Manager

Requests for copies of this report should be referred to

National Aeronautics and Space Administration
Scientific and Technical Information Facility
P. O. Box 33
College Park, Md. 20740

NASA CR-72799

TOPICAL REPORT

DEVELOPMENT OF SEAL RING CARBON-GRAPHITE MATERIALS

(TASKS I AND II)

by

N. J. Fechter and P. S. Petrunich

UNION CARBIDE CORPORATION
Carbon Products Division
12900 Snow Road
Parma, Ohio 44130

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS3-13211

NASA Lewis Research Center
Cleveland, Ohio
Lawrence P. Ludwig, Project Manager

TOPICAL REPORT

DEVELOPMENT OF SEAL RING CARBON-GRAPHITE MATERIALS
(TASKS I AND II)

by

N. J. Fechter and P. S. Petrunich

ABSTRACT

Four material formulations, from which seal ring carbon-graphite bodies with a performance goal of 3000 hours life at air temperatures to 1300°F are to be produced, were ultimately developed after preparation and characterization of twelve material systems and forty-seven material subsystems. The material systems and subsystems employed four particulate and four binder raw materials selected after a literature search. Experimental results have shown:

(1) The oxidation rate of carbon-graphite bodies baked to 2800°C and prepared with a particulate system which contains a high concentration of relatively pure graphite is significantly lower than that of a commercial grade typical of current practice.

(2) The strength and hardness of these materials are lower than that of the commercial grade.

(3) The phenolic resin and coal tar pitch studied were more effective as binders than the furfuryl alcohol and polyphenylene sulfide resin.

(4) "Graphite" fibers can be used as an admixture for strengthening compacts prepared with an artificial graphite filler.

FOREWORD

The work described herein was conducted at the Parma Technical Center, Carbon Products Division of Union Carbide Corporation, under NASA Contract NAS3-13211. Mr. Lawrence P. Ludwig, Fluid System Components Division, NASA Lewis Research Center, was the Project Manager. Mr. John E. Dilley, NASA Lewis Research Center, was the Contracting Officer.

TABLE OF CONTENTS

TABLE OF CONTENTS (CONT'D)

LIST OF FIGURES

LIST OF TABLES

SECTION I

SUMMARY

The purpose of this Contract is to develop a carbon-graphite seal ring material which will have a 3000 hour life while exposed to ambient air temperatures up to 1300°F. The carbon-graphite material is being developed for use as a self-acting seal in advanced gas turbine engines. This Topical Report covers Tasks I and II of the Contract. Task I includes a literature search for information relevant to carbon-graphite materials for high-temperature seal ring applications; selection of four particulate and four binder raw materials for experimental studies; and the selection, preparation, and screen testing of up to twelve material systems or subsystems. The results of Task I were used to select four approaches to the manufacture of seal ring carbon-graphite bodies under Task II.

The high operating air temperatures require high oxidation resistance for the seal ring. A survey of the literature indicated that the most oxidation resistant carbon-graphite bodies are produced by graphitizing formed articles which contain a high concentration of high purity graphite filler and an oxidation inhibitor. The oxidation resistance of the porous seal ring body can be further increased by impregnation with oxidation inhibiting treatments.

Since self acting seals experience relatively high speed sliding contact during limited periods of operation, good wear resistance is also a requirement. A literature search revealed that the inclusion of low concentrations of "hard" carbons such as furnace black and particulate glassy carbon with the particulate graphite produces material with good load carrying capacity and wear resistance. The addition of furnace black reportedly increases the strength and reduces the anisotropy of bulk graphite. The use of graphites of fine particle size also imparts strength to a carbon-graphite body. While no goal has been established for strength, the operating pressures, dimensional stability requirements, and the configuration of the seal ring (7-12 inches in diameter - 1/2 inch thick - .020 inch dam widths) require material with the maximum strength consistent with high oxidation resistance and good wear resistance.

Binders also play an important role in producing strong, oxidation resistant, carbon-graphite composites. Besides the commonly used coal tar pitch binder, furfuryl alcohol and phenolic resin binders have been found to produce strong carbon-graphite materials. The use of these two types of resin has resulted in the formation of compacts of relatively low porosity which should improve oxidation resistance. Polyphenylene sulfide resin also appeared to be a potentially promising carbon binder since this material has a high theoretical carbon content and leaves a large residue after pyrolysis.

Based on the literature survey, the following particulate and binder raw materials were initially selected for experimental evaluation during Task I:

(1) Union Carbide Corporation Grade CHP artificial graphite
(2) Union Carbide Corporation Grade ASO natural graphite
(3) Commercial Solvents Corporation Thermax furnace black
(4) Lockheed Company LMSC Glassy carbon
(5) Barrett No. 30 medium coal tar pitch
(6) Bakelite BRP-5095 phenol-formaldehyde resin
(7) Varcum 8251 furfuryl alcohol resin
(8) Ryton polyphenylene sulfide resin.

Later, a fiber prepared from Union Carbide Corporation Grade WCA graphite cloth was added to the list of selected raw materials.

Twelve material systems which employed the selected raw materials were approved for screen testing. The selected filler systems usually contained 80 pbw (parts by weight) of graphite and 20 pbw of either furnace black or graphite fibers. Some of the systems incorporated ground glassy carbon or boron carbide additives for increasing wear and oxidation resistance, respectively. The twelve material systems were designed to include an evaluation of the effectiveness of the four binder raw materials. Processing techniques were based primarily on the requirements of the binder used.

The initial compacts produced with the twelve material systems by using a technique for estimating an optimum binder level were found to be too weak for use as seal rings. Subsequently, forty-seven material subsystems were studied to determine the effects of changes in binder level, baking schedule, and molding temperature on the physical properties of compacts baked to graphitizing temperature (2800°C). The subsystems study was used to optimize the twelve material systems.

Final screening tests showed that the 1300°F oxidation rates of all but one of the optimized material systems were between six and seventeen times lower than that of commercial seal ring Grade CDJ. Introduction of selected impregnants into these material systems reduced oxidation rates approximately tenfold, whereas that of Grade CDJ was reduced less than threefold. The maximum flexural strength obtained with samples from the material systems was 4000 psi, that of comparable samples of Grade CDJ was 7700 psi. Both the No. 30 pitch and BRP-5095 resin binders produced stronger, harder, more oxidation resistant compacts than the other two resins. Of the four evaluated, the BRP-5095 resin appears to be the best overall binder for seal ring bodies. Compacts employing Grade WCA fiber as a minor filler component had a high strength and strength-to-weight ratio. The addition of glassy carbon to one of the pitch bonded material systems appeared to improve strength.

Based on the experimental results of Task I, four approaches for the processing of carbon-graphite seal ring bodies were selected during Task II. Attempts will be made to further increase oxidation resistance, wear resistance, and strength by working with these four material formulations during Task III. The chemical, physical, and wear properties of the materials manufactured during Task III will be characterized during Task IV.

SECTION II

INTRODUCTION

The use of carbon as a seal ring material dates back to the early 1930's when mechanical seals began to replace packings in automobile water pumps. Little progress was made in improving carbon seal ring materials until the chemical and petroleum industries began to require seals which could withstand high pressures and temperatures in corrosive environments. The need for improved materials which would perform under these more stringent operating conditions caused a number of companies to specialize in the manufacture of carbon-graphite seal rings. This specialization has advanced seal technology at a more rapid rate.

Introduction of the turbine aircraft engine has produced sealing problems so severe that carbon-graphite is one of the few engineering materials which can meet the requirements of this application. The carbon-graphite seals used in gas turbine engines can operate at sealed gas temperatures up to 800°F and at speeds as high as 350 ft/sec.(1), (2)* To assure reliability, sealed gas pressures are not more than 125 psi.(2)

There are many reasons for carbon-graphite bodies becoming important as a seal ring material, particularly in the aerospace industry. Carbon-graphite materials are self lubricating under most conditions; they have high strength per unit weight, corrosion resistance, thermal shock resistance, and dimensional stability at elevated temperatures. At 1200°F, carbon-graphite is superior to most engineering materials in strength-to-weight ratio. With no oil lubrication, carbon-graphite materials can rub against metals, ceramics, or themselves without galling or seizing. The non-galling property exists at temperatures ranging from those encountered in cryogenic applications to those bordering the softening point of heat-resistant metals.(3)

Introduction of the gas turbine engine has produced very severe seal operating conditions; and operating conditions will become more severe as gas temperatures and seal sliding speeds increase. Increased temperatures

---

* Denotes Reference Number

result from higher flight speeds or higher gas temperatures to improve engine efficiency; increased seal sliding speeds are the result of larger engines. Contact type seals with carbon-graphite seal rings are used in many current gas turbine engines. However, the limited pressure, speed, and temperature capability of the contact seal restricts this use to operation below 125 psi sealed pressure differential, 350 ft/sec. sliding speed, and 800°F sealed gas temperature. For more severe operating conditions labyrinth seals are used. The labyrinth seal systems have higher gas leakage than contact seals and, therefore, contribute to easier passage of debris and to greater losses in engine efficiency.

Recent studies have produced a face seal with self-acting lift augmentation. This seal operates without rubbing contact (except at start and stop); therefore, it has higher pressure, speed, and temperature capability than a conventional face contact seal. For this new generation of seals, pads are machined on the seal face which, during engine operation, act as a thrust bearing and cause the seal to lift off the seal seat and ride on a thin gas film.(4) The seal with self-acting lift augmentation ideally will experience mechanical wear only during start-up and shut-down of the engine. However, momentary periods of high speed sliding contact can occur because of the close dimensional tolerances associated with the thin gas films.(5) Therefore, the importance of wear resistance cannot be neglected when a carbon-graphite formulation is developed for use as a self-acting seal ring material. High hardness, strength, and modulus, together with the proper selection of impregnants and mating materials, are necessary for producing wear resistant carbon-graphite seal ring materials.(6) Increased oxidation resistance will become a major requirement of carbon-graphite seal rings as engine gas temperatures rise to 1200°F and above. Development of improved carbon-graphite seal ring materials which can operate in ambient air temperatures up to 1300°F for 3000 hours will make feasible seal designs which will contribute to improvements in engine performance.

Conventional carbon-graphite seal ring materials are prepared by mixing selected sizes and types of carbon and graphite fillers with a binder such as coal tar pitch. The mixtures are formed into compacts and baked to various temperatures which are adjusted to produce the desired physical properties of the finished material. Usually, the finished carbon-graphite seal ring contains additives or impregnants which help the seal to meet particular performance requirements (e. g., oxidation resistance). Specific raw materials or processing techniques are employed to obtain desired properties of the finished carbon-graphite material. Detailed descriptions of the raw materials and processes employed specifically for the preparation of carbon-graphite seal rings are not available in the literature.

This Topical Report covers Tasks I and II of the Contract. The scope of work for Task I includes both literature and bench scale studies of raw materials and processing methods for carbon-graphite materials. The experience gained during Task I was used to select four approaches to the manufacture of seal ring carbon-graphite bodies required during Task II. The four formulations were selected as the best candidates to meet the performance requirements of 3000 hours life at ambient air temperatures up to 1300° F.

SECTION III

CONCLUSIONS

(1) Carbon-graphite materials baked to 2800°C which contain a high purity graphite as a major filler constituent have significantly lower oxidation rates than that of commercial seal ring Grade CDJ. The flexural strength and hardness of these compacts are lower than those of Grade CDJ. Grade CDJ, which is manufactured by the Union Carbide Corporation, is widely used as a seal ring material in turbine engines powering commercial aircraft.

(2) A high purity artificial graphite filler (Grade CHP) produced a compact with better oxidation resistance than that of a similar material made with a high purity natural graphite (Grade ASO).

(3) When used as a minor filler component, graphite fibers strengthen compacts prepared from Grade CHP artificial graphite filler. Graphite fibers prepared from Grade WCA cloth produced a compact with strength equivalent to that of a similar compact in which Thermax carbon black was substituted for the fibers. The strength-to-weight ratio of the material prepared with fibers was higher than that of the material prepared with Thermax.

(4) Bakelite BRP-5095 phenol-formaldehyde resin had a higher coking value than No. 30 medium pitch and produced the highest strength carbon-graphite materials processed during the screening studies portion of Task I.

(5) The addition of boron carbide to a carbon-graphite material prior to forming can cause subsequent degradation of the oxidation resistance or the strength of the resulting compacts.

SECTION IV

RECOMMENDATIONS

Based on experience gained from the analyses of twelve material systems and forty-seven subsystems, the following four material formulations are recommended for the manufacture of carbon-graphite seal ring bodies during Task III.

Formulation No.	Particulate Solid Raw Material	Additive	Binder Raw Material
1	CHP Artificial Graphite (80 pbw) Thermax (20 pbw)	---	No. 30 Medium Pitch (60 pph)
2	CHP Artificial Graphite (80 pbw) Thermax (20 pbw)	Glassy Carbon (5 pbw)	No. 30 Medium Pitch (60 pph)
3	CHP Artificial Graphite (80 pbw) Thermax (20 pbw)	---	Bakelite BRP-5095 Phenolic Resin (58 pph)
4	CHP Artificial Graphite (80 pbw) WCA Fibers (20 pbw)	---	Bakelite BRP-5095 Phenolic Resin (67.5 pph)

Note: Final Bake Temperature = 2800°C

Proportions are parts by weight (pbw)

Binder proportions are parts (by weight) per 100 parts (by weight) particulate solid raw materials.

SECTION V

STUDY OF CONSTITUENT VARIABLES

(CATEGORY 1 -- TASK I)

A. Particulate Solid Raw Materials

1. Graphite

A graphite crystal has a highly oriented layer structure. The layer planes consist of closely spaced carbon atoms held together by strong valence bonds in a regular hexagonal array. Successive planes are parallel and held together at well-defined distances by relatively weak van der Waals forces. In the case of graphite, the hexagonal arrangement of carbon atoms in a plane line up directly with those in alternating planes. The structure of graphite accounts for its being a very anisotropic material.

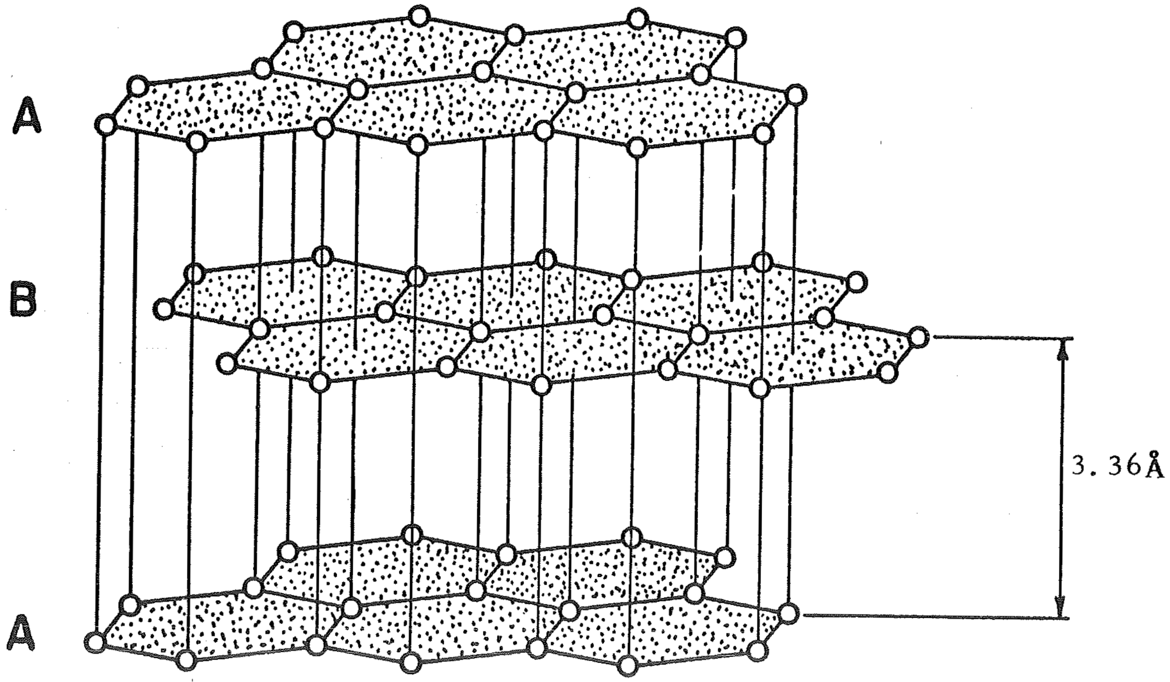


Figure 1. Structure of Graphite

G700253

Graphite is one of the few single-phase materials which exhibits good wear qualities. At one time, the self-lubricating ability of graphite was attributed to the ease of shearing the weak van der Waals forces between the layer planes. However, more recent work has shown that absorbed gases and water vapor within the layer lattices produce the lubrication properties.(7) Although graphite is one of the weaker forms of carbon, it has the highest oxidation threshold temperature: graphite begins to oxidize in air at 842°F (450°C), whereas "amorphous" carbon starts to oxidize at 662°F (350°C).(8)

Many different types of particulate graphite are commercially available. This report will divide the discussion of graphite fillers into three titled sections: Natural Graphite, Artificial Graphite, and Pyrolytic Graphite. As-deposited pyrolytic graphite is not so crystalline as either natural or artificial graphite. However, the crystallinity of some pyrolytic graphites that have been subjected to post-deposition heat treatment approaches that of natural and artificial graphite. Since pyrolytic graphites with wide variations in degree of crystallinity have been produced, it is difficult to categorize this material according to crystallinity. Therefore, pyrolytic graphite arbitrarily will be discussed under the graphite section.

a. Natural Graphite

Natural graphites are mined in different sections of the United States and in a number of foreign countries. The various forms of natural graphite include flakes, lumps, needles, and cryptocrystalline masses referred to as "amorphous graphite." The form and properties of the graphite vary greatly depending on where it is mined. After it has been mined, the raw graphite is mechanically processed to remove it from the metamorphic rock in which it is found in nature. Further purification is achieved by subjecting the graphite to multi-stage wet-chemical treatments with alkalis and acids. Subjecting a raw graphite with a carbon content of 20 percent to the mechanical and chemical purification processes can produce a finished graphite with an ash level of 10 - 30 ppm.(9)

Heindl and Mohler(10) measured the 900°C oxidation rates of 20 natural flake and amorphous graphites from eight foreign and three domestic deposits in an attempt to establish the most oxidation resistant natural graphite sources. The lowest oxidation rates were observed with Madagascar, Alabama, and Pennsylvania flake graphites. Large differences in oxidation rates were observed among Madagascar flake graphites obtained from various deposits. They found that correlation between the origin and the oxidation rate of graphite is difficult or impossible since information on the geologic origin of most graphite deposits is meager. They also concluded that the oxidation rate of graphite appears to be a characteristic property that does not depend on any one of the physical or chemical properties they monitored, but rather on a combination of two or more properties or possibly on some factor not yet explored. Flake graphites with a comparatively low ash content were found to oxidize more rapidly after an extended period of exposure to oxygen than those with a high ash level. Heindl and Mohler felt that the ash might possibly be forming a protective coating over the graphite particles and, thus, be retarding oxidation. The investigators also noted that coarser size fractions oxidized at a considerably slower rate than did the fine fractions from the same graphite deposit, an observation consistent with the expected increase reactivity of a higher surface area material.

Group CMF-13 of the Los Alamos Scientific Laboratory (LASL) has studied the grindability of various graphites.(11, 12) Included in their research was a Ceylon natural graphite which was found to be very easy to grind: the Ceylon natural graphite required only five passes through a Trost fluid-energy mill to reduce all the material to a particle size of less than 5μ. An extruded polycrystalline manufactured graphite, Grade YBF, purchased from the Union Carbide Corporation, Carbon Products Division, required 12 passes to achieve the same particle size. After each pass through the mill, the Ceylon natural graphite particles were very acicular and somewhat shredded in appearance.

As a continuation of their grinding research, LASL prepared hot-molded pitch-bonded graphite discs from the filler materials they had ground.(13) The optimum binder level for each filler material was estimated using a lubricant-evaporation technique. Six specimens were prepared for which the Ceylon natural graphite was used as the filler material. One of the molded specimens contained the as-received unground Ceylon natural graphite filler material. The five remaining specimens contained Ceylon natural graphite filler materials that had been passed through the Trost-fluid energy mill:one had filler materials that had passed once through the mill, another the filler that had passed twice through the mill, and so on. The fifth specimen, of course, had the smallest particle size filler since it had passed through the mill five times. All six molded specimens expanded during graphitization, the expansion being greatest for those made with the coarsest filler material. The density of the graphitized specimen which contained the unground Ceylon natural graphite was 1.952 g/cc, but the densities of the other five specimens decreased with increasing fineness of filler to a low of 1.850 g/cc. The apparent discrepancy between the coarser filler specimens experiencing the larger expansion during graphitization while still producing the higher densities was probably caused by the variation in the binder levels of the six molded materials. In spite of continuously decreasing density, the use of progressively finer natural graphite fillers reduced the number of interconnected voids, and the remaining isolated voids were progressively less damaging to the mechanical properties of the molded specimens. Crystalline anisotropy was high for the specimens which contained unground natural graphite (σ oz/σ ox = 2.02, M = 3.2) and it increased sharply with the first reduction (first mill pass) in filler particle size (σ oz/σ ox = 3.45, M = 7.0).

Considerable work has been done by LASL in developing a class of highly oriented polycrystalline graphites. Preliminary investigations(14, 15) indicated that the most promising type of material for initial development was a hot-molded, pitch-bonded graphite made from natural flake graphite and carbon black. Southwestern Graphite Company Grade 1651 natural graphite flakes, Thermax carbon black, and Barrett No. 30MH coal tar pitch were mixed together in various combinations.(16) While under pressure in the mold, the mixes were heated to 900°C in an 18-hour cycle, followed by graphitization at 2800°C. By using the natural graphite as the primary filler (80-90 percent of the total filler weight), LASL has produced materials with across-grain compressive strengths of 7000 to 8000 psi and with-grain flexural strengths approaching 5500 psi. These strengths are of the magnitude found in conventional seal ring materials.

The fact that natural graphite can readily be reduced to a fine particle size makes it attractive as a potential seal ring filler material. Fine particle size fillers help to strengthen a carbon-graphite material in two ways. Finer natural graphite filler reduces the number of interconnected voids which subsequently improves the mechanical properties of the molded materials. Secondly, the natural graphite particles tend to break at their weakest point as they are milled causing the remaining smaller particles to be progressively stronger as the reduction in particle size is continued. Although the use of an increasingly finer natural graphite filler will increase the strength of a molded carbon-graphite material, it also will increase the anisotropy of the physical, thermal, and chemical properties of the specimen. Therefore, the trade-off between strength and anisotropy must be considered in the formulation of a carbon-graphite seal ring material.

b. Artificial Graphite

The production of artificial graphite(17) consists of mixing an organic particulate solid raw material with a carbonaceous binder, forming the mixture into green plugs, and firing the plugs in a two-stage bake to temperatures of 2600°C and above. Petroleum coke is usually used as the particulate raw material, since it is readily graphitizable and leaves a high-carbon residue when heated to elevated temperatures. Likewise, a high-density, high-coking-value coal tar pitch is usually used as the binder material in the production of artificial graphite. Variations in the type of coke used or in the manufacturing processes employed will alter the physical properties of the final graphite product.

Many different types of petroleum coke, such as needle cokes and air-blown cokes, to name a few, are commercially available. The raw coke is usually prepared by the polymerization and distillation of the volatiles from heavy refinery oils. This process yields raw coke with a carbon content of approximately 95 percent. The raw coke must be calcined at a temperature of approximately 1300°C to drive off and burn large amounts of hydrocarbon gas and to preshrink the coke so that volume changes can be controlled during subsequent processing steps. The calcined coke is then crushed and screened, and the desired particle sizes are selected and blended together. Selection of the sizes and shapes of the coke particles is determined by the physical properties desired for the finished graphite product.

Mixing of the coke particles and the coal tar pitch can be accomplished in a number of different types of mixers. The mixing operation usually uses some standardized batch size and a specified length of time to control the physical properties of the graphite produced. To obtain a good pitch coating around the coke particles the mixing is usually carried out at temperatures of 150°C to 170°C. At these temperatures the viscosity of the pitch is low enough to get proper coating.

Extrusion or molding can be used to form the pitch-coke mixture into green plugs, but the choice of the forming technique affects the alignment of the coke particles in the green plugs. If extruded, the coke particles tend to line up with their longest dimensions parallel to the direction of the extrusion axis. When the green plugs are molded, the coke particles tend to line up with their longest dimension perpendicular to the molding force and the shortest dimension parallel to it. The alignment of the coke particles causes anisotropy in the physical properties of the finished graphite.

Graphitization of the green plugs is accomplished in a two-stage bake. In the first stage, commonly referred to as the gas bake, the green plugs are packed with coke or a sand-coke mixture in a furnace and carbonized at temperatures ranging from 750°C to 1000°C. The packing material is needed to prevent the plugs from slumping as they are heated through the temperature range during which the pitch is soft. As the temperature increases above 450°C, the binder becomes rigid and the plugs begin to shrink. Peak temperatures of the second-stage bake range from 2600°C to 3000°C, causing the graphitization of the gas-baked carbon plugs. During the second-stage bake, the plugs are packed in some form of carbonaceous material, such as coke or graphite particles, and/or an inert atmosphere is introduced around the plugs to protect them from oxidation. The purity of the plugs is improved during graphitization, since many of the ash constituents are vaporized.

Heating the gas-fired plugs to temperatures between 2500°C and 3000°C increases the degree of crystallinity of the graphite, resulting in a significant change in the physical properties. Upon graphitization, the specific electrical resistance decreases by a factor of 5, the thermal conductivity increases by a factor of 25, the coefficient of thermal expansion decreases by 50 percent, and the elastic modulus and strength decrease by 20 percent.(18) Manufacturing methods have been developed to produce nearly isotropic graphites.(19)

LASL has recently manufactured and characterized 0.5 inch diameter rods of an extruded, resin-bonded graphite identified as Lot AAQ1.(20) The primary filler component (85 parts by weight) was Great Lakes Grade 1008-S graphite flour, an artificial graphite made from a relatively non-acicular coke and a coal tar pitch binder. Approximately 60 percent by weight of the Grade 1008-S graphite flour passed through a 200 mesh screen. The remainder of the Lot AAQ1 filler (15 parts by weight) was Thermax carbon black. Varcum 8251 furfuryl alcohol resin (27 parts by weight) which contained maleic anhydride as a polymerization catalyst was used as the binder for Lot AAQ1 graphite. The average bulk density for 147 samples of the extruded, resin-bonded graphite was 1.901 g/cc. An average flexural strength of 4865 psi was measured during room temperature tests on four longitudinal samples of 0.5 inch diameter. A four-point loading over a four inch span was used to break the samples.

During the course of their work, LASL obtained a second lot of Grade 1008-S graphite flour in which the graphite particles were more acicular than those of the first lot.(21) Extruded rods containing the more acicular graphite particles were found to have a higher degree of preferred orientation when compared with the rods which contained the less acicular graphite flour.

An artificial graphite that is crushed and milled to a fine flour after its manufacture would make an excellent filler material for carbon-graphite seal rings. The properties of artificial graphite generally can be controlled to a greater degree than those of a natural graphite. Artificial graphite is less anisotropic than natural graphite, and it has a relatively high purity since most impurities are vaporized during graphitization. High purity is important since most impurities are oxidation accelerators.

c. Pyrolytic Graphite

The term pyrolytic graphite is used to describe a type of carbonaceous material deposited on a heated surface when a gaseous hydrocarbon is passed over it. The deposited material is referred to as pyrolytic graphite when the temperature is above 1900°C and pyrolytic carbon when the temperature is below 1900°C; the difference in designation is based upon the type of structure obtained.(22) Benzene, methane, and propane are some of the hydrocarbons most commonly used to produce pyrolytic graphite. A recent in-depth review of the materials science of pyrolytic carbons has been conducted by Bokros.(23)

The deposition process can be conducted in two distinct ways.(24) In the first technique, the gas is simply passed over the heated object to be coated. The second process consists of using the flowing gas itself to levitate small particles of the material to be coated in the hot zone of the deposition equipment. The flowing gas thus forms a fluidized bed within which there is excellent heat transfer. An advantage of the second process is that it is more controllable than the first. Since most objects to be coated are too large and heavy to be levitated by the flowing gas, both deposition techniques can be combined by suspending the large object to be coated in a fluidized bed, permitting the best features of both techniques to be utilized. Auriol et al.(25) have reported the deposition of high density isotropic structures using the latter technique with alumina, silica, and carbon as levitated particles of the fluidized bed.

A number of mechanisms have been proposed to explain the manner by which the pyrolytic carbon is deposited on a heated substrate. According to one of the proposed theories(26), the hydrocarbon gas dissociates when it comes in contact with the hot surface, with or without deposition of carbon, forming free radicals and possibly complex molecules which pass back into the gas phase. The products of the initial reaction undergo repeated decomposition on the hot surface and recombination in the gas phase, in the course of which carbon is deposited and aromatic carbon compounds produced. Although the aromatic planes formed are parallel with each other and with the surface of the hot substrate, the orientation of the imperfect hexagonal ring structures is random. Thus, pyrolytic graphite does not necessarily have the highly ordered stacking registry of the layer planes generally found in natural or artificial graphites. Also, the distance between adjacent planes is larger for pyrolytic graphite than it is in the more crystalline forms of graphite. The crystallinity of the pyrolytic graphites can be greatly increased (i. e., pyrolytic graphites can be "graphitized") by annealing at approximately 3000°C under shear stress, followed by annealing of still higher temperatures.(27)

Pyrolytic graphites are typically very anisotropic materials because of their laminar structure. The room temperature tensile and compressive yield strength of pyrolytic graphite measured along the layers is 15, 000 ± 5000 psi; across the layers, it has a compressive yield strength of 60, 000 ± 20, 000 psi.(28) Flexural strength is 20, 000 to 30, 000 psi. Low tensile strengths across layers (500 to 1000 psi), low shear strengths between layers (1500 ± 1000 psi), and susceptibility to delamination when subjected to thermal or mechanical stresses limit application of the anisotropic forms of pyrolytic graphite. However, isotropic and granular pyrolytic graphites can be produced by using the fluid bed technique and the proper type of gaseous hydrocarbon, gas flow, and deposition temperature. Isotropic deposits with flexural strengths in excess of 40, 000 psi and low elastic moduli have been produced.(29)

The oxidation rate of bulk pyrolytic graphite is significantly lower than that of conventional polycrystalline graphites. The principal reason for this advantage in oxidation resistance is the fact that pyrolytic graphite can be made essentially nonporous. Pyrolytic graphite co-deposited with boron displays improved strength and oxidation resistance.(30) Tominaga and Nagaoki(31) have studied the oxidation of pyrolytic graphite as a function of both the oxidation and deposition temperatures. These investigators found that the edge planes oxidize ten times faster than the basal planes for a pyrolytic graphite annealed at 3200°C. Experiments conducted on an unannealed pyrolytic graphite sample showed that the edge planes oxidize faster than the basal planes at lower oxidation temperatures (650°C), but the basal planes show the higher oxidation rates as the temperature is increased (950°C). Unlike those of the specimen annealed at 3200°C, the basal planes of the unannealed specimen developed pits which became progressively deeper, proceeding from the top layer down to the deposition face. Tominaga and Nagaoki found that the oxidation rate decreases as deposition temperature increases. The greatest oxidation resistance for both the edge and basal planes is obtained when the pyrolytic graphite is deposited at high temperature (approximately 2300°C), followed by annealing.

Cahn and Harris(32) reported that the wear characteristics of anisotropic pyrolytic graphite were "excellent"; however, Diefendorf and Stover(33) indicated that the wear rate of this material is below that of most conventional graphites. Wear rate is sensitive to sample orientation. The higher wear rate in the direction parallel to that of the basal plane has been associated with the low shear strength in that plane. The frictional and wear properties of pyrolytic graphite in sliding contact with a number of counterfaces have been studied.(34) Pike and Thompson(35) studied the friction and wear of anisotropic pyrolytic graphite used as a sliding electrical contact. The wear values they obtained were similar to those of "conventional" brush carbons. The combination of high flexural strength and low modulus has been suggested to impart "interesting" wear characteristics to isotropic coatings. Isotropic coatings alloyed with boron to enhance oxidation resistance may have potential application as high temperature seal ring materials if the required size and geometry can be attained.

This report has already discussed some of the work LASL has carried out in developing a class of highly oriented polycrystalline graphite.(36, 37) Part of that investigation included the use of ground pyrolytic graphite as a primary filler component (80 to 100 percent). The hot-molded graphite samples produced with the ground pyrolytic graphite as the primary filler material had considerably lower across-grain compressive strengths than the corresponding materials produced with natural graphite as the major filler component. For example, the specimen identified as 50I-I produced from ground pyrolytic graphite (80 pbw), needle coke flour (20 pbw), and Barrett 30 MH pitch (30 pbw) had an across-grain compressive strength of 3748 psi. A similar sample identified as 50Z-1 was produced from natural graphite flakes (80 pbw), needle coke flour (20 pbw), and Barrett 30 MH pitch (35 pbw). Specimen 50Z-1 had an across-grain compressive strength of 5469 psi. The pitch concentration was considered optimum for the respective particulate systems.

Ground pyrolytic graphite does not appear to be a good particulate raw material for producing carbon-graphite seal rings. Although bulk pyrolytic graphites apparently can have good wear characteristics, the work of LASL has shown that the strengths of compacts produced using ground pyrolytic graphite as the primary filler component appear to be lower than the range required for a good seal ring material. Furthermore, the excellent basal plane oxidation resistance inherent with an anisotropic nonporous bulk pyrolytic graphite coating could be adversely affected when the material is ground into a randomly oriented particulate raw material for incorporation into a conventional carbon-graphite body.

2. Less Crystalline Forms of Carbon

The word carbon, when used in the discussion of carbon-graphite materials, refers to the carbonaceous materials that do not have highly ordered crystal structures. The structure of carbon is often referred to as being turbostratic. The carbon crystals, built up from the basic layer of hexagonally bonded carbon atoms, generally do not possess the degree of regular, three-dimensional order found in graphite. Although the planes of a carbon crystal are parallel to each other and uniformly spaced, they may be arranged in many different ways to produce carbons which range from very hard to relatively soft.

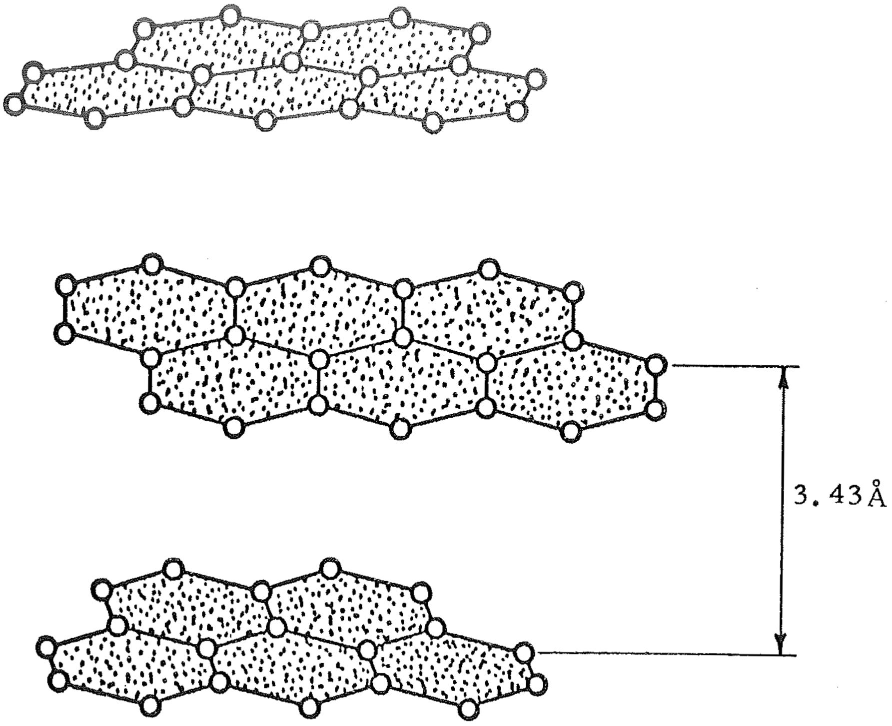


Figure 2. Structure of Turbostratic Carbon

G700254

Many types of carbon are commercially available. Some of the more common forms include petroleum cokes, carbon blacks, glassy carbon, and carbon/graphite fibers. Although petroleum cokes are readily "graphitizable", the latter three materials usually do not exhibit a high degree of graphitization when heat treated to temperatures of 3000°C. This section of the report will deal with the discussion of carbon/graphite fibers, carbon blacks, and glassy carbon. Petroleum cokes were discussed as intermediate products in the production of artificial graphite.

a. Carbon/Graphite Fibers

Carbon fibers are commercially produced by the controlled pyrolysis of organic fibers, which may be either natural or man-made. The general term carbon fiber covers all fibers which have been heat treated to temperatures substantially higher than the decomposition temperature of the precursor polymer. When used as a more specific term, carbon usually refers to fibers which have been heated to intermediate temperatures such as

1000°C to 1500°C whereas, *graphite* is used to denote fibers heated to higher temperatures, frequently above 2500°C.(38) Although *graphite* fibers have broader, more closely packed layers than *carbon* fibers, both fiber types have a turbostratic structure. *Carbon* fibers are usually 80-95 percent elemental carbon while *graphite* fibers are approximately 99 percent carbon.

The production of carbon fibers involves both chemical and thermal treatments of the precursor polymer.(39) Although rayon and polyacrylonitrile are the leading precursor materials for carbon fiber manufacture, a number of other organic fibers have been successfully converted into carbon fiber. The three primary criteria for the selection of the precursors are thermal decomposition without the presence of a melt phase, a high residual carbon content in the pyrolyzed structure, and high strength and flexibility of the carbonaceous residue. Rayon can be pyrolyzed in a moisture-free, reducing or inert atmosphere. During pyrolysis, the chain of the macromolecule is broken, producing volatile carbon, and carbon-like residues are formed by chain condensation. The two competing reactions occur simultaneously. Pyrolysis of rayon produces an intermediate product called laevoglucosan, which, upon further heating, forms a carbonaceous char and volatile tars. The tars decompose to give additional polymer carbon and a variety of gaseous products. Finally, cross-linking unites the carbon crystallites into a randomly oriented mass. Very high strength graphite fibers can be produced by applying tension to the fibers during the high temperature step. Fibers with a tensile strength of 500,000 psi and Young's modulus of 100 million psi have been prepared using this technique.(40)

Composites have been made from various textile forms of carbon fiber, such as graphite yarn and cloth. Fiber composites have been prepared which employ both pyrolyzed and unpyrolyzed resins as a matrix. The former material is usually referred to as a "carbon-carbon" composite, and the latter is called a "carbon-resin" composite. The application of the carbon-resin composite is usually limited by the degradation temperature of the resin. Graphite-cloth composites that incorporate a pyrolyzed matrix have been produced by using shredded Grade WCA graphite cloth and a resin binder.(41) The resin (50 parts per hundred parts cloth by weight) was spread over the graphite cloth, after which the resin treated cloth was charged into a mixer and macerated to a fibrous mass. Plugs were molded at 750 psi and pressure-cured for six hours at 130°C, followed by baking first to 800°C and then to 2800°C. The across-grain compressive strength of the compacts was 9100 psi after curing and 800 psi after baking to 2800°C. Recent advances in the technology of this type of composite have provided materials with flexural and impact strengths high enough to permit use as brake components for high performance aircraft.(42)

Graphite fibers appear to be a potential seal ring filler material because carbon-carbon fiber composites employing this material have exhibited high strengths and strength-to-weight ratios. When added as a minor filler component, graphite fibers may strengthen seal ring materials which contain natural or artificial graphite fillers.

b. Carbon Black

Carbon blacks are a class of particulate elemental carbons produced from gaseous or liquid hydrocarbons which undergo incomplete combustion in a flame or thermal decomposition in a furnace. The turbostratic structure of a carbon black particle may be represented as the resulting aggregate of some 1500 crystallites, each of which generally contains two to five parallel sheets of hexagonally packed carbon atoms in random orientation.(43) "Amorphous" carbon is present in the spaces between the crystallites. The particular type of carbon black formed depends on the raw materials and manufacturing processes employed. All of the different types of carbon blacks are generally grouped into five classifications: furnace black, lampblack, channel black, thermal black, and acetylene black.

Of the five types of carbon blacks commercially available, lampblack and furnace black are the two most commonly used in the manufacture of carbon-graphite materials. Lampblack is utilized in arc lamp electrodes and in brushes for various types of electric motors and generators. Furnace black is often used as a minor filler component to increase the density and hardness of artificial graphites. The coke particles used as a major filler component in the production of artificial graphite are seldom less than two microns in diameter. Furnace black particles, which are spherical in shape and approximately 0.3 micron in diameter, fill the voids between the coke particles, causing an increase in density and hardness. Replacing 20 percent of a fine-grained coke flour with furnace black has increased the density of carefully extruded small-diameter graphite rods from 1.84 g/cc to 1.91 g/cc.(44)

LASL has used Thermax in their research on carbon and graphite.(45) Thermax is a furnace black manufactured by the Thermatomic Carbon Division of Commercial Solvents Corporation. A helium density of 1.88 g/cc and a specific surface of 8.9 m^2/g were reported for this black. An electron micrograph has shown the individual Thermax particles to be smooth-shelled and nearly spherical, but many appear as aggregates, which may represent intergrowths of particles.

LASL has prepared several experimental graphites, identified as Series AAP, to investigate the effects of filler particle size and size distribution on the properties of manufactured graphites and on the manufacturing methods required.(46) Eight graphite flours of varying fineness were used individually as either the only filler material or as the major component in a binary filler system which incorporated Thermax as the second filler material. Varcum 8251 furfuryl alcohol resin containing maleic anhydride as a polymerization catalyst was used as the binder. The addition of the carbon black reduced the binder requirements and increased the densities of the products baked to graphitizing temperatures. One specimen which contained Great Lakes Grade 1008 graphite flour as the only filler material had a baked density of 1.77 g/cc. A similar sample which contained the same graphite flour (85 parts by weight) and Thermax (15 parts by weight) as the filler materials had a baked density of 1.88 g/cc. The addition of carbon black also reduced the tendency for cracks to form in the extruded graphites produced.

In an attempt to understand how carbon black affects the compaction behavior of a graphite flour, LASL compacted Great Lakes Grade 1008 graphite flour and Thermax carbon black in a steel die equipped with a vacuum system.(47) No binder materials were used. While under a pressure of 28,000 psi, the compact containing only graphite flour had a bulk density of 2.125g/cc (127.2 percent of the calculated packing density); the compact containing only Thermax carbon black had a density of 1.403 g/cc (98.8 percent of the calculated packing density). The calculated packing density, which equals 74 percent of the material's particle density, is the bulk density which would be achieved by the close packing of monosized spheres. The densities of both compacts decreased rapidly as the pressure was reduced, but the percent decrease in density or "spring-back" of the Thermax compact was appreciably less than that of the compact containing only graphite flour. Apparently, the graphite particles deform elastically to fill voids, a characteristic which accounts for the compacted bulk density being considerably greater than the calculated packing density.

While under pressure, the compacts which contained various combinations of the graphite flour and carbon black had densities ranging between those of the compacts containing the individual filler materials. The densities decreased with increasing Thermax content. After the pressure was removed, the densities of the compacts containing graphite and Thermax were higher than that of the compact containing only graphite flour. For example, the compact containing 80 parts graphite flour and 20 parts Thermax had a bulk density of 1.422 g/cc, compared with 1.351 g/cc for the compact containing only graphite flour. The reason for this density difference apparently was that the "spring-back" of the plugs containing graphite flour and Thermax was considerably less than that of the compact containing only graphite flour.

The effects of carbon black additions in ternary systems also were studied.(48) These studies indicate that the porosity and density of some material systems can be adjusted almost independently of each other.

The addition of carbon black reportedly reduces the anisotropy of manufactured graphites.(49) Hot molded compacts which contained various combinations of natural graphite flakes and Thermax carbon black as the filler were produced to study changes in anisotropy of the materials. The natural graphite had a fineness of 100 percent through a 325 mesh screen.

A specimen identified as 58E-1 contained no carbon black and had a Bacon Anisotropy Factor (σ oz/σ ox) of 4.11. Another sample identified as 59F-1 contained natural graphite flakes (70 parts by weight) and Thermax (30 parts by weight). Specimen 59F-1 had a Bacon Anisotropy Factor of 1.72. Carbon black additions of at least 10 to 15 percent were required to produce large changes in the anisotropies of the manufactured graphites. Carbon-black contents up to approximately 20 percent seem to stabilize the filler network against dimensional changes during graphitization.

Carbon blacks were once thought to be completely "ungraphitizable", but recent work has shown that they do graphitize to a small extent.(50) Electron microscopy examination of Thermax particles heated at 2800°C for 30 minutes has shown that they change in shape from spherical to polyhedral. The average carbon black crystallite size (L_c) increased from 17.4Å to 225Å and that the average interplanar spacing (d_{002}) decreased from 3.47Å to 3.378Å after the heat treatment.

Carbon black is a good particulate raw material for use as a minor filler component in a carbon-graphite seal ring formulation. A good seal ring material should have relatively high strength, modulus, and hardness and low porosity and anisotropy. The literature has shown that the addition of Thermax (10 to 30 parts by weight) to a graphite filler produces an increase in strength and hardness and a reduction in the porosity and anisotropy of the resultant compacts.

c. Glassy Carbon

Glassy carbon is a nonporous, isotropic, graphitization resistant material produced by the thermal degradation of organic polymers which display a high degree of cross-linking. Polyfurfuryl alcohol resins, phenol-formaldehyde resins, and cellulose are often used as raw materials in the production of glassy carbon. Not much detailed information concerning the production of glassy carbon is available, since the manufacturing processes have not been disclosed by the companies which produce this material. Although literature does point out that a glassy carbon which "proved satisfactory for a large variety of purposes" has been prepared by limiting the maximum heat-treatment temperature to 1800°C(51), the properties of glassy carbon are known to be influenced by heat treatment temperature. A recent review of the literature on glassy carbons has been conducted by Yamada.(52)

According to Noda et al.(53) the most probable structure of glassy carbon consists of carbon atoms held together by both triagonal and tetrahedral bonds. Small domains of two-dimensional graphite like arrangements are produced by the triagonally-bound carbon atoms. The small domains are held together by tetrahedral bonds, but the tetrahedrally-bound carbon atoms themselves make no domain of regular arrangement. A high degree of unordered, three-dimensional cross-linking probably accounts for glassy carbon's nongraphitizing characteristics and for its tendency to be isotropic.

Glassy carbon displays excellent physical and chemical properties.(54) Permeability to gases is roughly 13 orders of magnitude less than that of an electrode graphite and is comparable with that of hard glasses. With-grain and across-grain compressive strengths of 10,000 psi have been measured for glassy carbon. The electrical and thermal conductivities of glassy carbon resemble those of baked carbons but are considerably lower than those of the various forms of conventional polycrystalline graphite. The low permeability, negligible porosity, and low specific surface tend to make glassy carbon more chemically inert than most other forms of carbon. Its resistance to attack by hydrochloric, hydrofluoric, nitric, sulphuric, and chromic acids is better than that of the nonglassy carbons; however, glassy carbon does disintegrate in the presence of alkali metals.

Lewis(55) has conducted thermogravimetric studies of the oxidation of vitreous or glassy carbon. The glassy carbon specimens used for the investigation were prepared by the carbonization of thin discs of high purity phenol-formaldehyde resin. Carbonization was carried out in an inert atmosphere, usually with a maximum heat treatment temperature of 1800°C. The investigation established that pure grades of glassy carbon prepared from phenolic resins exhibit an oxidation rate lower than that of pyrolytic graphite, which is one of the most oxidation-resistant forms of carbon. During oxidation, the shiny appearance of vitreous carbon was usually maintained or even enhanced. Hemispherically shaped pits formed around impurities during oxidation. Lewis concluded that glassy carbons with even greater oxidation resistance could be produced if the purity of the phenolic resins were improved.

In addition to high cost, glassy carbon has several drawbacks which hinder commercial use. Glassy carbon presently cannot be made in sections thicker than approximately 8 mm, since conventional polymer-forming techniques are used to make the starting-shapes.(56) The formed piece must be, subsequently, heat-treated, probably at a very slow rate, to avoid disruption by the evolving gaseous products. Machining of glassy carbon is rather difficult, requiring diamond-grinding or ultrasonic techniques. Yamada(57) suggested that the poor resistance to mechanical shock exhibited by glassy carbons limits their use for dynamic applications. This observation would indicate that bulk glassy carbons probably could not be used as seal ring materials.

A patent describes the addition of small amounts of pulverized glassy carbon to carbonaceous mixes conventionally used for the production of electrographitic brushes.(58) A suitable glassy carbon for such use was prepared from a mixture of a phenol-formaldehyde resin (150 parts by weight) and furfural (200 parts by weight). The patent states that the glassy carbon should be pulverized to a fineness of 100 percent through a 100 mesh screen, preferably with 50 percent or more passing through a 200 mesh screen. The finely divided glassy carbon is added in amounts constituting from 0.5 percent to 10 percent by weight of the mix batch. Brush life was increased from 7300 hours for the brush containing no glassy carbon to 11,500 hours for the brush containing two percent glassy carbon. The brush containing ten percent glassy carbon had a life of 10,000 hours.

Ground glassy carbon appears to be a good particulate raw material for use as an additive in a carbon-graphite seal ring formulation. Addition of small amounts of ground glassy carbon to a carbon-graphite seal ring mix may increase the wear resistance of the resultant material; such an addition did enhance the wear resistance of electrographitic brushes. Since bulk glassy carbon is hard, strong, isotropic, and oxidation resistant, the addition of ground glassy carbon to a carbon-graphite seal ring formulation may increase the hardness, strength, and oxidation resistance of the resultant compacts and, at the same time, decrease anisotropy.

3. Selection of Four Particulate Solid Raw Materials for Experimental Screening Studies

At the conclusion of the literature search on particulate solid raw materials, four materials were selected to be used in "bench-scale" screening studies. During the selection of each of the four raw materials, consideration was given to the material's type, its source, its particle size and shape, the manufacturing methods required to produce it, and the role it would play in a carbon-graphite seal ring formulation. The selection of the four particulate solid raw materials required and received the approval of the NASA Project Manager; they are:

(1) Grade CHP Graphite - an artificial graphite of relatively high purity manufactured by the Union Carbide Corporation from a non-acicular petroleum coke and coal tar pitch binder.

(2) Grade ASO Graphite - a natural graphite purified by the Union Carbide Corporation.

(3) "Regular" Thermax - a furnace black manufactured by the Thermatomic Carbon Division of the Commercial Solvents Corporation. This material is the same carbon black used by Group CMF-13 of the Los Alamos Scientific Laboratory in their research on carbon and graphite.

(4) LMSC Glassy Carbon Powder - a material manufactured by the Lockheed Palo Alto Research Laboratory by using a 1000°C heat treatment temperature; it is pulverized to the desired fineness by the Contractor.

One point consistently brought out during the literature search was that a high concentration of graphite filler is required to produce the most oxidation resistant carbon-graphite materials. The use of this type of filler system also produces a specimen with excellent machinability and high thermal conductivity, at least in the with-grain direction. High thermal conductivity provides rapid transfer of deleterious frictional heat which can develop during periods of sliding contact. Since seal dam widths as small as 0.020 inches are inherent in the seal design, good machinability is a very desirable characteristic of the seal ring material. Because they met these filler requirements, Grade ASO natural graphite and Grade CHP artificial graphite were selected as two of the particulate solid raw materials for experimental evaluation. These high-purity graphites were selected because most metal impurities are known to be oxidation catalysts. Starting with a high concentration of high-purity graphite and adding known oxidation inhibitors should result in the formation of the most oxidation-resistant carbon-graphite seal ring materials.

Consideration was given to the effect of filler particle size on the properties of carbon-graphite bodies during selection of the comminution procedure for the ASO and CHP graphites. Both graphites were milled to very fine flours (ASO = 87 percent and CHP = 97 percent by weight through a 200 mesh "Tyler" screen). As mentioned during the discussion of particulate graphites, grain size and strength are inversely related. The use of fine particle size fillers, therefore, will enhance the strength of the carbon-graphite seal ring material. However, the fine particle size Grade ASO natural graphite will probably produce a relatively anisotropic compact. Grade CHP is a relatively isotropic artificial graphite filler because it is manufactured from a nonacicular coke. Molded carbon-graphite seal ring bodies prepared with this filler should be more isotropic than those prepared with ASO graphite.

Thermax furnace black was selected as a particulate raw material for use as a minor filler component in a carbon-graphite seal ring formulation. The literature has shown that the addition of Thermax to highly graphitic filler materials produces an increase in the strength of the resultant compacts, with a corresponding decrease in porosity and anisotropy. Since the rate-controlling mechanism for oxidation at 1300°F involves penetration of the reacting gas into the pores of the carbon-graphite body, a decrease in the porosity of the compacts will help increase oxidation resistance. The fact that an addition of Thermax reduces anisotropy may help to increase the across-grain thermal conductivity of highly graphitic seal rings. The addition of Thermax also will increase the wear resistance of highly graphititic seal rings, since "hard" carbons, such as Thermax, increase the load carrying capacity of the carbon-graphite body.

The LMSC 1000°C heat treated pulverized glassy carbon was selected as a particulate raw material to be used as an additive for carbon-graphite seal ring materials. Since the hardness of glassy carbon is inversely related to its heat treatment temperature, this low-temperature material should contribute greater hardness and wear resistance to the seal ring composition than a glassy carbon heat treated at high temperature e. g., 2000°C.

B. Binder Raw Materials

1. Coal Tar Pitch

Coal tar pitch is a thermoplastic material which has long been used as the principal binder in the manufacture of carbon-graphite materials. Coal tar pitch is a very complex mixture of dispersed solids and as many as 5000 different aromatic and heterocyclic compounds. Production of coal tar pitch consists of the distillation of coal tar (a viscous liquid mixture produced by the destructive distillation of coal) to remove the light oils, creosote, and anthracene oil. The nature and properties of coal tar pitch are affected by the type of coal used and the manufacturing procedures employed to produce it. The processes employed to manufacture coal tar pitch have been reviewed by Smith et al.(59) The wide range of commercially available pitches are generally grouped into three broad classifications entitled "soft pitch" (softening point 30°C or less) "medium-soft pitch" (softening point up to 78°C), and "hard pitch" (softening point between 80°C and 250°C). Pitches with softening points of 80°C to 100°C are the most commonly used binder materials in the United States. A survey of the literature on pitch binders for graphites has been conducted by Hooker.(60)

The characterization of a coal tar pitch usually includes a measurement of its coking value and its insoluble contents. Coking value is the proportion of the binder material remaining as residual carbon after pyrolysis. Benzene and quinoline are the solvents commonly used to extract the soluble residues from the pitch sample being characterized. The benzene-insolubles (BI) and quinoline-insolubles (QI) reflect the molecular weight distribution of the compounds in the pitch. Measurements of specific gravity, softening point, viscosity, ash content, and elemental analysis also are used to characterize coal tar pitches. A good pitch binder usually has a coking value of 45 percent or higher and must wet and adhere to filler material to effectively bond the carbon article. The effectiveness of a coal tar pitch binder has not been related solely to any single property. Binder effectiveness is determined ultimately by preparation and property characterization of test specimens.

The process of carbonizing a coal tar pitch binder is a complex combination of thermalytic cracking, condensation, and polymerization.(61) A basic understanding of the carbonization process can be acquired from the following simplified explanation. When the temperature of coal tar pitch reaches its softening point, the pitch becomes plastic. The pitch remains viscous enough to hold the formed compact together, but the compact must be supported to avoid sagging. As the baking temperature is increased to approximately 700°C, polymerization and dehydrogenation reactions occur which continue to increase the viscosity of the pitch until the structure is thermally set as coke. Additional heating to temperatures up to 3000°C causes increased crystal growth and additional loss of hydrogen. Carbon produced from the pyrolysis of coal tar pitch usually displays a relatively high degree of crystallinity when heated above 2800°C.

The behavior of coal tar pitch during pyrolysis can be altered by use of various additives. Small amounts of powdered sulfur are sometimes added to carbon-graphite mixes to increase the coking value of the pitch binder and, thereby, enhance the physical properties of the resultant carbon article. Edstrom et.al.(62) found that p-benzoquinone, chloranil, hydroquinone, hydrochloric acid, trichloroethylene, ferric chloride, and several inorganic persulfates, chlorates, and oxides increased the coking value of a pitch. The latter three types of material were found to be as effective "coking additives" as sulfur. However, the oxidation rates at 650°C of graphitized bodies incorporating the sulfur, ammonium persulfate, potassium persulfate, and sodium chlorate pitch additives all were significantly greater than that of bodies bonded with pitch alone. The use of the additives containing the nonfugitive metallic elements will also increase susceptibility to oxidation, since most metals are oxidation catalysts.

Presently, coal tar pitch is the principal binder for carbon-graphite seal ring materials. The high coking value of coal tar pitch enables preparation of strong seal ring bodies. Since coal tar pitch can be graphitized to a relatively high degree, it can contribute to the overall oxidation resistance of the carbon-graphite body.

Recent evidence suggests that petroleum pitch may be a suitable binder for carbon-graphite materials.(63) However, the strength of compacts prepared with this binder generally appear to be lower than that of compacts bonded with coal tar pitch.

2. Synthetic Resin Binders

Although coal tar pitch is the binder used most extensively for carbon-graphite bodies, a number of other materials have been successfully employed as binders. The Armour Research Foundation of the Illinois Institute of Technology has screened many synthetic hydrocarbons to determine their effectiveness as possible binders for carbon-graphite materials. A measurement of the carbon residue after pyrolysis was made on 50 materials, including several coal tar pitches and a large number of synthetic resins.(64) Based on the results of the coking value measurements, a liquid furfuryl alcohol resin, an unplasticized phenolformaldehyde resin, and a phenol-benzaldehyde resin were selected as the most promising synthetic resin binders. Further screening studies were conducted on the three synthetic resins by preparing small carbonized compacts in which the three resins were used as binders. Compacts bonded with Barrett No. 30 medium coal tar pitch were produced and used as standards for comparison with the three types of resin-bonded materials.

Synthetic resin binders have the advantage of being a more controllable raw material than coal tar pitches. A further advantage of employing synthetic thermosetting binders is that it is possible to bake the formed carbon-graphite compact without the support of a packing medium. More rapid processing of carbon-graphite materials, therefore, also may be effected by using these synthetic resins as binders.

a. Phenol-formaldehyde Resin

Phenol-formaldehyde resins are a specific category of phenolic materials. The term phenolic usually is used to describe thermosetting polymers which are formed by the condensation reaction of any number of aldehydes and monohydric or polyhydric phenols.

Phenol-formaldehyde resins are prepared by the condensation of phenol with formaldehyde employing either an acid or alkaline catalyst. The nature of the resultant product is dependent on the type of catalyst. When an alkaline catalyst is used with equimolar quantities of the two reactants, a material called a resole is formed. This material can be thermally cross-linked without addition of any other reactant. In acid catalyzed solutions containing an excess of phenol, a linear soluble fusible polymer called a novolac is formed. This polymer softens between 65°C and 95°C and must be reacted with formaldehyde to effect cross-linkage. Thermal decomposition of hexamethylene-tetramine generally provides the formaldehyde necessary to accomplish the cross-linking. Decomposition of hexamethylene-tetramine also produces ammonia, which catalyzes the reaction. Phenol-formaldehyde resins based on novalacs are usually called "two-stage" resins. Since hexamethylene-tetramine requires elevated temperatures for decomposition, two-stage resins are stable at room temperature. Resoles can polymerize at room temperature.

Although many general references to the use of "phenolic" resins as binders for carbon-graphite materials can be found in the literature, specific information as to the variety of resin used (i. e., type, manufacturer, method of preparation, grade, etc.) often is not included. This type of information was contained in the previously cited work of the Armour Research Foundation. Armour obtained a coking value of 50.2 percent for Bakelite BRP-5095 resin and 37.3 percent for the phenol-benzaldehyde resin.(65) The phenol-benzaldehyde resin will not be discussed in this report, since it is not a commercially available resin. The Armour Research Foundation produced small quantities of the phenol-benzaldehyde for their experimental work. The BRP-5095 material is a two-stage phenol-formaldehyde resin molding powder. Compacts were prepared by Armour by using the Bakelite BRP-5095 resin (60 parts by weight) and Texas Lockport No. 90 petroleum coke flour (100 parts by weight).(66) The resin was dissolved in acetone and mixed with coke in a cookie mixer until dry. Dissolving the resin in acetone produced a good coating of the binder around the particulate filler material. Chunks of the dry mixture were heated at 100°C for one hour to drive off any remaining acetone; the material was then ball milled and sifted through a No. 40 screen. The mixture was warm-molded (80°C) at pressures of 6000 psi to 16,000 psi, after which the compacts were first baked to 1000°C and then exposed to a graphitizing temperature of 2800°C.

Evaluation of the phenol-formaldehyde resin bonded compacts heat treated to 2800°C included a measurement of their bulk densities, electrical resistances, and porosities. Armour noted no pronounced tendency for the green densities of the compacts to increase as the molding pressure was increased. A sample identified as No. 119, which had been molded at 14,000 psi, had a green density of 1.59 g/cc. After the compacts were baked at 1000°C, physical dimensions decreased approximately eight percent for the phenol-formaldehyde compacts, compared with only 0.6 percent for the samples produced from the same coke flour (100 parts by weight) and a coal tar pitch binder (38 parts by weight). The 1000°C baked density of sample No. 119 was 1.43 g/cc. After being heat treated to 2800°C, sample No. 119 had a density of 1.70 g/cc and a total porosity of

24.9 percent, a porosity which is considerably lower than the 35.8 percent measured for one of the pitch-bonded compacts. Armour concluded that the binder phase of the phenol-formaldehyde bonded compacts underwent relatively large shrinkage during heat treatment. A careful examination of the electrical resistances obtained during the evaluation of the phenol-formaldehyde bonded compacts indicates that they did not graphitize so well as those made with coal tar pitch binder.

Later work indicates the crystallinity of resin binder carbon which has been heat treated to graphitization temperatures is influenced by the filler material. Smith(67) studied the graphitization behavior of binder residues derived from various thermosetting synthetic resins. In the first set of experiments, the resins were used as binders for carbon black. Heating to 2820°C produced a binder carbon residue which was not significantly graphitized. Repeating the same experiments with the substitution of glassy carbon for the carbon black produced a binder carbon residue which was reasonably well graphitized ($L_c = \sim 240Å$, $d_{002} = 3.36Å$). When the resins were used as binders for a well-graphitized filler, the binder carbon residue was found to be graphitized to an extent approximately equal to that of the graphite filler.

The high coking value of phenol-formaldehyde resin indicates that this material is a potentially promising binder for producing strong carbon-graphite seal rings. The high shrinkage during baking which may occur when a phenol-formaldehyde resin is used would contribute to low porosity in the phenolic-resin-bonded compacts and, therefore, should aid the oxidation resistance of a carbon-graphite seal ring.

b. Furfuryl Alcohol Resin

Furfuryl alcohol is a low viscosity liquid prepared by the hydrogenation of furfural, which is extracted from vegetable materials through acid treatment. The general term furan resin is often used to refer to condensation products in which one of the starting monomers is furfural or furfuryl alcohol. Furfuryl alcohol can be polymerized in the presence of an acid catalyst, usually with heat, through a hydrogenation-condensation reaction. Polymers varying from low-viscosity liquids to brittle, fusible solids may be obtained by altering reaction conditions. Neutralization and removal of water provides a stable product for storage. Curing of these resins is accomplished by addition of either mineral or organic acid. The strength of the acid and temperature determine the rate of resin cure. The cured resin is a brittle infusible solid.

High coking value, ability to wet filler material, and low shrinkage are characteristics accompanying the pyrolysis of some furfuryl alcohol resins which have prompted rather extensive recent research on the use of this material as a binder for carbon-graphite bodies. During earlier work, Armour Research Foundation reported a coking value of 49.1 percent for Durez 16470 RI-3385 resin, a furfuryl alcohol resin manufactured by the Hooker Electrochemical Company.(68) This furfuryl alcohol resin contained a five percent by weight of Durez 17932, a polymerization catalyst. Furfuryl alcohol resin-bonded compacts heat treated to graphitizing temperatures were prepared by Armour. Texas Lockport No. 90 petroleum coke flour (100 parts by weight) was mixed for two hours in a cookie mixer with the Durez 16470 RI-3385 resin (20 parts by weight). The furfuryl alcohol resin contained five percent by weight of the Durez 17932 accelerator. Within two hours after mixing, green compacts were warm-molded (125°C) at pressures of 8000 psi and 10,000 psi. Molding pressure was maintained for two minutes. The green plugs were subsequently baked to 1000°C and then heat treated to a graphitizing temperature of 2800°C.

Evaluation of the furfuryl alcohol, resin-bonded compacts also included measuring their bulk densities, electrical resistances, and porosities. A green compact identified as Sample No. 200 which was molded at 10,000 psi had a density of 1.74 g/cc. Of the four types of binders (including a coal tar pitch) evaluated by Armour, the furfuryl alcohol resin binder produced compacts with the highest green densities and greatest internal homogeneity. Baking to 1000°C produced a dimensional shrinkage of 0.9 percent for the compacts bonded with the furfuryl alcohol resin. Sample No. 200 had a baked density of 1.64 g/cc. After being heat treated at 2800°C, sample No. 200 had an apparent density of 1.71 g/cc and a total porosity of 26.2 percent, values which are comparable with those of the phenol-formaldehyde resin bonded compact discussed in the preceding section. Measurements of the electrical resistance indicated that the furfuryl alcohol resin bonded plugs "graphitized" to a relatively high degree. Armour concluded that, although liquid furfuryl alcohol and phenol-formaldehyde are both binders of considerable merit, liquid furfuryl alcohol appears to provide the best overall binder properties.

The Oak Ridge National Laboratory evaluated numerous pitches and resins during their investigation of methods to be used for fabricating nuclear fueled-graphite spheres.(69) A high coking value and solubility of the binder in a volatile liquid were the requirements stressed during the binder evaluation. A soluble binder was required, since the addition of a solvent would allow for mixing in a liquid medium, a necessary condition for good coating of the binder around the particles of the filler material. The "benzene-soluble fraction of Varcum, a furan resin" was selected as the binder having the best properties.

Edstrom et. al.(70) investigated a furfuryl alcohol resin binder which had 16 percent of the water from the condensation reaction removed after pre-polymerization by activated alumina. They employed para-toluene sulfonic acid as a catalyst; this high viscosity resin was submitted to them for evaluation by Armour Research.(71) Plugs prepared with this binder and a graphite filler cracked extensively when baked to 800°C. Fewer cracking problems were encountered with plugs made from a coke filler. The strengths and Young's moduli of the plugs bonded with this resin and heat treated to graphitizing temperatures were lower than those of plugs processed with a pitch-sulfur binder. These physical property differences were attributed to nonuniform dispersion of the resin on the filler particles and to high shrinkage and weight loss during baking.

LASL has used Varcum 8251 furfuryl alcohol resin extensively in their research on carbon and graphite. They have produced small diameter rods of an extruded, resin-bonded graphite identified as Lot AAQ1 using Varcum 8251 resin as the binder. This graphite lot has been discussed in the section of this report entitled "Artificial Graphite."

Maleic anhydride, in a proportion of four percent by weight of furfuryl alcohol resin, was included in the binder level of 27 parts by weight to act as a polymerization catalyst. Evaluation of Lot AAQ1 graphite has shown it to be relatively strong and very uniform. The binder phase of this material graphitized considerably after heat treatment at 2800°C.

Liquid furfuryl alcohol resin appears to be a potentially good raw material for use as a binder in a carbon-graphite seal ring formulation. The high coking value possible with a furfuryl alcohol resin indicates that this thermosetting material can produce strong carbon-graphite seal rings. This resin can wet filler materials and has produced high density graphite bodies. Furfuryl alcohol resin also appears to be a good binder for developing oxidation resistant carbon-graphite seal rings: the resin can be readily graphitized, and compacts made with the resin can have low porosity.

c. Polyphenylene Sulfide Resin

Polyphenylene sulfide resin appears to be a promising carbon binder material. The literature pointed out that polyphenylene sulfide has a relatively high theoretical carbon content (approximately 65 percent) and that thermal degradation of the material produces a large residue.(72) No reference to the use of this material as a binder for carbon-graphite materials was found. The high theoretical carbon content and the possibility of a large amount of residue remaining after pyrolysis may make polyphenylene sulfide a good binder for a carbon-graphite seal ring material.

The Phillips Petroleum Company produces a polyphenylene sulfide resin powder called Ryton which is available in developmental quantities.(73) This material is a free flowing white powder of nominal 10 micron particle size. Heating the material in air at temperatures of 650°F to 700°F causes thermal cross-linking, a condition which greatly increases molecular weight and is a vital processing step for molding. Although the material is not a true thermoset, it is thermosetting in nature since it will not soften until heated to the temperature reached during curing. Some softening is always possible if the resin is subjected to sufficient heat.

The Phillips Petroleum Company reports that the unpyrolyzed resin has unusually good wetting action on most substrates and all common fillers, resulting in filled parts and laminates of very high strength.

The brochure issued by the Phillips Petroleum Company on the polyphenylene sulfide resin describes some compacts which have been prepared by using the unpyrolized resin as the binder. Fillers used included ground glass, asbestos, and mineral powders; no carbon or graphite was used. The polyphenylene sulfide resin was dry blended with the fillers in the desired proportions. After the mixtures were blended, they were heated in a 650°F to 700°F circulating air oven for approximately one hour. The air circulating through the mixtures produced cross-linking of the resin and wetting of the fillers. Compacts were molded at temperatures between 600°F and 700°F; pressures of 1000 psi or greater were applied for five minutes. The compacts were cooled to 300°F while under pressure and then ejected.

3. Selection of Four Binder Materials for Experimental Screening Studies

At the conclusion of the literature search on binder raw materials, four materials were selected to be used in further experimental "bench scale" screening studies. Coking value was one of the primary considerations for selection of the four binder materials, since a high coking value binder is required to produce strong carbon-graphite seal rings. The selection of the four binder raw materials required the approval of the NASA Project Manager.

The four binder raw materials approved by the NASA Project Manager are:

(1) Barrett No. 30 MH Coal Tar Pitch--Manufactured by the Allied Chemical Company. The Los Alamos Scientific Laboratory has used this thermoplastic material to prepare carbon-graphite compacts..

(2) Varcum 8251 -- A dark, thermosetting, liquid resin manufactured by Reichold Chemicals Incorporated. The Los Alamos Scientific Laboratory has studied Varcum 8251 extensively as a binder material for carbon-graphite bodies.

(3) Bakelite BRP-5095 Resin -- An unplasticized two-stage phenol-formaldehyde resin powder manufactured by the Union Carbide Corporation. The Armour Research Foundation has studied this thermosetting material as a binder for carbon bodies.

(4) Ryton Resin -- A polyphenylene sulfide resin powder manufactured by the Phillips Petroleum Company.

Barrett No. 30 MH (medium hard) coal tar pitch was selected as one of the four binder raw materials because LASL had previously used the pitch to produce strong carbon-graphite compacts. Difficulties arose when the Contractor attempted to order Barrett No. 30 MH coal tar pitch. Allied Chemical Company presently produces No. 30 medium pitch (softening point approximately 98°C to 103°C) and No. 30 hard pitch (softening point approximately 108°C to 113°C); however, the production of No. 30 MH pitch was discontinued in June, 1967. The problem was resolved by gaining the approval of the NASA-Project Manager to substitute Barrett No. 30 medium pitch for the Barrett No. 30 MH pitch which initially had been approved.

The coking value of 52 percent measured for No. 30 medium pitch by the Armour Research Foundation indicates that this pitch is a potentially good binder for producing strong carbon-graphite seal rings. The relatively low softening point of No. 30 medium pitch will permit good dispersion of this binder on the filler particles by using conventional hot mixing techniques. The softening point should be sufficiently high to minimize distortion problems during baking. The fact that this pitch can be readily graphitized will enhance the oxidation resistance of molded compacts. Since coal tar pitch is the most commonly used commercial carbon binder, Barrett No. 30 medium pitch will be used as a baseline in the evaluation of binder effectiveness during the experimental screening studies.

Varcum 8251 furfuryl alcohol resin was selected as a binder raw material warranting experimental evaluation for carbon-graphite seal ring formulations. This resin binder is a liquid and can be dispersed readily on the filler for good coating of the filler particles. Varcum 8251 resin binder was used by LASL to produce a uniform lot of high density, high strength graphite. When used as a carbon binder, this resin has produced relatively low porosity compacts. Lowering the porosity of carbon-graphite seal rings should enhance their oxidation resistance. The fact that the Varcum 8251 resin can be readily graphitized when in the presence of a graphite filler should also enhance the oxidation resistance of molded carbon-graphite seal ring materials.

Bakelite Grade BRP-5095 resin also was selected as a binder raw material for experimental evaluation. This phenol-formaldehyde resin powder can be readily dissolved in liquids for mixing with the filler particles. Grade BRP-5095 resin has a high coking value and has produced relatively low porosity carbon bodies. This resin may produce a glassy binder carbon which should enhance the wear and oxidation resistance of the seal ring material.

Ryton polyphenylene sulfide resin was selected as a potential carbon binder, since this type of resin has a high theoretical carbon content and can leave a large residue after undergoing thermal degradation. This latter characteristic may make Ryton resin a good binder for carbon-graphite seal rings.

C. Oxidation-Inhibiting Impregnants and Additives

Finished carbon-graphite seal rings almost always contain additives or impregnants which help them meet the requirements of a particular sealing application. Resins, metals, and ceramics are common impregnants for pump seals. Insoluble inorganic compounds from the fluoride or sulfide family can be used as film-forming additives for carbon-graphite seal rings. Aircraft seals are exposed to very high ambient air temperatures and, therefore, require impregnation with, or the addition of, temperature stable inorganic salts which act as anti-oxidants. Since the purpose of this Contract is to develop oxidation-resistant carbon-graphite seal ring materials, this section of the report will be limited to the discussion of oxidation-inhibiting impregnants and additives.

The oxidation of carbon and graphite materials is a heterogeneous reaction between a gas and a porous solid. The oxidation rate may be controlled by one or more of the following steps:

(1) mass transport of the oxidizing gas and the products of oxidation across a boundary layer of relatively stagnant gas which exists at the outer surface of the solid;

(2) mass transport of the oxidizing gas from the exterior surface to an active site within the solid and mass transport of the oxidation products to the outer surface; and

(3) chemisorption of the oxidizing gas at an active site, rearrangement of the chemisorbed gas on the surface to a desorbable product, and desorption of the products from the surface.

A number of factors determine which oxidation mechanism controls the reaction. Temperature is one of these factors. At the temperatures that can be encountered by the seal ring materials developed for this Contract (up to 1300°F), the third mechanism will probably dominate.

The process by which a carbon-graphite seal ring is impregnated with an oxidation inhibiting treatment consists basically of vacuum evacuation, impregnation, pressurization, and curing. There are three mechanisms by which the impregnant may retard oxidation:

(1) the impregnant may form a glass which wets the carbon and impurities to form an impervious barrier against the oxidizing gas,

(2) the impregnant may seal off the opening to a pore and prevent entrance of the oxidizing gas, and

(3) the impregnant may react with those impurities which are oxidation accelerators to convert them to inactive impurities or even inhibitors.

The impurity content of a graphite has a significant effect on the rate at which it oxidizes. Most metals are known to be catalysts for the oxidation of graphite, whereas, all known oxidation inhibitors are either nonmetals or nonmetallic in nature. Rakszawski and Parker, who studied the effects of Group IIIA-VIA (periodic table) elements and their oxides on graphite oxidation(74) found that boric oxide and phosphorous rather significantly reduce the oxidation of graphite at temperatures up to 800°C. A patent held by the Union Carbide Corporation(75) which pertains to the No. 83 treatment states ". . . . the useful life of phosphoric acid as an oxidation retardant can be extended by reacting it 'in situ' with colloidal silica to form a silicon-phosphorous-oxygen complex (example, silico phosphate) in the pores of graphite articles." Hastings and Zeitsch have reported that a graphite composite known as Grade JTA has oxidation protection for the full temperature range to approximately 3500°F.(76) The starting material for Grade JTA is a blend of powdered graphite, pitch, zirconium diboride, and silicon.

As previously indicated, the addition of boron enhances the oxidation resistance of graphitic materials. Boronated graphites generally are produced by adding B_4C particles to the mix early in the manufacturing process. At the melting point of B_4C (approximately 2450°C), the maximum solubility of boron in graphite is approximately 2.3 atomic percent.(77) When boronated graphites are exposed to oxidizing conditions, molten B_2O_3 forms on the surface of the graphite. The surface coating of B_2O_3 masks the active sites of the graphite and, therefore, reduces the oxidation rate. Although the addition of boron reduces the activation energy of graphite, increasing boron content will produce enough of the protective B_2O_3 to overshadow the catalytic effect of the reduced activation energy. The oxidation rate of boronated graphites decreases with increasing boron content. Theoretically, moisture in the air should strip off the accumulated B_2O_3 by the formation of volatile HBO_2. However, recent experiments have shown that the accumulated B_2O_3 was not stripped away from boronated graphite samples when they were oxidized in the presence of moist oxygen.(78)

Trask has prepared boronated graphites by starting with a mixture of coke and coal tar pitch to which B_4C was added in percentages varying between 0.5 and 7.5.(79) This investigator noted the decrease in oxidation rate as a function of the increase in boron content. He also observed that, when the boron-containing materials were heated to 2200°C, they had interlayer spacings and crystallite sizes equivalent to the non-additive graphite heated to 2750°C. The observation indicates that the B_4C additive acted as a graphitization catalyst.

Since the use of B_4C as an oxidation-inhibiting additive warranted additional experimental study, it was included as an additive in the material systems produced for the experimental screening studies. The material systems are discussed in a later section of this report.

A recent study of fluoride solid lubricants was conducted at the NASA Lewis Research Center. The NASA investigators found that CaF_2-BaF_2 mixtures can be used as a coating on bearing cages or as a filler in porous-bearing cages to produce lubricated ball bearings which will operate successfully in air at temperatures from 1200°F to 1500°F.(80,81) Graphite fluoride $(CF_x)_n$ also was investigated as a potential solid lubricant.(82) The NASA personnel found that graphite fluoride will lubricate in moist air, dry air, or dry argon to a temperature of approximately 400°C. Stainless-steel discs lubricated with graphite fluoride were found to have a longer wear life than those lubricated with either graphite or MoS_2.

The results of the NASA investigation on solid lubricants may have potential use in the development of self-lubricating carbon-graphite seal rings. However, temperature limitations of the $(CF_x)_n$, MoS_2, and CaF_2-BaF_2 solid lubricants have eliminated their possible use as additives or binders for the carbon-graphite seal ring formulations to be produced under this Contract. The carbon-graphite materials to be produced will be graphitized at 2800°C so that the high oxidation resistance required to withstand the 1300°F operating air temperature will be obtained.

Oxidation inhibiting impregnants and additives sometimes aid the performance of carbon-graphite seal rings by the promotion of a surface film on the counterface. Presently, the mechanism by which these surface films aid performance is not fully understood. A review of the literature on boundary lubrication by Godfrey revealed that no adequate theory presently exists that completely defines the mechanisms associated with boundary lubrication.(83) However, Godfrey concluded that the formation of a solid film appears to be essential for effective lubrication.

D. Materials Processing

The Contractor reviewed the literature to ascertain processing techniques that could be used to prepare compacts from the four particulate and four binder raw materials selected for further experimental studies. Reports issued by the Los Alamos Scientific Laboratory and the Armour Research Foundation were used as primary sources, since they gave some of the most detailed descriptions of techniques employed to produce carbon-graphite compacts. However, the two institutions were primarily preparing relatively small carbon-graphite bodies for their research work and, thus, they employed some equipment which is usually not used commercially to process carbon-graphite materials. For example, the Armour Research Foundation used a cookie mixer to prepare its materials, and the Los Alamos Scientific Laboratory incorporated a meat grinder as part of the mixing operation. The literature search did indicate that the binder system plays a key role in determining the processing techniques required.

The Contractor's knowledge of carbon-graphite material processing, augmented by information gained through the literature survey, dictated the initial methods to be used for producing the materials required under the scope of this Contract. Four different manufacturing cycles were devised to suit the processing requirements imposed by each of the four approved binder materials. The processing methods were devised to employ the type of equipment commercially used to process carbon-graphite materials.

Molding was selected as the forming process to be used, since this forming method produces a less anisotropic structure than that obtained by extrusion. Higher forming pressures than those usually applied during conventional extrusion are generally preferred for seal ring compositions. Although isostatic forming offers further opportunity for obtaining a material with more nearly isotropic properties, the proper selection of raw materials and the use of molding were considered adequate to sufficiently minimize anisotropy. Since the use of shear during molding may tend to increase the anisotropy of the formed body, it will not be used.

The following processing methods were selected for the screening studies.

(1) Materials Bonded with Coal Tar Pitch: (a) Blend filler raw materials for one hour.(b) Mix filler and binder in a sigma blade mixer for one hour. Preheat filler and mixer to 150°C before adding pitch. (c) Crush cooled mix. (d) Micromill crushed material. (e) Blend milled material for one hour. (f) Mold the milled material at room temperature by using a hydraulic press. (g) Pack green compacts with coke in a sagger and bake green compacts at 10°C/hour to 1000°C. (h) Using graphite particles as the packing medium, heat the baked compacts to 2800°C in an induction furnace.

(2) Materials Bonded with Phenol-Formaldehyde Resin: (a) Blend filler raw materials for one hour. (b) Dissolve binder in equal volume of acetone and mix with filler in a sigma blade mixer for one hour at room temperature. (c) Heat material in a 75°C circulating air oven until all the acetone is evaporated. (d) The remaining processing steps are the same as those used with the coal tar pitch-bonded materials, starting with the crushing of the material (pitch bonded Step c).

(3) Materials Bonded with Furfuryl Alcohol Resin: (a) Blend filler raw materials for one hour. (b) Dissolve maleic anhydride (4 percent by weight of the furfuryl alcohol included in the binder level) in the binder and mix with filler in a sigma blade mixer for one hour at room temperature.

(c) Force the material through a 10 to 20 mesh screen to break up any mix agglomerates. (d) Mold the screened material at room temperature by using a hydraulic press. (e) The other processing steps are the same as those used with the coal tar pitch bonded materials starting with baking the compacts to 1000°C (pitch bonded Step g).

(4) Materials Bonded with Polyphenylene Sulfide Resin: (a) Blend filler raw materials for one hour. (b) Dry blend the resin with the filler for one hour in a twin-shell blender equipped with an intensifier bar.
(c) Heat the mix for one hour at 650-700°F in a circulating air oven.
(d) The other processing steps are the same as those used with the coal tar pitch bonded materials starting with the crushing of the material (pitch bonded Step c).

Porous carbon bodies often are impregnated with tars, pitches, synthetic resins, or combinations of these materials when the application requires a material with low porosity, high density, and high strength. Infiltration of the pores with carbon deposited by a hydrocarbon gas (pyrolytic carbon) has been recently investigated.(84) The materials are usually introduced by a vacuum-pressure impregnation procedure. Impregnation is followed by carbonization and, in most cases, exposure to graphitization temperatures. This type of impregnation was considered for materials produced during this program (see discussion of the screening studies).

E. Selection of Twelve Materials Systems for Experimental Screening Studies

After the NASA Project Manager approved the selection of the particulate and binder raw materials, 12 material systems for experimental screening studies were proposed. The systems initially submitted for approval are listed in Table I. Glassy carbon, one of the approved particulate solid raw materials, is listed as an additive in the table since it will be used in relatively low concentrations. The 12 material systems were selected to permit a binder evaluation, a graphite evaluation, an evaluation of boron carbide as an oxidation inhibiting additive, and an evaluation of ground glassy carbon as an additive for increasing seal life. An attempt was to be made to proportion the solid raw materials (by weight), employing the method used by Lewis and Goldman for determining optimum particle packing.(85) The optimum binder concentrations for the particulate raw materials were to be estimated by the "stearic acid" technique developed by LASL.(86)

TABLE I. - TWELVE PROPOSED MATERIAL SYSTEMS

Material System	Particulate Solid Raw Materials	Additive	Binder Raw Material
1	CHP Artificial Graphite & Thermax	---	No. 30 Medium Pitch
2	CHP Artificial Graphite & Thermax	---	Varcum 8251 Resin
3	CHP Artificial Graphite & Thermax	---	Bakelite BRP-5095 Resin
4	CHP Artificial Graphite & Thermax	---	Ryton Polyphenylene Sulfide Resin
5	ASO Natural Graphite & Thermax	---	No. 30 Medium Pitch
6	ASO Natural Graphite & Thermax	---	Varcum 8251 Resin
7	CHP Artificial Graphite & Thermax	Boron Carbide	No. 30 Medium Pitch
8	ASO Natural Graphite & Thermax	Boron Carbide	No. 30 Medium Pitch
9	CHP Artificial Graphite & Thermax	Glassy Carbon	No. 30 Medium Pitch
10	CHP Artificial Graphite & Thermax	Glassy Carbon	Varcum 8251 Resin
11	CHP Artificial Graphite & Thermax	Glassy Carbon	Bakelite BRP-5095 Resin
12	CHP Artificial Graphite, ASO Natural Graphite & Thermax	---	No. 30 Medium Pitch

After having reviewed the proposed material systems, the NASA Project Manager requested a de-emphasis of the use of ASO natural graphite, emphasis on the use of ground glassy carbon, and inclusion of graphite fiber as a filler. Approval was given for the first five material systems listed in Table I. The Contractor proposed that 20 parts Thermax be used for all the filler systems incorporating Thermax, since the possibility exists that the Lewis and Goldman method could not be applied to the approved particulate solid raw materials. A number of previously cited works indicate that a 20-percent addition of Thermax should reduce the anisotropy, improve the strength, and increase the hardness of a graphite material without impairing oxidation resistance. The NASA Project Manager agreed to the use of 20 parts of Thermax for the filler, but requested that the Lewis and Goldman method be used as a means of material characterization.

The Sharples Micromerograph normally is used to determine the particle size distributions required for the calculation of optimum particle packing. Approximately one-half of the sample was recovered when a micromerograph analysis of a filler material was conducted. This sample recovery is considered typical for the micromerograph apparatus. The precision of the sample statistics for particle size distributions derived from the micromerograph data, therefore, may be questionable. In order to obtain a more accurate measurement of the particle size distributions of the four particulate raw materials, a MSA Sedimentation Particle Size Analysis was recommended rather than the micromerograph analysis. The term MSA is the trademark of the Mine Safety Appliance Company, which manufactures the apparatus used in the Sedimentation Particle Size Analysis.

The original selection of the 12 material systems was revised to incorporate the requests made by the NASA Project Manager. Table II presents the 12 material systems approved by the NASA Project Manager.

TABLE II. - TWELVE APPROVED MATERIAL SYSTEMS

Material System	Particulate Solid Raw Material	Additive	Binder Raw Material
1	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	---	No. 30 Medium Pitch
2	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	---	Varcum 8251 Resin
3	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	---	Bakelite BRP-5095 Resin
4	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	---	Ryton Polyphenylene Sulfide Resin
5	ASO Natural Graphite (80 pbw) & Thermax (20 pbw)	---	No. 30 Medium Pitch
6	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	Glassy Carbon (2 pbw)	No. 30 Medium Pitch
7	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	Glassy Carbon (10 pbw)	No. 30 Medium Pitch
8	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	Glassy Carbon (10 pbw)	Varcum 8251 Resin
9	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	Boron Carbide (1 pbw)	No. 30 Medium Pitch
10	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	Boron Carbide (7.5 pbw)	No. 30 Medium Pitch
11	Glassy Carbon (80 pbw) & Thermax (20 pbw)	---	Varcum 8251 Resin
12	CHP Artificial Graphite (80 pbw) & WCA Graphite Fibers (20 pbw)	---	Varcum 8251 Resin

Note: Proportions are parts by weight (pbw)

SECTION VI

EXPERIMENTAL DATA ON APPROXIMATE ROLES OF MATERIALS AND VARIABLES

(CATEGORY 2 TASK I)

A. Characterization of Raw Materials

This section presents the results of all characterization tests of the raw materials used in this program. The test procedures are described in Appendix I.

1. CHP Artificial Graphite

Helium Density = 2.22 g/cc

Surface Area = 6.7 m^2/g

Screen Analysis

On 35 mesh = 0%
On 65 mesh = 0%
On 100 mesh = 0%
On 150 mesh = 0.08%
On 200 mesh = 3.30%
On Pan = 96.62%

Chemical Analysis

% Ash = 0.066
% Moisture = 0.039

Emission Spectrographic Analysis (Semi-Quantitative)

Al = 7 ppm
Ti = 37 ppm
V = 23 ppm
Fe = 44 ppm
Ni < 5 ppm
Cr < 5 ppm
Si = 60 ppm
Ca = 162 ppm
Mg < 5 ppm
Pb < 5 ppm
Sn < 5 ppm
Ag < 5 ppm
B = 6 ppm
Na < 5 ppm
Cu < 5 ppm

2. ASO Natural Graphite

Helium Density = 2.26 g/cc

Surface Area = 3.0 m^2/g

Screen Analysis

On 35 mesh =	0%
On 65 mesh =	0%
On 100 mesh =	.04%
On 150 mesh =	1.37%
On 200 mesh =	11.29%
On Pan =	87.30%

Chemical Analysis

% Ash = 0.016
% Moisture = 0.007

Emission Spectrographic Analysis (Semi-Quantitative)

Al < 5 ppm
Ti = 12 ppm
V = 4 ppm
Fe = 32 ppm
Ni < 5 ppm
Cr < 5 ppm
Si = 12 ppm
Ca < 5 ppm
Mg < 5 ppm
Pb = 6 ppm
Sn < 5 ppm
Ag < 5 ppm
B = 9 ppm
Na = 7 ppm
Cu < 5 ppm

3. Thermax Carbon Black

Helium Density = 1.84 g/cc

Surface Area = 8.1 m^2/g

Screen Analysis*

On 35 mesh = 3.97%
On 65 mesh = 36.91%
On 100 mesh = 15.74%
On 150 mesh = 13.44%
On 200 mesh = 10.84%
On Pan = 19.10%

Chemical Analysis

% Ash = 0.022
% Moisture = 0.027

Emission Spectrographic Analysis (Semi-Quantitative)

Al < 5 ppm
Ti < 5 ppm
V < 5 ppm
Fe < 5 ppm
Ni < 5 ppm
Cr < 5 ppm
Si = 33 ppm
Ca = 11 ppm
Mg = 5 ppm
Pb = 5 ppm
Sn < 5 ppm
Ag < 5 ppm
B = 5 ppm
Na = 23 ppm
Cu < 5 ppm

---

* The presence of aggregates appears to have a significant effect on the results of the screen analysis.

4. Ground Glassy Carbon

Helium Density = 1.91 g/cc*

Surface Area = 5.6 m^2/g

Screen Analysis

On 35 mesh =	0%
On 65 mesh =	0%
On 100 mesh =	0.41%
On 150 mesh =	18.42%
On 200 mesh =	21.98%
On Pan =	59.19%

Chemical Analysis

% Ash = 0.92
% Moisture = 0.85

Emission Spectrographic Analysis (Qualitative)**

+ Major-	+ Minor-	+ Trace-
←Fe	Mn	Mg→
Cr	Sn→	Ag→
Ni	Si	
	Al	
	Ca	
	Cu	

---

* Sample drifted considerably and, therefore, the results are questionable.

** No standards available to run semi-quantitative analysis.

5. WCA Graphite Fibers

Helium Density = 1.43 g/cc*

Surface Area = 1.3 m^2/g

Chemical Analysis

% Ash = 0.04
% Moisture = 0.03

Emission Spectrographic Analysis Semi-Quantitative

Al < 5 ppm
Ti = 5 ppm
V < 5 ppm
Fe < 5 ppm
Ni < 5 ppm
Cr < 5 ppm
Si = 7 ppm
Ca < 5 ppm
Mg < 5 ppm
Pb < 5 ppm
Sn < 5 ppm
Ag < 5 ppm
B < 5 ppm
Na = 13 ppm
Cu < 5 ppm

---

* Sample drifted considerably; therefore, results are questionable.

6. Barrett No. 30 Medium Coal Tar Pitch

Helium Density = 1.33 g/cc

Coking Value = 57.4%

Benzene Insoluble = 32.1%

Quinoline Insoluble = 13.1%

Softening Point = 100.3°C

Elemental Chemical Analysis

C = 93.62%
H = 4.29%
O = 1.56%
N = 0.92%
S = 0.44%

Emission Spectrographic Analysis (Qualitative)*

+ Major-	+ Minor-	+ Trace-
	Fe	Mg
	Pb→	Mn
	Si	
	Al	Cu→
	Ca→	
	Ti→	
	Zn→	

Differential Thermal Analysis

Endotherm at 55°C.
Endotherm at 440°C.
Exothermic jump at 535°C. which is coincidental with 3% weight loss.
Exothermic rise maximum at 645°C.

Thermal Gravimetric Analysis

Essentially constant weight to 200°C.
Gradual loss between 200°C and 260°C.
-1% at 260°C.
Increasing rate of loss between 260°C and 335°C
Steady rate of loss from 335°C to 460°C and 605°C to 800°C with a slightly lower rate of loss between 460°C and 605°C.
-10% at 370°C.
Overall loss of 83% at cut off of 800°C

Volume Change After Baking**

$$\frac{\text{1000°C Baked Volume}}{\text{Green Volume}} = 0.871$$

$$\frac{\text{2800°C Graphitized Volume}}{\text{Green Volume}} = 0.843$$

---

* No standards available to run semi-quantitative analysis.

** Measured for compacts containing 80 pbw CHP graphite, 20 pbw Thermax, and 60 pph No. 30 Med. Pitch.

7. Bakelite BRP-5095 Phenol-formaldehyde Resin

Helium Density = 1.28 g/cc

Coking Value = 65.4%

Elemental Chemical Analysis

C = 75.86%
H = 6.13%
O = 16.80%
N = 2.44%
S = None

Emission Spectrographic Analysis (Qualitative)*

+ Major-	+Minor-	+Trace-	
	←Ca	←Fe	Cu
	Si→	Al	←Ni
	Mg	Cr→	
		Mn→	

Differential Thermal Analysis

Small exotherm at 165°C which is just at the beginning of 5% weight loss.
Very broad exothermic rise beginning at 540°C.

Thermal Gravimetric Analysis

Essentially constant weight to 160°C.
Gradual loss between 160°C and 265°C.
Plateau between 265°C and 370°C at approximately 5% loss.
-10% at 445°C.
Steady loss between 370°C and 540°C.
Increasing rate of loss to 600°C.
Steady loss rate to cut off at 750°C.
Overall loss of 88% at cut off of 750°C.

Volume Change After Baking**

$$\frac{\text{1000°C Baked Volume}}{\text{Green Volume}} = 0.704$$

$$\frac{\text{2800°C Graphitized Volume}}{\text{Green Volume}} = 0.649$$

---

* No standards available to run semi-quantitative analysis.

** Measured for compacts containing 80 pbw CHP graphite, 20 pbw Thermax, and 58 pph Bakelite BRP 5095 resin.

8. Varcum 8251 Furfuryl Alcohol Resin

Helium Density = 1.196 g/cc

Coking Value

Varcum 8251 = 20.6%
Varcum 8251 (96%) & ZZLA-0334 Bakelite Hardener (4%) = 22.2%
Varcum 8251 (98%) & Oxalic Acid (2%) = 35.1%
Varcum 8251 (96%) & Maleic Anhydride (4%) = 37.9%

Elemental Chemical Analysis

C = 66.09%
H = 5.87%
O = 28.00%*
N = 0.04%
S = None

Emission Spectrographic Analysis (Qualitative)**

+ Major-	+ Minor-	+ Trace-
	Ca→	Si
	Fe→	←Mg
	Sn→	Cu

Differential Thermal Analysis

Major exotherm @ 490°C peak temperature.
Initial "break temp" approximately 410°C to 440°C.

Thermal Gravimetric Analysis

Weight loss neglibible to 75°C.
-1% at 90°C.
Steady loss between 75°C and 200°C.
-10% at 145°C.
Plateau between 200°C and 375°C (-39% at 250°C).
Accelerating rate of loss between 375°C and 500°C.
Weight loss complete (100%) at 715°C.

Volume Change After Baking***

$$\frac{\text{1000°C Baked Volume}}{\text{Green Volume}} = 0.944$$

$$\frac{\text{2800°C Graphitized Volume}}{\text{Green Volume}} = 0.869$$

---

* Oxygen determined by difference.
** No standards available to run semi-quantitative analysis.
***Measured for compacts containing 80 pbw CHP, 20 pbw Thermax, and 54 pph Varcum 8251 resin containing 2% by weight Oxalic Acid.

9. Ryton Polyphenylene Sulfide Resin

Helium Density = 1.39 g/cc

Coking Value = 58.5%

Elemental Chemical Analysis

C = 65.95%
H = 3.91%
O = 1.39%
N = 0.18%
S = 28.31%

Emission Spectrographic Analysis (Qualitative)*

+ Major-		+ Minor-		+ Trace-
	Al→	Na	Ca	←Mn
			←Fe	
			Si	
			Mg	
			Cu→	
			Ni	
			Cr	

Differential Thermal Analysis

Endotherm at 305°C.
Exothermic rise at 505°C coincident with beginning of weight loss.
Exothermic rise at 615°C.

Thermal Gravimetric Analysis

-1% at 295°C.
Lost only 1.2% weight at 400°C.
Rapid loss from 505°C to 580°C (28% loss).
-10% at 525°C.
Plateau at 580° to 615°C (-33% at 600°C).
Rapid loss in weight between 615° and 750°C.
Overall loss of 90% at cut off of 750°C.

Volume Change After Baking**

$$\frac{\text{1000°C Baked Volume}}{\text{Green Volume}} = 1.005$$

$$\frac{\text{2800°C Graphitized Volume}}{\text{Green Volume}} = 0.927$$

---

* No standards available to run semi-quantitative analysis.

** Measured for compacts containing 80 pbw CHP, 20 pbw Thermax, and 48 pph Ryton polyphenylene sulfide resin.

B. Particle Packing Theory (Lewis and Goldman Method)

Lewis and Goldman(87) of the Los Alamos Scientific Laboratory have prepared a detailed report covering theoretical small-particle statistics. The report discusses the measurement of particle size distributions based on the use of techniques such as microscopic count, screen analysis, micromerograph analysis, and Coulter counter. Included in the report is a discussion of the methods used to compare the different types of particle size data measured by the various techniques. For example, the particle size data generated by a screen analysis are measured on a weight basis and must be converted to a frequency basis for comparison with that measured by a microscopic count. A portion of the report pertains to the development of a general mixture theory. The mixture theory describes the method for producing mixes of increased packing density by properly proportioning two or more particulate materials for which the particle size distributions have been measured.

The particle size distributions of the four approved particulate raw materials were measured by using the MSA Sedimentation Particle Size Analysis. Table III displays the particle size distributions measured for CHP artificial graphite, ASO natural graphite, Thermax carbon black, and ground glassy carbon. Like the micromerograph analysis, the MSA method is based on the use of Stokes Law. However, the MSA method uses a number of different centrifuges running at different speeds to settle the material which is suspended in a liquid. Since the MSA technique yields nearly 100 percent recovery of the sample, sample statistics derived from the data should be more meaningful than those derived from micromerograph data from which a sample recovery of approximately 50 percent is considered typical. Table IV presents the sample statistics calculated from the MSA results displayed in Table III. An explanation of the sample statistics is presented in Appendix II.

TABLE III. MSA - SEDIMENTATION PARTICLE SIZE ANALYSIS

Particle Size (Microns)	CHP Graphite (%bw > size)	ASO Graphite (%bw > size)	Thermax (%bw > size)	Ground Glassy Carbon (%bw > size)
100.0	0.0	0.0	0.0	11.0
80.0	0.0	0.0	0.0	32.0
60.0	8.0	1.0	0.0	59.0
50.0	15.0	3.0	0.0	72.0
40.0	22.0	6.5	0.0	83.0
35.0	31.0	12.2	0.0	86.0
30.0	40.0	17.8	0.0	89.0
25.0	49.0	25.2	0.0	91.0
20.0	56.0	35.0	0.0	94.0
18.0	61.0	43.0	0.0	95.0
16.0	66.0	52.0	0.0	96.0
14.0	67.0	59.0	0.0	96.0
12.0	70.0	68.0	0.0	97.0
10.0	73.0	74.0	0.0	98.0
8.0	79.0	80.0	0.0	98.0
6.0	86.0	87.0	0.0	99.0
5.0	92.0	95.5	2.3	99.0
4.0	95.0	98.5	4.1	100.0
3.0	97.0	98.5	6.5	100.0
2.0	100.0	99.5	12.0	100.0
1.0	100.0	100.0	52.0	100.0
0.8	100.0	100.0	60.0	100.0
0.7	100.0	100.0	69.0	100.0
0.6	100.0	100.0	76.0	100.0
0.5	100.0	100.0	87.0	100.0
0.3	100.0	100.0	97.0	100.0
0.2	100.0	100.0	100.0	100.0

Note: %bw - Percent by weight.

TABLE IV. MSA - SAMPLE STATISTICS

Sample MSA Statistics	CHP Graphite	ASO Graphite	Thermax	Ground Glassy Carbon
$\hat{\mu}_{x3}$	3.000	2.800	0.000	4.110
$\hat{\sigma}^2_x$	0.774	0.407	0.446	0.185
$\hat{\mu}_x$	0.678	1.579	-1.338	3.555
$\bar{d}_3$	29.6μ	20.3μ	1.25μ	66.5μ
$S^2_{d_3}$	1020.0μ^2	210.0μ^2	0.878μ^2	900.0μ^2
$\bar{d}$	2.90μ	5.95μ	0.317μ	3.85μ
S^2_d	9.89μ^2	17.6μ^2	0.068μ^2	297.7μ^2
CV_d	1.085	0.706	0.823	0.449

Limitations placed on the size distributions of the components and resultant mixture to which the mixture theory is most applicable require that the following equation be satisfied:

$$\left| \hat{\mu}_{x(1)} - \hat{\mu}_{x(2)} \right| < 2.5 \; \hat{\sigma}^2_{x(2)}$$

where $\hat{\sigma}^2_{x(2)}$ is the value of the smaller variance.

If the equation is not satisfied, the mixture tends to be bimodal, and the suitability of this method becomes questionable. An attempt was made to use the Lewis and Goldman general mixture theory to determine the optimum proportion of Thermax in three binary mixtures which contain CHP graphite, ASO graphite, and ground glassy carbon as the second filler component, respectively. For each of the three binary mixes, incorporation of the MSA sample statistics in the above equation produced an absolute value of the difference between the means that was greater than 2-1/2 times the value of the smaller variance. For this reason, the Lewis and Goldman method was not used to compute the proportions for these three binary mixtures.

C. Estimation of Optimum Binder Levels

The optimum binder levels for the filler materials listed in Table II were estimated by using the "stearic acid" technique discussed in the Los Alamos Scientific Laboratory Report No. 3, LA-3821(88) and are displayed in Table V. This technique consists of blending stearic acid with the desired filler materials and molding the blend at a temperature above the melting point of the stearic acid. The die used has a loose-fitting plunger which allows the excess stearic acid to be forced out. While under pressure, the die is cooled to a temperature at which the stearic acid solidifies. The ejected compact is then weighed, heated in an inert atmosphere to evaporate the stearic acid, and reweighed. Knowing the weight loss and the density of the stearic acid allows one to calculate the volume of the compact occupied by the stearic acid. Multiplying the occupied volume by the density of the binder material to be used produces the weight of binder required per unit weight of filler.

TABLE V. - ESTIMATED OPTIMUM BINDER LEVEL

CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)

Binder	Estimated Optimum Binder Level (pph)
No. 30 Medium Pitch	30
Varcum 8251 Resin	27
Bakelite BRP5095 Resin	29
Ryton Polyphenylene Sulfide Resin	32

ASO Natural Graphite (80 pbw) & Thermax (20 pbw)

Binder	Estimated Optimum Binder Level (pph)
No. 30 Medium Pitch	27
Varcum 8251 Resin	24
Bakelite BRP5095 Resin	26
Ryton Polyphenylene Sulfide Resin	28

CHP Artificial Graphite (80 pbw) & WCA Graphite Fibers (20 pbw)

Binder	Estimated Optimum Binder Level (pph)
No. 30 Medium Pitch	47
Varcum 8251 Resin	42
Bakelite BRP5095 Resin	45
Ryton Polyphenylene Sulfide Resin	49

Ground Glassy Carbon (80 pbw) & Thermax (20 pbw)

Binder	Estimated Optimum Binder Level (pph)
No. 30 Medium Pitch	54
Varcum 8251 Resin	49
Bakelite BRP5095 Resin	52
Ryton Polyphenylene Sulfide Resin	57

Note: pbw - Parts by weight

pph - Parts (wt.) binder per hundred parts (wt.) filler

In order to permit a direct comparison with the material systems containing no additives, it was decided that no adjustments of binder levels would be made for the materials containing additives. All additives were to be used in relatively low concentrations. Thus, the additives were ignored in the estimation of the optimum binder levels.

Compacts of material systems Nos. 1, 2, 3, and 5 (Table II) were prepared by using the estimated binder levels. All materials (except No. 2, which contained Varcum 8251 resin) were processed through the 1000°C bake according to the procedures listed in Section V-D of this report (Material Processing). It was originally planned to use maleic anhydride to polymerize the Varcum 8251 resin. However, maleic anhydride can be a strong body irritant, and the maleic anhydride vapors which come in contact with the eyes can cause photophobia and double vision. A survey of less toxic polymerization catalysts was conducted and oxalic acid was found to be a good material for polymerizing Varcum 8251 resin. The furfuryl alcohol bonded material presently being discussed was produced by adding four percent by weight of the oxalic acid to the resin. Later experimental work showed that up to two percent oxalic acid would completely dissolve in the Varcum 8251 resin. The furfuryl alcohol bonded material was heated at 75°C for one hour prior to molding to partially polymerize the resin. This procedure was used to improve the strength of the green plug. Room temperature molded compacts were prepared for all four material systems by using molding pressures that were increased in 5000 psi increments between 10,000 psi and 35,000 psi.

So that the effectiveness of the binder might be determined, a cursory investigation of the 1000°C baked compacts molded for the four material systems was conducted. The bulk densities of the baked compacts were measured, and the molded plugs were cut open to examine their internal structures. The pieces containing ASO natural graphite which were molded at pressures of 30,000 psi and 35,000 psi were found to be laminated. Laminations occur when the internal structure of a molded compact is so tightly packed that the binder volatiles cannot escape during baking. The highest density unlaminated compacts molded from each of the four materials were selected, and their flexural strengths and hardness were measured. Table VI presents the results of the examination.

TABLE VI. - RESULTS OF PRELIMINARY PHYSICAL PROPERTY MEASUREMENTS

Material	Molding Pressure (psi)	Green Density (gr./cc)	1000°C Baked Density (gr./cc)	Rockwell Hardness R_r	Rockwell Hardness R_s	Flexural Strength psi	Flexural Strength (N/cm)
CHP Artificial Graphite (80 pbw) & Thermax (20 pbw) No. 30 Medium Pitch (30 pph)	30,000	1.744	1.408	9-8-9	----	540	370
	30,000	1.746	1.418	15-16-15	----	510	350
	35,000	1.765	1.416	17-16-14	----	540	370
	35,000	1.759	1.471	17-16-14	----	860	590
ASO Natural Graphite (80 pbw) & Thermax (20 pbw) No. 30 Medium Pitch (27 pph)	25,000	1.834	1.696	74-74-74	34-33-34	1670	1150
	25,000	1.828	1.676	68-70-70	31-31-31	1750	1210
CHP Artificial Graphite (80 pbw) & Thermax (20 pbw) Bakelite BRP5095 Resin (29 pph)	30,000	1.627	1.466	75-76-76	39-40-41	1660	1150
	30,000	1.629	1.469	78-74-76	41-42-40	1660	1150
	35,000	1.650	1.456	78-76-78	43-42-43	1890	1300
	35,000	1.649	1.475	78-78-78	43-44-42	1870	1290
CHP Artificial Graphite (80 pbw) & Thermax (20 pbw) Varcum 8251 Resin (27 pph)	30,000	1.578	1.430	13-13-13	----	310	210
	35,000	1.613	1.467	35-34-34	----	270	190

Note: R_r = 1/2" Dia. ball and 60 Kg load

R_s = 1/2" Dia. ball and 100 Kg load

Flexural strength obtained with grain

All four of the materials were too weak and too soft to be used as seal ring materials. However, the preliminary results did reflect the relative effectiveness of the three binders used.

It was initially felt that the use of the "stearic-acid" technique for estimating optimum binder levels would be a good approach for developing the carbon-graphite seal ring materials. However, the binder levels estimated by the "stearic-acid" technique were too low. The inadequacy may be due to the fact that the lubricating properties, surface tension, and viscosity of the binders are different from those of the stearic acid. Traditionally, optimum binder levels have been determined by systematically changing the binder level of the carbon-graphite material. Recent work reported by Froberg(89) has confirmed the fact that the physical properties of a carbon-graphite material can be improved by increasing the binder level and slowing the baking schedule. It was decided to attempt to improve the physical properties listed in Table VI by systematically increasing the binder levels and varying the baking schedules. Warm molding also was to be investigated as a possible method for improving physical properties.

D. Materials Subsystem Study

A material subsystem study was conducted to optimize each of the 12 approved material systems presented in Table II. Forty-one subsystems, which were variations of the approved nonadditive material systems, were initially produced to study the effects of increased binder level, slower baking schedule, and warm molding of the physical properties of the graphitized compacts. Material systems containing additives were not included in the subsystems study, since they are simply counterparts of the nonadditive material systems. A numbering system containing the prefix "SS" was used to identify the material subsystems.

The compositions of the 41 subsystems are displayed in Table VII. Subsystem SS-6 had two versions identified as A and B. The high binder level of SS-18 required that those compacts be molded at 60°C.

TABLE VII - MATERIAL SUBSYSTEM IDENTIFICATION

Material Subsystem	Filler Material	Binder Material	Binder Level	Molding Pressures (psi)	Molding Temp.	1000°C Bake Rate
SS-1	80 pbw CHP-20 pbw Thermax	Polyphenylene Sulfide	32 pph*	10,000 to 35,000	R.T.	10°C/Hr.
SS-2	"	"	"	"	"	5°C/Hr.
SS-3	"	"	"	"	700°F	"
SS-4	80 pbw CHP-20 pbw Thermax	No. 30 Med. Pitch	30 pph*	20,000 to 35,000	R.T.	10°C/Hr.
SS-5	"	"	"	"	"	5°C/Hr.
SS-6A	"	"	"	"	125°C	"
SS-6B	"	"	"	"	60°C	"
SS-7	80 pbw CHP-20 pbw Thermax	No. 30 Med. Pitch	35 pph	20,000 to 35,000	R.T.	10°C/Hr.
SS-8	"	"	"	"	"	5°C/Hr.
SS-9	"	"	"	"	125°C	"
SS-10	80 pbw CHP-20 pbw Thermax	No. 30 Med. Pitch	40 pph	20,000 to 35,000	R.T.	10°C/Hr.
SS-11	"	"	"	"	"	5°C/Hr.
SS-12	"	"	"	"	125°C	"
SS-13	80 pbw CHP-20 pbw Thermax	No. 30 Med. Pitch	45 pph	15,000 to 35,000	R.T.	10°C/Hr.
SS-14	"	"	"	"	"	5°C/Hr.
SS-15	"	"	"	"	125°C	"
SS-16	80 pbw CHP-20 pbw Thermax	No. 30 Med. Pitch	60 pph	10,000 to 35,000	R.T.	10°C/Hr.
SS-17	"	"	"	"	"	5°C/Hr.
SS-18	"	"	"	"	60°C	"
SS-19	80 pbw CHP-20 pbw Thermax	Bakelite BRP-5095	29 pph*	20,000 to 35,000	R.T.	10°C/Hr.
SS-20	"	"	"	"	"	5°C/Hr.
SS-21	"	"	"	"	80°C	"
SS-22	80 pbw CHP-20 pbw Thermax	Bakelite BRP-5095	43.5 pph*	15,000 to 35,000	R.T.	10°C/Hr.
SS-23	"	"	"	"	"	5°C/Hr.
SS-24	"	"	"	"	80°C	"
SS-25	80 pbw CHP-20 pbw Thermax	Bakelite BRP-5095	58 pph	10,000 to 35,000	R.T.	10°C/Hr.
SS-26	"	"	"	"	"	5°C/Hr.
SS-27	"	"	"	"	80°C	"
SS-28	80 pbw ASO-20 pbw Thermax	No. 30 Med. Pitch	27 pph*	10,000 to 25,000	R.T.	5°C/Hr.
SS-29	"	"	"	"	125°C	"
SS-30	80 pbw ASO-20 pbw Thermax	No. 30 Med. Pitch	40.5 pph	10,000 to 25,000	R.T.	5°C/Hr.
SS-31	"	"	"	"	125°C	"
SS-32	80 pbw ASO-20 pbw Thermax	No. 30 Med. Pitch	54 pph	10,000 to 25,000	R.T.	5°C/Hr.
SS-33	"	"	"	"	125°C	"
SS-34	80 pbw CHP-20 pbw Thermax	Polyphenylene Sulfide	48 pph	15,000 to 35,000	R.T.	5°C/Hr.
SS-35	"	"	64 pph	10,000 to 15,000	"	"
SS-36	80 pbw CHP-20 pbw WCA fibers	Bakelite BRP-5095	45 pph*	20,000 to 35,000	R.T.	10°C/Hr.
SS-37	"	"	67.5 pph	10,000 to 25,000	"	"
SS-38	80 pbw Glassy Carbon-20 pbw Thermax	Bakelite BRP-5095	52 pph*	10,000 to 35,000	R.T.	10°C/Hr.
SS-39	80 pbw CHP-20 pbw Thermax	Varcum 8251 - 2% Oxalic Acid	40.5 pph	20,000 to 35,000	"	"
SS-40		"	54 pph	10,000 to 25,000	"	"

Note: pbw - Parts by weight

pph - Parts (weight) binder per hundred parts (weight) filler

* Determined by "stearic acid" technique

It was impossible to successfully eject the plugs from the die when they were molded at higher temperatures. The SS-6B version was designed to be comparable with SS 18. Except for SS-18, the selection of molding temperatures was based on the literature search of material processing. The binder levels of corresponding subsystems usually were 1.0, 1.5, or 2.0 times those determined by the "stearic acid" technique. Molding pressures were increased in 5000 psi increments between the limits presented in Table VII. All of the subsystem compacts were baked to a final temperature of 2800°C after they had been baked from room temperature to 1000°C according to the baking rate presented for each subsystem in Table VII.

Bakelite BRP-5095 resin bonded subsystems SS-36, 37, and 38 are variations of approved material systems Nos. 11 and 12, although the two material systems as listed in Table II show Varcum 8251 resin as the binder. This change was proposed because the BRP 5095 resin consistently produced the strongest compacts during the initial segment of the screening studies. The characterization data (Section VI A, 7-8) also show that the coking value of the Bakelite BRP-5095 resin is far superior to that of the Varcum 8251 resin. The NASA Project Manager gave his approval of the binder substitution. Material system No. 8 (Table II) was also approved for the binder substitution.

After the samples were baked to 2800°C, the highest density unlaminated plug was selected from each of the 41 material subsystems, and some of its physical properties were measured. Table VIII shows the green, 1000°C baked, and "graphitized" bulk densities; the Rockwell hardness; and the flexural strengths of the selected compacts. The table also presents the highest molding pressure for each material subsystem from which unlaminated plugs were obtained.

TABLE VIII. - MATERIAL SUBSYSTEM PROPERTY EVALUATION

Material Subsystem	Optimum Molding Pressure (psi)	Green Density (g/cc)	1000°C Density (g/cc)	2800°C Density (g/cc)	Rockwell Hardness		Flexural Strength	
					R_r	R_s	(psi)	(N/cm^2)
SS-1	35,000	1.635	1.293	1.397	Too soft	---	430	300
SS-2	30,000	1.624	1.402	1.476	37 - 57	---	1,030	710
SS-3	Pieces all had deep surface cracks							
SS-4	35,000	1.770	1.429	1.451	Too soft	---	340	230
SS-5	35,000	1.773	1.507	1.536	11 - 9	---	460	320
SS-6A	30,000	1.784	1.645	1.666	61 - 60	---	1,210	830
SS-6B	25,000	1.753	1.504	1.525	Too soft	---	500	340
SS-7	25,000	1.735	1.406	1.428	Too soft	---	630	430
SS-8	30,000	1.740	1.486	1.510	23 - 25	---	1,070	740
SS-9	25,000	1.752	1.638	1.688	84 - 81	56 - 55	2,270	1,560
SS-10	30,000	1.719	1.431	1.462	14 - 11	---	930	640
SS-13	30,000	1.732	1.534	1.570	60 - 59	---	1,250	860
SS-12	30,000	1.729	1.680	1.676	91 - 91	67 - 67	2,670	1,840
SS-13	35,000	1.722	1.484	1.513	39 - 37	---	1,190	820
SS-14	35,000	1.710	1.561	1.613	64 - 61	---	1,700	1,170
SS-15	Pieces were all laminated							
SS-16	15,000	1.642	1.618	1.649	85 - 87	61 - 60	2,460	1,690
SS-17	10,000	1.616	1.634	1.665	90 - 92	64 - 67	2,650	1,830
SS-18	Pieces were all laminated						(For SS-17)	
SS-19	35,000	1.670	1.464	1.532	47 - 44	---	1,030	710
SS-20	30,000	1.662	1.494	1.575	66 - 60	---	1,340	920
SS-21	35,000	1.672	1.645	1.713	83 - 81	56 - 57	2,650	1,830
SS-22	30,000	1.574	1.590	1.685	89 - 90	62 - 66	2,610	1,800
SS-23*	20,000	1.556	1.619	1.722	96 - 93	74 - 75	2,850	1,960
SS-24	Pieces were badly deformed							
SS-25	15,000	1.461	1.584	1.706	94 - 92	73 - 74	4,290	2,960
SS-26	Pieces were deformed							
SS-27	Pieces were badly deformed							
SS-28	20,000	1.826	1.712	1.723	26 - 29	---	1,660	1,140
SS-29	20,000	1.816	1.727	1.731	28 - 30	---	1,680	1,160
SS-30	Pieces were all laminated							
SS-31	Pieces were all laminated							
SS-32	Pieces were all laminated							
SS-33	Pieces were all laminated							
SS-34	35,000	1.614	1.327	1.420	31 - 35	---	1,460	1,010
SS-35	Pieces were all laminated							
SS-36*	30,000	1.523	1.352	1.391	57 - 61	---	3,710	2,560
SS-37*	15,000	1.413	1.350	1.432	70 - 72	36 - 40	3,940	2,710
SS-38**	15,000	1.212	0.926	1.032	13 - 15	---	1,910	1,320
SS-39	Pieces all crumbled after graphitization							
SS-40*	15,000	1.476	1.257	1.356	29 - 35	---	1,300	900

---

*Plugs slightly deformed after baking to 1000°C.

**Plugs badly deformed and a coating of packing coke was strongly adhering to plugs after baking to 1000°C. Plugs were ground prior to density measurements.

Flexural strengths measured on a sample of .200" x .200" cross-sectional area using a 0.950" span.

R_r Scale = 1/2" diameter ball and 60 Kg maj. load.
R_s Scale = 1/2" diameter ball and 100 Kg maj. load.

Increasing binder level, using a slower baking schedule, and using a warm molding technique all helped to increase the strengths of the pitch-bonded compacts containing CHP artificial graphite and Thermax (SS-4 to SS-18). Figure 3 is a plot of flexural strength versus binder level for the unlaminated plugs with the highest baked density. The highest flexural strength (SS-12 and SS-17) can be obtained by two pressing techniques. The SS-12 compact was warm molded at 125°C and 30,000 psi. The SS-17 compact was molded at room temperature but had a much higher binder level. The latter system was selected as a superior system because it is easier to process and the high binder level should prevent binder deficiency in the modification of the system that contains the additive.

Because of time limitations, the pitch-bonded compacts of the subsystems SS-28 to SS-33 containing ASO natural graphite and Thermax were all baked to 1000°C on the slower baking schedule. Those subsystems apparently represented the one approved material system for which the "stearic acid" technique did predict the optimum binder level. Subsystem SS-28 was selected as an optimized material system, since the warm-molding employed to form the SS-29 compact produced no significant increase in strength.

Bakelite BRP-5095 resin appears to be an excellent binder for carbon-graphite seal ring materials. The BRP-5095 resin bonded compacts of SS-25 and SS-37 had the highest flexural strengths measured during the subsystem study. The flexural strength of the SS-25 compact was greater than 1.5 times that of the comparable SS-17 compact which was bonded with coal tar pitch. The shrinkage of the SS-25 compact was significantly greater than that of the SS-37 material. Apparently, the presence of the fibers inhibited shrinkage of the binder phase. Bakelite BRP-5095 resin-bonded compacts had a tendency to deform while being baked to 1000°C, especially at the higher binder levels when baked at 5°C per hour. The SS-25 and SS-37 versions were selected as optimized material systems because of their high strength values.

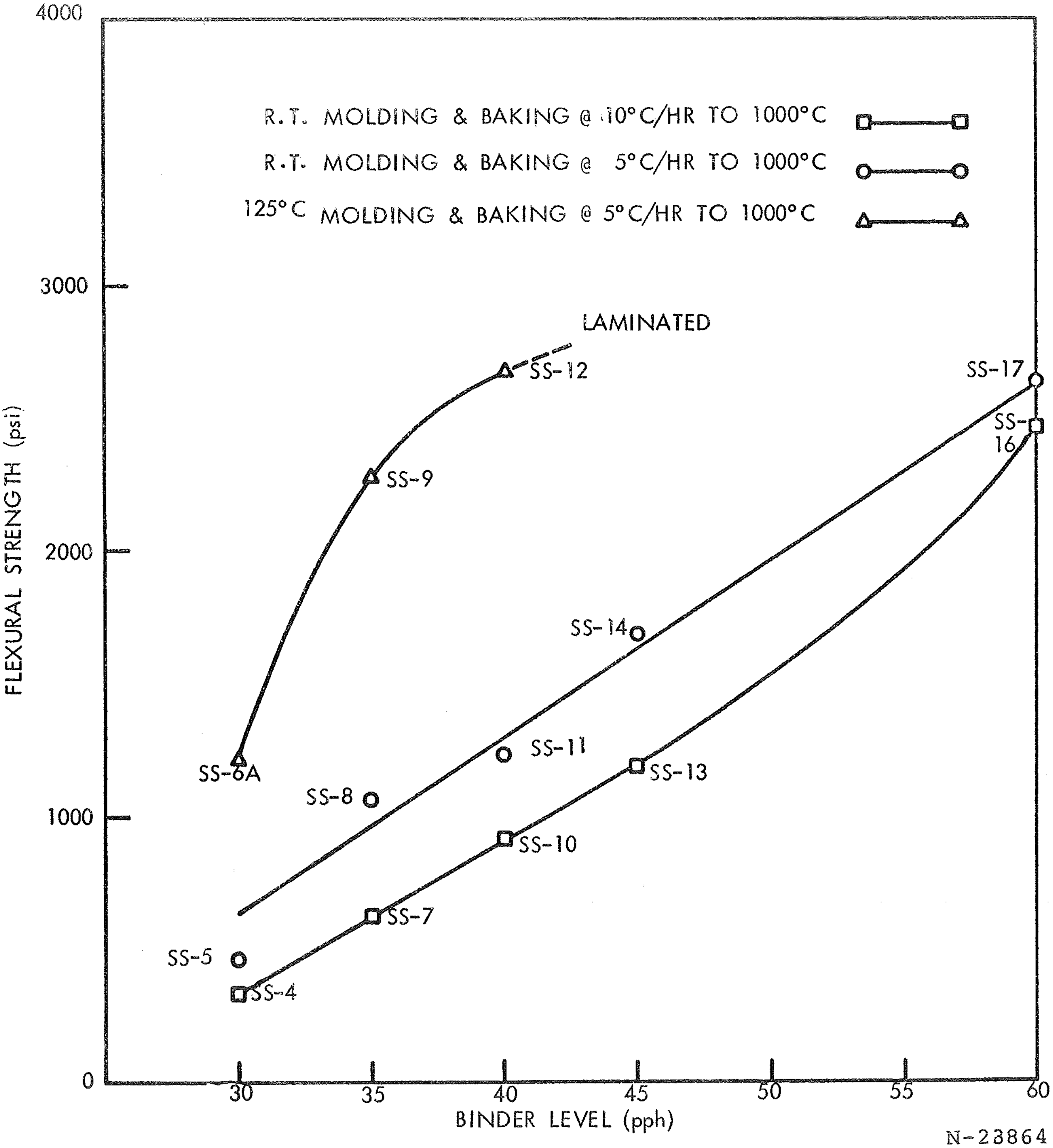


Figure 3. Effects of Variables on Flexural Strength.

The SS-38 compact was also bonded with Bakelite BRP-5095 resin, but glassy carbon was used instead of graphite as the main filler component. The internal structure of the SS-38 compact was much more porous than the plugs of any of the other subsystems, a condition which causes its low density and flexural strength. After the SS-38 compacts were baked at 1000°C, they were badly deformed and had a coating of packing coke strongly adhering to them. The plugs had to be ground before density measurements could be made. The SS-38 version was selected as an optimized material, since it was the only material of its type produced during the subsystem evaluation.

The physical properties of the compacts prepared with Ryton polyphenylene sulfide resin and Varcum 8251 furfuryl alcohol resin as the binder materials were very poor. None of the variations investigated during the subsystem studies greatly enhanced the strength and hardness of compacts prepared with those binders. The SS-39 and SS-40 Varcum 8251 resin-bonded compacts were molded at room temperature from mixes which had been heated at 100°C for 16 hours prior to crushing and milling. Ryton resin-bonded SS-34 and Varcum 8251 resin-bonded SS-40 were selected as optimized material systems.

A numbering system containing the prefix "MS" was used to identify the optimized material systems. Table IX lists the original identifications of the 12 optimized material systems and gives the proportions of filler and binder materials, the molding temperature and pressure, and the room temperature-to-1000°C baking schedule to be used for producing each of the material systems. To determine to some extent the reproducibility and spread of the physical properties, the decision was made to produce and analyze several compacts of each of the 12 optimized material systems.

TABLE IX. - ORIGINAL IDENTIFICATION OF OPTIMIZED MATERIAL SYSTEMS

Optimized Material System	Subsystem Derived From	Particulate Solid Raw Materials	Binder Raw Material	Additive	Molding Temp.	Molding Pressure	1000°C Bake Rate
MS-1	SS-17	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	No. 30 Med. Pitch (60 pph)	---	R.T.	10,000 psi	5°C/Hr.
MS-2	SS-17	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	No. 30 Med. Pitch (60 pph)	Boron Carbide (1 pbw)	R.T.	10,000 psi	5°C/Hr.
MS-3	SS-17	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	No. 30 Med. Pitch (60 pph)	Boron Carbide (7.5 pbw)	R.T.	10,000 psi	5°C/Hr.
MS-4	SS-17	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	No. 30 Med. Pitch (60 pph)	Glassy Carbon (2 pbw)	R.T.	10,000 psi	5°C/Hr.
MS-5	SS-17	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	No. 30 Med. Pitch (60 pph)	Glassy Carbon (10 pbw)	R.T.	10,000 psi	5°C/Hr.
MS-6	SS-28	ASO Natural Graphite (80 pbw) & Thermax (20 pbw)	No. 30 Med. Pitch (27 pph)	---	R.T.	20,000 psi	5°C/Hr.
MS-7	SS-25	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	Bakelite BRP-5095 (58 pph)	---	R.T.	15,000 psi	10°C/Hr.
MS-8	SS-25	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	Bakelite BRP-5095 (58 pph)	Glassy Carbon (10 pbw)	R.T.	15,000 psi	10°C/Hr.
MS-9	SS-37	CHP Artificial Graphite (80 pbw) & WCA Graphite Fibers (20 pbw)	Bakelite BRP-5095 (67.5 pph)	---	R.T.	15,000 psi	10°C/Hr.
MS-10	SS-38	Glassy Carbon (80 pbw) & Thermax (20 pbw)	Bakelite BRP-5095 (52 pph)	---	R.T.	15,000 psi	10°C/Hr.
MS-11	SS-34	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	Polyphenylene Sulfide (48 pph)	---	R.T.	35,000 psi	5°C/Hr.
MS-12	SS-40	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	Varcum 8251 (54 pph)	---	R.T.	15,000 psi	10°C/Hr.

Note: Final baking temperature is 2800°C for all materials: Room temperature to 900°C @ 400°C/Hr., 900°C to 1600°C @ 200°C/Hr., 1600°C to 2800°C @ 300°C/Hr., hold 1 hour @ 2800°C.

Several samples were prepared for each of the material systems MS-1 to MS-6. The molded plugs were packed with coke in a sagger and baked from room temperature to 1000°C at 5°C per hour. Apparently, oxygen got into the pack during baking, causing the MS-1 to MS-6 pitch-bonded compacts to discolor and crack. The literature search on material processing had revealed that charcoal or coke can be used to protect carbons from oxidation during baking.(90) A second series of compacts was molded. The plugs were tightly packed with coke in a sagger, and a layer of charcoal was placed at the top of the pack. The same firing schedule was used. All but two of the 1000°C baked MS-1 to MS-6 samples were in satisfactory condition. Two of the five MS-5 compacts were laminated, but that problem could be corrected by molding at a slightly lower green density.

Plugs for material systems MS-7 and MS-8 were molded, packed with coke in a sagger, and baked from room temperature to 1000°C at 10°C per hour. Examination of the baked compacts showed that they had sagged during baking and that their internal structures were disrupted, apparently due to an outgassing problem. The MS-7 and MS-8 samples were not laminated, but they were extremely porous inside.

The sagging problem and the porous internal structure of the MS-7 and MS-8 compacts very likely can be attributed to the fact that Bakelite BRP-5095 is a two-stage resin. The sagging and outgassing problems probably occurred between the time the thermoplastic novolac of the first stage softened and the time when the hexamethylene-tetramine hardening agent reacted with the novolac. The Differential Thermal Analysis of the Bakelite BRP-5095 resin showed a small exotherm at 165°C which is probably related to the hexamethylene-tetramine reacting with the novolac. Two possible ways to remedy the problems would be to use the fastest possible heating rate through the portion of the baking cycle (R. T. to 150°C) during which the resin is soft and/or to partially polymerize the mix before molding. Compacts were prepared for the six material subsystems listed in Table X in an attempt to find a solution to the sagging and outgassing problems.

TABLE X. - IDENTIFICATION OF MATERIAL SUBSYSTEMS SS-41 TO SS-46

Material Subsystems	Mix	Molding Procedure
SS-41	MS-7	Same procedure as before (Table IX)
SS-42	MS-7	Mix heated 2 hours at 110°C before molding plugs
SS-43	MS-7	Plugs molded and placed in 110°C oven for 2 hours
SS-44	MS-7	Plugs molded and placed in 150°C oven for 2 hours
SS-45	MS-8	Same procedure as before (Table IX)
SS-46	MS-8	Mix heated 2 hours at 110°C before molding plugs

All the plugs were room temperature molded at a pressure of 15,000 psi.

Baking Schedule

Rush to 150°C, 150°C to 1000°C at 10°C per hour, hold at 1000°C for 4 hours.

The physical properties of the graphitized plugs of subsystems SS-41 to SS-46 are displayed in Table XI. None of the compacts experienced any sagging or outgassing problems. The properties for material subsystem SS-25 have been included in Table XI, since it was the material initially assigned the MS-7 designation. The physical properties of material subsystem SS-41, which was the same as SS-25 except for the fast baking schedule between room temperature and 150°C, were consistent with those of SS-25. Data obtained for material subsystems SS-42, SS-43, and SS-44 indicate that partial polymerization of the MS-7 mix before molding, or curing of the plugs in air before baking, degraded the physical properties of the graphitized compacts. The results obtained with subsystems SS 45 and SS-46 showed that the material system having the glassy carbon additive (10 pbw) requires reductions in molding pressure and/or partial polymerization of the mix before molding to avoid lamination of the finished compacts. Optimized material system designations MS-7 and MS-8 were re-assigned to subsystems SS-41 and SS-46, respectively.

Based on the results of the work with material subsystems SS-1 to SS-46, the optimization for the 12 approved material systems was completed. Table XII presents the identification of the revised optimized material systems. The table displays the composition of the materials, the molding procedure for the plugs, and the 1000°C baking schedule. Unless otherwise stated, the 1000°C bake rate is to be used between room temperature and 1000°C. The charcoal packing procedure is used for all systems. The same firing schedule between 1000°C and 2800°C is used for all 12 materials.

TABLE XI. - PROPERTY EVALUATION OF MATERIAL SUBSYSTEMS SS-41 TO SS-46

Material Subsystem	Molding Pressure (psi)	Green Density (g/cc)	1000°C Density (g/cc)	2800°C Density (g/cc)	Rockwell Hardness		Flexural Strength	
					R_r	R_s	(psi)	(N/cm^2)
*SS-25	15,000	1.461	1.584	1.706	94-92	73-74	4290	2960
*SS-41	15,000	1.446	1.558	1.669	90-92	68-69	4120	2840
*SS-42	15,000	1.445	1.501	1.623	76-80	51-52	2510	1730
*SS-43	15,000	1.452	1.522	1.650	83-84	58-62	3410	2350
*SS-44	15,000	1.453	1.519	1.646	89-92	61-62	3610	2490
**SS-45	15,000	Pieces were all laminated						
**SS-46	15,000	1.402	1.456	1.578	78-79	45-48	2750	1890

Note: * Contains (MS-7) mix which is composed of CHP artificial graphite (80 pbw), Thermax (20 pbw), + Bakelite BRP-5095 resin (58 pph).

** Contains (MS-8) mix which is composed of CHP artificial graphite (80 pbw), Thermax (20 pbw), Glassy Carbon (10 pbw), Bakelite BRP-5095 resin (58 pph).

Flexural strengths measured on a sample of .200" x .200" cross-sectional area using a 0.950" span.

R_r Scale = 1/2" diameter ball and 60 Kg maj. load.

R_s Scale = 1/2" diameter ball and 100 Kg maj. load.

TABLE XII. - REVISED DESCRIPTION OF OPTIMIZED MATERIAL SYSTEMS

Optimized Material System	Particulate Solid Raw Materials	Binder Raw Material	Additive	Molding Temp.	Molding Pressure	1000°C Bake Rate
MS-1	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	No. 30 Med. Pitch (60 pph)	---	R.T.	10,000 psi	5°C/Hr.
MS-2	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	No. 30 Med. Pitch (60 pph)	Boron Carbide (1 pbw)	R.T.	10,000 psi	5°C/Hr.
MS-3	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	No. 30 Med. Pitch (60 pph)	Boron Carbide (7.5 pbw)	R.T.	10,000 psi	5°C/Hr.
MS-4	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	No. 30 Med. Pitch (60 pph)	Glassy Carbon (2 pbw)	R.T.	10,000 psi	5°C/Hr.
MS-5	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	No. 30 Med. Pitch (60 pph)	Glassy Carbon (10 pbw)	R.T.	10,000 psi	5°C/Hr.
MS-6	ASO Natural Graphite (80 pbw) & Thermax (20 pbw)	No. 30 Med. Pitch (27 pph)	---	R.T.	20,000 psi	5°C/Hr.
MS-7	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	Bakelite BRP-5095 (58 pph)	---	R.T.	15,000 psi	*10°C/Hr.
MS-8	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	Bakelite BRP-5095 (58 pph)	Glassy Carbon (10 pbw)	R.T.	15,000 psi	*10°C/Hr.
MS-9	CHP Artificial Graphite (80 pbw) & WCA Graphite Fibers (20 pbw)	Bakelite BRP-5095 (67.5 pph)	---	R.T.	15,000 psi	**10°C/Hr.
MS-10	Glassy Carbon (80 pbw) & Thermax (20 pbw)	Bakelite BRP-5095 (52 pph)	---	R.T.	15,000 psi	**10°C/Hr.
MS-11	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	Polyphenylene Sulfide (48 pph)	---	R.T.	35,000 psi	5°C/Hr.
MS-12	CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	Varcum 8251 (54 pph)	---	R.T.	15,000 psi	10°C/Hr.

---

* Rush to 150°C, 150°C to 1000°C at 10°C/Hr.

** Suggest that bake be rushed to 150°C, 150°C to 1000°C at 10°C/Hr.

Final baking temperature is 2800°C for all materials: Room temperature to 900°C @ 400°C/Hr., 900°C to 1600°C @ 200°C/Hr., 1600°C to 2800°C @ 300°C/Hr., hold 1 hour @ 2800°C.

MS-8 mix partially polymerized at 110°C before molding.

E. Final Screening Studies

1. Evaluation of Physical Properties

Table XIII lists the physical properties of several compacts of each of the 12 optimized material systems. The table presents the range and the average of the physical properties determined for each material system. The bulk densities were measured on five plugs for each of the material systems MS-1 to MS-4 and MS-6 to MS-7, and on four plugs for each of the material systems MS-8 to MS-12. Only three plugs of MS-5 were analyzed, since two of the five green plugs originally molded were found to have laminated during baking to 1000°C. For each system, two with-grain flexural strength samples were prepared from the highest density plug, two from the lowest density plug, and two from the plug which had a density closest to the average density. The range and average of the flexural strength presented for each material system in Table XIII are, therefore, based on the results of six tests. The hardness measurements for each material system are based on three readings taken on the plug which had a density closest to the average density of the material system.

The strengths and hardnesses measured for the 12 optimized material systems are considerably lower than those of commercial seal ring Grade CDJ. An average flexural strength of 7680 psi has been measured for Grade CDJ by loading 0.200 inch x 0.200 inch cross-sectional dimension samples on a 1.875 inch span. The flexural strength measured for Grade CDJ would probably have been higher had the samples been broken on the 0.950 inch span used for the evaluation of the 12 optimized material systems. This smaller span had to be used because of limitation imposed by the size of the test compacts. Grade CDJ is a very hard material with a Rockwell "E" scale hardness of 105 to 112 (the R_e scale involves the use of a 1/8 inch diameter ball with a 100 kilogram major load). Lower strengths and hardnesses than those of Grade CDJ are to be expected for the 12 optimized material systems, since Grade CDJ is not baked to graphitizing temperatures. Baking to graphitizing temperatures increases the oxidation resistance of a carbon-graphite material at the expense of strength and hardness.

TABLE XIII. - PHYSICAL PROPERTIES MEASURED FOR TWELVE OPTIMIZED MATERIAL SYSTEMS

Physical Property	MS-1 CHP Graphite (80 pbw) Thermax (20 pbw) No. 30 Med Pitch (60 pph)	MS-2 CHP Graphite (80 pbw) Thermax (20 pbw) Boron Carbide (1 pbw) No. 30 Med Pitch (60 pph)	MS-3 CHP Graphite (80 pbw) Thermax (20 pbw) Boron Carbide (7.5 pbw) No. 30 Med Pitch (60 pph)	MS-4 CHP Graphite (80 pbw) Thermax (20 pbw) Glassy Carbon (2 pbw) No. 30 Med Pitch (60 pph)
Green Density (g/cc)				
Range	1.602 to 1.607	1.611 to 1.615	1.625 to 1.631	1.595 to 1.602
Average	1.604	1.613	1.627	1.599
1000°C Density (g/cc)				
Range	1.653 to 1.660	1.662 to 1.681	1.724 to 1.739	1.642 to 1.659
Average	1.656	1.673	1.730	1.652
2800°C Density (g/cc)				
Range	1.691 to 1.704	1.676 to 1.692	1.655 to 1.678	1.686 to 1.699
Average	1.696	1.682	1.666	1.693
Flexural Strength (in units of psi)				
Range	3,180 to 3,870	3,190 to 3,670	2,460 to 3,330	3,720 to 4,220
Average	3,440	3,440	2,840	4,020
Standard Deviation	252	176	375	185
(in units of N/cm²)				
Range	2,190 to 2,670	2,200 to 2,530	1,690 to 2,290	2,560 to 2,910
Average	2,370	2,370	1,960	2,770
Standard Deviation	174	121	258	127
Rockwell Hardness				
R_R	96, 95, 95	98, 100, 97	82, 76, 81	100, 100, 101
R_S	76, 76, 77	75, 76, 75	43, 43, 44	85, 82, 84

Note: Flexural Strength - Total of six samples for each material system. Two samples were cut from the highest density plug, two from the lowest density plug, and two from the plug that had a density closest to the average density of the material system being analyzed. Samples were ground parallel to the length dimension Cross sectional area = 0.200" x 0.200". Span = 0.950"

Rockwell Hardness - Measured on plug that had a density closest to the average density of the material system being analyzed.
R_R scale = 1/2" dia. ball & 60 kg. maj. load
R_S scale = 1/2" dia. ball & 100 kg. maj. load

TABLE XIII (Cont'd.) - PHYSICAL PROPERTIES MEASURED FOR TWELVE OPTIMIZED MATERIAL SYSTEMS

Physical Property	MS-5* CHP Graphite (80 pbw) Thermax (20 pbw) Glassy Carbon (10 pbw) No. 30 Med Pitch (60 pph)	MS-6 ASO Graphite (80 pbw) Thermax (20 pbw) No. 30 Med Pitch (27 pph)	MS-7 CHP Graphite (80 pbw) Thermax (20 pbw) Bakelite BRP-5095 (58 pph)	MS-8 CHP Graphite (80 pbw) Thermax (20 pbw) Glassy Carbon (10 pbw) Bakelite BRP-5095 (58 pph)
Green Density (g/cc)				
Range	1.560 to 1.561	1.827 to 1.831	1.443 to 1.450	1.402 to 1.407
Average	1.560	1.828	1.445	1.405
1000°C Density (g/cc)				
Range	1.601 to 1.634	1.729 to 1.739	1.534 to 1.568	1.456 to 1.460
Average	1.604	1.735	1.555	1.458
2800°C Density (g/cc)				
Range	1.646 to 1.653	1.737 to 1.749	1.648 to 1.692	1.567 to 1.585
Average	1.650	1.741	1.672	1.578
Flexural Strength (in units of psi)				
Range	3,830 to 4,120	1,590 to 2,160	3,310 to 3,660	2,710 to 2,970
Average	3,980	1,870	3,450	2,830
Standard Deviation	136	203	156	98
(in units of N/cm²)				
Range	2,640 to 2,840	1,100 to 1,490	2,280 to 2,520	1,870 to 2,050
Average	2,740	600	2,380	1,950
Standard Deviation	94	140	107	68
Rockwell Hardness				
R_R	103, 100, 103	39, 42, 43	89, 92, 91	78, 78, 79
R_S	84, 85, 84	---	67, 67, 65	45, 48, 52

---

*Two of the five plugs molded laminated when baked to 1000°C. The two laminated plugs were in the bottom layer of the pack. Probably should back off on green density to 1.540 - 1.550 in an attempt to avoid lamination.

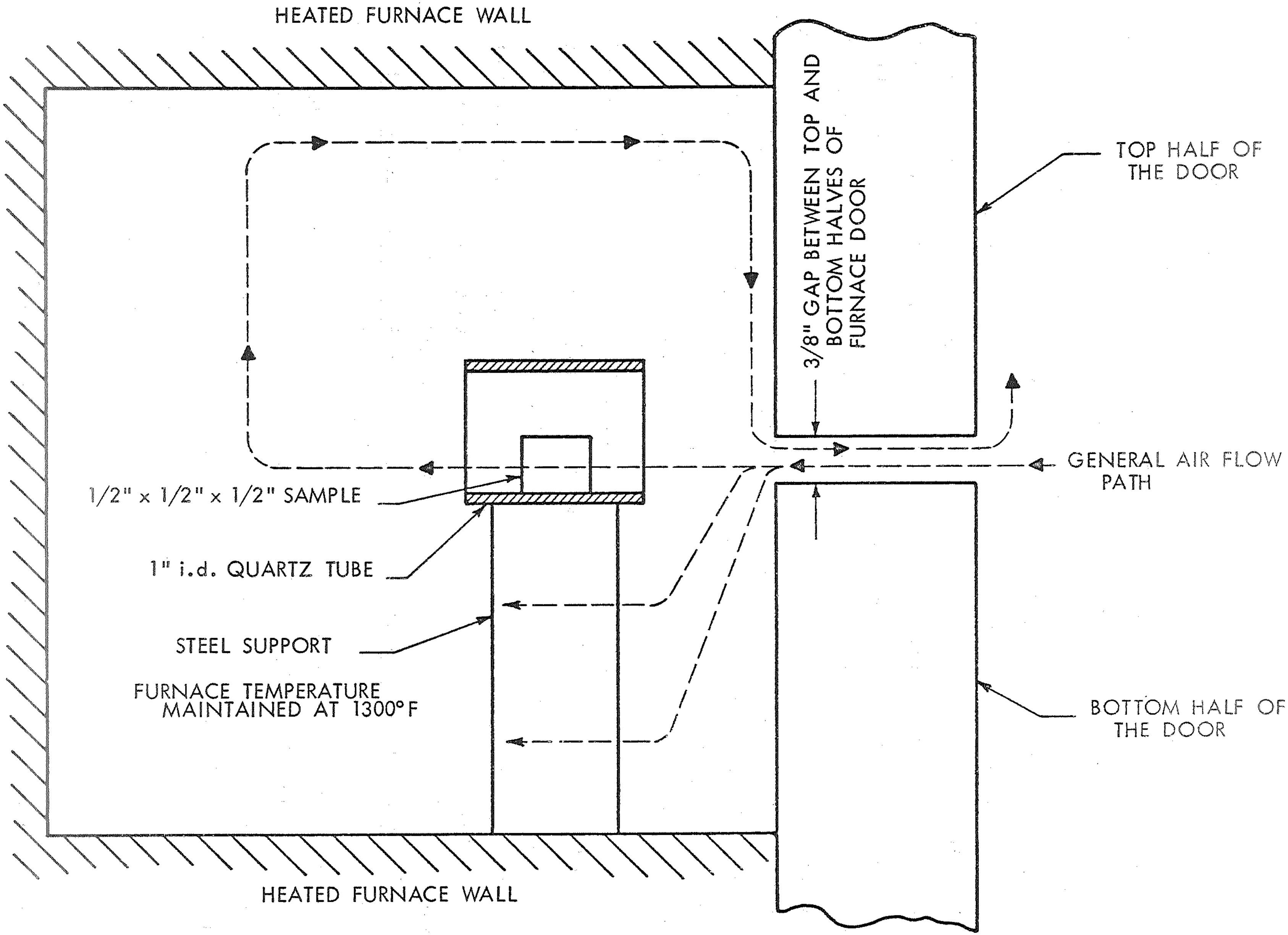
TABLE XIII (Cont'd.) - PHYSICAL PROPERTIES MEASURED FOR TWELVE OPTIMIZED MATERIAL SYSTEMS

Physical Property	MS-9 CHP Graphite (80 pbw) WCA Fibers (20 pbw) Bakelite BRP-5095 (67.5 pph)	MS-10 Glassy Carbon (80 pbw) Thermax (20 pbw) Bakelite BRP-5095 (52 pph)	MS-11 CHP Graphite (80 pbw) Thermax (20 pbw) Polyphenylene Sulfide (48 pph)	MS-12 CHP Graphite (80 pbw) Thermax (20 pbw) Varcum 8251 (54 pph) (2% oxalic acid)
Green Density (g/cc)				
Range	1.412 to 1.415	1.208 to 1.212	1.613 to 1.616	1.476 to 1.482
Average	1.413	1.211	1.615	1.479
1000°C Density (g/cc)				
Range	1.350 to 1.391	0.923 to 0.936	1.327 to 1.341	1.257 to 1.276
Average	1.366	0.930	1.334	1.267
2800°C Density (g/cc)				
Range	1.422 to 1.464	1.032 to 1.052	1.416 to 1.426	1.347 to 1.376
Average	1.438	1.041	1.422	1.362
Flexural Strength				
(in units of psi)				
Range	3,630 to 4,110	1,840 to 2,290	1,170 to 2,240	1,210 to 1,670
Average	3,910	2,050	1,520	1,460
Standard Deviation	181	157	434	171
(in units of N/cm²)				
Range	2,501 to 2,830	1,270 to 1,586	810 to 1,540	830 to 1,150
Average	2,690	1,400	1,047	1,010
Standard Deviation	125	108	299	118
Rockwell Hardness				
R_R	78, 79, 81	31, 12, 19	31, 33, 34	31, 34, 29
R_S	47, 48, 50	---	---	---

The flexural strength samples used in the final screening studies of the twelve optimized material systems were ground differently from those used in the subsystem analyses. When the 0. 200 inch x 0. 200 inch cross-section flexural samples were prepared for the subsystem studies, the grinding wheel traversed the samples perpendicular to their longest dimension to facilitate more rapid grinding of the large number of samples. The 0. 200 inch x 0. 200 inch cross-section flexural samples used in the final screening studies were ground parallel to their longest dimension. Grinding parallel to the length dimension tends to give fewer notches on the edges of the flexural sample, a condition which, in turn, tends to provide more reliable data by reducing the possibility of premature fracture. In general, the change in grinding techniques produced slight increases in the flexural strengths measured for the optimized material systems compared with those measured for the corresponding subsystems. Material system MS-7 was the one material which showed a significant decrease in flexural strength as a result of the change in grinding procedure. System MS-7 had a flexural strength of 4120 psi (SS-41, Table XI) when ground perpendicular to the length dimension compared with a value of 3450 psi when ground longitudinally. The surfaces of the longitudinally ground MS-7 samples appeared to have ridges in them (perpendicular to length dimension) which were probably caused by chattering of the grinding wheel. Ridges in the surfaces of flexural samples produce high stress concentrations which cause the samples to break at loads smaller than those required to fracture samples having smooth surfaces.

2. Oxidation Testing

As a part of the final screening studies, oxidation tests were conducted at 1300°F with the 12 optimized material systems. Seal ring Grade CDJ was used as the standard for comparison. During testing, the samples were placed in one-inch i. d. quartz tubes, which subsequently were supported in a small electrically heated furnace. The quartz tubes were used to keep the samples from contacting the metal support (which might have acted as an oxidation catalyst for the "graphitized" materials) and to allow the removal of the oxidation samples from the furnace without damaging them. Figure 4 is a schematic of the oxidation testing apparatus.



N-23865

Figure 4. Oxidation Testing Apparatus.

The furnace has a split door which was propped open during oxidation testing so that a 3/8 inch gap was maintained across the entire face of the furnace between the upper and lower halves of the door. The quartz tubes containing the samples were supported so that the samples were in line with the gap between the two sections of the door. Air passing through the gap in the door also flowed around the samples, as shown in Figure 4. At the beginning of the test, the samples were weighed and placed into the quartz tubes, after which the tubes containing the samples were weighed and placed inside the 1300°F furnace chamber. After 1/2 hour of exposure to the oxidizing conditions, the quartz tubes containing the samples were removed from the furnace, cooled to room temperature, weighed, and placed back inside the furnace for another 1/2 hour. This procedure was continued until the samples had been exposed to the oxidizing conditions for a total of three hours. Due to size limitations of the furnace, only five samples could be oxidized at one time. A preliminary test had shown that the weight of the empty quartz tubes remained constant when exposed to the 1300°F temperature.

Untreated samples were used in the first series of 1300°F oxidation tests. Table XIV lists the percent weight losses determined for samples of the optimized material systems and for samples of Grade CDJ. The results presented in the table are based on the averages from the oxidation testing of two samples for each of the 12 material systems and six samples of Grade CDJ. Except for MS-10, the oxidation resistances of the optimized material systems were between 6 and 17 times better than that of Grade CDJ. The results presented in Table XIV point out an interesting phenomenon concerning the use of B_4C as an oxidation inhibiting additive. The MS-2 and MS-3 mixes were prepared by adding 1 pbw and 7.5 pbw, respectively, of B_4C to the milled mix of material system MS-1. Apparently, the 1 pbw addition of B_4C did not produce enough of the protective B_2O_3 surface coating to counteract the decrease in activation energy caused by the presence of the additive and, therefore, the oxidation losses experienced by the MS-2 samples were higher than those measured for the MS-1 samples. The MS-3 samples contained enough B_4C to produce oxidation losses which were lower than those experienced by the MS-1 samples.

TABLE XIV. - OXIDATION TEST DATA FOR UNTREATED MATERIALS

Material System	Cumulative Percent Weight Loss					
	1/2 Hr.	1 Hr.	1-1/2 Hr.	2 Hr.	2-1/2 Hr.	3 Hr.
MS-1	0.51	1.03	1.60	2.48	3.71	4.63
MS-2	0.83	1.66	2.64	4.06	5.68	7.60
MS-3	0.21	0.46	0.85	1.60	2.50	3.53
MS-4	0.48	1.04	1.64	2.50	3.43	4.52
MS-5	0.50	1.13	1.86	2.78	3.79	4.97
MS-6	0.82	1.83	2.94	4.30	5.76	7.38
MS-7	0.24	0.56	0.96	1.57	2.31	3.23
MS-8	0.46	1.18	2.08	3.26	4.57	6.25
MS-9	0.67	1.56	2.58	3.76	5.12	6.48
MS-10	2.01	4.62	7.82	11.34	15.50	19.99
MS-11	0.72	1.80	3.10	4.91	6.86	8.76
MS-12	0.96	1.89	2.86	3.96	5.26	6.50
CDJ	6.34	14.87	24.05	34.03	44.42	54.42

Sample size = 1/2" x 1/2" x 1/2"

Oxidation temperature = 1300°F

Samples which had been impregnated with an oxidation-inhibiting treat were used for the second series of 1300°F oxidation tests. Union Carbide Corporation's No. 83 treatment was employed. Table XV presents the percent weight losses determined for treated samples of the material systems and Grade CDJ. The results are based on the oxidation testing of one treated sample for each of the material systems and three treated samples of Grade CDJ. The last column of Table XV displays the differences in percent weight loss measured after 1/2 hour and three hours of exposure to the oxidizing conditions. Apparently, absorbed moisture was driven off during the first 1/2 hour, producing higher incremental weight losses than those experienced in the succeeding 1/2 hour exposure periods. A more realistic picture of the oxidation behavior of the materials is obtained by ignoring the first 1/2 hour of testing. The percent weight losses measured for the treated samples were appreciably lower than those determined for the corresponding untreated samples.

The percent total porosity and No. 83 treat pickups for the twelve optimized material systems are shown in Table XVI. The treat pickups measured for samples of MS-1 to MS-8 reflect the absence of large differences in the porosity of these compacts. The MS-7 material which was prepared with the BRP-5095 resin binder had the lowest porosity. Both the porosity and pickup data indicate that the MS-10 to MS-12 compacts are considerably more porous than the MS-1 to MS-8 samples. The MS-10 compacts are extremely porous, a condition which would account for the material's poor oxidation resistance compared with that of the other eleven material systems. The MS-9 sample had a total porosity only slightly greater than that of the MS-6 material. In spite of this comparatively small difference in porosity, the MS-9 sample had a much higher treat pickup than the MS-6 material. Apparently, the size of the pores present in the MS-9 material, which contains 20 percent WCA fibers, makes them more accessible to the impregnant than those of the MS-6 compact.

TABLE XV. - OXIDATION TEST DATA FOR NO. 83 TREATED MATERIALS

Material System	Cumulative Percent Weight Loss						Δ% Weight
	1/2 Hr.	1 Hr.	1-1/2 Hr.	2 Hr.	2-1/2 Hr.	3 Hr.	Loss 1/2-3 Hrs.
MS-1	0.94	1.03	1.06	1.19	1.22	1.28	0.34
MS-2	1.02	1.11	1.12	1.23	1.26	1.29	0.27
MS-3	0.67	0.69	0.70	0.73	0.73	0.74	0.07
MS-4	0.94	1.03	1.05	1.17	1.21	1.26	0.32
MS-5	0.84	0.91	0.91	1.01	1.04	1.11	0.27
MS-6	1.98	2.41	2.54	2.82	3.01	3.25	1.27
MS-7	0.75	0.82	0.82	0.89	0.93	0.99	0.24
MS-8	0.91	1.02	1.02	1.14	1.21	1.30	0.39
MS-9	1.44	1.48	1.58	1.61	1.77	1.85	0.41
MS-10	3.86	4.10	4.39	4.59	5.07	5.46	1.60
MS-11	2.13	2.16	2.26	2.33	2.56	2.74	0.61
MS-12	2.37	2.42	2.52	2.58	2.78	2.90	0.53
CDJ	1.14	3.34	6.75	11.01	16.37	22.67	21.53

Sample size = 1/2" x 1/2" x 1/2"

Oxidation temperature = 1300°F

TABLE XVI. - PERCENT TOTAL POROSITY AND NO. 83 TREAT PICKUPS

Material System	% Total Porosity	Weight % Treat Pickup
MS-1	16.6	2.91
MS-2	17.6	3.21
MS-3	18.3	3.18
MS-4	16.2	2.91
MS-5	15.7	2.98
MS-6	19.3	3.14
MS-7	14.6	2.64
MS-8	16.2	3.00
MS-9	22.1	5.37
MS-10	36.6	12.96
MS-11	31.2	6.66
MS-12	31.4	7.19

$$\text{Percent Total Porosity} = \frac{\text{Helium Density} - \text{Bulk Density}}{\text{Helium Density}} \times 100$$

SECTION VII

DISCUSSION OF RESULTS AND MATERIAL FORMULATION (CATEGORY 3 -- TASK II)

A. Selection of Four Material Formulations

At the conclusion of Task I, the Contract Work Plan called for the selection of four approaches to the processing and manufacture of seal ring carbon-graphite bodies. The selection of the four material formulations, which include the required processing techniques, was based on the results of the final screening studies and was aimed at providing material that would meet the 3000 hour life and 1300°F ambient air temperature requirements. Since the carbon-graphite bodies are to be used as self acting seal rings, reduction in strength and hardness could be tolerated to enhance oxidation resistance. Results of the oxidation tests indicate the carbon-graphite materials prepared during the screening studies were more oxidation-resistant than commercial seal ring Grade CDJ. However, since potential seal ring materials must be made as strong and wear resistant as possible the four formulations that would produce materials with the best combination of strength, hardness, and oxidation resistance were selected.

The final screening studies resulted in eliminating material systems MS-6, MS-10, MS-11, and MS-12 from further consideration. Systems MS-2 and MS-3 were subsequently eliminated because of the detrimental effects produced by the addition of B_4C to the MS-1 mix. Although the 1 pbw addition of B_4C did not affect the physical properties of the MS-2 compacts, it caused oxidation losses that were greater than those measured for the MS-1 samples. The 7.5 pbw addition of B_4C in the MS-3 sample tended to increase oxidation resistance, but it degraded the strength. Examination of the internal structures of the MS-3 compacts showed that they contained several small spherically-shaped voids. Apparently, the voids were produced by the dissolution of carbon in the B_4C during graphitization, a condition which subsequently produced hollow pockets when the carbon precipitated and coalesced as highly crystalline graphite during the cooling cycle. The presence of the internal voids very likely produced the degradation of the physical properties.

The addition of glassy carbon to the pitch bonded MS-1 mix slightly improved the physical properties of the resultant compacts. Flexural strengths measured for the MS-4 (2 pbw glassy carbon) and MS-5 (10 pbw glassy carbon) compacts were approximately 600 psi greater than those measured for the MS-1 plugs. Further testing will be required to determine whether the 600 psi is statistically significant. Increasing the addition of glassy carbon from 2 pbw to 10 pbw did not produce a corresponding increase in the strength of the "graphitized" material. The hardness of both material system compacts containing glassy carbon was greater than that of the MS-1 samples. These glassy carbon bearing bodies had the highest hardnesses of the 12 materials. The addition of up to 10 pbw glassy carbon did not significantly affect oxidation behavior. The MS-1, MS-4, and MS-5 samples all experienced some of the lower oxidation losses measured during the final screening studies. A formulation interpolated from those of material systems MS-4 and MS-5 was selected as one of the four to be used for producing seal ring bodies. The new material is the same as MS-1 except for a 5 pbw addition of glassy carbon. An addition of 5 pbw was chosen since this amount should be sufficient to determine if the presence of glassy carbon increases wear resistance. The 5 pbw addition also should be low enough to avoid the lamination problems encountered during the production of the MS-5 compacts. Material system MS-1 was selected as the second formulation to be manufactured, since it was one of the stronger materials developed. Also, seal ring bodies of MS-1 would be needed as standards to determine the effect of the 5 pbw addition of glassy carbon on performance.

Material systems MS-7 and MS-9 were selected as the remaining two formulations from which carbon-graphite seal ring bodies are to be produced. System MS-7 was chosen because samples of the material had shown excellent oxidation resistance, and compacts from its corresponding subsystems (SS-25 and SS-41) had the highest flexural strengths measured during the subsystems studies. The lower-than-expected flexural strengths determined during the final screening studies for the MS-7 samples were apparently due to a sample preparation problem. Although the oxidation behavior of the MS-9 compacts was not quite so good as that of the other selected material systems, flexural strength was comparable. The addition of WCA graphite fibers produced a material having relatively high strength and low density; high strength-per-unit weight is a desirable characteristic of a seal ring material.

The four material formulations listed in Table XVII were approved by the NASA Project Manager. Impregnation of material formulations No. 3 and 4 with a Bakelite BRP-5095 resin and acetone solution prior to baking to 2800°C was recommended as a route to increase strength, hardness, and wear resistance. The impregnations would reduce porosity and further enhance oxidation resistance. The impregnation studies are to be carried out on a best-efforts basis and may be extended to formulations No. 1 and 2 if time and funding permit.

The decision concerning the oxidation-inhibiting treatments to be employed in the four seal ring formulations will be made at a later date. The 1300°F oxidation tests were also run on samples treated with the Union Carbide No. 121 treatment. Table XVIII presents the results of oxidation tests conducted on No. 121 treated samples of the four types of materials selected for the manufacturing of seal ring bodies. One sample of each material was tested. The oxidation test procedure was the same as that used during the final screening studies.

B. Processing of the Material Formulations

Since this Topical Report describes "bench-scale" work, the compacts prepared for analysis were of relatively small size. Compacts of varying size were prepared and analyzed during the different investigations cited in the literature search phase of Task I. LASL produced some of the largest compacts, with diameters varying between 2.50 inches and 4.0 inches and thicknesses generally ranging from 1.25 to 2.50 inches.

TABLE XVII. - IDENTIFICATION OF THE FOUR MATERIAL FORMULATIONS

Formulation No.	Particulate Solid Raw Material	Additive	Binder Raw Material	Approximate[1] Nominal Green Density g/cc	Final Bake Temp. °C
1	CHP Artificial Graphite (80 pbw)-Thermax (20 pbw)	---	No. 30 Medium Pitch (60 pph)	1.60	2800
2	CHP Artificial Graphite (80 pbw)-Thermax (20 pbw)	Glassy Carbon (5 pbw)	No. 30 Medium Pitch (60 pph)	1.60	2800
3	CHP Artificial Graphite (80 pbw)-Thermax (20 pbw)	---	Bakelite BRP-5095 Phenolic Resin (58 pph)	1.44	2800
4	CHP Artificial Graphite (80 pbw)-WCA Fibers (20 pbw)	---	Bakelite BRP-5095 Phenolic Resin (67.5 pph)	1.41	2800

Note: Proportions are parts by weight (pbw).

Binder proportions are parts (by weight) per 100 parts (by weight) particulate raw materials.

(1) Actual green density to be established through test baking.

TABLE XVIII. - TREAT PICKUPS AND OXIDATION TEST DATA FOR NO. 121 TREATED MATERIALS

Material System	Weight % Treat Pickup	Cumulative Percent Weight Loss After						Δ% Weight Loss 1/2 - 3 Hrs.
		1/2 Hr.	1 Hr.	1-1/2 Hr.	2 Hr.	2-1/2 Hr.	3 Hr.	
MS-1	2.09	0.51	0.59	0.72	0.86	0.94	1.01	0.50
MS-4	1.86	0.47	0.54	0.65	0.77	0.83	0.89	0.42
MS-7	1.51	0.39	0.44	0.53	0.63	0.70	0.76	0.37
MS-9	3.76	1.07	1.12	1.23	1.34	1.40	1.42	0.35
CDJ		1.21	2.07	8.20	14.13	20.20	27.82	26.61

Sample size = 1/2" x 1/2" x 1/2"

Oxidation temperature = 1300°F

The compacts produced for the screening studies reported here were 2.50 x 1.25 x 1.0 inches as molded (green). During Task III, six 7.25 inch o.d. x 5.75 inch i.d. x 0.50 inch thick ring blanks must be made for each of the four material formulations. The large size of the ring blanks may cause some processing problems that were not encountered during the preparation of the smaller compacts for the screening studies. The same processing techniques used to develop the four material formulations will be applied to the manufacture of the large bodies; required processing changes will be made if problems are encountered.

The following processing steps will be employed in producing compacts of the four material formulations:

Formulation No. 1 - CHP Artificial Graphite (80 pbw) - Thermax (20 pbw) - No. 30 Medium Pitch (60 pph): a) Blend filler raw materials for one hour. b) Preheat filler and mixer to 150°C, add pitch, and mix filler and binder in a sigma blade mixer for one hour. c) Crush material by using a hammer pulverizer. d) Micromill material. e) Blend milled material for one hour in a ribbon blender. f) Mold the milled material at room temperature by using a hydraulic press. g) Pack green compacts with coke in a sagger, place a layer of charcoal on the top of the pack, and bake green compacts between room temperature and 1000°C at 5°C/hr., followed by a 4-hour hold at 1000°C. h) Using graphite particles as the packing medium, fire the 1000°C baked compacts to 2800°C in an induction furnace, use the following schedule: room temperature to 900°C at 400°C/hr., 900°C to 1600°C at 200°C/hr., 1600°C to 2800°C at 300°C/hr., and hold 1 hour at 2800°C.

Formulation No. 2 - CHP Artificial Graphite (80 pbw) - Thermax (20 pbw) Glassy Carbon (5 pbw) - No. 30 Medium Pitch (60 pbw): a) Blend small batches of filler containing CHP artificial graphite (16 lbs), Thermax (4 lbs), and glassy carbon (1 lb) for one hour in a small blender. b) Blend all the smaller filler batches (Step a) for one hour in a large blender. c) The other processing steps are the same as those listed for Formulation No. 1, starting at Step b (mixing).

Formulation No. 3 - CHP Artificial Graphite (80 pbw) - Thermax (20 pbw)-Bakelite BRP-5095 Resin (58 pph): a) Blend filler raw materials for one hour. b) Dissolve binder in equal volume of acetone and mix with filler in a sigma blade mixer for one hour at room temperature. c) Heat material in a 75°C circulating air oven until all the acetone is evaporated. d) The other processing steps, except for the 1000°C baking schedule, are the same as those listed for Formulation No. 1, starting at Step c (crushing). The 1000°C baking schedule to be used for Formulation 3 is: rush to 150°C, raise from 150°C to 1000°C at 10°C/hr, and hold at 1000°C for 4 hrs.

Formulation No. 4 - CHP Artificial Graphite (80 pbw) - WCA Fibers (20 pbw) - Bakelite BRP-5095 Resin (67.5 pph): a) Blend shredded WCA cloth, with graphite for one hour. b) Micromill the blended filler material, c) Blend milled filler material for one hour. d) The other processing steps are the same as those listed for Formulation No. 3, starting at Step b (mixing).

APPENDIX I

PROCEDURES USED TO CHARACTERIZE RAW MATERIALS

Helium Density-	Measured with Beckman pycnometer
Surface Area-	B. E. T. method
Screen Analysis-	Tyler standard screen sieve analysis
Chemical Analysis-	Ash measured per ASTM C561 except 680°C overnight. Moisture measured by drying at 105°C overnight. Modification of ASTM C562
Emission Spectrographic Analysis-	Conducted using Jerrell Ash emission spectrograph
Coking Value-	Modified Conradson technique (ASTM D-189-52). Modification is furnace instead of gas burner for heat
Benzene Insoluble-	Method based on ASTM D2317
Quinoline Insoluble-	Method based on ASTM D2318
Softening Point-	Method based on ASTM D2319
Elemental Chemical Analysis-	(C) Combustion techniques using gravimetric analysis (H) Combustion techniques using gravimetric analysis (O) LECO oxygen analyzer (N) Kjeldahl method (S) X-ray fluorescence
Differential Thermal Analysis-	Mettler thermal analyzer
Thermal Gravimetric Analysis-	Mettler thermal analyzer

APPENDIX II

DEFINITION OF TERMS AND SYMBOLS

σ_{oz}/σ_{ox}	Bacon Anisotropy Factor; Bacon, G. E., "A Method for Determining the Degree of Orientation of Graphite," Journal of Applied Chemistry, Volume 6, page 477 (1956). Used by Group CMF-13 of the Los Alamos Scientific Laboratory to measure the overall anisotropy of a molded material.
M	The exponent in the cosine function $I(\phi) = I_0 \cos^M \phi$, which best describes the change in concentration of basal planes with angle relative to molding axis. Group CMF-13 of the Los Alamos Scientific Laboratory used M as a measurement of preferred orientation.
d	A linear particle dimension characteristically measureable for all particles in the population of particles.
$\hat{\mu}_{x_3}$	The value of $x = \ln d$ at $\frac{w_i}{W} = 0.5$ obtained from a log probability plot of weight fraction $\frac{w_i}{W}$ data (as measured by a micromerograph, a screen or a MSA Sedimentation Particle Size analysis).
$\hat{\sigma}^2_{x_3}$	Variance of $x = \ln d$ obtained from a log probability plot of weight fraction $\frac{w_i}{W}$ data. Its value equals the square of the difference between the values of $x = \ln d$ at $\frac{w_i}{W} = 0.8413$ and $\frac{w_i}{W} = 0.5$.
$\hat{\sigma}^2_{x}$	Variance of $x = \ln d$ obtained from a log probability plot of relative frequency $\frac{n_i}{N}$ data (as measured by a microscopic count). Its value equals the square of the difference between the values of $x = \ln d$ at $\frac{n_i}{N} = 0.8413$ and $\frac{n_i}{N} = 0.5$. Lewis and Goldman have said to assume that $\hat{\sigma}^2_{x} \approx \hat{\sigma}^2_{x_3}$ when calculating sample statistics.

APPENDIX II (Cont'd)

$\hat{\mu}_x$	The value of $x = \ln d$ at $\frac{n_i}{N} = 0.5$ obtained from a log probability plot of relative frequency $\frac{n_i}{N}$ data. $\hat{\mu}_{x_3} = \hat{\mu}_x + 3\hat{\sigma}^2_x$
$\bar{d}_3$	Sample mean computed from weight fraction $\frac{w_i}{W}$ data. $\bar{d}_3 \approx \exp\,[\hat{\mu}_{x_3} + 0.5\hat{\sigma}^2_x]$
$S^2_{d_3}$	Sample variance computed from weight fraction $\frac{w_i}{W}$ data. $S^2_{d_3} \approx \exp\,[2\hat{\mu}_x + 8\hat{\sigma}^2_x] - \exp\,[2\hat{\mu}_x + 7\hat{\sigma}^2_x]$
$\bar{d}$	Sample mean computed from relative frequency $\frac{n_i}{N}$ data. $\bar{d} \overset{\circ}{\approx} \exp\,[\hat{\mu}_x + 0.5\hat{\sigma}^2_x]$
S^2_d	Sample variance computed from relative frequency $\frac{n_i}{N}$ data. $S^2_d \overset{\circ}{\approx} \exp\,[2\hat{\mu}_x + 2\hat{\sigma}^2_x] - (\bar{d})^2$
CV_d	Coefficient of variation. $CV_d = S_d/\bar{d}$

Note: $\approx$ means approximately equal to

$\overset{\circ}{\approx}$ means estimates or is estimated by

REFERENCES

1. Paxton, R. R., "Carbon and Graphite Materials for Seals, Bearings, and Brushes," Electrochemical Technology, Volume 5, page 175, May - June, 1967.
2. Parks, A. J., McKibbin, R. H., and Ng, C. C. W., "Development of Main Shaft Seals for Advanced Air Breathing Propulsion Systems," NAS3-7609, Final Report Phase I (August, 1967), NASA CR72338, page 49.
3. Paxton, R. R. and Shobert, W. R., "Carbon-Graphite for Aerospace Seals," Soc. Automotive Engineers, Aerospace Fluid Power Systems and Equipment Conference, Los Angeles, California, Proc., (SAE paper, 650302), pages 149 - 152, May 18 - 20, 1965.
4. Johnson, Robert L., and Ludwig, Lawrence P., "Shaft Face Seal with Self-Acting Lift Augmentation for Advanced Gas Turbine Engines," NASA-TN-D-5170, NASA Lewis Research Center, Cleveland, Ohio, April, 1969.
5. Strom, Thomas N., Allen, Gordon P., and Johnson, Robert L., "Wear and Friction of Impregnated Mechanical Carbons at Temperatures to 1400°F (760°C) in Air or Nitrogen," NASA-TN-D-3958, page 2, NASA Lewis Research Center, Cleveland, Ohio, May, 1967.
6. Lauzau, W. R., Shelton, B. R., and Waldheger, R. A., "The Use of Carbon-Graphite in Mechanical Seals," Lubrication Engineering, Volume 19, pages 201 - 209, May, 1963.
7. Baskey, Raymond H., "A Research Program on the Investigation of Seal Materials for High Temperature Application," WADC-TR-58-181 (AF33(616)-3891), (AD 155 689), page 5, June, 1958.
8. Loc cit, Reference 5.

REFERENCES (Cont'd)

9. Lipsdorf, K., Schafer, R., Spener, G., and Wege E., "Reactor Graphite of Low Permeability and of High Density," in Int. Atomic Energy Agency, Fuel element fabrication...proc..., page 181, 1960.

10. Heindl, R. A. and Mohler, N. F., "Oxidation Studies of Some Natural Graphites," Journal of the American Ceramic Society, Volume 38, No. 3, pages 89 - 94, March 1, 1955.

11. Smith, Morton C., "CMF-13 Research on Carbon and Graphite," Los Alamos Scientific Laboratory, LA-3821 (W-7405-ENG. 36) (Report No. 3) (Summary of Progress from August 1 to October 31, 1967) pages 6 - 7, November 15, 1967.

12. Smith, Morton C., "CMF-13 Research on Carbon and Graphite," Los Alamos Scientific Laboratory, LA-3872 (W-7405-ENG. 36) (Report No. 4) (Summary of Progress from November 1, 1967 to January 31, 1968) pages 16 - 17, February 9, 1968.

13. Smith, Morton C., "CMF-13 Research on Carbon and Graphite," Los Alamos Scientific Laboratory, LA-3989 (W-7405-ENG. 36) (Report No. 6) (Summary of Progress from May 1 to July 31, 1968) pages 8 - 11, September 4, 1968.

14. Smith, Morton C., "CMF-13 Research on Carbon and Graphite," Los Alamos Scientific Laboratory, LA-4057 (W-7405-ENG. 36) (Report No. 7) (Summary of Progress from August 1 to October 31, 1968) pages 5 - 7, December 31, 1968.

15. Smith, Morton C., "CMF-13 Research on Carbon and Graphite," Los Alamos Scientific Laboratory, LA-4128 (W-7405-ENG. 36) (Report No. 8) (Summary of Progress from November 1, 1968 to January 31, 1969) pages 3 - 5, March 21, 1969.

REFERENCES (Cont'd)

16. Smith, Morton C., "CMF-13 Research on Carbon and Graphite," Los Alamos Scientific Laboratory, LA-4237 (W-7405-ENG. 36) (Report No. 10) (Summary of Progress from May 1 to July 31, 1969) pages 14 - 17, September 3, 1969.

17. Currie, L. M., Hamister, V. C., and MacPherson, H. G., "The Production and Properties of Graphite for Reactors," Volume VIII P/534 USA, L. M. Currie et al., pages 451 - 455.

18. *Ibid,* page 458.

19. Brockway, M. Clifford, "Carbons and Graphites - Their Production and Use," Battelle Tech. Rev., Vol. 13, page 5, March, 1964.

20. Smith, Morton C., "The Manufacture and Properties of an Extruded, Resin-Bonded Graphite, CMF-13 Lot AAQ1," Los Alamos Scientific Laboratory, LA-3981 (W-7405-ENG. 36), October 31, 1968.

21. Smith, Morton C., "CMF-13 Research on Carbon and Graphite," Los Alamos Scientific Laboratory, LA-3758 (W-7405-ENG. 36) (Report No. 2) (Summary of Progress from May 1 to July 1, 1967) page 11, September 15, 1967.

22. Peggs, I. D., "Carbon, Graphite, and Some Carbides for Superheat Service: Literature Survey," AECL-3069 (Atomic Energy of Canada Limited), Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, page 32, March, 1968.

23. Bokros, J. C., "Deposition, Structure, and Properties of Pyrolytic Carbon" Chemistry and Physics of Carbon (Edited by Walker, P. L.), Volume 5, Marcel Dekker, Inc., New York (1969), pages 1 - 118.

24. Cahn, R. W. and Harris, B., "Newer Forms of Carbon and Their Uses," Nature, Volume 221, page 135, January 11, 1969.

REFERENCES (Cont'd)

25. Auriol, A., Mavrel, G., Tannenberger, H., Rappeneau, J., and Yuars, M., "Preparation of Solid Pyrocarbons in a Fluidized Bed-Physical Properties of These Pyrocarbons," Carbon, Volume 4, pages 509 - 529 (1966).

26. Nightengale, R. W., Nuclear Graphite, Academic Press, New York, and London, page 435, 1962.

27. Loc cit., Reference 24, page 136.

28. Diefendorf, R. J. and Stover, E. R., "Pyrolytic Graphites...How Structure Affects Properties," Metal Progress, page 106, May, 1962.

29. Loc cit, Reference 23, page 107.

30. Bourdeau, R. G., "New Pyrolytic Materials," Materials in Design Engineering, Volume 56 (August, 1962), page 107.

31. Tominaga, Y. And Nagaoki, T., "Oxidation of Pyrolytic Graphite," In Carbon Soc. Japan, Symposium on Carbon...pp. VIII-4-1 to VIII-4-4, 1964.

32. Loc cit., Reference 24, page 136.

33. Loc cit., Reference 28.

34. Arnell, R. D., Midgley, J. W., and Teer, D. G., "The Development of Surface Orientation on Rubbed Pyrolytic Carbon and Their Relation to the Friction and Wear," British Journal of Applied Physics, Volume 1, (Series 2), pages 1543 - 1548 (1968).

35. Pike, E. C. and Thompson, J. E., "On the Possible Application of Pyrolytic Graphite As A Brush Material and A Critical Assessment of The Use of Brushes With Truncated Conical Tips to Study The Running Characteristics of Graphite Materials," Wear, Volume 13, No. 4/5, pages 247 - 255.

REFERENCES (Cont'd)

36. Loc cit., Reference 14, pages 5 - 7.

37. Loc cit., Reference 15, pages 3 - 5.

38. Bacon, R., "An Introduction to Carbon/Graphite Fibers," Applied Polymer Symposia, Volume 9, pages 213 - 214 (1969).

39. Loc cit., Reference 24, page 138.

40. Bacon, R., and Schalamon, W. A., "Physical Properties of High Modulus Graphite Fibers Made From A Rayon Precursor," Applied Polymer Symposia, Volume 9, pages 285 - 299 (1969).

41. Beasley, W. C., McHenry, E. R., and Piper, E. L., "Fabrication and Properties of Carbonized Cloth Composites," Prepared by Union Carbide Corporation, WADD Technical Report 61-72, Vol. IX, Contract AF 33(616)-6915, pages 3 - 6, August, 1963.

42. Stover, E. R., "Evaluation of Structural Characteristics of Carbon/ Carbon Composites," Proceedings of the Tenth Annual Carbon Composite Technology Symposium (University of New Mexico), pp. 55-88 (1970).

43. Slaniceau, R. D., "Carbon Black Technology," Research Council of Alberta (Canada), Information Service, No. 39, pp. 113-116, 1962.

44. Loc cit., Reference 17, pp. 455-456.

45. Loc cit., Reference 20, pp. 6-8.

46. Loc cit., Reference 12, pp. 18-19.

47. Smith, Morton C., "CMF-13 Research on Carbon and Graphite," Los Alamos Scientific Laboratory, LA-3932 (W-7405-ENG. 36) (Report No. 5) (Summary of Progress from February 1 to April 30, 1968) pages 28 - 32, (May 20, 1968).

48. Loc cit., Reference 14, pp. 11-16.

49. Loc cit., Reference 16, pp. 14-17.

50. Loc cit., Reference 20, page 7.

REFERENCES (Cont'd)

51. Cowlard, F. C. and Lewis, J. C., "Vitreous Carbon - A New Form of Carbon," Journal of Materials Science 2, page 508, 1967.

52. Yamada, S., "A Review of Glasslike Carbons," Defense Ceramic Information Center, DCIC Report 68-2, April, 1968.

53. Noda, Tokiti; Inagaki, Michio; and Yamada, Shigehiko; "A Comment on the Structure of Glassy Carbon," Chem. Soc. Japan, Bull., Vol. 41, pp. 3023 - 3024, June 4, 1968.

54. Loc cit., Reference 51, pp. 508-510.

55. Lewis, J. C., "Comparative Study of the Gaseous Oxidation of Vitreous Carbon and Various Graphites," presented at the Second Conference on Industrial Carbon and Graphite, London, pp. 258-268, April, 1965.

56. Loc cit., Reference 24, page 138.

57. Loc cit., Reference 52, page 38.

58. Krellner, Walter G., United States Patent No. 3,284,371; Nov. 8, 1966.

59. Smith, F. A. Eckle, T. F., Osterholm, R. J. and Stickel, R. M., "Manufacture of Coal Tar and Pitches," Bituminous Materials: Asphalts, Tars, and Pitches (Edited by Hoiberg, A. J.), Volume III, John Wiley and Sons, New York (1966), pp. 57-116.

60. Hooker, J. R. "Pitch Binders for Graphite - A Survey of the Literature," GA-3985, General Atomic Division General Dynamics Corporation, San Diego, California, March 7, 1963.

61. Bradstreet, S. W., "Graphite Technology," Armour Research Foundation, AF 33(616)-5185, Proj. G-033, Progress Report No. 3, pp. 4-5, (August 1 to October 1, 1957).

62. Edstrom, T., Lewis, I. C., Racicot, R. L. and Stout, C. F., "Research and Development on Advanced Graphite Materials," AF 33(616)-6915, Technical Report No. WADD TR61-72, Vol. XXXII, pp. 1-15, May, 1964.

63. King, L. F. and Robertson, W. D., "A Comparison of Coal Tar and Petroleum Pitch as Electrode Binders," Fuel, Volume XLVII (1968), pp. 197-212.

64. Riesz, C. H. and Susman, S., "Synthetic Binders for Carbon and Graphite," Proceedings of the Fourth Carbon Conference, University of Buffalo, pp. 609-612, 1959.

65. Ibid page 610.

66. Bradstreet, S. W., "Graphite Technology," Armour Research Foundation, AF 33(616)-5185, Proj. G-033, Progress Report No. 6, pp. 38, 46-49, (February 1 to April 1, 1958).

67. Loc cit., Reference 15, pp. 22-23.

68. Loc cit., Reference 66, pp. 38, 50-52.

69. Robbins, J. M., and Taylor, A. J., "Fabrication of Fueled Graphite," U. S. Oak Ridge National Laboratory ORNL-3302, Gas-Cooled Reactor Program, Quarterly Progress Report, pp. 184-186, July 16, 1962.

70. Loc cit., Reference 62, pp. 18-21.

71. Boquist, C. W., Nielsen, E. R., O'Neil, H. J., and Putcher, R. E., "Alumina - Condensed Furfuryl Alcohol Resins," Technical Report No. WADD TR61-72, Volume XV.

72. Christopher, N. S. J., Cotter, J. L., Knight, G. J., and Wright, W. W., "Thermal Degradation of Poly (phenylene sulfide) and Perfluoropoly (phenylene sulfide)," Journal of Applied Polymer Science, Vol. 12 pp. 863-870, 1968.

73. Phillips Petroleum Company, "RYTON* Polyphenylene Sulfide Resins," (*trademark of PPC), A new product information brochure issued by Commercial Development Division of the Phillips Petroleum Company, Bartlesville, Oklahoma, Second Edition, April, 1969.

REFERENCES (Cont'd)

74. Radszawski, J. F. and Parker, W. E., "The Effect of Group IIIA-VIA Elements and Their Oxides on Graphite Oxidation," Carbon, Vol. 2, pp. 53-63, 1964.

75. Fisher, J. C., United States Patent No. 2,897,102, July 28, 1959.

76. Hastings, P. J. and Zeitsch, K. J., "Graphite Base Composites for Oxidation Resistance up to Approximately 3500°F," from manuscript for oral presentation made by P. J. Hastings at the 18th Pacific Coast Regional Meeting of the American Ceramic Society held at the International Hotel, Los Angeles, October 27-29, 1965.

77. Woodley, R. E., "The Oxidation of Boronated Graphite," Carbon, Volume 6, pp. 617-618, 1968.

78. Allardice, D. J. and Walker, P. L. Jr., "The Effect of Substitutional Boron on the Kinetics of the Graphite-Oxygen Reaction," Defense Ceramic Information Center; Summary of papers for Ninth Biennial Conference on Carbon, Co-sponsored by the American Carbon Committee and Boston College, Chestnut Hill, Massachusetts, page 113, June 16-20, 1969.

79. Trask, R. B., "Effect of Boron Addition on Some Properties of Synthetic Graphites," Fuel, Volume 47, pp. 397-402, September, 1968.

80. Sliney, Harold E., Strom, Thomas N., Allen, Gordon, P., "Fluoride Solid Lubricants for Extreme Temperatures and Corrosive Environments," American Society of Lubrication Engineers, Preprint No. 65 AM 5C5, 1965.

81. "Coatings Help Lubricate Bearings at High Temperatures," Product Engineering, page 152, June 16, 1969.

82. Fusaro, Robert L. and Sliney, Harold E., "Preliminary Investigation of Graphite Fluoride $(CF_x)_n$ As A Solid Lubricant," NASA TN D-5097, NASA Lewis Research Center, Cleveland, Ohio, March, 1969.

REFERENCES (Cont'd)

83. Godfrey, D., "Boundary Lubrication," Interdisciplinary Approach to Friction and Wear, National Aeronautics and Space Adminstration, Washington, D. C., page 353, 1968.

84. Beatty, R. L., "Gas Impregnation of Graphite With Carbon," U. S. Oak Ridge National Laboratory Metals and Ceramics Division Annual Progress Report for period ending June 30, 1969, ORNL-4470, (W-7405-ENG. 26), October, 1969, pp. 195-197.

85. Lewis, H. D., Goldman, A., "Theoretical Small-Particle Statistics: A Summary of techniques for Data Analysis with Recent Developments in Data Comparison, Notation, and Mixture Theory," Los Alamos Scientific Laboratory, LA-3656 (W-7405-ENG. 36), November 8, 1968.

86. Loc cit., Reference 11, pp. 8-13.

87. Loc cit., Reference 85.

88. Loc cit., Reference 86.

89. Froberg, Robert W., "Development of Improved Bulk Polycrystalline Graphite for Re-entry Vehicle Componentry," Technical Report SCC-TR-69-100, Contract No. F33615-69-C-1786, August, 1969.

90. Mantell, Charles L., Carbon and Graphite Handbook, Interscience Publishers, New York, page 450, C 1968.

BIBLIOGRAPHY

Bradstreet, S. W. "Graphite Technology," Armour Research Foundation, AF 33(616)-5185, Proj. G-033, Progress Report No. 5, December 1, 1957 to February 1, 1958).

Brown, A. R. G. and Watt, W., "The Preparation and Properties of High-Temperature Pyrolytic Carbon," Industrial Carbon and Graphite. Papers read at the Conference held in London on September 24-26, 1957, Society of Chemical Industry, London, pp. 86-100, 1958.

Carson, Robert W., "Selecting High-Temperature Sleeve Bearings," Product Engineering, Vol. 36, pp. 76-82, January 4, 1965.

Ewbank, W. J. "Dynamic Seals - A Review of the Recent Literature," ASME Paper 67-WA/LUB-24 (1967); Paper presented at ASME Winter Annual Meeting and Energy Systems Exposition, Pittsburgh, Pa., November 12-17, 1967.

Fischbach, Dr. D. B., "Kinetics of Graphitization of a Petroleum Coke," Nature, Volume 200, pp. 1281-1283, December 28, 1963.

Lindsey, M. H., "Mechanical Seals: Carbon's Key Role," Chemical Engineering, Volume 74, pp. 160-166, February 27, 1967.

Ruhl, Fremont F., Wendt, Arthur B., and Dalenberg, Paul N., "A New Approach to Face Type Sealing," Lubrication Engineering, Volume 23, pp. 241-244, June, 1967.

Schaeffer, W. D., Smith, W. R., Polley, M. H., "Structure and Properties of Carbon Black," Industrial Eng. Chemistry, Vol. 45, No. 8, pp. 1721-1725, August, 1953.

Smith, Morton C., "CMF-13 Research on Carbon and Graphite," Los Alamos Scientific Laboratory, LA-3693 (W-7405-ENG. 36) (Report No. 1) (Summary of Progress to May 1, 1967) (June 1, 1967).

BIBLIOGRAPHY (Cont'd)

Smith, Morton C., "CMF-13 Research on Carbon and Graphite," Los Alamos Scientific Laboratory, LA-4171 (W-7405-ENG. 36) (Report No. 9) (Summary of Progress from February 1 to April 30, 1969) (May 13, 1969)

Swikert, Max A. and Johnson, Robert L., "Wear of Carbon-Type Seal Materials with Varied Graphite Content," ASLE Trans., Volume 1, pp. 115-120, 1958.

Yamada, Shigehiko, "Actual Circumstances as to the Application of Glassy Carbon," American Carbon Commission. Carbon Conference, 8th 1967, Abstr. No. P-79.