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DEVELOPMENT OF SEAL RING CARBON-GRAPHITE MATERIALS (TASKS V, VI, and VII)

by

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16. Abstract

Carbon-graphite seal ring bodies for operation at air temperatures to 1300°F (704°C) were manufactured from three select formulations. Selection was based on the results of screening studies and an analysis of prior work. Mechanical and thermal properties, porosities, and oxidation rates were measured. The results have shown:

1. Major property improvements anticipated from the screening studies were not realized because of processing problems associated with the scale-up in material size and probable deterioration of a phenolic resin binder.

2. The mechanical properties of a phenolic resin-bonded, carbon-graphite material can be improved by applying high pressure during carbonization.

3. The textile form of graphite fiber used as the minor filler component in a carbon-graphite material can beneficially affect mechanical properties.

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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. Leonard W. Schopen, NASA-Lewis Research Center, was the Contracting Officer.

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SECTION I

SUMMARY

The purpose of this Contract is to develop a carbon-graphite seal ring material which will have significantly greater life than conventional carbon-graphite seal materials at ambient air temperature up to 1300°F (704°C). The carbon-graphite material is being developed for use in a self-acting seal in advanced gas turbine engines. Although high oxidation resistance is the primary requirement of the materials being developed, high strength and good wear resistance are also needed. Good wear resistance is necessary, since self-acting seals experience relatively high speed sliding contact during limited periods of operation. High thermal conductivity also is a very desirable property for the carbon-graphite seal material, since it will provide rapid dissipation of the frictional heat generated during periods of sliding contact.

Topical Reports NASA CR-72799 (Tasks I and II) and NASA CR-72986 (Tasks III and IV) cover the earlier work done under this program. Tasks I and II included the selection of four base material systems from a total of 12 which were derived from a literature survey and bench-scale tests. Task III covered the fabrication of seal rings made from seven carbon-graphite materials whose final heat-treatment temperature was 2800°C: the four formulations selected above plus resin-impregnated versions of three of the four formulations. Four of the formulations were selected for property and performance evaluation which was performed in Task IV. Three of the materials had oxidation resistance, thermal conductivity, and thermal expansion superior to that of a widely used commercial grade. Strength and hardness were low but could be satisfactory for the self-acting seal.

This Topical Report covers Tasks V, VI, and VII of the program. Task V efforts were directed at improving the strength, mechanical erosion resistance (hardness) and uniformity of the best materials from Task IV, while maintaining oxidation resistance. Eight material/process systems were studied of which three were selected for manufacture of seal rings under Task VI. Selected properties of the three materials were determined under Task VII and samples were delivered to NASA-Lewis Research Center for evaluation.

The Task V screening studies covered various resin impregnants and baking techniques. Graphite fibers were investigated as a minor filler component in a carbon-graphite seal ring material. The following conclusions were drawn:

a. Bakelite BRP-5095 phenolic resin-furfuryl alcohol appears to be a more suitable resin impregnant than the Bakelite BRP-5095 resin-acetone solution used during Task III.

b. Pressure baking improved the mechanical properties of a resin-bonded, carbon-graphite material.

c. The density and hardness of a resin-bonded material containing fibers as its minor filler component can be increased by substituting Union Carbide Corporation (UCC) Grade WFA graphite fibers for those prepared from UCC Grade WCA graphite cloth.

For Task VI, three formulations listed below were selected for the manufacture of improved carbon-graphite seal ring bodies. Particulate raw materials included UCC Grade CHP artificial graphite, UCC Grade WFA graphite fibers, and Commercial Solvents Corporation Thermax furnace black.

Formulation	Filler Material	Binder Material
No. 1Y	CHP Artificial Graphite (80 pbw) Thermax (20 pbw)	Barret No. Medium Pitch (60 pph)
No. 5Y	CHP Artificial Graphite (80 pbw) Thermax (20 pbw)	Bakelite BRP-5095 Resin (58 pph)
No. 6Y	CHP Artificial Graphite (80 pbw) WFA Graphite Fibers (20 pbw)	Bakelite BRP-5095 Resin (70 pph)

Compacts baked to 1000°C were impregnated with BRP-5095 resin (35 pbw)-furfuryl alcohol (50 pbw) before heat-treatment at 2800°C.

pbw = parts by weight

pph = parts (by weight) per hundred parts filler

Several major processing problems resulted from the use of the furfuryl alcohol-Bakelite BRP-5095 resin-impregnant. The impregnant filled the open porosity of the large 1000°C baked compacts so completely that some of them cracked during rebaking as the volatiles from the resin-impregnant tried to escape. This problem prevented the manufacture of the formulation No. 1Y and some of the formulation No. 6Y compacts. Formulation No. 1Z was substituted for formulation No. 1Y. The resin impregnation for formulation No. 1Z was applied to 2800°C baked compacts of the base material and was followed by a very slow rebaking schedule.

Processing problems also were encountered during the attempt to manufacture seal ring bodies from formulation No. 5Y. The formulation No. 5 compacts were prepared from one-year-old mix remaining from one of the Task III formulations. The BRB-5095 resin binder in the mix apparently had deteriorated, causing most of the formulation No. 5 compacts to crack and laminate during baking to 1000°C. The deterioration of the old mix was first noted during the Task V screening studies of baking techniques. Only a few seal ring bodies of formulation No. 5 were successfully manufactured during Task VI. None of the compacts were resin-impregnated prior to final heat-treatment at 2800°C.

Before testing, some of the formulations were given the No. 121 oxidation inhibiting treat. The formulation No. 1Z-121 material had comparable mechanical and thermal properties and was at least as oxidation resistant as a similar material manufactured during Task III. Formulation No. 6Y-121 material had comparable mechanical properties and oxidation resistance along with a higher thermal conductivity and a lower coefficient of thermal expansion than those of a similar material manufactured during Task III. These improvements indicate that the materials manufactured from formulations Nos. 1Z-121 and 6Y-121 may be better suited for use as rings for self-acting seals than the similar materials manufactured during Task III.

SECTION II

INTRODUCTION

Introduction of the gas turbine 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. Operating conditions will become more severe as gas temperatures and seal sliding speeds increase. Increased temperatures result from the higher flight speeds or higher gas temperatures used to improve engine efficiency; increased seal sliding speeds result from the use 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 (86 N/cm^2) sealed pressure differential, 350-ft/sec. (107 meter/sec.) sliding speed, and 800°F (427°C) sealed gas temperature.(1)* 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 resulted in the production of a face seal with self-acting lift augmentation. Since this seal operates without rubbing contact (except at start and stop), 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.(2) 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 may occur because of the close dimensional tolerances associated with the thin gas films.(3) 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.

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* Denotes Reference Number

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.(4) Increased oxidation resistance will become a major requirement of carbon-graphite seal rings as engine gas temperatures rise to 1200°F (649°C) and above. Development of improved carbon-graphite seal ring materials which can operate in ambient air temperatures up to 1300°F (704°C) 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 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.

Topical Report NASA CR-72799(5) covered the work done during Tasks I and II of this Contract. Task I included a literature search for information relevant to carbon-graphite materials for high-temperature seal ring applications. Task I also provided for selection of four particulate and four binder raw materials for experimental studies and for the selection, preparation, and screen testing of 12 material systems. Forty-seven material/process subsystems were produced and evaluated to optimize the selected 12 material systems. Small compacts measuring 2.5 inch x 1.25 inch x 1.0 inch (6.35 cm x 3.18 cm x 2.54 cm) were prepared from the 12 optimized material systems and used for all the screen studies conducted during Task I. The screen testing of the compacts of the 12 optimized material systems consisted of measuring their bulk densities, flexural strengths, and hardnesses at room temperature and their oxidation rates in air at 1300°F (704°C).

The experience gained during Task I was used to select four approaches to the manufacture of seal ring carbon-graphite bodies during Task II. Tests indicated that the compacts prepared during the screen testing were significantly more oxidation resistant than commercial seal ring Grade CDJ. Since 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.

Topical Report NASA CR-72986(6) covered the work done during Tasks III and IV of this Contract. Task III included the manufacture of carbon-graphite seal ring bodies from the four formulations selected during Task II. The number, size, and shape of these bodies were determined by the delivery requirements of Task III and the testing requirements of Task IV. Seven materials were ultimately produced during Task III: the selected four formulations and a second version for three of those formulations in which the 1000°C baked compacts were impregnated with a phenolic resin prior to final heat treatment at 2800°C. During Task IV, four of the seven materials manufactured under Task III were selected and their material properties determined. The selection was based on the preliminary mechanical property measurements made on all seven materials.

This Topical Report covers Tasks V, VI, and VII of the Contract. The scope of work for Task V consisted of the screen testing of up to eight material/process systems or subsystems for the purpose of optimizing the particulate systems, binder concentrations, carbonizable impregnants, and processing techniques studied during Tasks I through IV. The experience gained during the Task V screening studies was used to select three approaches to the manufacture of seal ring carbon-graphite bodies with improved properties. Seal ring bodies were manufactured during Task VI, but processing problems necessitated some modification of the formulations. Selected material properties were determined for the manufactured materials during Task VII.

SECTION III

CONCLUSIONS

1. Improvements in mechanical properties anticipated from the screening studies were not realized because of processing problems encountered during scale-up in material size. Problems included rupture and chipping of compacts during pyrolysis of a furfuryl alcohol-phenolic resin-impregnant and lamination during baking of compacts bonded with a phenolic resin.

2. Pressure curing and pressure baking of a phenolic resin-bonded carbon-graphite material effects improved mechanical properties.

3. A phenolic resin-bonded, carbon-graphite material prepared with chopped graphite yarn has better mechanical and thermal properties than a similar material prepared with chopped graphite cloth.

4. The materials manufactured from formulations Nos. 1Z (pitch binder) and 6Y (phenolic resin binder) show potential as useful primary rings for self-acting seals. Both formulations incorporate artificial graphite as the major filler component (80 weight percent); the former contains furnace black and the latter chopped graphite yarn as the minor filler component (20 weight percent). A furfuryl alcohol-phenolic resin impregnant is introduced prior to final heat-treatment at 2800° C.

SECTION IV

SCREENING STUDIES AND SEAL RING CARBON-GRAPHITE MATERIAL FORMULATION (TASK V)

A. Screening Studies

The carbon-graphite seal ring materials developed during Tasks I through IV(5,6) of this Contract (Table I) have oxidation resistance several times greater than that of a widely used commercial grade, but their flexural strengths are 40 to 50 percent lower than that of the commercial grade. These oxidation resistant carbon-graphite materials were developed for use as self-acting seal rings. Since self-acting seals normally employ metal-retaining bands, the strengths of these materials were judged acceptable. Erosion resistance may also be an important requirement for self-acting seal materials. Debris passing through the gas film formed between the sealing dam and the seat is responsible for the erosion of the seal face. Increases in strength would mitigate the necessity of metal-retaining bands and increases in hardness would improve erosion resistance. These improvements would enable broader application of the carbon-graphite seal ring materials. The purpose of this phase of the Contract was thus to improve the uniformity, strength, and hardness of the materials manufactured during Task III(6) while maintaining or improving their oxidation resistance. Included in the new effort was a review and analysis of the previous Contract work and a screening study to optimize the particulate systems, binder concentrations, carbonizable impregnants, and processing techniques studied during Tasks I through IV.(5,6)

The Task V screening study consisted of three parts. A study of various resin impregnants and baking techniques comprised the first two parts. The third part consisted of the manufacture and characterization of five material subsystems aimed at improving the uniformity and properties of the formulation No. 4 material. The composition of the formulation No. 4 material, along with those of the other materials produced during Task III,(6) is displayed in Table I. All the materials presented in Table I were manufactured from particulate and binder raw materials that had been characterized during Task I.(5) The results for the characterization of the raw materials also are included in this section of the report. Descriptions of the test procedures used to characterize the raw materials are presented in Appendix I.

TABLE I

Material Formulations Developed Under Tasks I Through IV

	Base Material			Impregnants	
Formulation No.	Particulate Solid Raw Material	Additive	Binder Raw Material	Resin Impregnant*	Oxidation Inhibiting Treatment**
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)	----	----
1X	Formulation No. 1 Base Material			Bakelite BRP-5095 Phenolic Resin	----
2X	Formulation No. 2 Base Material			Bakelite BRP-5095 Phenolic Resin	----
4X	Formulation No. 4 Base Material			Bakelite BRP-5095 Phenolic Resin	----
1X-121	Formulation No. 1 Base Material			Bakelite BRP-5095 Phenolic Resin	No. 121 Treatment
2X-121	Formulation No. 2 Base Material			Bakelite BRP-5095 Phenolic Resin	No. 121 Treatment
3 -121	Formulation No. 3 Base Material			----	No. 121 Treatment
4X-121	Formulation No. 4 Base Material			Bakelite BRP-5095 Phenolic Resin	No. 121 Treatment

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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.

* Dissolve resin in an equal weight of acetone, impregnate 1000°C baked compacts, pressure cure at 150°C, rebake to 1000°C, and final bake to 2800°C.

** Impregnate with oxidation inhibiting treatment after desired configuration has been finish machined from 2800°C baked stock.

Some of the carbon-graphite materials produced during the Task V screening study employed two particulate raw materials which had previously not been used during the Contract work. The two new raw materials were Grade VFA carbon fibers and Grade WFA graphite fibers. Both types of fibers are produced by pyrolyzing continuous filament rayon yarn which is subsequently chopped to the desired lengths. The fibers previously used for the Contract work were prepared from Grade WCA graphite cloth which is produced by the pyrolysis of rayon cloth. Although the two new types of fibers were not characterized during Task V, some of their properties were obtained from "Union Carbide Corporation Technical Information Bulletin No. 465-213 cj." The brochure lists a density (water immersion) of 1. 8 g/cc and a weight percent ash of 0. 8 for the Grade VFA carbon fibers. Grade WFA graphite fibers are reported to have a density (water immersion) of 1. 4 g/cc, a surface area of $2m^2/g$, and a weight percent ash of 0. 01.

1. Union Carbide Corporation Grade 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. Commercial Solvents Corporation Thermax Furnace 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

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

3. Lockheed Company LMSC Glassy Carbon (Ground)

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	

---

* A prolonged period was required for the Beckman pycnometer to reach equilibrium conditions and, therefore, the results are questionable.

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

4. Union Carbide Corporation Grade WCA Graphite Cloth

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

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* A prolonged period was required for the Beckman pycnometer to reach equilibrium conditions and, therefore, the results are questionable.

5. 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**

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

$$\frac{\text{2800°C Heat-Treated Volume}}{\text{Green Volume}} = 0.843$$

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* 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.

6. 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**

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

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

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* 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.

1. Study of Resin-Impregnants

Carbonization of a resin-impregnant was found during Task III(6) to significantly improve the strength, hardness, and modulus of a carbon-graphite material. The resin-impregnant used during Task III(6) was a solution of Bakelite BRP-5095 resin (50 pbw [parts by weight]) and acetone (50 pbw). After the compacts were baked to 1000°C, they were impregnated with the resin solution by using a vacuum-pressure technique. The resin-impregnated compacts were subsequently pressure-cured at 150°C and rebaked to 1000°C prior to final baking to 2800°C.

A screening study of various resin-impregnants was conducted during Task V to find a more suitable resin-impregnant than that used during Task III.(6) The principal objective of this investigation was to find a liquid resin to replace the acetone as the vehicle for dissolving the Bakelite BRP-5095 resin. A liquid resin would contribute to the coking value of the resin-impregnant, whereas, the acetone contributes nothing, since it is completely driven off during curing. The investigation was begun by determining the solubility of the Bakelite resin in various liquid resins. Varcum 8251 (partially polymerized furfuryl alcohol) was found to be a poor resin for dissolving the Bakelite resin. Only 25 pbw of the Bakelite resin could be dissolved in 50 pbw of the Varcum 8251 resin, and the resultant solution was too viscous to be used as an impregnant. Furfuryl alcohol monomer was found to be better than the Varcum 8251 resin. A solution suitable for use as an impregnant was obtained by dissolving 35 pbw of the Bakelite resin in 50 pbw of the furfuryl alcohol. A second solution suitable for use as an impregnant was prepared by dissolving 50 pbw of the Bakelite resin in 50 pbw of furfural.

The second portion of the resin-impregnation study consisted of impregnating small (4-inch x 1/2-inch x 1/4-inch [10.2 cm x 1.3 cm x 0.6 cm]) 1000°C baked samples of the formulation No. 1 material (Table I). Three resin-impregnants were investigated: the two in which furfuryl alcohol and furfural were used to dissolve the Bakelite BRP-5095 resin and a third consisting of Varcum 8251 (98 pbw) and oxalic acid (2 pbw). The formulation No. 1 samples were vacuum evacuated, impregnated, pressure-cured to 150°C or pressure-baked to 550°C, and rebaked to 1000°C. The results of the resin-impregnation studies are displayed in Table II. After the samples were rebaked to 1000°C, the measured increases in weight ranged between 4.5 and 6.5 percent for the three types of resin-impregnated materials. These increases in weight resulted in improvements of 26 to 45 percent in the 1000°C baked flexural strengths. The Bakelite BRP-5095 resin (50 pbw) and acetone (50 pbw) solution used during Task III(6) effected only a 1.6 percent increase in the weight of the formulation No. 1 material after it was rebaked to 1000°C. The higher yields of residual carbon from the three resin impregnants thus produced greater improvements in physical properties than did the Bakelite resin-acetone solution used during Task III.(6) Although these improvements were determined for 1000°C baked material, they were expected to carry over to the 2800°C baked material as well.

The goal of this investigation was to find a resin impregnant which would effect large improvements in the strength, hardness, and modulus of a carbon-graphite material. Of the resin impregnants studied, the one consisting of furfuryl alcohol (50 pbw) and Bakelite BRP-5095 resin (35 pbw) appeared to be the best for fulfilling this goal. This investigation also showed that pressure-curing a resin impregnant to 150°C produced the same strength and hardness as that obtained by pressure baking to 550°C. This observation was made for the formulation No. 1 samples impregnated with the furfural (50 pbw)-Bakelite BRP-5095 resin (50 pbw) solution (Table II).

2. Study of Baking Techniques

Pressure curing and pressure baking were two techniques investigated to improve the properties of the materials developed under Tasks I through IV.(5,6) The baking of a pitch-bonded, carbon-graphite body while subjecting it to a mechanical constraint at elevated pressure exerted by an inert gas has been shown to result in an improvement in mechanical properties.(7) The improvements are due in part to an increased coke yield from the pitch binder phase.

TABLE II

Mechanical Properties - Resin-Impregnated Materials

	1000°C Baked Density (g/cc)	Flexural (psi)	Strength (N/cm^2)	Rockwell R_s	Hardness R_m
Formulation No. 1-No Impregnant					
Maximum	1.657	5430	3740	97	61
Minimum	1.650	4880	3360	94	55
Average	1.653	5170	3560	96	59
Standard Deviation	0.003	231	159	1	2
n	4	4	4	8	8
Formulation No.1-Impregnated With Varcum 8251 (98 pbw) + Oxalic Acid (2 pbw)-Pressure Cured Prior to Baking to 1000°C					
Maximum	1.750	7350	5060	118	99
Minimum	1.722	6150	4240	116	94
Average	1.742	6750	4650	117	96
Standard Deviation	0.013	556	383	1	2
n	4	4	4	8	8
Formulation No. 1-Impregnated With Furfuryl Alcohol (50 pbw) + Bakelite BRP-5095 (35 pbw)-Pressure Cured Prior to Baking to 1000°C					
Maximum	1.748	7890	5440	116	96
Minimum	1.740	7160	4930	108	88
Average	1.744	7500	5170	114	95
Standard Deviation	0.004	301	207	3	3
n	4	4	4	8	8
Formulation No. 1-Impregnated With Furfural (50 pbw) + Bakelite BRP-5095 (50 pbw)-Pressure Cured to 150°C Prior to Baking to 1000°C					
Maximum	1.759	7050	4860	118	98
Minimum	1.754	6080	4190	116	96
Average	1.757	6510	4490	117	97
Standard Deviation	0.002	411	283	1	1
n	4	4	4	8	8
Formulation No. 1-Impregnated With Furfural (50 pbw) + Bakelite BRP-5095 (50 pbw)-Pressure Baked to 550°C Prior to Baking to 1000°C					
Maximum	1.767	7250	5000	118	99
Minimum	1.763	5740	3950	116	96
Average	1.765	6510	4490	117	98
Standard Deviation	0.002	641	442	1	1
n	4	4	4	8	8

Note: Density, flexural strength, and hardness measured on 1/4" x 1/2" x 4" (0.6 cm x 1.3 cm x 10.2 cm) samples. Flexural samples broken on 1.875" (4.76 cm) span.

R_s Scale = 1/2" (1.3 cm) Diameter ball and 100 Kg Maj. load. Two readings per sample.

R_m Scale = 1/4" (0.6 cm) Diameter ball and 100 Kg Maj. Load. Two readings per sample.

Pressure-curing done using 100 psig Air. While under pressure, temperature maintained for 1 hour at 125°C and 1 hour at 150°C.

During pressure-baking, temperature rushed to 150°C, followed by a 10°C/hour rate between 150°C and 550°C. Temperature held 4 hours at 550°C.

During the Task V baking studies, the one-year-old resin-bonded formulation No. 3 mix (Table I) remaining from Task III(6) was used. Twelve green compacts measuring 2.5-inch x 1.25-inch x 1.0-inch (6.35 cm x 3.18 cm x 2.54 cm) were molded from the formulation No. 3 mix. The compacts were molded to a green bulk density range of 1.400 to 1.415 g/cc, a range which had been determined during Task III(6) to be the optimum molding condition for the formulation No. 3 material. Four of the green compacts subsequently were pressure-cured at 150°C and four were pressure-baked to 550°C. These eight compacts and the remaining four green compacts were then baked to 1000°C by employing the standard packing procedure and baking schedule (10°C/hr) used to bake the formulation No. 3 material during Task III.(6) The twelve compacts were not baked to 2800°C but, instead, were analyzed after they had been baked to 1000°C.

The mechanical properties of the three variations of the formulation No. 3 material are displayed in Table III. The results show that both the pressure-curing and pressure-baking techniques yielded improved mechanical properties. Incorporation of the two techniques into the processing of the formulation No. 3 material resulted in increased coke yields and greater shrinkage during baking, both of which contributed to the improvements in mechanical properties. However, the pressure baking to 550°C prior to baking to 1000°C resulted in the greater improvement.

The results presented in Table III do show the benefits of employing pressure baking, but the 1000°C baked density listed for the formulation No. 3 standards was much lower than that (1.519 g/cc) measured for the same material during Task III.(6) The reduction in baked density indicated that the resin in the formulation No. 3 mix may have deteriorated during the one-year period between mix manufacture (Task III(6)) and the Task V work.

TABLE III

Mechanical Properties-Pressure Cured and Baked Formulation No. 3 Material

	Green Density (g/cc)	Pressure Cured* Density (g/cc)	Pressure Baked** Density (g/cc)	1000°C Baked Density (g/cc)	Flexural (psi)	Strength (N/cm^2)	Rockwell "S" Hardness
Formulation No. 3-Green Compacts Baked to 1000°C.							
Maximum	1.410	-----	-----	1.431	3320	2290	62
Minimum	1.405	-----	-----	1.421	2820	1940	58
Average	1.408	-----	-----	1.427	3150	2170	60
Standard Deviation	0.002	-----	-----	0.004	231	159	2
n	4	-----	-----	4	4	4	12
Formulation No. 3-Green Compacts Pressure Cured to 150°C Prior to Baking to 1000°C.							
Maximum	1.412	1.413	-----	1.500	4900	3380	76
Minimum	1.401	1.406	-----	1.489	3040	2090	67
Average	1.407	1.410	-----	1.493	4020	2770	72
Standard Deviation	0.005	0.003	-----	0.005	784	540	3
n	4	4	-----	4	4	4	12
Formulation No. 3-Green Compacts Pressure Baked to 550°C Prior to Baking to 1000°C							
Maximum	1.407	-----	1.496	1.554	5120	3530	90
Minimum	1.403	-----	1.468	1.531	3890	2680	83
Average	1.406	-----	1.477	1.539	4770	3290	87
Standard Deviation	0.002	-----	0.013	0.010	594	409	2
n	4	-----	4	4	4	4	12

Note: Densities Calculated From Physical Dimensions and Weights Measured for Compacts.
Flexural Strengths Measured Using 0.200" x 0.200" x 2.0" (0.51cm x 0.51cm x 5.1cm) Samples.
Flexural Samples Broken on a 0.950" (2.41cm) Span.
R_s Scale = 1/2"(1.3cm) Diameter Ball and 100Kg Maj. Load. Six Readings were Taken on Each of Two Samples.

* Pressure Curing Done Using 100 psig Air. While Under Pressure, Temperature Maintained for 1 Hour at 125°C and 1 Hour at 150°C.

** During Pressure Baking Temperature Rushed to 150°C, Followed by a 10°C/Hour Rate Between 150°C and 550°C. Temperature Held 4 Hours at 550°C.

The pressure baking (550°C) analysis discussed thus far involved the use of the small samples of the formulation No. 3 material. No problems were encountered when pressure-baking the small samples. Problems occurred during the initial pressure-baking trials with large compacts of the formulation No. 3 material. Several of the 5-inch (12.7 cm) diameter greenplugs and the large green ring blanks molded from the formulation No. 3 mix during Task III(6) were pressure-baked to 550°C during Task V. All the large compacts were found to have cracked and/or laminated during pressure-baking, and they all possessed a pungent odor characteristic of ammonia. Ammonia is one of the compounds formed when the hexamethylene-tetramine ("hexa") hardening agent reacts with the thermoplastic novolac of the first stage of the Bakelite BRP-5095 resin binder raw material. Apparently, the products of reaction were given off suddenly during pressure-baking, resulting in cracking and laminating of the compacts. The large compacts of the formulation No. 3 material could be successfully pressure-baked to 550°C if they were first pressure-cured at 150°C for several hours. The pressure-curing partially decomposes the "hexa" and allows the reaction by-products to be evolved without disrupting the internal structure of the molded material.

The formulation No. 3 material had the lowest oxidation rate of the carbon-graphite materials characterized during Task IV,(6) but its mechanical properties and related wear resistance were rather poor. The results of the Task V study of baking techniques indicated that the pressure-baking might be used to improve the properties of the formulation No. 3 material in spite of the apparent resin deterioration. Incorporation of pressure-baking into the processing of the formulation No. 3 material would increase the coke yield and shrinkage of the material during baking, thus producing an improvement in mechanical properties and a reduction in total open porosity. Increased oxidation resistance should result from the reduction in total open porosity.

3. Material Subsystem Study

The compositions of the five material subsystems analyzed during Task V are listed in Table IV. The five materials were processed in an attempt to optimize the composition of the formulation No. 4 base material (Table I). Specifically, changes in the minor filler component and binder concentration were investigated which could yield improvements in the uniformity, strength, hardness, and oxidation resistance of the resultant material.

All five material subsystems were similar to formulation No. 4 in that they included some form of fiber as a minor filler component. Grade WFA graphite fibers chopped from yarn were used in subsystems SS-47, SS-48, SS-49, and SS-51 rather than the fibers prepared from Grade WCA graphite cloth. The latter type of fiber was used as the minor filler component in the formulation No. 4 material. Subsystem SS-50 incorporated Grade VFA chopped carbon fibers as the minor filler component. The individual Grade VFA and WFA fiber filaments were approximately 1/4-inch (0. 64 cm) long prior to milling. Subsystems SS-47 to SS-51 were all bonded with Bakelite BRP-5095 resin.

Small green compacts measuring 2. 5-inch x 1. 25-inch x 1. 0-inch (6. 35 cm x 3. 18 cm x 2. 54 cm) were molded from the mixes manufactured from subsystems SS-47 to SS-51. After the compacts were baked to 1000°C, their bulk densities were measured and their internal structures examined. The 1000°C baked compacts of subsystems SS-48, SS-49, and SS-51 were all found to be extremely porous, apparently due to an outgassing problem. This same outgassing problem had been noted during Task I,(8) but was remedied at that time by revising the baking schedule. The binder levels of subsystems SS-48, SS-49, and SS-51 were apparently too high for the respective particulate filler systems, since the revised baking schedule did not prevent the outgassing problem. Based on the analysis of the 1000°C baked compacts, molding pressures of 15,000 psi (10, 340 N/cm^2) and 10, 000 psi (6890 N/cm^2) were selected as the optimum molding conditions for the SS-47 and SS-50 materials, respectively. The compacts molded at these pressures were subsequently final baked to 2800°C.

TABLE IV

Identification of Material Subsystems SS-47 to SS-51

Material Subsystem	Filler Material	Binder Material	Binder Level	Molding Pressure (psi)	Molding Temp.	1000°C Bake Rate
SS-47	80 pbw CHP-20 pbw WFA	Bakelite BRP-5095	67.5 pph	10,000 to 35,000	R.T.	Rush to 150°C 10°C/Hr to 1000°C
SS-48	"	"	80 pph	"	"	"
SS-49	80 pbw CHP-20 pbw WFA-5 pbw B_4C	"	"	"	"	"
SS-50	80 pbw CHP-20 pbw VFA	"	"	"	"	"
SS-51	80 pbw CHP-10 pbw WFA-10 pbw Thermax	"	67.5 pph	"	"	"

Note: All Materials Baked to Final Temperature of 2800°C.
pbw - Parts by Weight.
pph - Parts (Weight) Binder per Hundred Parts (Weight) Filler.

Table V displays the mechanical properties measured for the small, 2800°C baked compacts of subsystems SS-47 and SS-50 (the properties measured for small compacts of formulation No. 4 have been included for comparison). The SS-47 material was found to shrink more than the formulation No. 4 material during baking. The total porosity of the SS-47 material was 17.6 percent compared with 22.1 percent for the formulation No. 4 material. (The procedure for calculating the percent total porosity of a material is explained in Section VI-D of this report.) The SS-47 material also had a higher 2800°C baked bulk density and hardness, and the properties were more uniform than those of the formulation No. 4 material. The mechanical properties of the SS-50 material, which contained Grade VFA carbon fibers, were not so uniform nor quite so good as those of the SS-47 material.

Table VI presents the 1300°F (704°C) oxidation test results generated when untreated samples of materials SS-47, SS-50, formulation No. 4, and commercial Grade CDJ were examined. The oxidation test procedure was the same as that used during Tasks I and IV.(9,10) Due to the required rebuilding of the furnace used for oxidation testing,(11) it would be misleading to compare the Task I oxidation test results with those displayed in Table VI. The oxidation rate determined for the SS-47 material was the same as that measured for the formulation No. 4 material. Since Grade VFA carbon fibers are not so crystalline as Grade WFA graphite fibers, they should not be so oxidation resistant. Therefore, the lower oxidation rate determined for the SS-50 material probably can be attributed to the higher binder level (80 pph) of the material rather than the use of Grade VFA carbon fibers.

The purpose of the Task V subsystem study was to produce a formulation No. 4 type material with improved and more uniform material properties. The SS-47 material was found to be the best one for fulfilling the goal of the subsystem study. Although no further improvement in oxidation resistance was achieved, subsystem SS-47 resulted in a material with more uniform and slightly better mechanical properties than those of the formulation No. 4 material.

TABLE V

Mechanical Properties - SS-47, SS-50, and Formulation No. 4 Materials

	Material					
	SS-47		SS-50		Formulation No. 4	
Bulk Density*						
Green Density (g/cc)						
Maximum	1.445		1.343		1.431	
Minimum	1.442		1.334		1.426	
Average	1.444		1.338		1.428	
Standard Deviation	0.002		0.005		0.002	
n	3		3		3	
1000°C Density (g/cc)						
Maximum	1.442		1.352		1.364	
Minimum	1.428		1.330		1.345	
Average	1.434		1.343		1.356	
Standard Deviation	0.007		0.012		0.007	
n	3		3		3	
2800°C Density (g/cc)						
Maximum	1.494		1.489		1.437	
Minimum	1.485		1.449		1.416	
Average	1.490		1.472		1.428	
Standard Deviation	0.005		0.021		0.008	
n	3		3		3	
Flexural Strength**	(psi)	(N/cm²)	(psi)	(N/cm²)	(psi)	(N/cm²)
Maximum	4610	3180	4480	3090	4590	3160
Minimum	4080	2810	3390	2340	3680	2540
Average	4270	2940	3860	2660	4020	2770
Standard Deviation	199	137	392	270	325	224
n	6	6	6	6	6	6
Rockwell "S" Hardness***						
Maximum	51		39		38	
Minimum	43		21		23	
Average	49		32		32	
Standard Deviation	3		7		6	
n	8		8		8	

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* Calculated from physical dimensions and weights measured for compacts.

** Measured using 0.200"x0.200"x2.00"(0.51cm x 0.51 cm x 5.1 cm) samples. Flexural samples broken on 0.950" (2.41 cm) span.

*** R_s Scale 1/2" (1.3cm) diameter ball and 100 Kg Maj. load. Four readings on two samples of each material.

TABLE VI

Oxidation Test Results

Material	Average Cumulative Percent Weight Loss					
	1/2 Hr	1 Hr	1-1/2 Hr	2 Hr	2-1/2 Hr	3 Hr
SS-47*	5.47	14.25	23.15	35.42	45.84	53.14
SS-50*	3.02	7.56	12.45	19.63	28.46	34.33
Formulation No. 4**	7.99	18.20	26.58	36.56	45.22	53.06
CDJ**	8.84	26.33	43.16	59.40	72.17	80.70

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* Three untreated samples tested.

** Two untreated samples tested.

Sample size 1/2" x 1/2" x 1/2" (1.3cm x 1.3cm x 1.3cm).

Oxidation temperature 1300°F (704°C).

B. Seal Ring Carbon-Graphite Material Formulation

At the conclusion of the Task V screening studies, three approaches were selected for the manufacture of seal ring carbon-graphite bodies. The selection of the three material formulations, which included the required processing techniques, was based on the results of the Task V screening studies and review of the work done under Tasks I through IV.(5, 6) The three selected formulations represented the most promising approaches for improving the uniformity, strength, and oxidation resistance of the seal ring materials manufactured during Task III.(6) Two of the formulations were to be manufactured by using in-process material remaining from Task III.(6) Table VII displays the compositions of the selected three material formulations.

TABLE VII

Material Formulations Nos. 1Y, 5Y, and 6Y

Formulation Number	Particulate Solid Raw Material	Binder Raw Material	Resin Impregnant	Baking Procedure
1Y	CHP Artificial Graphite (80 pbw) Thermax (20 pbw)	No. 30 Medium Pitch (60 pph)	Furfuryl Alcohol (50 pbw) Bakelite BRP-5095 Resin (35 pbw)	Bake Green Compacts to 1000°C. Impregnate Compacts with Resin-Solution, Pressure Cure at 150°C, and Rebake to 1000°C. Final Bake to 2800°C.
5Y	CHP Artificial Graphite (80 pbw) Thermax (20 pbw)	Bakelite BRP-5095 Resin (58 pph)	Furfuryl Alcohol (50 pbw) Bakelite BRP-5095 Resin (35 pbw)	Pressure Cure Green Compacts at 150°C. Pressure Bake Compacts to 550°C. Bake Compacts to 1000°C. Impregnate Compacts with Resin Solution, Pressure Cure at 150°C, and Rebake to 1000°C. Final Bake to 2800°C.
6Y	CHP Artificial Graphite (80 pbw) WFA Graphite Fibers (20 pbw)	Bakelite BRP-5095 Resin (70 pph)	Furfuryl Alcohol (50 pbw) Bakelite BRP-5095 Resin (35 pbw)	Same as that used for Formulation No. 5Y.

Note: Proportions are parts by weight (pbw)

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

Formulation No. 1Y is the same as formulation No. 1X (Table I) except for the resin impregnant. The letter "Y" following the formulation number was used to denote impregnation of the 1000°C baked compacts with a solution consisting of furfuryl alcohol (50 pbw) and Bakelite BRP-5095 resin (35 pbw). The resin impregnant was found to be the best of those studied during Task V for producing significant improvements in the density, strength, and hardness of the formulation No. 1 base material. Impregnation of the formulation No. 1 base material with the furfuryl alcohol - Bakelite resin solution yielded considerably more residual carbon after baking to 1000°C than that obtained when the same material was impregnated with the Bakelite BRP-5095 resin (50 pbw)-acetone (50 pbw) solution during Task III.(6) The formulation No. 1X material, which was impregnated with the Bakelite resin-acetone solution, was felt to be the best material of those characterized during Task IV(6) for meeting the requirements of a self-acting seal material. Due to the higher residual carbon yield resulting from the use of the new resin impregnant, the formulation No. 1Y material was expected to be a significant improvement over the formulation No. 1X material. The formulation No. 1Y material was to be manufactured from the formulation No. 1 mix remaining from Task III.(6)

The formulation No. 5Y material was to be manufactured from the formulation No. 3 mix (Table I) remaining from Task III.(6) As mentioned previously in Section IV-A-2, the resin binder in the one-year-old formulation No. 3 mix apparently had degraded during the time between manufacture of the mix and reuse during the Task V baking studies. Although the "aged" formulation No. 3 mix produced a low-density baked material, the use of the mix in the manufacture of the formulation No. 5Y material was felt to be a valuable addition to the further development of the pressure baking and resin-impregnation techniques. The formulation No. 5 base material was the same as that manufactured from formulation No. 3 with the exception that formulation No. 5 incorporated pressure curing and pressure baking in its processing. Pressure baking was included in the formulation No. 5 processing, since that technique had been found during Task V to yield significant improvements in the mechanical properties of the resin-bonded formulation No. 3 material. Pressure curing was included, since it had been found during Task V to be a required step before pressure baking large compacts. The use of the furfuryl alcohol-Bakelite BRP-5095 resin impregnating solution was to be extended to the processing of the formulation No. 5Y material.

Formulation No. 6Y was similar to formulation No. 4X (Table I) from which material was manufactured during Task III.(6) The formulation No. 6Y material, however, was to be impregnated with the furfuryl alcohol-Bakelite BRP-5095 resin solution rather than the Bakelite BRP-5095 resin-acetone solution used in the processing of the formulation No. 4X material. The use of pressure curing and pressure baking was extended to the processing of the formulation No. 6 base material. Unlike the formulation No. 4 base material which contained a minor filler component (20 pbw) of fibers prepared from Grade WCA graphite cloth, the formulation No. 6 base material included Grade WFA chopped graphite fibers as a minor filler constituent (20 pbw). The Task V subsystem study revealed that the use of Grade WFA fiber results in an increase in the shrinkage of the material during baking. Due to the increase in shrinkage and reduction in porosity, the material (SS-47) containing the Grade WFA graphite fibers had more uniform and slightly better mechanical properties than those of the formulation No. 4 material. Although the formulation No. 6 base material also was to be bonded with Bakelite BRP-5095 resin, its binder level (70 pph) was slightly higher than that of the formulation No. 4 material (67.5 pph). The binder level was increased in an attempt to further improve material properties.

SECTION V

MANUFACTURING OF CARBON-GRAPHITE MATERIALS

(TASK VI)

A. Identification of Materials Manufactured

Carbon-graphite seal ring bodies were to be manufactured during Task VI from material formulations Nos. 1Y, 5Y, and 6Y. Since processing problems were encountered during the manufacture of the three materials, some adjustments in processing had to be made. The processing problems and the required revisions in the processing procedures are discussed in Section V-B with detailed descriptions of the techniques employed to manufacture the carbon-graphite materials during Task VI. The manufacturing problems resulted primarily from the scale-up in the size of the compacts being manufactured. Many of the processing techniques employed during Task VI had been developed during the Task V sceening studies in the preparation of small 2.5-inch x 1.25-inch x 1.0-inch (6.35cm x 3.18cm x 2.54cm) compacts. Although these processing techniques had been used successfully to manufacture the small compacts, they resulted in some problems during Task VI when attempts were made to manufacture considerably larger compacts: 5-inch (12.7 cm) diameter x 1.4-inch (3.6 cm) thick solid plugs and 8.6-inc (21.8 cm) o.d. x 5.8-inch (14.7 cm) i.d. x 1.3-inch (3.3 cm) thick ring blanks. All dimensions listed are for the green compacts.

Table VIII presents the identification of the three basic formulations and their impregnated versions from which carbon-graphite seal ring bodies were manufactured during Task VI. Formulation No. 1Y was replaced by formulation No. 1Z when processing problems prevented the manufacture of the formulation No. 1Y material. Except for the use of the Grade WFA graphite fibers, the carbon-graphite materials produced during Task VI were manufactured from the particulate and binder raw materials characterized during Task I.(5) The results of the Task I(5) characterization tests and some of the properties of the Grade WFA graphite fibers were presented previously in Section IV-A of this report.

TABLE VIII

Identification of the Three Basic Material Formulations and Their Impregnated Versions

	Base Material			Impregnants	
Formulation No.	Particulate Solid Raw Material	Binder Raw Material	Baking Procedure	Resin Impregnant	Oxidation Inhibiting Treatment***
1	CHP Artificial Graphite (80 pbw) Thermax (20 pbw)	No. 30 Medium Pitch (60 pph)	Bake Green Compacts to 1000°C and Final Bake to 2800°C	---	---
5	CHP Artificial Graphite (80 pbw) Thermax (20 pbw)	Bakelite BRP-5095 Resin (58 pph)	Pressure Cure Green Compacts at 150°C, Pressure Bake to 550°C, Bake to 1000°C, and Final Bake to 2800°C	---	---
6	CHP Artificial Graphite (80 pbw) WFA Graphite Fibers (20 pbw)	Bakelite BRP-5095 Resin (70 pph)	Same as that used for Formulation No. 5	---	---
1Z	Formulation No. 1 Base Material			Furfuryl Alcohol (50 pbw) Bakelite BRP-5095 Resin (35 pbw)*	---
6Y	Formulation No. 6 Base Material			Furfuryl Alcohol (50 pbw) Bakelite BRP-5095 Resin (35 pbw)**	---
1Z-121	Formulation No. 1 Base Material			Furfuryl Alcohol (50 pbw) Bakelite BRP-5095 Resin (35 pbw)*	No. 121 Treatment
5-121	Formulation No. 5 Base Material			---	No. 121 Treatment
6Y-121	Formulation No. 6 Base Material			Furfuryl Alcohol (50 pbw) Bakelite BRP-5095 Resin (35 pbw)**	No. 121 Treatment

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 (pph).
*Impregnate 2800°C baked compacts with resin solution, pressure cure at 150°C, rebake to 1000°C, and final bake to 2800°C.
**Impregnate 1000°C baked compacts with resin solution, pressure cure at 150°C, rebake to 1000°C, and final bake to 2800°C.
***Impregnate with oxidation-inhibiting treatment after desired configuration has been finished machined from 2800°C baked stock.

B. Processing of Materials Formulations

Two different types of compacts were prepared for the materials manufactured during Task VI: 5-inch (12.7 cm) diameter x 1.4-inch (3.6 cm) thick solid plugs and 8.6-inch (21.8 cm) o.d. x 5.8-inch (14.7 cm) i.d. x 1.3-inch (3.3 cm) thick ring blanks. The dimensions listed are for the green compacts. The material property samples and the rod specimens submitted to the NASA Project Manager were machined from the solid plugs.

Several test bakes were conducted to determine the best molding conditions for each of the materials manufactured during Task VI. The mixes of formulations Nos. 1 and 3, which were employed during Task VI for the manufacture of two materials, had been test baked when they were manufactured during Task III.(6) The formulation No. 6 mix was manufactured and test baked during Task VI. The test bake procedure consisted of molding small compacts of each material at 5000 psi (3450 N/cm^2) pressure increments between 10,000 psi (6890 N/cm^2) and 35,000 psi (24,100 N/cm^2). After the compacts were baked to 1000°C, their densities were measured and their internal structures were examined for laminations. The green density that resulted in a 1000°C baked compact having the highest baked density and sound internal structure was selected as the molding condition for each material. The processing techniques employed to manufacture compacts from the materials produced during Task VI are as follows:

1. Formulation No. 1Y - CHP Artificial Graphite (80 pbw) - Thermax (20 pbw) - No. 30 Medium Pitch (60 pph) - 1000°C Baked Compacts Impregnated with Solution Consisting of Furfuryl Alcohol (50 pbw) and Bakelite BRP-5095 Resin (35 pbw)
    - a) Blend filler raw materials for one hour.
    - b) Preheat filler and mixer to 150°C, add pitch, and mix filler and binder in sigma blade mixer for one hour.
    - c) Crush cooled mix by using a hammer pulverizer.
    - d) Micromill crushed mix.
    - 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, place a layer of charcoal on the top of the pack, and bake green compacts between room temperature and 1000°C at a rate of 5°C per hour, followed by a 4-hour hold at 1000°C.

h) Impregnate 1000°C baked compacts with a furfuryl alcohol (50 pbw) - Bakelite BRP-5095 resin (35 pbw) solution by using the following procedure.

1. Place compacts in autoclave and evacuate for 1 hour at 27 to 29-inch (9.1 to 9.8 N/cm^2) Hg vacuum.
2. Impregnate compacts with resin solution.
3. Pressurize autoclave containing compacts with 80 to 85 psig (55 to 59 N/cm^2) air for 1 hour.
4. Remove compacts from solution.
5. Place compacts in an autoclave, pressurize with 100 psig (69 N/cm^2) air, rush temperature to 125°C and hold 1 hour, and rush temperature to 150°C and hold 1 hour. Remove compacts from autoclave and place them in a 150°C circulating-air oven for 2 hours to complete resin cure.

i) Pack resin impregnated compacts with coke in a sagger and rebake to 1000°C according to the following schedule: rush to 150°C, 150°C to 1000°C at 10°C per hour, and hold 4 hours at 1000°C.

j) Using graphite particles as the packing medium, fire the 1000°C baked compacts to 2800°C in an induction furnace, using the following schedule: room temperature to 900°C at 400°C per hour, 900°C to 1600°C at 200°C per hour, 1600°C to 2800°C at 300°C per hour, and hold 1 hour at 2800°C.

Processing problems were encountered during the manufacture of the formulation No. 1Y compacts. Eight 5-inch (12.7 cm) diameter x 1.4-inch (3.6 cm) thick solid green plugs were successfully baked from room temperature to 1000°C. The 1000°C baked compacts were then impregnated with the furfuryl alcohol - Bakelite BRP-5095 resin solution. A 7.7 percent average increase in weight was measured for the resin-impregnated compacts following pressure curing at 150°C. After they were pressure cured, these compacts were rebaked to 1000°C at a rate of 10°C per hour. The baking schedule was apparently too fast, since large chips of material broke off during baking. The force produced by the volatiles from the resin-impregnant trying to escape through the internal structure of the compacts probably caused the chipping. The 10°C per hour rate was the same as that used during the Task V resin impregnation studies in which smaller resin-impregnated samples (4.0-inch x 0.5-inch x 0.25-inch (10.2 cm x 1.3 cm x 0.6 cm)) of formulation No. 1Y were successfully rebaked to 1000°C. Final baking (2800°C) of the damaged 1000°C rebaked formulation No. 1Y compacts resulted in their completely breaking apart, apparently due to undetected microcracks which had formed during the rebaking of the compacts to 1000°C. The formulation No. 1Y compacts were being manufactured from the limited quantity of formulation No. 1 mix remaining from Task III.(6) This supply of mix was exhausted with the manufacture of the solid plugs of formulation No. 1Y.

The processing problems encountered during the manufacture of the formulation No. 1Y compacts necessitated the revising of the original work plan for Tasks VI and VII. Formulation No. 1Y was replaced by formulation No. 1Z. Formulation No. 1Z was basically the same as formulation No. 1Y with the exception that formulation No. 1Z specified resin impregnation of 2800°C baked compacts and a much slower baking schedule to rebake the resin-impregnated compacts to 1000°C.

2. Formulation No. 1Z - CHP Artificial Graphite (80 pbw) - Thermax (20 pbw) - No. 30 Medium Pitch (60 pph) - 2800°C Baked Compacts Impregnated with Solution Consisting of Furfuryl Alcohol (50 pbw) and Bakelite BRP-5095 Resin (35 pbw):

a) Bake compacts to 2800°C by using the same processing as that used for formulation No. 1Y except for the elimination of steps h and i.

b) Impregnate 2800°C baked compacts with the furfuryl alcohol (50 pbw) - Bakelite BRP-5095 resin (35 pbw) solution, using same procedure employed to resin impregnate 1000°C baked compacts of formulation No. 1Y (Step h).

c) Pack resin impregnated compacts with coke in a sagger and bake to 1000°C according to the following schedule: room temperature to 500°C at 2.5°C per hour, 500 to 1000°C at 5°C per hour, and hold 4 hours at 1000°C.

d) Using graphite particles as the packing medium, fire 1000°C baked compacts to 2800°C in an induction furnace according to the firing schedule used for the formulation No. 1Y compacts.

Three of the large ring blanks and seven solid plugs were manufactured from formulation No. 1Z. Existing 2800°C baked formulation No. 1 compacts remaining from Task III(6) were used to manufacture the formulation No. 1Z material. A 10.6 percent average increase in weight was measured for the compacts following resin impregnation and pressure curing at 150°C. Although the resin-impregnated formulation No. 1Z compacts were rebaked to 1000°C by using a very slow baking schedule, the large resin pickup resulted in the chipping of some of the compacts during baking. However, the resin-impregnated compacts of formulation No. 1Z were in much better condition after rebaking to 1000°C than those of formulation No. 1Y. The formulation No. 1Z compacts experienced no further damage during final baking to 2800°C. Although some of the formulation No. 1Z compacts experienced chipping problems during processing, the quantity of material that was successfully manufactured was sufficient to fulfill the delivery and testing requirements for Tasks VI and VII.

3. Formulation No. 5 - CHP Artificial Graphite (80 pbw) - Thermax (20 pbw) - Bakelite BRP-5095 Resin (58 pph):

a) Blend filler raw materials for one hour.

b) Dissolve Bakelite BRP-5095 resin binder in equal volume of acetone and mix with filler in a sigma blade mixer for one hour at room temperature.

c) Dry mixed material at 75°C for 16 hours.

d) Crush material by using a hammer pulverizer. The material may still be rather soft and pliable after Step c, due to entrapped acetone, in which case the mix must be chilled at -20°C to harden it before crushing.

e) Place crushed mix in an autoclave and vacuum - evacuate for 16 hours while maintaining the temperature at 50°C. The step will remove the residual acetone.

f) Crush material again by using a hammer pulverizer. The step can be omitted if the mix does not agglomerate during Step e.

g) Micromill crushed material.

h) Blend milled material for 1 hour.

i) Mold the milled material at room temperature by using a hydraulic press.

j) Pressure cure green compacts at 150°C by using the following procedure: place compacts in autoclave, apply 100 psig (69 N/cm^2) air pressure, rush temperature to 125°C, hold for 1 hour, rush temperature to 150°C and hold 3 hours. The cure is completed by heating the pressure cured compacts in a circulating-air oven for 1 hour at 100°C, 1 hour at 125°C, and 3 hours at 150°C.

k) Pressure bake cured compacts according to the following schedule: rush to 150°C and hold 1/2 hour, raise at 5°C per hour between 150°C and 550°C, and hold at 550°C for 4 hours. During pressure baking, an inert gas is used to apply 50 to 100 atmospheres pressure.

l) Pack pressure baked compacts with coke in a sagger, place a layer of charcoal on the top of the pack, and bake to 1000°C according to the following schedule: rush to 150°C, raise at 10°C per hour between 150°C and 500°C, hold 2 hours at 500°C, raise at 5°C per hour between 500°C and 1000°C, and hold 4 hours at 1000°C.

m) Using graphite particles as the packing medium, fire the 1000°C baked compacts to 2800°C in an induction furnace according to the firing schedule used for the formulation No. 1Y compacts.

Since major processing problems were encountered during the manufacture of the formulation No. 5 base material, no attempt was made to manufacture the resin impregnated version of the material (formulation No. 5Y). As reported for the Task V baking studies (Section IV-A-2), scale up in the size of the compacts resulted in cracking problems. The large green formulation No. 3 compacts fractured when they were pressure baked to 550°C. At that time, it was discovered that the large green compacts could be successfully pressure baked to 550°C if they were first pressure cured at 150°C. The large green formulation No. 3 compacts used during the Task V baking studies had been molded a year before during Task III(6) and had since been resting on a bench in an air-conditioned room. The formulation No. 3 mix from which the formulation No. 5 compacts were molded during Task VI, had spent the past year in an unheated storage area. Hence, the mix had been exposed to temperatures ranging from 100°F (38°C) during the summer to below 0°F (-18°C) during the winter. The large variation in temperature may have affected the Bakelite BRP-5095 resin used to bond the formulation No. 3 mix or the resin binder may have deteriorated with age. The result was that all 20 of the 5-inch (12.7 cm) diamter x 1.4-inch (3.6 cm) thick green formulation No. 5 compacts cracked and/or laminated when pressure cured at 150°C followed by pressure baking to 550°C.

Absorbed moisture was also suspected as a possible cause of the processing problems encountered during the manufacture of the formulation No. 5 material. However, an analysis of the one-year-old formulation No. 3 mix showed that it contained only 0.6 percent (by weight) absorbed moisture.

This value was obtained by weighing a sample of the mix before and after it had been vacuum evacuated for 7 hours at a temperature of 50°C. Furthermore, the dried sample of mix was found to re-absorb 0.5 percent moisture during its first hour exposure to room temperature conditions. Due to the relatively small amount of absorbed moisture present in the mix, it was ruled out as being a major cause of the processing problems experienced during the manufacture of the formulation No. 5 material.

In view of the processing difficulties experienced during the manufacture of the formulation No. 5 material, the NASA Project Manager requested that the work on this material not be continued. The remaining program efforts were to be directed to completion of the manufacture and characterization of the other two materials (formulations Nos. 1Z and 6Y). Only a few formulation No. 5 compacts were completely processed through baking to 2800°C. The compacts included two ring blanks and several small pieces salvaged from the solid plugs which had experienced cracking problems during pressure baking. The formulation No. 5 compacts were not resin-impregnated prior to final baking to 2800°C to avoid any further processing problems which might result from the use of the furfuryl alcohol-Bakelite BRP-5095 resin impregnant. Because of the processing problems encountered during Task VI, the quantity of formulation No. 5 material which was produced was not sufficient to fulfill the delivery requirements.

4. Formulation No. 6 - CHP Artificial Graphite (80 pbw)-
<u>WFA Fibers (20 pbw) - Bakelite BRP-5095 Resin (70 pph):</u>

a) Blend Grade WFA chopped graphite fibers with the CHP artificial graphite for one hour.

b) Micromill the blended filler material.

c. Blend milled filler material for one hour.

d) Follow the other processing steps listed for formulation No. 5, starting at mixing (Step b).

5. Formulation No. 6Y - CHP Artificial Graphite (80 pbw)-WFA Fibers (20 pbw) - Bakelite BRP-5095 Resin (70 pph)-1000°C Baked Compacts Impregnated with Solution Consisting of Furfuryl Alcohol (50 pbw) and Bakelite BRP-5095 Resin (35 pph):

a) Bake the green compacts to 1000°C in the same manner as that used for formulation No. 6.

b) Follow the other processing steps listed for formulation No. 1Y, starting at the impregnation of the 1000°C baked compacts (Step h).

Ring blanks were manufactured from formulation No. 6 after processing problems prevented the manufacture of the resin-impregnated formulation No. 6Y ring blanks. The processing problems resulted from the large resin pickup experienced by the formulation No. 6Y ring blanks. An increase in weight of 11.1 percent was measured for the 1000°C baked ring blanks following resin impregnation and pressure curing at 150°C. This resin pickup was ten times that measured for the 5-inch (12.7 cm) diameter solid plugs of the formulation No. 6Y material at the same stage in processing. The impregnant apparently filled the open porosity of the 1000°C baked ring blanks so completely that they broke apart during rebaking to 1000°C as the volatiles from the resin impregnant tried to escape through the internal structures of the compacts. Due to their low resin pickup, no problems were encountered during the processing of the formulation No. 6Y solid plugs through final baking to 2800°C.

The resin pickups measured for the solid plugs and ring blanks of formulation No. 6Y indicated that there may have been a difference in the surface condition of the two types of compacts prior to impregnation. The 1000°C baked solid plugs of the formulation No. 6 base material apparently had a very low porosity surface condition which prevented the resin solution from freely entering the stock during impregnation. The 1000°C baked ring blanks of the formulation No. 6 base material did not appear to have the low porosity surface condition, since they readily accepted the resin during impregnation.

If indeed there was a difference in the surface porosity of the two types of compacts, the difference would probably be related to the difference in their surface-to-volume ratios. The surface-to-volume ratio of the ring blanks was approximately 1.4 times that of the solid plugs, indicating that the volatiles would experience greater difficulty in escaping from the resin binder through the solid plugs during baking. The difficulty of removing the volatiles and the fact that phenolic resins yield low porosity carbonaceous materials after pyrolysis possibly could account for the formation of a low porosity envelope around the solid plugs of formulation No. 6 during baking to 1000°C.

SECTION VI

MATERIAL PROPERTIES

(TASK VII)

A. Property Requirements of Seal Ring Carbon-Graphite Materials

The goal of this contract is the development of a carbon-graphite material for use as a self-acting seal in advanced gas turbine engines. High oxidation resistance is a primary requirement of the material if it is to withstand the high operating temperatures. Since self-acting seals experience relatively high speed sliding contact during limited periods of operation, good wear resistance is also a requirement. 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. High hardness also is required to ensure the erosion resistance of the material. Erosion resistance is an important requirement for a self-acting seal material, since debris passing through the gas film formed between the self-acting seal and the seat during engine operation tends to score and erode the primary ring. A carbon-graphite material used as a self-acting seal must also have a high thermal conductivity to provide rapid transfer of deleterious frictional heat which can develop during periods of sliding contact. Dimensional stability is a desirable property of a seal ring material, although thermal expansion is not critical for this application, since the carbon will be controlled by an outer shrink ring during operation.

Aside from the material properties that are essential for good performance, a seal ring material should also be readily machinable, since seal dam widths as small as 0.020-inches (.05 cm) often are present in seal design. The compacts manufactured from formulations Nos. 1Z, 5, 6, and 6Y during Task VI were all found to be more easily machinable than commercial seal ring Grade CDJ. The good machinability of the carbon-graphite articles manufactured during Task VI resulted from the use of a large proportion of particulate graphite in the filler systems and a final heat-treatment temperature of 2800°C.

Under the scope of Task VII, the Contractor determined the following material properties for the carbon-graphite seal ring bodies manufactured during Task VI:

1. Mechanical Properties
    a. Density before and after impregnation with an oxidation inhibiting treatment.
    b. Flexural strength.
    c. Elastic modulus.
2. Thermal Properties
    a. Thermal conductivity.
    b. Coefficient of thermal expansion.
3. Oxidation Resistance and Related Porosity
    a. Oxidation resistance compared with that of carbon-graphite seal material currently in use.
    b. Total porosity, pore size and size distribution, uniformity of impregnation, and structural uniformity.

This section of the report is divided into subsections. The next subsection discusses the mechanical properties determined for the materials manufactured during Task VI. The remaining subsections cover the thermal properties, the porosities, and the oxidation rates determined for the materials.

B. Mechanical Properties

The literature search conducted during Task I(5) indicated that high hardness, strength, and modulus are necessary requirements for producing wear-resistant carbon-graphite seal ring materials. Hardness greatly affects performance, since the load-carrying capacity of a carbon-graphite seal ring material is directly related to its hardness. High hardness also is needed to prevent scoring and erosion of the seal face when debris passes between the self-acting seal and the seat during engine operation. Although no goal was established for the strength of the material to be developed under the scope of this Contract, the operating pressures, dimensional stability requirements, and the configuration of the seal ring (7-12 inches (18-30 cm) in diameter, 1/2-inch (1.3 cm) in thickness, and 0.020-inch (.05 cm) in dam width) require a material with maximum strength and hardness consistent with high oxidation resistance.

Tables IX, XI, and XIII display the green, 1000°C baked, and 2800°C baked bulk densities; the flexural strengths; the elastic moduli, and the hardnesses determined for the carbon-graphite seal ring bodies manufactured from formulations Nos. 1Z, 5, and 6Y. Except for the hardness measurement, these mechanical properties were the ones which the Contractor was required to measure. The hardness measurement was included, since it is one of the physical properties commonly specified for commercially available carbon-graphite seal ring materials. Appendix II described the procedures used to determine the material properties. The ASTM methods were used where applicable.

A complete listing of the mechanical properties determined for the formulation No. 1Z material is displayed in Table IX. Table X presents a comparison of the average mechanical properties measured for the formulation No. 1Z material with those determined during Task IV(6) for the materials manufactured from formulations Nos. 1 and 1X (compositions listed in Table I). Although the formulation No. 1Z material had a significantly higher 2800°C baked bulk density, its other mechanical properties were not quite so good as those determined for the formulation No. 1X material. The mechanical properties of the formulation No. 1Z material were slightly more uniform than those of the formulation No. 1X material.

TABLE IX

Mechanical Properties - Formulation No. 1Z Material

Bulk Density*

	Green (g/cc)	1000°C Baked (g/cc)	2800°C Baked (g/cc)	Resin Impregnated - 1000°C Rebaked (g/cc)	Resin Impregnated - 2800°C Rebaked (g/cc)
5"(12.7cm)Diameter Plugs					
Maximum	1.602	1.669	1.711	1.796	1.794
Minimum	1.593	1.660	1.701	1.788	1.791
Average	1.597	1.664	1.707	1.793	1.792
Standard Deviation	0.003	0.003	0.005	0.003	0.002
n	5	5	5	5	5
Ring Blanks					
Maximum	1.593	1.666	1.705	1.799	1.798
Minimum	1.592	1.657	1.702	1.794	1.794
Average	1.593	1.662	1.704	1.797	1.796
n	2	2	2	2	2

Flexural Strength**

	(psi)	(N/cm^2)
Maximum	4300	2960
Minimum	3870	2660
Average	4070	2800
Standard Deviation	172	119
n	6	6

Rockwell "S" Hardness***

Maximum	82
Minimum	78
Average	80
Standard Deviation	1
n	6

Elastic Modulus**

	(10^6 psi)	(10^{5}N/cm^2)
Maximum	1.42	9.78
Minimum	1.39	9.58
Average	1.41	9.71
Standard Deviation	0.01	0.07
n	6	6

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* Calculated from physical dimensions and weights measured for compacts.

** Measured using 4.5" x 1.0" x 0.5" (11.4 cm x 2.5 cm x 1.30 cm) samples. Flexural samples broken on a 3.0" (7.6 cm) span per ASTM procedure C651-70.

*** R_s Scale = 1/2" (1.3 cm) diameter ball and 100 Kg Maj. load. Two measurements made on each of the 6 flexural samples.

TABLE X

Comparison of Mechanical Properties - Formulations Nos. 1, 1X, and 1Z Material

	Formulation No. 1Z		Formulation No. 1*		Formulation No. 1X*	
Bulk Density (g/cc)**						
Green (Average)	1.597		1.597		1.592	
Standard Deviation	0.003		0.003		0.003	
n	5		5		4	
2800°C Baked (Average)	1.792		1.707		1.733	
Standard Deviation	0.002		0.005		0.003	
n	5		5		4	
Flexural Strength***						
	(psi)	(N/cm²)	(psi)	(N/cm²)	(psi)	(N/cm²)
Average	4070	2800	3810	2630	4480	3090
Standard Deviation	172	119	242	167	220	152
n	6	6	6	6	6	6
Elastic Modulus***						
	(10^6 psi)	(10^5N/cm²)	(10^6 psi)	(10^5N/cm²)	(10^6 psi)	(10^5N/cm²)
Average	1.41	9.71	1.31	9.03	1.47	10.13
Standard Deviation	0.01	0.07	0.03	0.21	0.03	0.21
n	6	6	6	6	6	6
Rockwell "S" Hardness****						
Average	80		80		85	
Standard Deviation	1		5		2	
n	6		6		6	

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* Materials manufactured during Task III. Compositions of Formulations Nos. 1 and 1X were presented in Table I of this report.

** Calculated from physical dimensions and weights measured for compacts.

*** Measured using 4.5" x 1.0" x 0.5" (11.4 cm x 2.5 cm x 1.3 cm) samples. Flexural samples broken on a 3.0" (7.6 cm) span per ASTM procedure C651-70.

**** R_s Scale = 1/2" (1.3 cm) diameter ball and 100 Kg. Maj. load. Two measurements made on each of the flexural samples.

The strength, hardness, and modulus of the formulation No. 1Z material initially had been expected to be better than those of the formulation No. 1X material. This result was expected since the formulation No. 1Z resin impregnant yielded three times more residual carbon (by weight) after baking as that obtained from the formulation No. 1X resin impregnant. The large amount of residual carbon resulting from the resin impregnant was reflected in the 2800°C baked bulk density measured for the formulation No. 1Z material. The lack of improvement in the strength, hardness, and modulus of the formulation No. 1Z material may have been the result of a number of different factors. Perhaps the furfuryl alcohol-BRP-5095 resin solution did not wet nor adhere to the substrate carbon so well as did the BRP-5095 resin-acetone solution used to manufacture the formulation No. 1X material. The lack of improvement also might indicate that the residual carbon formed from the resin impregnant in the formulation No. 1Z material may have had a higher degree of crystallinity after baking to 2800°C than that formed in the formulation No. 1X material. This increased degree of crystallinity, which could have resulted from the impregnation of 2800°C baked rather than 1000°C baked formulation No. 1 compacts, would cause the residual carbon to be softer than that formed in the formulation No. 1X material, thus contributing little to the strength and hardness. The lack of improvement could also be due to a difference in the pore size distribution of the formulation No. 1Z material as compared with that of the formulation No. 1X material. This possibility will be discussed further in Section VI-D of this report.

Table XI displays a listing of the mechanical properties determined for the formulation No. 5 material. Table XII presents a comparison of the average mechanical properties measured for the formulation No. 5 material and those determined during Task IV(6) for the material manufactured from formulation No. 3 (composition listed in Table I). Although pressure baking was included as a part of the processing, the formulation No. 5 material was found to have mechanical properties similar to those determined for the formulation No. 3 material. This result was probably due to the fact the formulation No. 5 compacts were manufactured from the one-year-old formulation No. 3 mix remaining from Task III.(6) The Bakelite BRP-5095 resin used to bond the formulation No. 3 mix apparently had deteriorated with age.

TABLE XI

Mechanical Properties - Formulation No. 5 Material

Bulk Density[*]

	Green (g/cc)	550°C Pressure Baked (g/cc)	1000°C Baked (g/cc)	2800°C Baked (g/cc)
5" (12.7 cm) Diameter Plugs				
Maximum	1.410	-----	-----	1.682
Minimum	1.406	-----	-----	1.649
Average	1.408	-----	-----	1.668
Standard Deviation	0.001	-----	-----	0.012
n	13	-----	-----	10
Ring Blanks				
Maximum	1.406	1.502	1.565	1.659
Minimum	1.405	1.496	1.554	1.656
Average	1.406	1.499	1.560	1.658
n	2	2	2	2

Flexural Strength[**]

	(psi)	(N/cm^2)	Rockwell "S" Hardness[***]	
Maximum	3780	2600	Maximum	69
Minimum	2950	2030	Minimum	37
Average	3390	2340	Average	57
Standard Deviation	278	192	Std. Dev.	10
n	6	6	n	6

Elastic Modulus[**]

	(10^6 psi)	($10^5 N/cm^2$
Maximum	1.24	8.54
Minimum	1.10	7.58
Average	1.20	8.27
Standard Deviation	0.05	0.34
n	6	6

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[*] Calculated from physical dimensions and weights measured for compacts. 2800°C baked bulk densities listed for 5" (12.7 cm) diameter plugs were determined for segments salvaged from solid plugs damaged during pressure baking.

[**] Measured using 4.5" x 1.0" x 0.5" (11.4 cm x 2.5 cm x 1.3 cm) samples. Flexural samples broken on a 3.0" (7.6 cm) span per ASTM procedure C651-70.

[***] R_s Scale = 1/2" (1.3 cm) diameter ball and 100 KG Maj. load. Two measurements made on each of the 6 flexural samples.

TABLE XII

Comparison of Mechanical Properties - Formulations Nos. 3 and 5 Material

	Formulation No. 5		Formulation No. 3*	
Bulk Density (g/cc)**				
Green (average)	1.408		1.407	
Standard Deviation	0.001		<0.001	
n	13		6	
2800°C Baked (average)	1.668		1.644	
Standard Deviation	0.012		0.005	
n	10		6	
Flexural Strength***	(psi)	(N/cm^2)	(psi)	(N/cm^2)
Average	3390	2340	3480	2400
Standard Deviation	278	192	118	81
n	6	6	6	6
Elastic Modulus***	(10^6 psi)	(10^{5}N/cm^2)	(10^6 psi)	(10^{5}N/cm^2)
Average	1.20	8.27	1.15	7.92
Standard Deviation	0.05	0.34	0.02	0.14
n	6	6	6	6
Rockwell "S" Hardness****				
Average	57		58	
Standard Deviation	10		2	
n	6		6	

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* Material manufactured during Task III. Composition of formulation No. 3 was presented in Table I of this report.

** Calculated from physical dimensions and weights measured for compacts. 2800°C baked bulk density listed for formulation No. 5 was measured for segments salvaged from solid plugs damaged during pressure baking.

*** Measured using 4.5" x 1.0" x 0.5" (11.4cm x 2.5cm x 1.3cm) samples. Flexural samples broken on a 3.0" (7.6cm) span per ASTM Procedure C651-70.

**** R_s Scale = 1/2" (1.3cm) diameter ball and 100 Kg. Maj. load. Two measurements made on each of the flexural samples.

The apparent deterioration of the resin binder was reflected in the 1000°C baked densities measured for the small formulation No. 3 compacts manufactured during the Task V baking studies (Section IV-A-2). These compacts, which had been molded from the one-year-old formulation No. 3 mix, had an average 1000°C baked bulk density of 1.427 g/cc. Although the same processing techniques had been employed, the compacts manufactured from the formulation No. 3 mix during Task III(6) had an average 1000°C baked bulk density of 1.519 g/cc. The apparent deterioration of the resin binder prohibited the formulation No. 5 material from gaining the full benefit of pressure baking.

Since complete property characterization of the formulation No. 5 material was not warranted, only selected mechanical properties and oxidation rate were determined. The oxidation testing, which is discussed in a later section of this report, was conducted by using samples impregnated with the No. 121 oxidation-inhibiting treatment.

A complete listing of the mechanical properties of the formulation No. 6Y material is presented in Table XIII. These mechanical properties were determined for samples prepared from the 2800°C baked solid plugs of formulation No. 6Y. Due to the apparent formation of a low porosity surface condition during processing, the solid plugs of formulation No. 6Y experienced only a 1.1 percent average increase in weight after resin impregnation. The average increase in weight decreased to 0.26 percent after the resin-impregnated solid plugs were rebaked to 1000°C. Since the solid plugs of formulation No. 6Y experienced such a small resin pickup, the mechanical properties displayed in Table XIII are essentially the same as those which would be measured for the solid plugs of the non-resin-impregnated formulation No. 6 base material. The formulation No. 6 ring blanks manufactured during Task VI had 2800°C baked bulk densities ranging between 1.564 and 1.569 g/cc. The larger surface-to-volume ratio of the formulation No. 6 ring blanks may have been responsible for their 2800°C baked bulk density being higher than that measured for the solid plugs of the same material.

TABLE XIII

Mechanical Properties - Formulation No. 6Y Material

Bulk Density*	Green (g/cc)	550°C Pressure Baked (g/cc)	1000°C Baked (g/cc)	Resin Impregnated-1000°C Rebaked (g/cc)	2800°C Baked (g/cc)
5" (12.7 cm) Diameter Plugs					
Maximum	1.458	1.391	1.459	1.463	1.506
Minimum	1.452	1.383	1.447	1.452	1.496
Average	1.455	1.388	1.453	1.458	1.502
Standard Deviation	0.002	0.003	0.005	0.004	0.004
n	7	7	7	7	7
Flexural Strength**					
	(psi)	(N/cm^2)		Rockwell "S" Hardness***	
Maximum	5240	3610		Maximum	70
Minimum	4300	2960		Minimum	36
Average	4660	3210		Average	48
Standard Deviation	339	234		Standard Deviation	6
n	8	8		n	8
Elastic Modulus**					
	(10^{6}psi)	(10^{5}N/cm^2)			
Maximum	1.43	9.85			
Minimum	1.26	8.68			
Average	1.33	9.16			
Standard Deviation	0.06	0.04			
n	8	8			

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* Calculated from physical dimensions and weights measure for compacts.

** Measured using 4.5" x 1.0" x 0.5" (11.4cm x 2.5cm x 1.3cm) samples. Flexural samples broken on a 3.0" (7.6cm) span per ASTM Procedure C651-70.

*** R_s Scale = 1/2" (1.3cm) diameter ball and 100 Kg Maj. load. Two measurements made on each of the 8 flexural samples.

Table XIV shows a comparison of the average mechanical properties measured for the formulation No. 6Y material and those determined during Task IV(6) for similar materials manufactured from formulations Nos. 4 and 4X (compositions listed in Table I). The mechanical properties of the formulation No. 6Y material were significantly better than those determined for the non-resin-impregnated formulation No. 4 material. The formulation No. 6Y material had mechanical properties similar to but more uniform than those of the resin-impregnated formulation No. 4X material, even though the latter had gained considerably more residual carbon from the carbonization of its resin impregnant. An average increase of 4 percent had been measured during Task III(6) after the resin-impregnated formulation No. 4X compacts were rebaked to 1000°C. As mentioned previously, the mechanical properties of the formulation No. 6 base material should be approximately the same as those measured for the resin-impregnated formulation No. 6Y material. Formulation No. 6 thus results in a non-resin-impregnated material with properties similar to those of the resin-impregnated formulation No. 4X material. This improvement is significant, since deletion of resin-impregnation reduces processing,

The goal of the Tasks V, VI, and VII was to develop carbon-graphite materials having improved strength, hardness, and uniformity. The goal was not completely achieved, since the scale-up in the size of the compacts produced during Task VI resulted in processing problems. These processing problems prevented the gains in mechanical properties anticipated from the techniques developed during the Task V screening study. Seal ring bodies manufactured from formulations Nos. 1Z and 6Y possessed mechanical properties similar to those determined for the compacts of formulations Nos. 1X and 4X, respectively. The mechanical properties of the latter two materials had been judged during Task IV(6) to be adequate for use as a self-acting seal ring material. Although no improvements in strength and hardness were obtained, the formulation No. 6 material was more uniform than the formulation No. 4X material manufactured during Task III.(6) The mechanical properties determined for the carbon-graphite seal ring bodies manufactured from formulations Nos. 1X, 1Z, 4X, and 6Y were, however, all lower than the corresponding values specified for commercial seal ring Grade CDJ-83.

TABLE XIV

Comparison of Mechanical Properties - Formulations Nos. 4, 4X, and 6Y Material

	Formulation No. 6Y		Formulation No. 4		Formulation No. 4X	
Bulk Density (g/cc)[*]						
Green (average)	1.455		1.434		1.430	
Standard Deviation	0.002		0.005		0.004	
n	7		6		5	
2800°C Baked (average)	1.502		1.441		1.457	
Standard Deviation	0.004		0.008		0.012	
n	7		6		5	
Flexural Strength[**]	(psi)	(N/cm^2)	(psi)	(N/cm^2)	(psi)	(N/cm^2)
Average	4660	3210	3380	2670	4470	3080
Standard Deviation	339	234	244	168	313	216
n	8	8	6	6	6	6
Elastic Modulus[**]	(10^6 psi)	(10^{5}N/cm^2)	(10^6 psi)	(10^{5}N/cm^2)	(10^6 psi)	(10^{5}N/cm^2)
Average	1.33	9.16	1.19	8.20	1.49	10.27
Standard Deviation	0.06	0.41	0.01	0.07	0.11	0.76
n	8	8	6	6	6	6
Rockwell "S" Hardness[***]						
Average	48		26		59	
Standard Deviation	6		2		12	
n	8		6		6	

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[*] Calculated from physical dimensions and weights measure for compacts.

[**] Measured using 4.5" x 1.0" x 0.5" (11.4cm x 2.5cm x 1.3cm) samples. Flexural samples broken on a 3.0" (7.6cm) span per ASTM procedure C651-70.

[***] R_s Scale = 1/2" (1.3cm) diameter ball and 100 Kg Maj. load. Two measurements made on each of the flexural samples.

Grade CDJ-83 has a nominal bulk density of 1.76 g/cc, a flexural strength of 8800 psi (6100 N/cm^2), an elastic modulus of 3.2 x 10^6 psi (2.2 x 10^6 N/cm^2), and a Rockwell "E" hardness of 105. As discussed in Topical Report NASA CR-72799$^{(5)}$, some sacrifice in strength and hardness was necessary during the development of the oxidation resistant, carbon-graphite materials.

C. Thermal Properties

As a part of the material characterization program, the Contractor determined the thermal conductivities and the coefficients of thermal expansion for the materials manufactured from formulations Nos. 1Z and 6Y. Both of the thermal properties affect the performance of a carbon-graphite seal ring material. Self-acting seals experience limited periods of sliding contact. However to mitigate thermal deformation, they require a carbon-graphite material having a high thermal conductivity so that any frictional heat generated during sliding contact will be rapidly dissipated and thus proper interfacial geometry will be maintained to prevent high speed rubbing contact.$^{(12)}$ A low coefficient of thermal expansion is thus very desirable, even though the expansion of some self-acting seals will be controlled by an outer metal shrink ring.

Table XV lists the thermal conductivities measured for the carbon-graphite seal ring bodies manufactured from formulations Nos. 1Z and 6Y. The table also displays the thermal conductivities measured during Task IV$^{(6)}$ for the materials manufactured from formulations Nos. 1X and 4X (compositions presented in Table I.) The materials manufactured from similar formulations Nos. 1X and 1Z had approximately the same with-grain thermal conductivity, but the latter material had a considerably higher thermal conductivity in the across-grain direction. This improvement in across-grain thermal conductivity may have resulted from the higher 2800°C baked bulk density of the formulation No. 1Z material (1.792 g/cc) as compared with that of the formulation No. 1X material (1.733 g/cc). Formulation No. 6Y resulted in a more isotropic material with higher with-grain and across-grain thermal conductivities than those of the similar material manufactured from formulation No. 4X. All the thermal conductivities listed in Table XV, which were measured at room temperature by using the laser flash method (Appendix II), are considerably higher than the typical value of 4.4 BTU-ft/ft^2-hr-°F (0.018 cal/cm-sec-°C) for commercial seal ring Grade CDJ-83.

TABLE XV

Thermal Conductivities-Formulations Nos. 1X, 1Z, 4X, and 6Y Material

	THERMAL CONDUCTIVITY					
Formulation	Cal/cm-sec-°C		BTU-ft/ft²-hr-°F		Joule/meter-sec-°K	
	W.G.	A.G.	W.G.	A.G.	W.G.	A.G.
No. 1Z	0.187	0.185	45.25	44.77	78.4	77.3
No. 1X*	0.181	0.149	43.80	36.06	75.8	62.3
No. 6Y	0.173	0.116	41.87	28.07	72.6	48.8
No. 4X*	0.145	0.082	35.09	19.84	60.7	34.3

Formulation	Anisotropy Ratio**
No. 1Z	1.01
No. 1X	1.21
No. 6Y	1.49
No. 4X	1.77

Note: W.G. - with grain

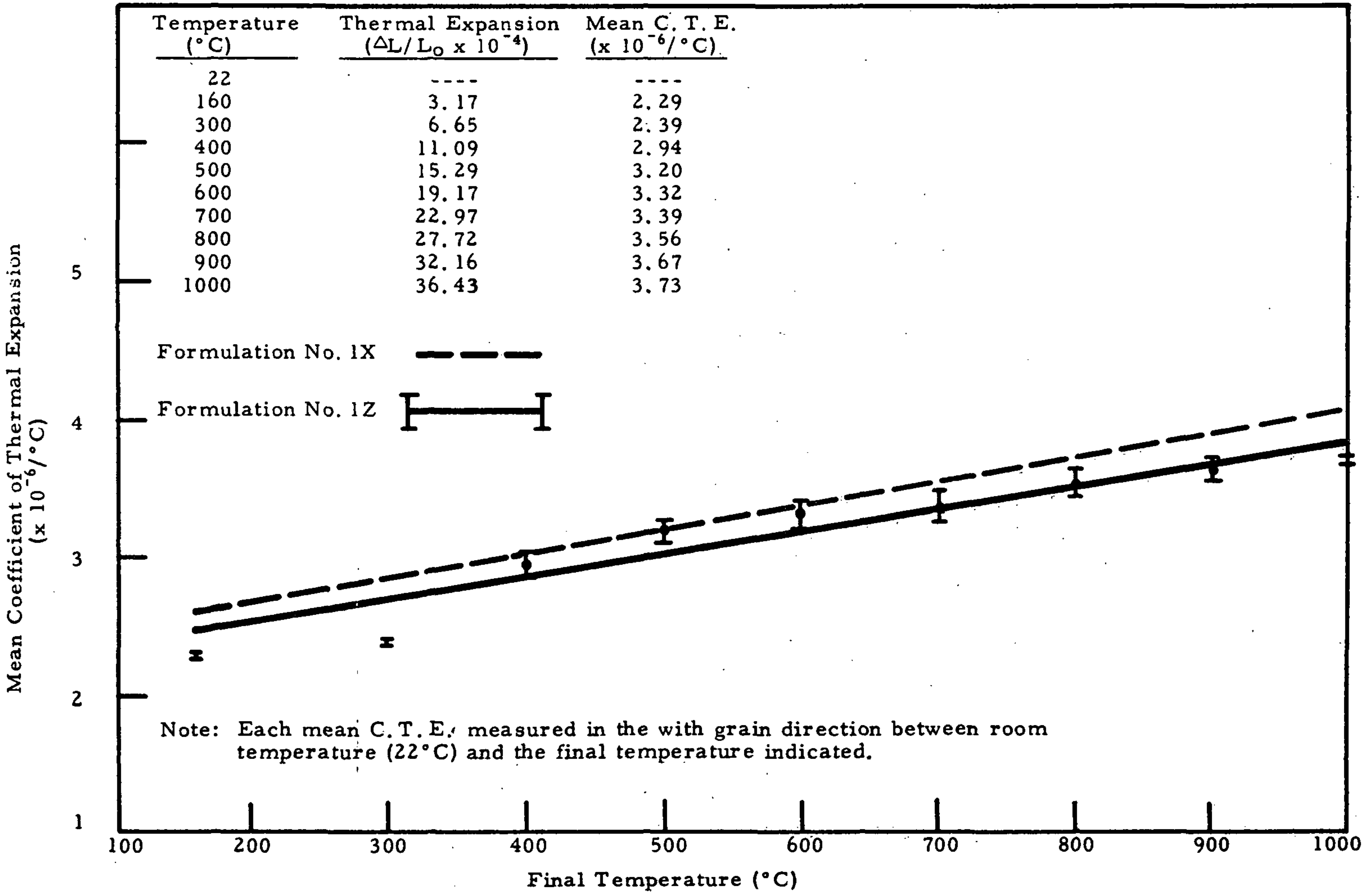
A.G. - across grain

* Measured during Task IV.

** Anisotropy ratio = Thermal conductivity (W.G.)/ Thermal conductivity (A.G.)

Figures 1 and 2 are plots of the coefficients of thermal expansion determined for the compacts of formulations Nos. 1Z and 6Y. Each plot represents the average of two tests conducted on samples machined on the with-grain direction. Figure 3 is a plot of the coefficient of thermal expansion of commercial seal ring Grade CDJ-83, which has been included for purposes of comparison. All the materials analyzed showed an increasing coefficient of thermal expansion with increasing temperature. The coefficient of thermal expansion of Grade CDJ-83 is considerably higher than those of the other materials tested. Figure 1 presents a comparison of the coefficient of thermal expansion of the formulation No. 1Z material to that determined during Task IV(6) for the formulation No. 1X material. The coefficients of thermal expansion of the two materials are comparable. Figure 2 shows that formulation No. 6Y resulted in a material having a considerably lower coefficient of thermal expansion than that of the similar formulation No. 4X material.

Based on the measured thermal properties, the material manufactured from formulation No. 6Y is a potentially better seal ring material than that prepared from the comparable formulation No. 4X. The higher thermal conductivity of the formulation No. 6Y material as compared with that of the formulation No. 4X material will provide more rapid dissipation of the frictional heat generated during periods of sliding contact. The lower coefficient of the thermal expansion of the formulation No. 6Y material is beneficial from a thermal deformation standpoint. Although a metallic shrink ring controls the thermal deformation of the carbon ring in some cases, if no shrink ring is used (as on small turbine engine seals), thermal deformation is mitigated by using high thermal conductivity and low thermal expansion carbon-graphite materials.



Temperature (°C)	Thermal Expansion ($\Delta L/L_o \times 10^{-4}$)	Mean C. T. E. (x 10^{-6}/°C)
22	----	----
160	3.17	2.29
300	6.65	2.39
400	11.09	2.94
500	15.29	3.20
600	19.17	3.32
700	22.97	3.39
800	27.72	3.56
900	32.16	3.67
1000	36.43	3.73

Note: Each mean C.T.E. measured in the with grain direction between room temperature (22°C) and the final temperature indicated.

Figure 1. Mean Coefficient of Thermal Expansion-Formulation No. 1Z Material.

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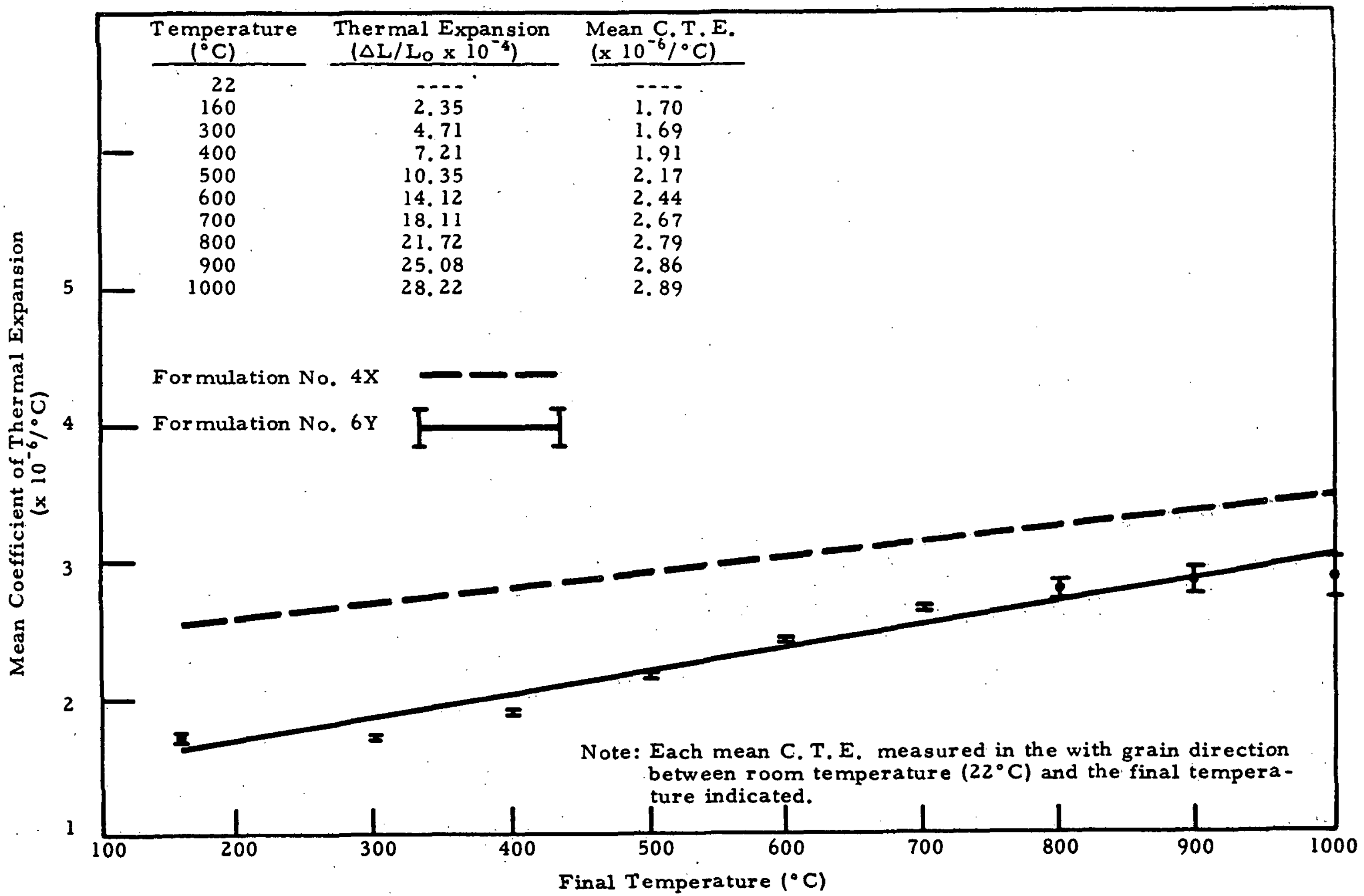

Temperature (°C)	Thermal Expansion ($\Delta L/L_o \times 10^{-4}$)	Mean C.T.E. (x 10^{-6}/°C)
22	----	----
160	2.35	1.70
300	4.71	1.69
400	7.21	1.91
500	10.35	2.17
600	14.12	2.44
700	18.11	2.67
800	21.72	2.79
900	25.08	2.86
1000	28.22	2.89

Note: Each mean C.T.E. measured in the with grain direction between room temperature (22°C) and the final temperature indicated.

Figure 2. Mean Coefficient of Thermal Expansion-Formulation No. 6Y Material.

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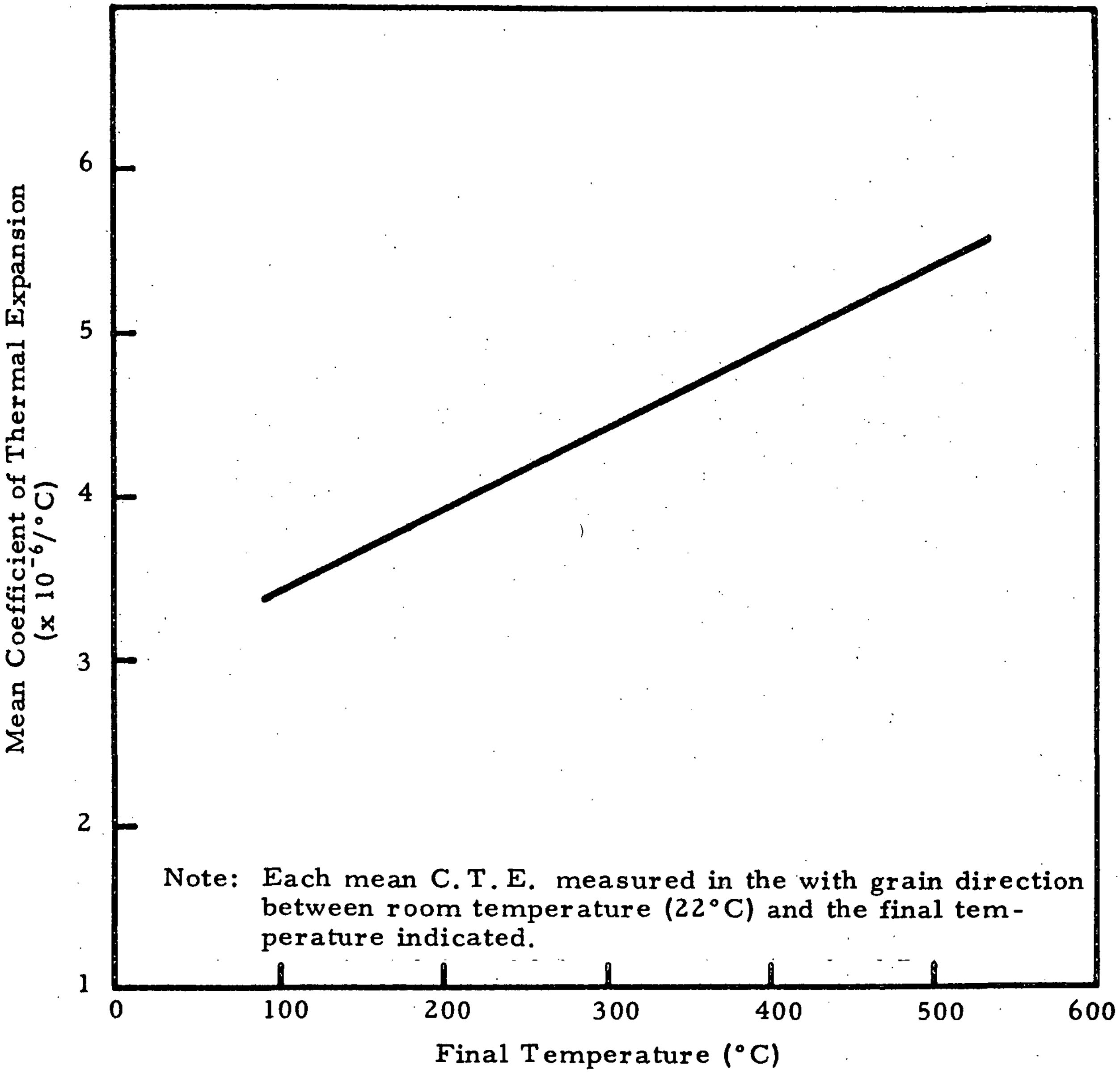

Note: Each mean C.T.E. measured in the with grain direction between room temperature (22°C) and the final temperature indicated.

Figure 3. Mean Coefficient of Thermal Expansion - Grade CDJ-83.

G 710432

D. Porosities

Carbon-graphite seal ring bodies must be low porosity materials so that they will be impervious to the fluids which they seal. As demonstrated during the experimental portion of Task I,(5) the mechanical properties and oxidation resistance of a carbon-graphite compact are greatly affected by the choice of raw materials, composition, and final baking temperature used for its manufacture. Although the degree of crystallinity of a carbon-graphite body greatly affects its material properties, the porosity of the compact also has some effect. Reducing the porosity of a formed article should result in an improvement in the mechanical and chemical properties. The carbonization of a resin impregnant has been found to be a good way to reduce the porosity of a carbon-graphite compact. Resin impregnation has been found to be better than the conventional pitch-type impregnation, since the resins, with their lower viscosities and increased wettings, tend to block the pores, as well as the larger open volumes.(13) Decreasing the porosity of a compact reduces the number of interconnected voids, and the remaining isolated voids are less damaging to the mechanical properties. Reducing the porosity of a carbon-graphite compact also should increase its oxidation resistance.

Table XVI presents the percent total porosities calculated for the compacts of formulations Nos. 1, 1X, 1Z, 4, 4X, and 6Y. The values presented for the materials manufactured from formulations Nos. 1, 1X, 4 and 4X were determined during Task IV,(6) but have been included for purposes of comparison. Table XVI also displays the percent total porosity determined for commercial seal ring Grade CDJ. These values were calculated by using the following equation:

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

The value obtained by using this equation is the ratio of the total open pore volume to the volume occupied by the pores and the carbonaceous material in the compact being analyzed.

TABLE XVI

Percent Total Porosities-Formulations Nos. 1, 1X, 1Z, 4, 4X, and 6Y Material

Formulation	Helium Density (g/cc)	Bulk Density (g/cc)	Percent Total Porosity
No. 1	2.050	1.710	16.6
No. 1X	1.940	1.730	10.8
No. 1Z	2.042	1.790	12.3
No. 4	1.900	1.441	22.1
No. 4X	1.765	1.466	16.9
No. 6Y	1.790	1.496	16.4
Grade CDJ	1.841	1.756	4.6

Formulations Nos. 1X and 1Z were resin-impregnated versions of formulation No. 1. Formulation No. 1X involved the impregnation of 1000°C baked formulation No. 1 compacts with a Bakelite BRP-5095 resin (50 pbw)-acetone (50 pbw) solution. Formulation No. 1Z involved the impregnation of 2800°C baked formulation No. 1 compacts with a furfuryl alcohol (50 pbw)-Bakelite BRP-5095 resin (35 pbw) solution. As mentioned during the discussion of mechanical properties (Section VI-B), the carbonaceous residue remaining after the formulation No. 1Z resin impregnant was baked to 2800°C may have had a higher degree of crystallinity than that obtained from the formulation No. 1X resin impregnant. A more "graphitizable" resin impregnant could account for the formulation No. 1Z material having a higher bulk density with a higher total porosity than those of the formulation No. 1X material. Although a higher helium density generally indicates a greater degree of crystallinity for a fine particulate material, this result may not necessarily occur for bulk carbon-graphite materials. Rather than indicating a difference in the degrees of crystallinity of the two materials, the difference in the helium densities of the materials manufactured from formulations Nos. 1X and 1Z could be a result of a difference in the accessibility of helium into the pore structures of the two materials.

The formulation No. 1Z material may be more oxidation resistant than formulation No. 1X material, even though the total porosity of the former is slightly greater. The helium density measurements indicate the formulation No. 1Z material is less accessible to helium than the formulation No. 1X material and, therefore, may be less accessible to oxidizing gases. Greater oxidation resistance also would be expected if the formulation No. 1Z material is more "graphitic" than the formulation No. 1X material, since the degree of crystallinity greatly affects the rate at which a carbon-graphite material oxidizes.

The data displayed in Table XVI show that the percent total porosity of the formulation No. 6Y material was similar to that measured for the formulation No. 4X material (Table I) and lower than that of the formulation No. 4 material (Table I). The reduced porosity of the formulation No. 6Y material was probably primarily effected through processing changes other than resin impregnation, since the resin pickup of the formulation No. 6Y compacts was low. The total porosities of the materials manufactured from formulations Nos. 4X and 6Y related to their mechanical properties: both materials had significantly better mechanical properties than those of the formulation No. 4 material. The total porosities of all these materials are significantly higher than that of commercial Grade CDJ.

Tables XVII and XVIII present the results of the pore volume and pore size distribution measurements made on compacts of formulations Nos. 1Z and 6Y by using mercury intrusion. Figures 4 to 7 are the corresponding plots of the pore volume and cumulative pore volume versus pore diameter for the two materials. The mercury intrusion method is used to determine the distribution of the pores ranging between 0.02 and 100.0 microns (μ) in diameter. For the range of pores measured, the formulation No. 1Z material was found to have the largest average pore diameter (5.2μ) with an intruded pore volume of 0.082 cc/g.

TABLE XVII

Pore Volume and Distribution by Mercury Intrusion-Formulation No. 1Z Material

SAMPLE WEIGHT = 7.3069 GRAMS.
SAMPLE VOLUME = 4.1580 CC.
SURFACE AREA = 0.972 SQUARE METERS PER GRAM.
TOTAL VOLUME INTRUDED = 0.6012 CC.
~~AVERAGE PORE RADIUS = 2.599 MICRONS.~~

BULK DENSITY AT 100 MICRONS = 1.7573 G/CC.
BULK DENSITY AT 0.02 MICRONS = 2.0543 G/CC.
VOLUME OF PORES BETWEEN 100 MICRONS AND 0.020 MICRONS = 0.0822 CC/G.

RANGE PORE DIAMETEP MICRONS	AVERAGE PORE DIAMETER MICRONS	PORE VOLUME CC/CC	CUMULATIVE PORE VOLUME CC/CC	PER CENT CUMULATIVE PORE VOLUME CC/CC	PORE VOLUME CC/CC/MICRON	PORE VOLUME CC/GRAM	CUMULATIVE PORE VOLUME CC/GRAM
~~100.000- 50.000~~	~~75.0000~~	~~0.00536~~	~~0.00536~~	~~3.70~~	~~0.00010~~	~~0.0030~~	~~0.0822~~
50.000- 25.000	37.5000	0.00156	0.00692	4.79	0.00006	0.0008	0.0792
25.000- 20.000	22.5000	0.00099	0.00791	5.47	0.00019	0.0005	0.0783
20.000- 15.000	17.5000	0.00208	0.01000	6.91	0.00041	0.0011	0.0777
15.000- 10.000	12.5000	0.00294	0.01294	8.95	0.00058	0.0016	0.0765
10.000- 5.000	7.5000	0.00302	0.01597	11.04	0.00060	0.0017	0.0749
~~5.000- 4.000~~	~~4.5000~~	~~0.00097~~	~~0.01695~~	~~11.72~~	~~0.00097~~	~~0.0005~~	~~0.0731~~
4.000- 3.000	3.5000	0.00039	0.01735	11.99	0.00039	0.0002	0.0726
3.000- 2.000	2.5000	0.02512	0.04247	29.37	0.02512	0.0142	0.0724
2.000- 1.000	1.5000	0.05263	0.09511	65.77	0.05263	0.0299	0.0581
1.000- 0.800	0.9000	0.01234	0.10745	74.31	0.06172	0.0070	0.0281
0.800- 0.600	0.7000	0.00998	0.11744	81.21	0.04994	0.0056	0.0211
~~0.600- 0.500~~	~~0.5500~~	~~0.00387~~	~~0.12132~~	~~83.90~~	~~0.03879~~	~~0.0022~~	~~0.0154~~
0.500- 0.400	0.4500	0.00488	0.12620	87.27	0.04884	0.0027	0.0132
0.400- 0.350	0.3750	0.00220	0.12841	88.80	0.04417	0.0012	0.0104
0.350- 0.300	0.3250	0.00123	0.12964	89.65	0.02461	0.0007	0.0092
0.300- 0.280	0.2900	0.00076	0.13040	90.18	0.03805	0.0004	0.0085
0.280- 0.260	0.2700	0.00085	0.13126	90.77	0.04297	0.0004	0.0080
~~0.260- 0.240~~	~~0.2500~~	~~0.00058~~	~~0.13185~~	~~91.18~~	~~0.02914~~	~~0.0003~~	~~0.0075~~
0.240- 0.220	0.2300	0.00039	0.13224	91.45	0.01981	0.0002	0.0072
0.220- 0.200	0.2100	0.00062	0.13286	91.88	0.03104	0.0003	0.0070
0.200- 0.180	0.1900	0.00053	0.13340	92.25	0.02662	0.0003	0.0066
0.180- 0.160	0.1700	0.00036	0.13376	92.50	0.01835	0.0002	0.0063
0.160- 0.140	0.1500	0.00018	0.13395	92.63	0.00933	0.0001	0.0061
~~0.140- 0.120~~	~~0.1300~~	~~0.00059~~	~~0.13454~~	~~93.04~~	~~0.02959~~	~~0.0003~~	~~0.0060~~
0.120- 0.100	0.1100	0.00036	0.13491	93.29	0.01822	0.0002	0.0057
0.100- 0.080	0.0900	0.00137	0.13628	94.24	0.06869	0.0007	0.0055
0.080- 0.060	0.0700	0.00063	0.13691	94.68	0.03164	0.0003	0.0047
0.060- 0.050	0.0550	0.00030	0.13722	94.89	0.03049	0.0001	0.0043
0.050- 0.040	0.0450	0.00170	0.13892	96.07	0.17028	0.0009	0.0041
~~0.040- 0.030~~	~~0.0350~~	~~0.00181~~	~~0.14073~~	~~97.32~~	~~0.18104~~	~~0.0010~~	~~0.0032~~
0.030- 0.020	0.0250	0.00386	0.14460	99.99	0.38666	0.0022	0.0022

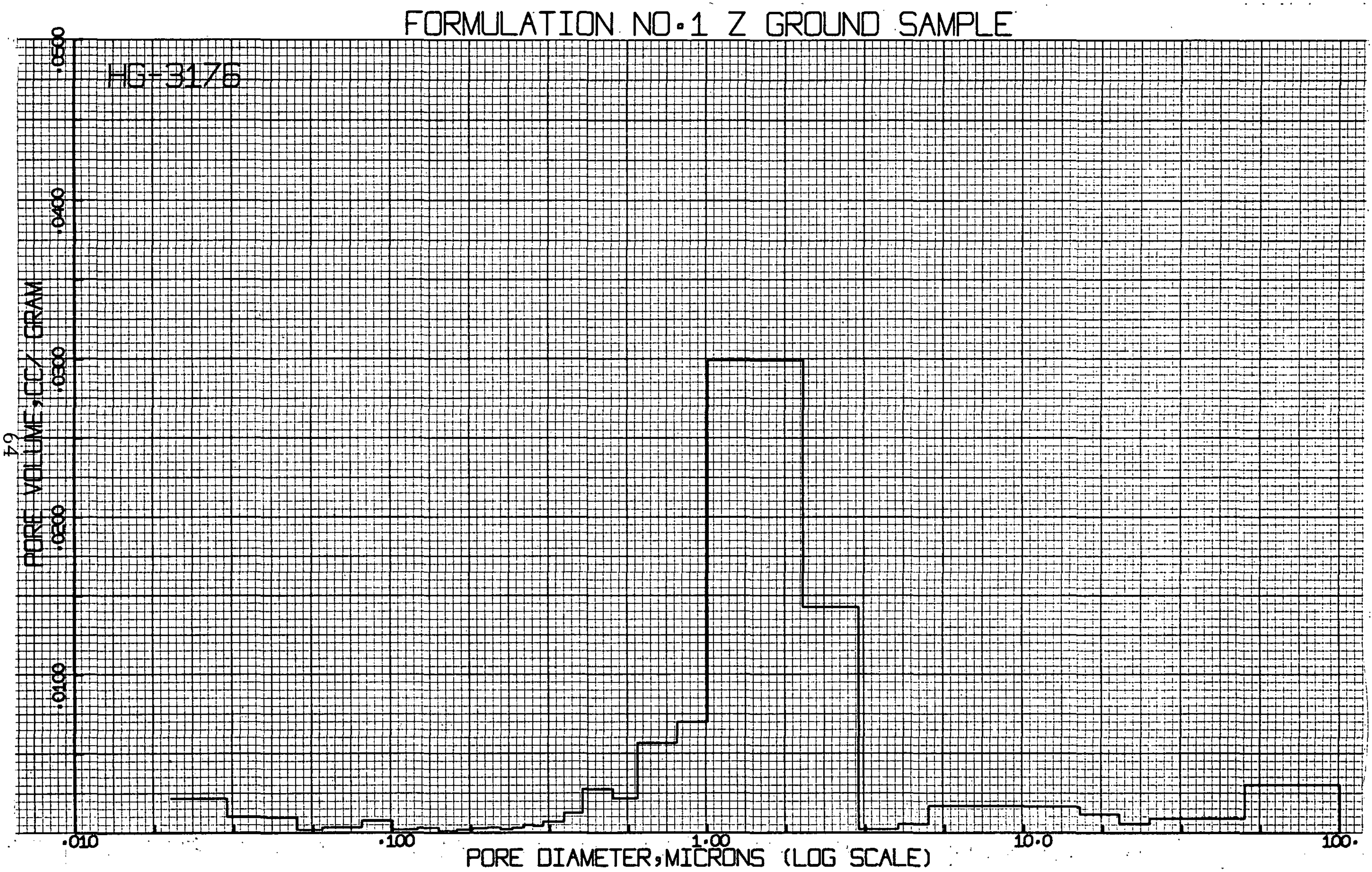

Figure 4. Pore Volume Versus Pore Diameter by Mercury Intrusion-Formulation No. 1Z Material.

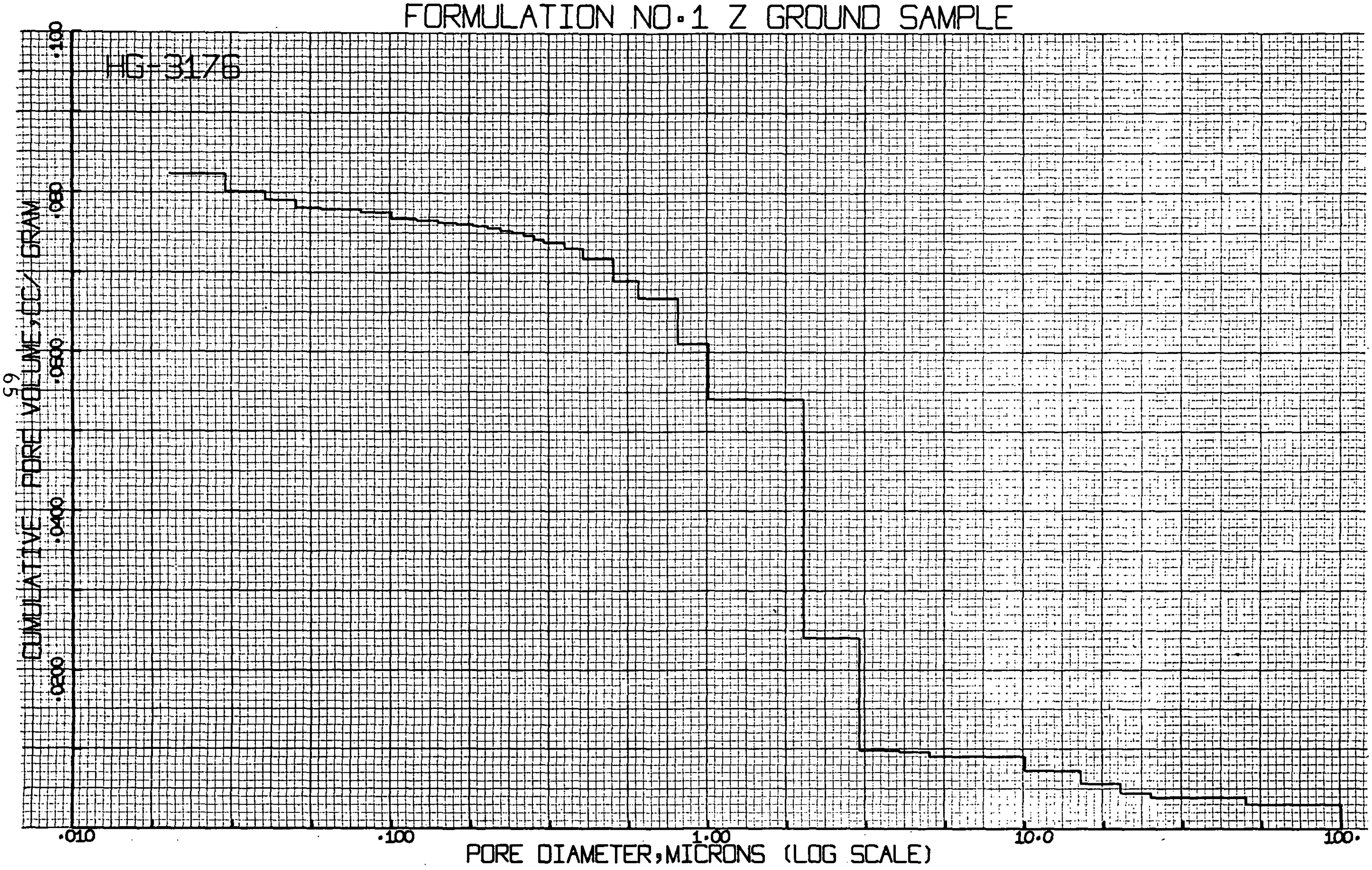

Figure 5. Cumulative Pore Volume Versus Pore Diameter by Mercury Intrusion - Formulation No. 1Z Material.

TABLE XVIII

Pore Volume and Distribution by Mercury Intrusion-Formulation No. 6Y Material

SAMPLE WEIGHT = 6.5447 GRAMS.
SAMPLE VOLUME = 4.4275 CC.
SURFACE AREA = 4.824 SQUARE METERS PER GRAM.
TOTAL VOLUME INTRUDED = 1.0188 CC.
AVERAGE PORE RADIUS = 1.258 MICRONS.

BULK-DENSITY AT 100 MICRONS = 1.4781 G/CC.
BULK DENSITY AT 0.02 MICRONS = 1.9200 G/CC.
VOLUME OF PORES BETWEEN 100 MICRONS AND 0.020 MICRONS = 0.1556 CC/G.

RANGE PORE DIAMETER MICRONS	AVERAGE PORE DIAMETER MICRONS	PORE VOLUME CC/CC	CUMULATIVE PORE VOLUME CC/CC	PER CENT CUMULATIVE PORE VOLUME CC/CC	PORE VOLUME CC/CC/MICRON	PORE VOLUME CC/GRAM	CUMULATIVE PORE VOLUME CC/GRAM
100.000- 50.000	75.0000	0.00049	0.00049	0.21	0.00000	0.0003	0.1556
50.000- 25.000	37.5000	0.00074	0.00124	0.53	0.00002	0.0005	0.1553
25.000- 20.000	22.5000	0.00024	0.00148	0.64	0.00004	0.0001	0.1548
20.000- 15.000	17.5000	0.00251	0.00400	1.74	0.00050	0.0017	0.1546
15.000- 10.000	12.5000	0.00754	0.01155	5.01	0.00150	0.0051	0.1529
10.000- 5.000	7.5000	0.01395	0.02550	11.08	0.00279	0.0094	0.1478
5.000- 4.000	4.5000	0.00500	0.03050	13.25	0.00500	0.0033	0.1384
4.000- 3.000	3.5000	0.01654	0.04705	20.44	0.01654	0.0111	0.1350
3.000- 2.000	2.5000	0.03933	0.08638	37.54	0.03933	0.0266	0.1238
2.000- 1.000	1.5000	0.04086	0.12725	55.29	0.04086	0.0276	0.0972
1.000- 0.800	0.9000	0.00750	0.13475	58.55	0.03751	0.0050	0.0695
0.800- 0.600	0.7000	0.00962	0.14438	62.74	0.04813	0.0065	0.0645
0.600- 0.500	0.5500	0.00577	0.15015	65.25	0.05779	0.0039	0.0579
0.500- 0.400	0.4500	0.00344	0.15360	66.75	0.03444	0.0023	0.0540
0.400- 0.350	0.3750	0.00158	0.15519	67.44	0.03177	0.0010	0.0517
0.350- 0.300	0.3250	0.00245	0.15764	68.50	0.04903	0.0016	0.0506
0.300- 0.280	0.2900	0.00152	0.15917	69.17	0.07647	0.0010	0.0490
0.280- 0.260	0.2700	0.00104	0.16021	69.62	0.05215	0.0007	0.0479
0.260- 0.240	0.2500	0.00083	0.16105	69.98	0.04194	0.0005	0.0472
0.240- 0.220	0.2300	0.00061	0.16167	70.25	0.03098	0.0004	0.0467
0.220- 0.200	0.2100	0.00209	0.16377	71.17	0.10481	0.0014	0.0462
0.200- 0.180	0.1900	0.00236	0.16613	72.19	0.11835	0.0016	0.0448
0.180- 0.160	0.1700	0.00219	0.16833	73.15	0.10999	0.0014	0.0432
0.160- 0.140	0.1500	0.00172	0.17006	73.90	0.08634	0.0011	0.0417
0.140- 0.120	0.1300	0.00287	0.17293	75.15	0.14352	0.0019	0.0406
0.120- 0.100	0.1100	0.00288	0.17582	76.40	0.14427	0.0019	0.0386
0.100- 0.080	0.0900	0.00411	0.17993	78.19	0.20567	0.0027	0.0367
0.080- 0.060	0.0700	0.00636	0.18629	80.95	0.31802	0.0043	0.0339
0.060- 0.050	0.0550	0.00438	0.19067	82.86	0.43820	0.0029	0.0296
0.050- 0.040	0.0450	0.01000	0.20067	87.20	1.00001	0.0067	0.0266
0.040- 0.030	0.0350	0.01227	0.21294	92.54	1.22714	0.0083	0.0199
0.030- 0.020	0.0250	0.01716	0.23011	99.99	1.71633	0.0116	0.0116

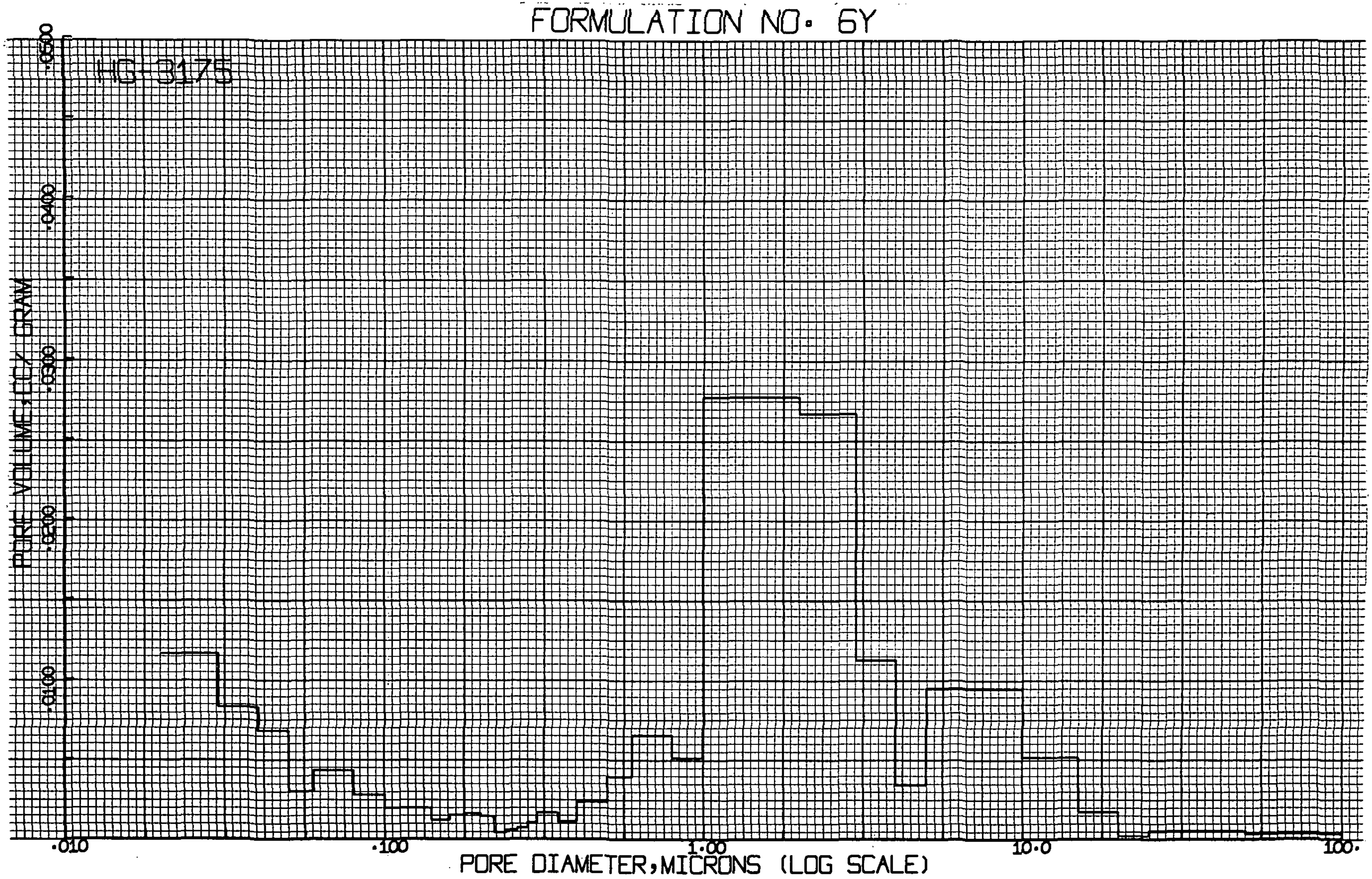

Figure 6. Pore Volume Versus Pore Diameter by Mercury Intrusion-Formulation No. 6Y Material.

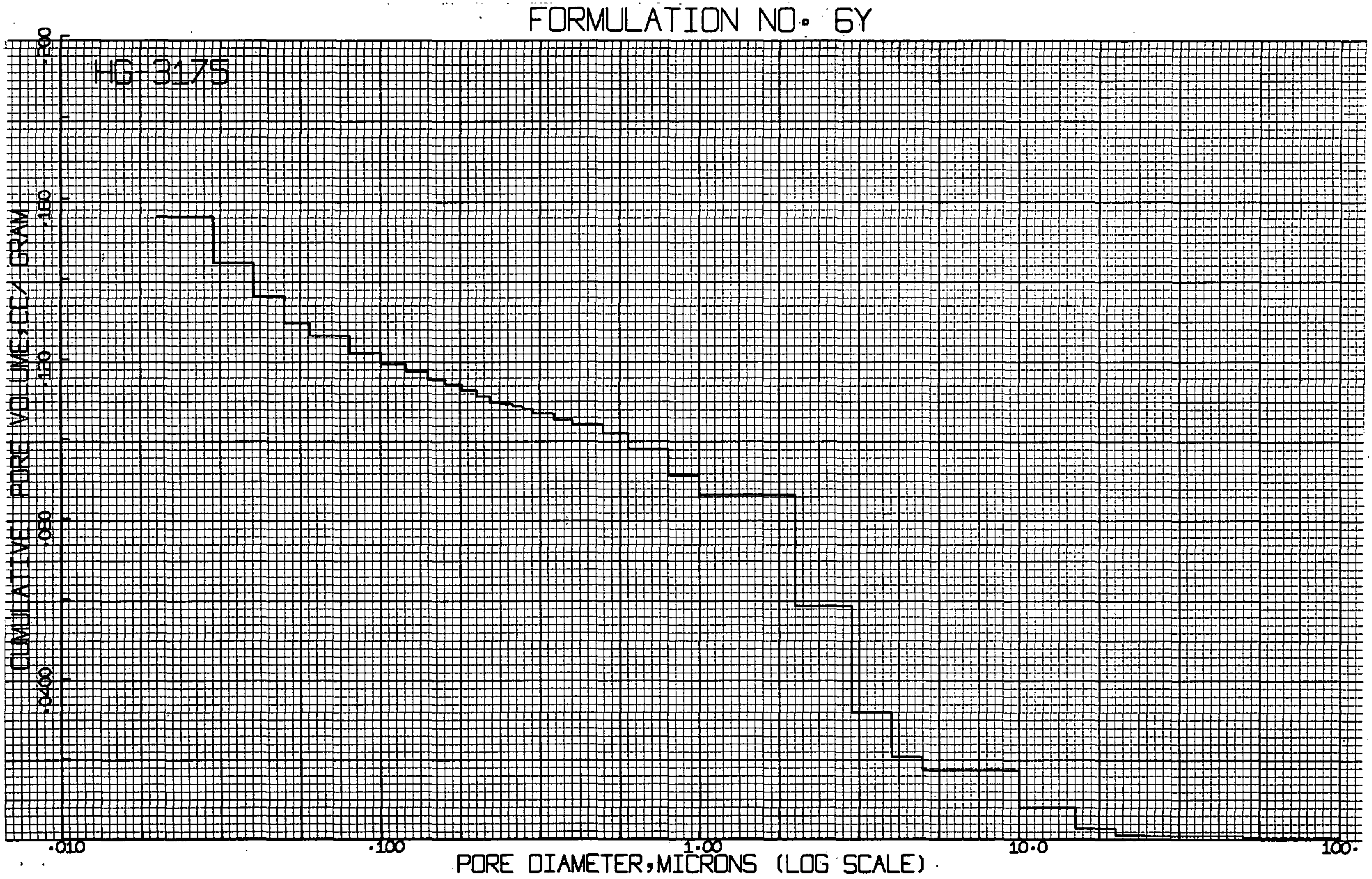

Figure 7. Cumulative Pore Volume Versus Pore Diameter by Mercury Intrusion - Formulation No. 6Y Material.

The similar material manufactured from formulation No. 1X had been found during Task IV(6) to have an average pore diameter of 4.4μ with an intruded pore volume of 0.076 cc/g. The larger average pore diameter and greater intruded pore volume of the formulation No. 1Z material could account for the slight reduction in strength and hardness compared with those of the formulation No. 1X material (Section VI-B). Formulation No. 6Y produced a material having an average pore diameter of 2.6μ, which was approximately half the average pore diameter (5.6μ) determined during Task IV(6) for the similar formulation No. 4X material. The formulation No. 6Y material had an intruded pore volume of 0.156 cc/g, which was a little larger than the 0.139 cc/g value determined for the formulation No. 4X material. The material manufactured from formulation No. 6Y appears to have a larger volume of pores measuring less than 0.060μ in diameter than does the formulation No. 4X material. Since the mercury intrusion method does not accurately measure the distribution of pores smaller than 0.060μ in diameter, a more accurate determination of this difference was made by the nitrogen desorption method.

Table XIX displays the pore volume and pore size distribution determined by mercury intrusion for Grade CDJ. Figures 8 and 9 are the corresponding plots of pore volume and cumulative pore volume versus pore diameter. The sample of Grade CDJ had an average pore diameter of 1.2μ and an intruded pore volume of 0.025 cc/g, both of which are significantly smaller than the corresponding values determined for the seal ring bodies of formulations Nos. 1X, 1Z, 4X, and 6Y.

Tables XX and XXI display the results of nitrogen pore volume measurements made on compacts of formulations Nos. 1Z and 6Y. Figures 10 and 11 are the corresponding plots of percent pore volume and cumulative percent pore volume versus pore diameter. The nitrogen desorption method is used to measure the size distribution of pores with diameters in the range of 20-600 Angstroms (Å). For the range of pore sizes measured by nitrogen desorption (too small to be accurately measured by mercury intrusion), the formulation No. 1Z material was found to have an average pore diameter of 125Å with a total pore volume of 0.0011 cc/g.

TABLE XIX

Pore Volume and Distribution by Mercury Intrusion-Grade CDJ

SAMPLE WEIGHT = 7.7586 GRAMS.
SAMPLE VOLUME = 4.4696 CC.
SURFACE AREA = 0.261 SQUARE METERS PER GRAM.
TOTAL VOLUME INTRUDED = 0.1922 CC.
AVERAGE PORE RADIUS = 0.617 MICRONS.

BULK DENSITY AT 100 MICRONS = 1.7358 G/CC.
BULK DENSITY AT 0.02 MICRONS = 1.8139 G/CC.
HELIUM DENSITY = 1.8410 G/CC.
APPARENT DENSITY = 1.7560 G/CC.
VOLUME OF PORES BETWEEN 100 MICRONS AND 0.020 MICRONS = 0.0247 CC/G.
VOLUME OF PORES UNDER 0.020 MICRONS = 0.0081 CC/G.
VOID FRACTION = 0.043

RANGE PORE DIAMETER MICRONS	AVERAGE PORE DIAMETER MICRONS	PORE VOLUME CC/CC	CUMULATIVE PORE VOLUME CC/CC	PER CENT CUMULATIVE PORE VOLUME CC/CC	PORE VOLUME CC/CC/MICRON	PORE VOLUME CC/GRAM	CUMULATIVE PORE VOLUME CC/GRAM
100.000- 50.000	75.0000	0.00010	0.00010	0.23	0.00000	0.0000	0.0247
50.000- 25.000	37.5000	0.00028	0.00039	0.90	0.00001	0.0001	0.0247
25.000- 20.000	22.5000	0.00007	0.00046	1.07	0.00001	0.0000	0.0245
20.000- 15.000	17.5000	0.00005	0.00052	1.19	0.00001	0.0000	0.0245
15.000- 12.000	13.5000	0.00039	0.00091	2.11	0.00013	0.0002	0.0244
12.000- 11.000	11.5000	0.00009	0.00101	2.33	0.00009	0.0000	0.0242
11.000- 10.000	10.5000	0.00000	0.00101	2.33	0.00000	0.0000	0.0242
10.000- 9.000	9.5000	0.00000	0.00101	2.33	0.00000	0.0000	0.0242
9.000- 8.000	8.5000	0.00000	0.00101	2.33	0.00000	0.0000	0.0242
8.000- 7.500	7.7500	0.00000	0.00101	2.33	0.00000	0.0000	0.0242
7.500- 7.000	7.2500	0.00003	0.00105	2.42	0.00007	0.0000	0.0242
7.000- 6.500	6.7500	0.00004	0.00110	2.53	0.00009	0.0000	0.0241
6.500- 6.000	6.2500	0.00006	0.00117	2.68	0.00012	0.0000	0.0241
6.000- 5.500	5.7500	0.00000	0.00117	2.68	0.00000	0.0000	0.0241
5.500- 5.000	5.2500	0.00000	0.00117	2.68	0.00000	0.0000	0.0241
5.000- 4.500	4.7500	0.00000	0.00117	2.70	0.00001	0.0000	0.0241
4.500- 4.000	4.2500	0.00008	0.00125	2.88	0.00016	0.0000	0.0241
4.000- 3.500	3.7500	0.00024	0.00149	3.44	0.00048	0.0001	0.0240
3.500- 3.000	3.2500	0.00000	0.00149	3.44	0.00000	0.0000	0.0239
3.000- 2.500	2.7500	0.00002	0.00152	3.50	0.00005	0.0000	0.0239
2.500- 2.000	2.2500	0.00008	0.00161	3.70	0.00017	0.0000	0.0239
2.000- 1.500	1.7500	0.00012	0.00173	3.98	0.00024	0.0000	0.0238
1.500- 1.000	1.2500	0.00046	0.00219	5.05	0.00093	0.0002	0.0237
1.000- 0.800	0.9000	0.00193	0.00412	9.48	0.00965	0.0010	0.0235
0.800- 0.600	0.7000	0.01193	0.01606	36.91	0.05969	0.0067	0.0224
0.600- 0.500	0.5500	0.01360	0.02966	68.16	0.13600	0.0077	0.0156
0.500- 0.400	0.4500	0.00837	0.03804	87.41	0.08374	0.0047	0.0078
0.400- 0.350	0.3750	0.00167	0.03972	91.26	0.03359	0.0009	0.0031
0.350- 0.300	0.3250	0.00069	0.04041	92.87	0.01393	0.0003	0.0021
0.300- 0.280	0.2900	0.00029	0.04071	93.54	0.01461	0.0001	0.0017
0.280- 0.260	0.2700	0.00022	0.04093	94.05	0.01122	0.0001	0.0016
0.260- 0.240	0.2500	0.00017	0.04111	94.46	0.00893	0.0001	0.0014
0.240- 0.220	0.2300	0.00015	0.04127	94.83	0.00793	0.0000	0.0013
0.220- 0.200	0.2100	0.00013	0.04141	95.15	0.00691	0.0000	0.0012
0.200- 0.180	0.1900	0.00018	0.04159	95.57	0.00910	0.0001	0.0012
0.180- 0.160	0.1700	0.00013	0.04172	95.87	0.00656	0.0000	0.0010
0.160- 0.140	0.1500	0.00017	0.04190	96.27	0.00883	0.0001	0.0010
0.140- 0.120	0.1300	0.00018	0.04208	96.71	0.00942	0.0001	0.0009
0.120- 0.100	0.1100	0.00016	0.04225	97.09	0.00833	0.0000	0.0008
0.100- 0.080	0.0900	0.00025	0.04251	97.68	0.01297	0.0001	0.0007
0.080- 0.060	0.0700	0.00019	0.04271	98.13	0.00974	0.0001	0.0005
0.060- 0.050	0.0550	0.00008	0.04279	98.33	0.00869	0.0000	0.0004
0.050- 0.040	0.0450	0.00021	0.04300	98.82	0.02101	0.0001	0.0004
0.040- 0.030	0.0350	0.00015	0.04316	99.18	0.01586	0.0000	0.0002
0.030- 0.020	0.0250	0.00035	0.04352	99.99	0.03547	0.0002	0.0002

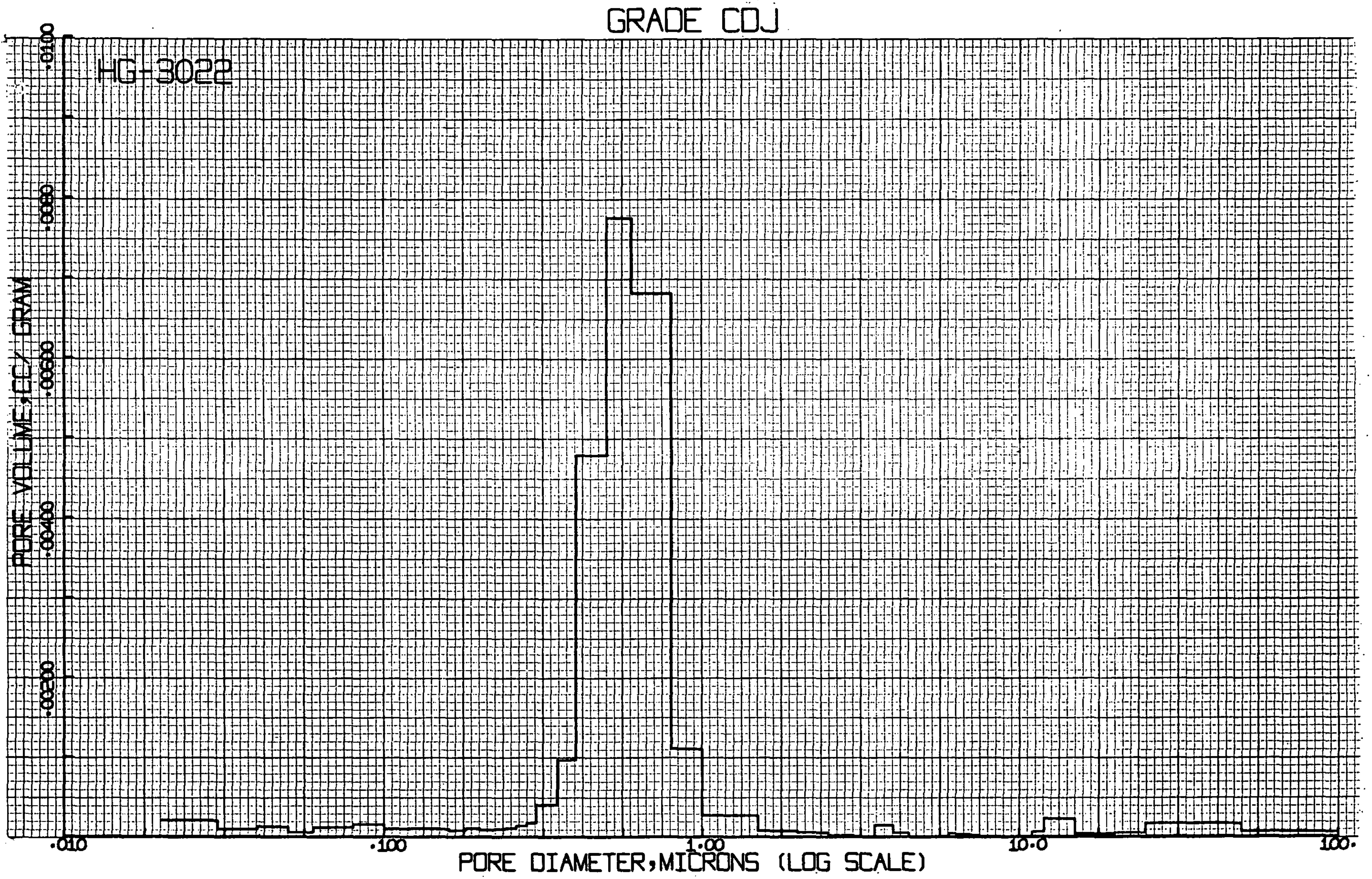

Figure 8. Pore Volume Versus Pore Diameter by Mercury Intrusion-Grade CDJ.

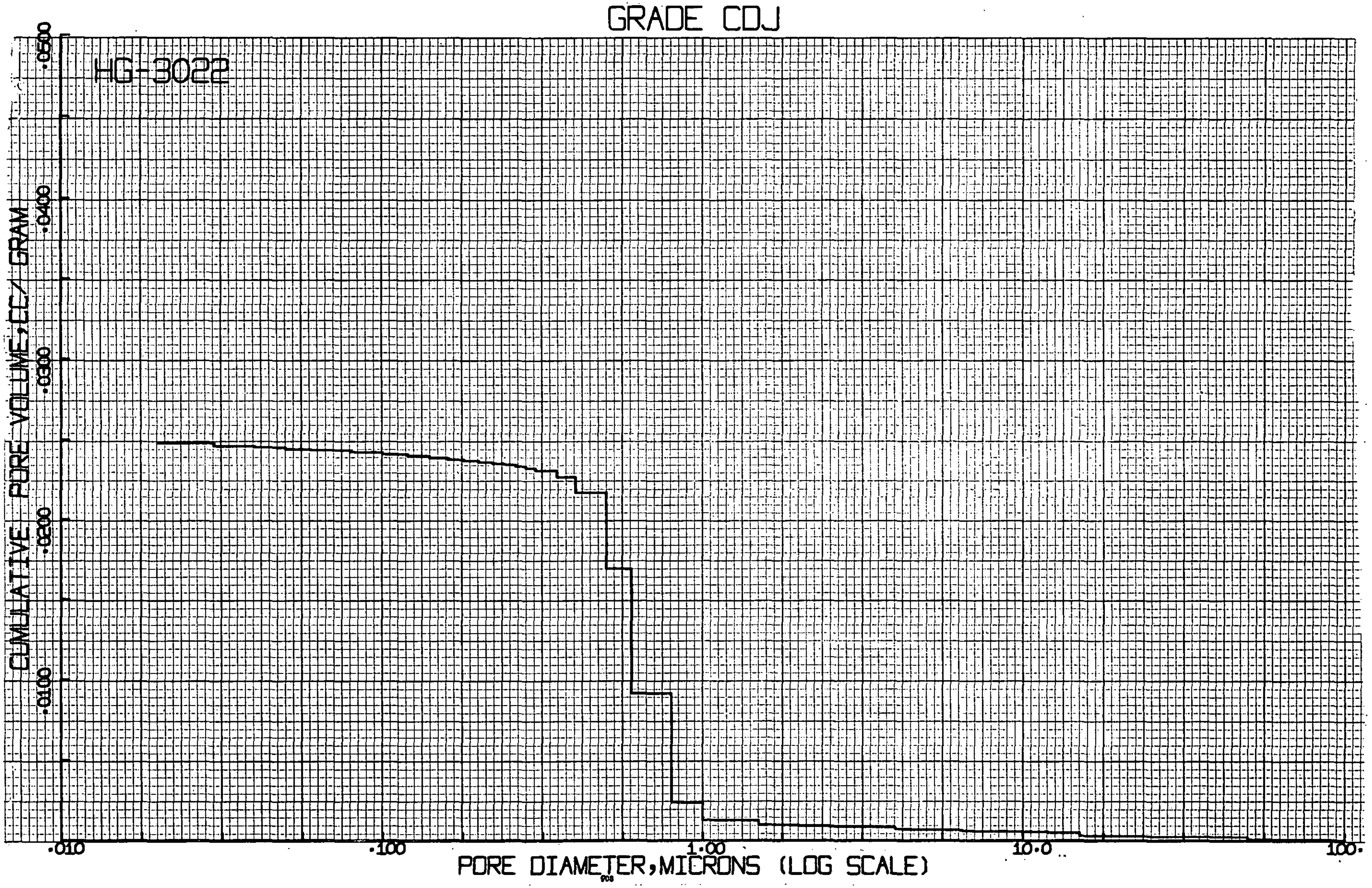

Figure 9. Cumulative Pore Volume Versus Pore Diameter by Mercury Intrusion - Grade CDJ.

TABLE XX

Pore Volume and Distribution by Nitrogen Desorption-Formulation No. 1Z Material

SAMPLE WEIGHT = 21.66900 GRAMS.

BET SURFACE AREA = 0.6 SQUARE METERS PER GRAM.
TOTAL PORE VOLUME = 0.00108 ML PER GRAM.

RANGE PORE DIAMETER,A	AVERAGE PORE DIAMETER,A	PER CENT PORE VOLUME CC/G	PER CENT PORE VOLUME CC/G/A	PER CENT CUMULATIVE PORE VOLUME CC/G
600- 500	550.0	9.387	0.0938	9.387
500- 450	475.0	4.010	0.0802	13.397
450- 400	425.0	4.628	0.0925	18.025
400- 350	375.0	5.187	0.1037	23.213
350- 300	325.0	5.256	0.1051	28.469
300- 280	290.0	2.072	0.1036	30.542
280- 260	270.0	2.175	0.1087	32.717
260- 240	250.0	2.410	0.1205	35.128
240- 220	230.0	2.318	0.1159	37.446
220- 200	210.0	2.456	0.1228	39.903
200- 180	190.0	2.326	0.1163	42.230
180- 160	170.0	2.477	0.1238	44.707
160- 150	155.0	1.125	0.1125	45.833
150- 140	145.0	1.422	0.1422	47.255
140- 130	135.0	1.159	0.1159	48.414
130- 120	125.0	1.600	0.1600	50.015
120- 110	115.0	1.672	0.1672	51.687
110- 100	105.0	3.180	0.3180	54.867
100- 95	97.5	1.432	0.2865	56.300
95- 90	92.5	1.103	0.2206	57.403
90- 85	87.5	1.976	0.3953	59.380
85- 80	82.5	0.258	0.0516	59.639
80- 75	77.5	1.152	0.2304	60.791
75- 70	72.5	1.209	0.2419	62.001
70- 65	67.5	4.044	0.8089	66.046
65- 60	62.5	1.459	0.2918	67.505
60- 55	57.5	0.000	0.0000	67.505
55- 50	52.5	0.000	0.0000	67.505
50- 45	47.5	0.000	0.0000	67.505
45- 40	42.5	0.000	0.0000	67.505
40- 35	37.5	0.000	0.0000	67.505
35- 30	32.5	0.000	0.0000	67.505
30- 25	27.5	0.000	0.0000	67.505
25- 20	22.5	3.883	0.7766	71.388
BELOW 20	10.0	28.611	1.4305	100.000

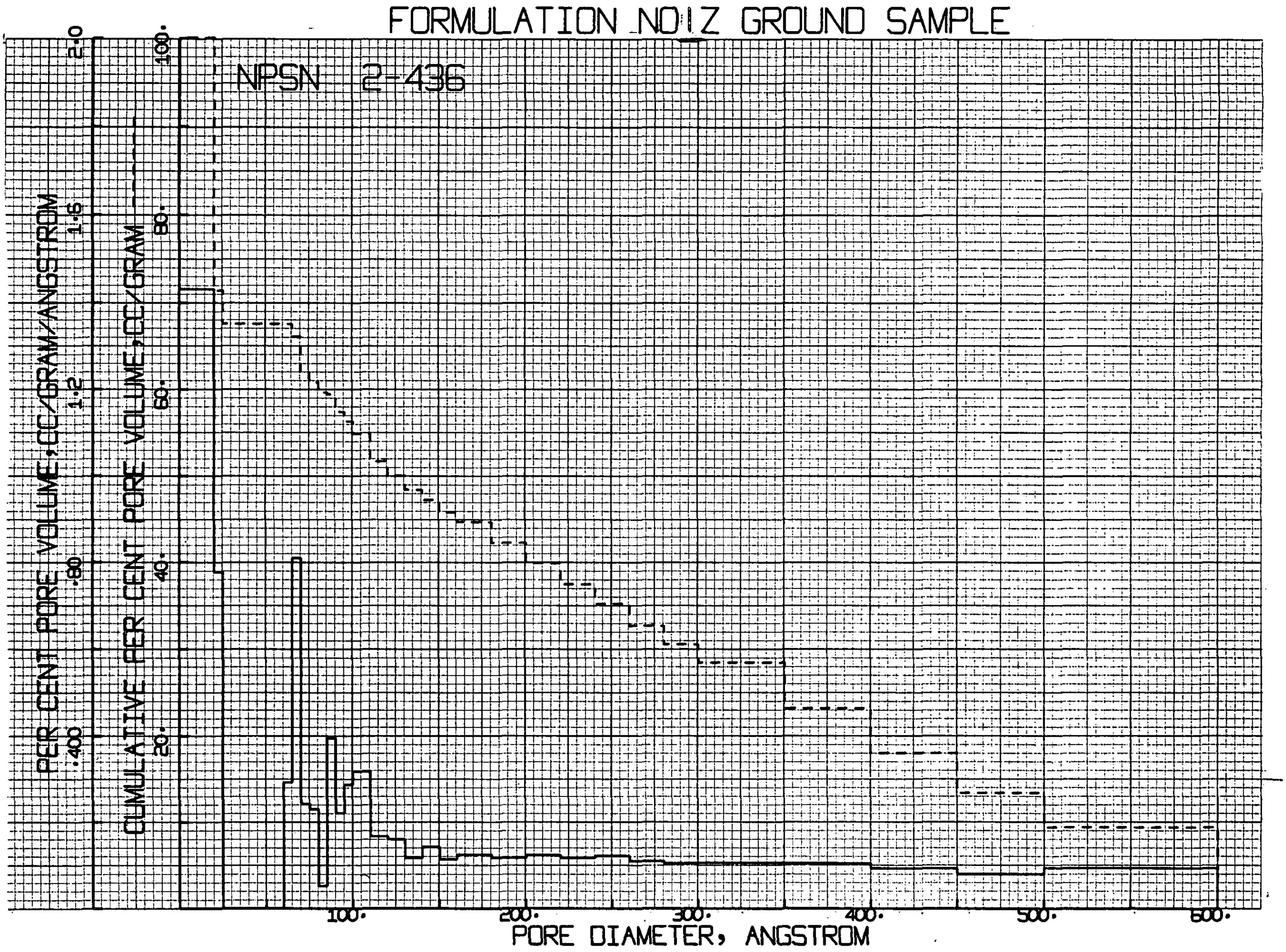

Figure 10. Percent Pore Volume and Cumulative Percent Pore Volume Versus Pore Diameter by Nitrogen Desorption - Formulation No. 1Z Material.

TABLE XXI

Pore Volume and Distribution by Nitrogen Desorption-Formulation No. 6Y Material

Sample Weight = 14.68020 grams.
BET Surface Area = 0.17 square meters per gram.
Total Pore Volume = 0.00106 ml per gram.

Range Pore Diameter, Å	Average Pore Diameter, Å	Percent Pore Volume cc/g	Percent Pore Volume cc/g/Å	Percent Cumulative Pore Volume cc/g
600-500	550.0	8.930	0.0893	8.930
500-450	475.0	5.123	0.1024	14.054
450-400	425.0	4.983	0.0996	19.038
400-350	375.0	5.904	0.1180	24.943
350-300	325.0	5.925	0.1185	30.868
300-280	290.0	2.527	0.1263	33.396
280-260	270.0	3.011	0.1505	36.407
260-240	250.0	2.727	0.1363	39.135
240-220	230.0	3.216	0.1608	42.351
220-200	210.0	3.014	0.1507	45.366
200-180	190.0	3.918	0.1959	49.284
180-160	170.0	3.586	0.1793	52.871
160-150	155.0	2.228	0.2228	55.100
150-140	145.0	1.985	0.1985	57.086
140-130	135.0	2.409	0.2409	59.495
130-120	125.0	2.135	0.2135	61.631
120-110	115.0	2.262	0.2262	63.893
110-100	105.0	2.513	0.2513	66.407
100-95	97.5	1.343	0.2687	67.751
95-90	92.5	1.372	0.2745	69.123
90-85	87.5	1.329	0.2659	70.453
85-80	82.5	1.902	0.3804	72.356
80-75	77.5	1.913	0.3827	74.269
75-70	72.5	2.421	0.4843	76.691
70-65	67.5	2.423	0.4847	79.115
65-60	62.5	2.195	0.4390	81.310
60-55	57.5	2.225	0.4450	83.535
55-50	52.5	2.492	0.4985	86.027
50-45	47.5	2.098	0.4197	88.126
45-40	42.5	2.688	0.5377	90.815
40-35	37.5	7.976	1.5953	98.792
35-30	32.5	0.464	0.0929	99.256
30-25	27.5	0.000	0.0000	99.256
25-20	22.5	0.000	0.0000	99.256
Below 20	10.0	0.743	0.0371	100.000

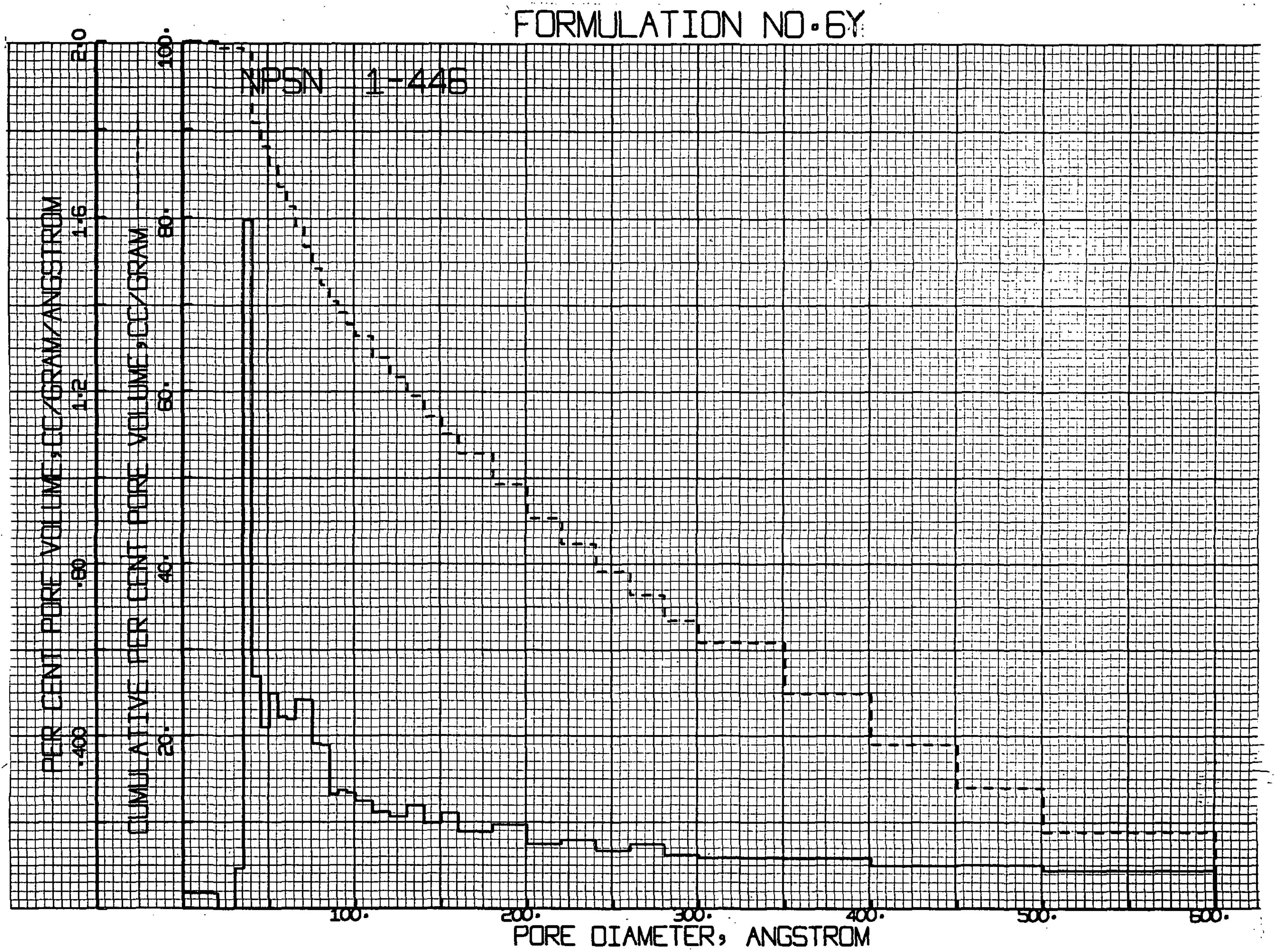

Figure 11. Percent Pore Volume and Cumulative Percent Pore Volume Versus Pore Diameter by Nitrogen Desorption-Formulation No. 6Y Material.

The similar formulation No. 1X material had been found during Task IV(6) to have both a larger average pore diameter and a larger total pore volume (average pore diameter = 240Å, total pore volume is 0.0014 cc/g). The formulation No. 6Y material had an average pore diameter of 180Å, which was considerably larger than the 50Å value measured during Task IV(6) for the similar formulation No. 4X material. However, the total pore volumes of the materials manufactured from formulation Nos. 4X and 6Y were very similar, i.e., 0.00099 cc/g and 0.0011 cc/g, respectively.

Table XXII presents the results of the nitrogen pore volume measurement made on a sample of Grade CDJ. Figure 12 is the corresponding plot of percent pore volume and cumulative percent pore volume versus pore diameter. The sample of Grade CDJ was found to have an average pore diameter of 240Å and a total pore volume of 0.0013 cc/g. The microporosity determined for Grade CDJ is almost identical to that of the formulation No. 1X compact examined during Task IV.(6)

The internal structures of the carbon-graphite seal ring bodies manufactured from formulations Nos. 1Z and 6Y appeared by visual examination to be very homogeneous and fine-grained. No large pores or voids were noted in the compacts examined. The formulation No. 5 compacts, however, were found to have internal structures containing localized areas of relatively high porosity. These "punky" areas were visible to the naked eye. A measure of the uniformity of the structures is obtained by examining the percent increases in weight of the compacts after impregnation with the No. 121 oxidation-inhibiting treatment. The uniformity of impregnation reflects the uniformity of the internal structure of the impregnated material. Table XXIII lists the treat pickups measured for the 1/2-inch (1.3 cm) cubes of formulations Nos. 1X, 1Z, 3, 5, 4X and 6Y after impregnation with the No. 121 oxidation-inhibiting treatment. The materials impregnated with the oxidation-inhibiting treatment were identified (Tables I and VIII) by the formulation number followed by the Number 121 (e.g., formulation No. 1X-121). Table XXIII displays the coefficient of variation for the treat pickups ("V" in Table XXIII). Based on the calculated coefficients of variation, the formulation No. 1Z material was more uniform than the similar formulation No. 1X material, the formulation No. 5 material was considerably less uniform than the similar formulation No. 3 material, and the uniformity of the formulation No. 6Y material was comparable with that of the formulation No. 4X material.

TABLE XXII

Pore Volume and Distribution by Nitrogen Desorption - Grade CDJ

Sample Weight = 24.03020 grams.
BET Surface Area = 0.2 square meters per gram.
Total Pore Volume = 0.00126 ml per gram.

Range Pore Diameter, Å	Average Pore Diameter, Å	Percent Pore Volume cc/g	Percent Pore Volume cc/g/Å	Percent Cumulative Pore Volume cc/g
600- 500	550.0	13.880	0.1388	13.880
500- 450	475.0	6.967	0.1393	20.848
450- 400	425.0	6.706	0.1341	27.554
400- 350	375.0	6.502	0.1300	34.057
350- 300	325.0	6.296	0.1259	40.353
300- 280	290.0	2.386	0.1193	42.740
280- 260	270.0	2.439	0.1219	45.179
260- 240	250.0	2.207	0.1103	47.387
240- 220	230.0	2.951	0.1475	50.339
220- 200	210.0	2.496	0.1248	52.835
200- 180	190.0	3.136	0.1568	55.972
180- 160	170.0	2.879	0.1439	58.851
160- 150	155.0	1.831	0.1831	60.682
150- 140	145.0	2.195	0.2195	62.878
140- 130	135.0	1.551	0.1551	64.430
130- 120	125.0	2.158	0.2158	66.589
120- 110	115.0	2.134	0.2134	68.723
110- 100	105.0	2.458	0.2458	71.181
100- 95	97.5	1.121	0.2243	72.303
95- 90	92.5	1.412	0.2825	73.716
90- 85	87.5	1.091	0.2183	74.808
85- 80	82.5	1.516	0.3033	76.325
80- 75	77.5	1.563	0.3127	77.889
75- 70	72.5	1.001	0.2002	78.890
70- 65	67.5	1.998	0.3996	80.888
65- 60	62.5	2.029	0.4058	82.918
60- 55	57.5	1.478	0.2957	84.397
55- 50	52.5	3.280	0.6560	87.677
50- 45	47.5	0.364	0.0728	88.041
45- 40	42.5	2.504	0.5008	90.545
40- 35	37.5	4.392	0.8785	94.938
35- 30	32.5	1.372	0.2745	96.311
30- 25	27.5	0.000	0.0000	96.311
25- 20	22.5	0.000	0.0000	96.311
Below 20	10.0	3.688	0.1844	100.000

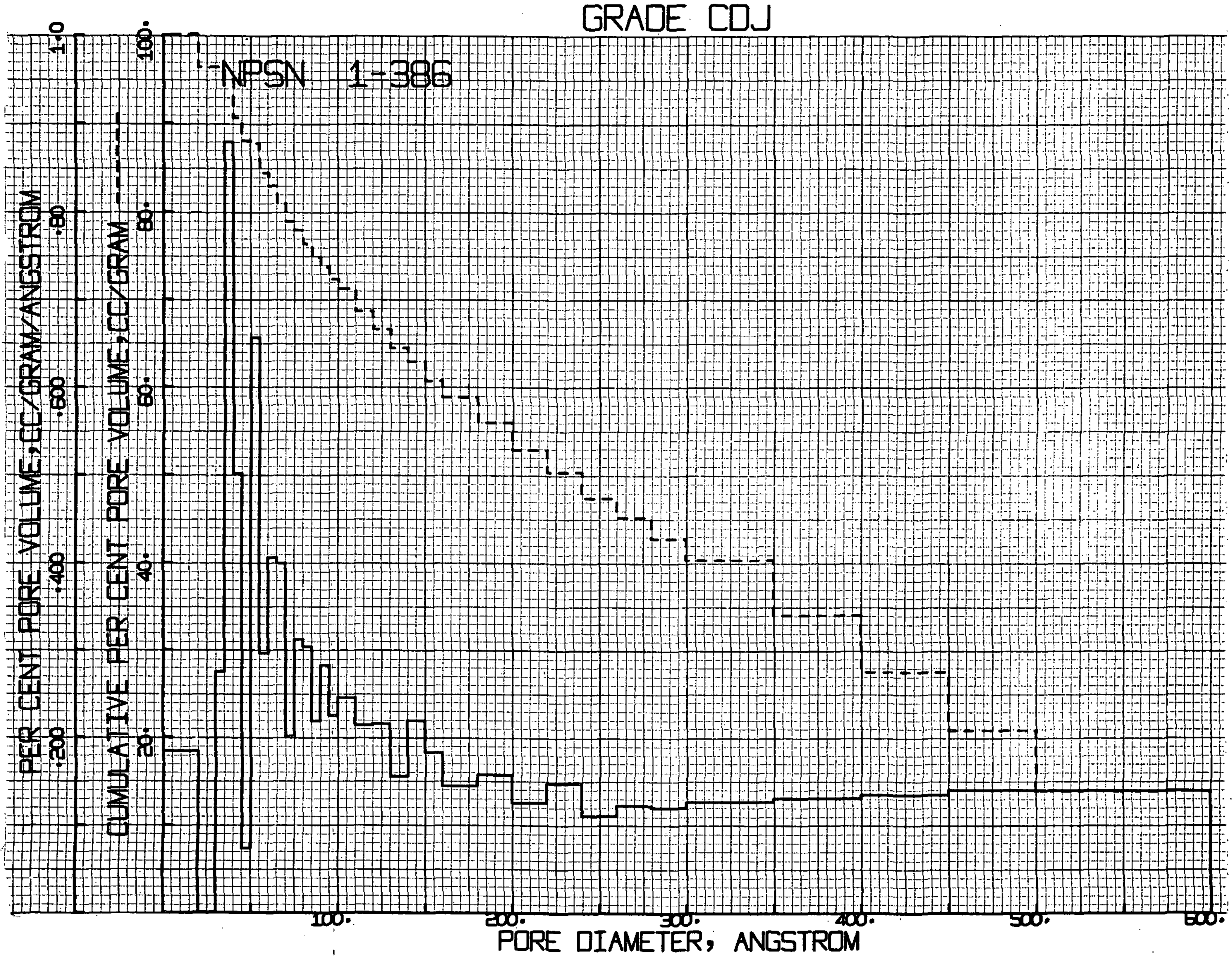

Figure 12. Percent Pore Volume and Cumulative Percent Pore Volume Versus Pore Diameter by Nitrogen Desorption-Grade CDJ.

TABLE XXIII

Weight Pickups for Materials Impregnated with No. 121 Oxidation-Inhibiting Treatment

	Formulation No. 1Z-121	Formulation* No. 1X-121	Formulation No. 5-121	Formulation* No. 3-121	Formulation No. 6Y-121	Formulation* No. 4X-121
Weight Percent Treat Pickup**						
Maximum	1.84	1.68	3.03	2.19	4.10	5.52
Minimum	1.73	1.41	1.93	1.97	2.94	4.07
Average	1.77	1.59	2.53	2.07	3.28	4.56
Standard Deviation	0.05	0.10	0.41	0.09	0.43	0.62
V***	2.9	6.2	16.1	4.5	13.10	13.6
n ****	6	6	6	6	6	6
By Mercury Intrusion						
Average Pore Diameter (μ)	5.2	4.4	---	8.7	2.6	5.6
Intruded Pore Volume (cc/g)	0.082	0.076	---	0.097	0.156	0.139
Normalized Data						
Average No. 121 Treat Pickup	1.11	1.00	---	1.30	2.06	2.87
Average Pore Diameter	1.18	1.00	---	1.98	0.59	1.27
Intruded Pore Volume	1.08	1.00	---	1.28	2.05	1.83

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* Measured During Task IV

** Weight percent treat pickup = 100X $\left(\frac{\text{Weight of Sample After Treatment-Original Weight of Sample}}{\text{Original Weight of Sample}}\right)$

*** V = coefficient of variation = 100 x σ /average

**** The number of 1/2" cubes (oxidation testing samples) impregnated with the No. 121 treatment.

Comparison of the pore volume data determined by mercury intrusion (Table XXIII) with that of the No. 121 oxidation-inhibiting treat pickups shows the expected trend of increasing treat pickup with increasing pore volume. As noted during Task IV, (14) normalization of the data presented in Table XXIII with respect to the formulation No. 1X-121 material shows a disproportionately high treat pickup for the formulation No. 4X material based on its intruded pore volume. The similar material manufactured from formulation No. 6Y experienced a treat pickup directly proportional to its pore volume determined by mercury intrusion, i.e., the formulation No. 6Y material had a normalized intruded pore volume of 2.05 and a normalized treat pickup of 2.06. This phenomenon is probably related to the large difference in the average pore diameters of the materials manufactured from formulations Nos. 4X and 6Y. The treat pickups for the formulations Nos. 1X-121, 1Z-121, and 3-121 materials also were directly proportional to their respective pore volumes determined by mercury intrusion.

The data listed in Table XXIV show that the impregnation of the samples of formulations Nos. 1Z, 5, and 6Y with the No. 121 oxidation-inhibiting treatment increased their respective final densities. The impregnation with the No. 121 treatment probably had little effect on the strengths and hardness of the materials, since the pickups are relatively low and since no additional carbonaceous material was added to the compacts as in the case when a resin-impregnant is carbonized. The densities listed in Table XXIV were measured for the treated 1/2-inch (1.3 cm) cubes which were later used during the oxidation testing of the three materials.

The pore structures determined for the seal ring bodies of formulations Nos. 1Z and 6Y indicate that both are potentially good carbon-graphite seal ring materials. Both of the formulations resulted in fine-grain materials with relatively low porosity.

TABLE XXIV

Bulk Densities of Materials Impregnated with No. 121 Oxidation-Inhibiting Treatment (Grams/Cubic Centimeter)

	Formulation No. 1Z	Formulation No. 1Z-121
Maximum	1.794	1.825
Minimum	1.783	1.816
Average	1.789	1.821
Standard Deviation	0.004	0.004
n	6	6
	Formulation No. 5	Formulation No. 5-121
Maximum	1.696	1.729
Minimum	1.653	1.703
Average	1.675	1.717
Standard Deviation	0.016	0.010
n	6	6
	Formulation No. 6Y	Formulation No. 6Y-121
Maximum	1.514	1.574
Minimum	1.501	1.547
Average	1.507	1.556
Standard Deviation	0.005	0.011
n	6	6

E. Oxidation Tests

High oxidation resistance is a primary requirement for a carbon-graphite seal ring material which is exposed to ambient air temperatures up to 1300°F (704°C). A material with a high degree of crystallinity is needed, since the crystallinity of a carbon-graphite material greatly affects the rate at which it oxidizes. Formulation Nos. 1Z, 5, and 6Y were designed to yield carbon-graphite seal ring bodies with high degrees of crystallinity. Further increases in oxidation resistance are obtained by impregnating the seal ring bodies with oxidation-inhibiting treatments, such as the No. 121 treatment. Oxidation tests were conducted at 1300°F (704°C) with 1/2-inch (1.3 cm) cubes prepared from the seal ring bodies of formulation Nos. 1Z, 5, and 6Y. Commercial seal ring Grade CDJ was used as a standard for the oxidation testing. The 1/2-inch (1.3 cm) cubes were impregnated with the No. 121 treatment before being exposed to the oxidizing conditions; the No. 121 treat pickups were presented in Table XXIII.

The oxidation test procedure and equipment employed during Task VII were the same as those used during the Tasks I and IV oxidation studies.(9,10) 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) and to allow the removal of the oxidation samples from the furnace without damaging them. Figure 13 is a schematic of the oxidation testing apparatus. The furnace has a split door which was propped open during oxidation testing so that a 3/8-inch (0.95 cm) 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 13. 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 (704°C) furnace chamber. After 1/2-hour exposure to the oxidizing condition, 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 period. This procedure was continued until the samples had been exposed to the oxidizing conditions for a total of three hours. A preliminary test had shown that the weight of the empty quartz tubes remained constant when exposed to the 1300°F (704°C) temperature.

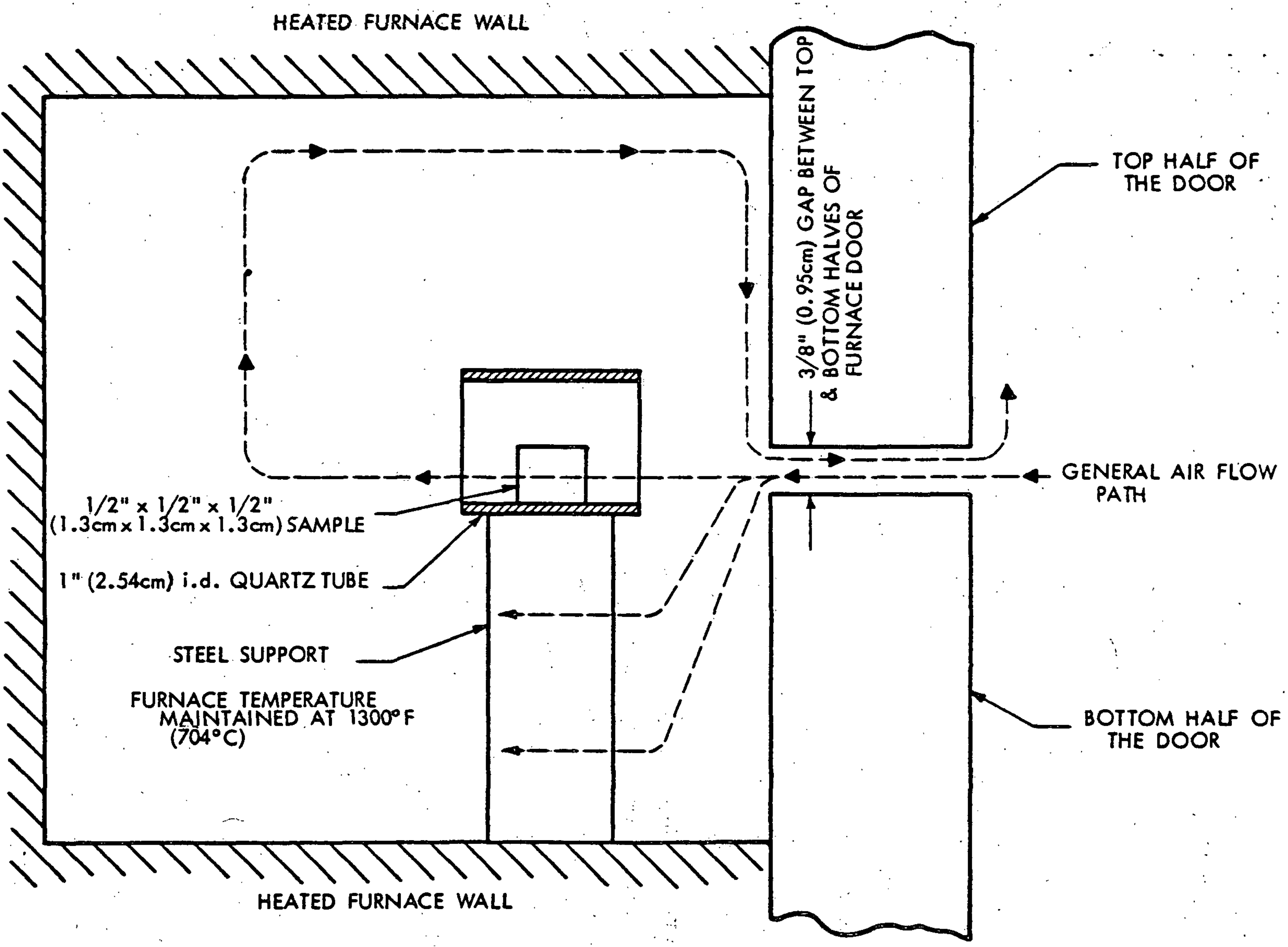

Figure 13. Oxidation Testing Apparatus

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Three oxidation tests were conducted during Task VII using the No. 121 treated samples. During each test, one sample of each of the formulations Nos. 1Z-121, 5-121, and 6Y-121 and one sample of Grade CDJ-121 were exposed to the 1300°F (704°C) temperature for a three-hour period. The relative positions of the four materials in the furnace were changed for each test to avoid any possible position-to-position variation in the oxidizing conditions. One of the tests was extended to include weight measurements after 4-1/2 hours and six hours of exposure, and two tests were extended to include seven-hour readings. The agreement between the oxidation rates determined for the Grade CDJ-121 standards during the Tasks IV and VII oxidation studies indicated that the oxidation results from the two series of tests can be compared directly.

Figures 14 to 16 are semi-logarithmic plots of the average percent weight loss versus exposure time at 1300°F (704°C) for the samples of formulations Nos. 1Z-121, 5-121, and 6Y-121. Each figure includes the control Grade CDJ-121 oxidation curve. The oxidation rates for all three of the No. 121 treated materials manufactured during Task VI were significantly lower than that of Grade CDJ-121. Also included in each figure is the oxidation curve determined during Task IV(10) for a similar material manufactured during Task III.(6)

Figure 14 is a plot of the oxidation rate for the formulation No. 1Z-121 material. This material oxidized at a slower average rate than that determined for the similar formulation No. 1X-121 material manufactured during Task III.(6) The presence of a slightly greater amount of absorbed moisture probably accounted for the higher weight losses experienced with the formulation No. 1Z-121 material during the initial one-half hour of exposure. One common method of characterizing the oxidation resistance of a carbon-graphite material is to specify the exposure time at temperature required to produce a 5-percent loss in the weight of the material. The formulation No. 1Z-121 material experienced a 5-percent weight loss after being exposed to the 1300°F (704°C) ambient air for 6.7 hours. This result was an improvement over the formulation No. 1X-121 material, which required only 4.7 hours to achieve the 5-percent weight loss when tested under the same conditions.

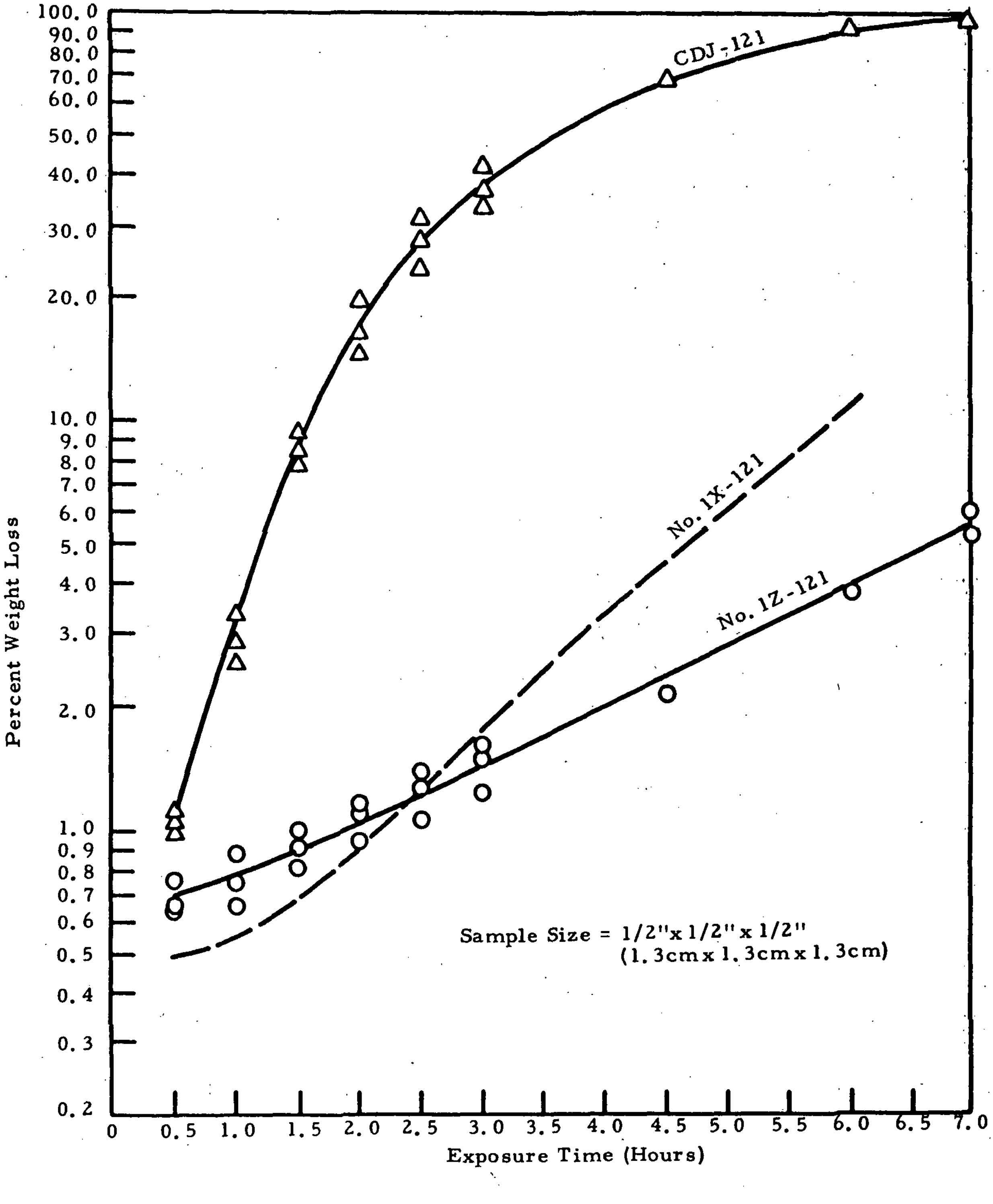

Figure 14. Percent Weight Loss Versus Exposure Time at 1300°F (704°C) - Formulation No. 1Z-121 Material.

G720399

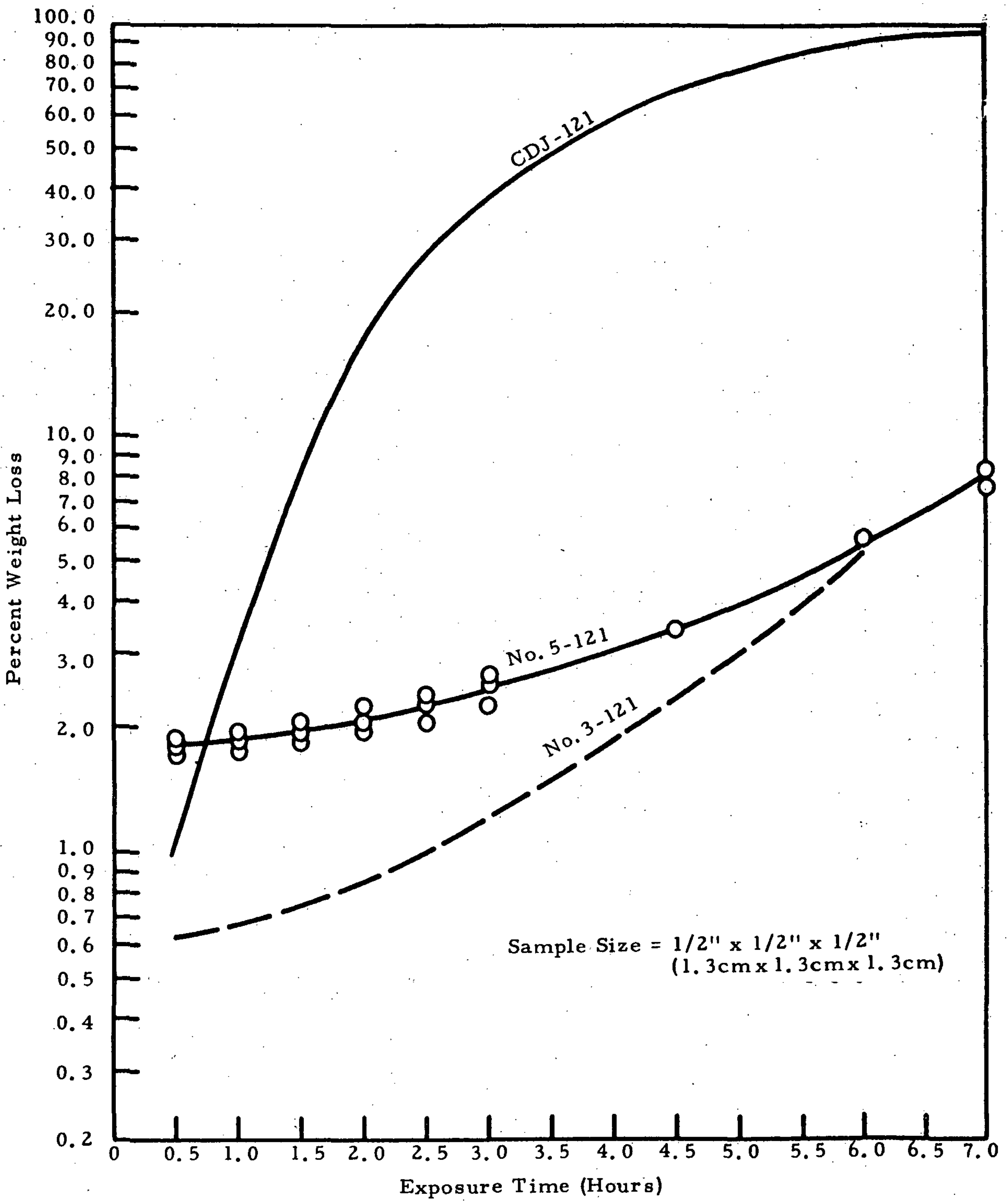

Figure 15. Percent Weight Loss Versus Exposure Time at 1300°F (704°C) - Formulation No. 5-121 Material.

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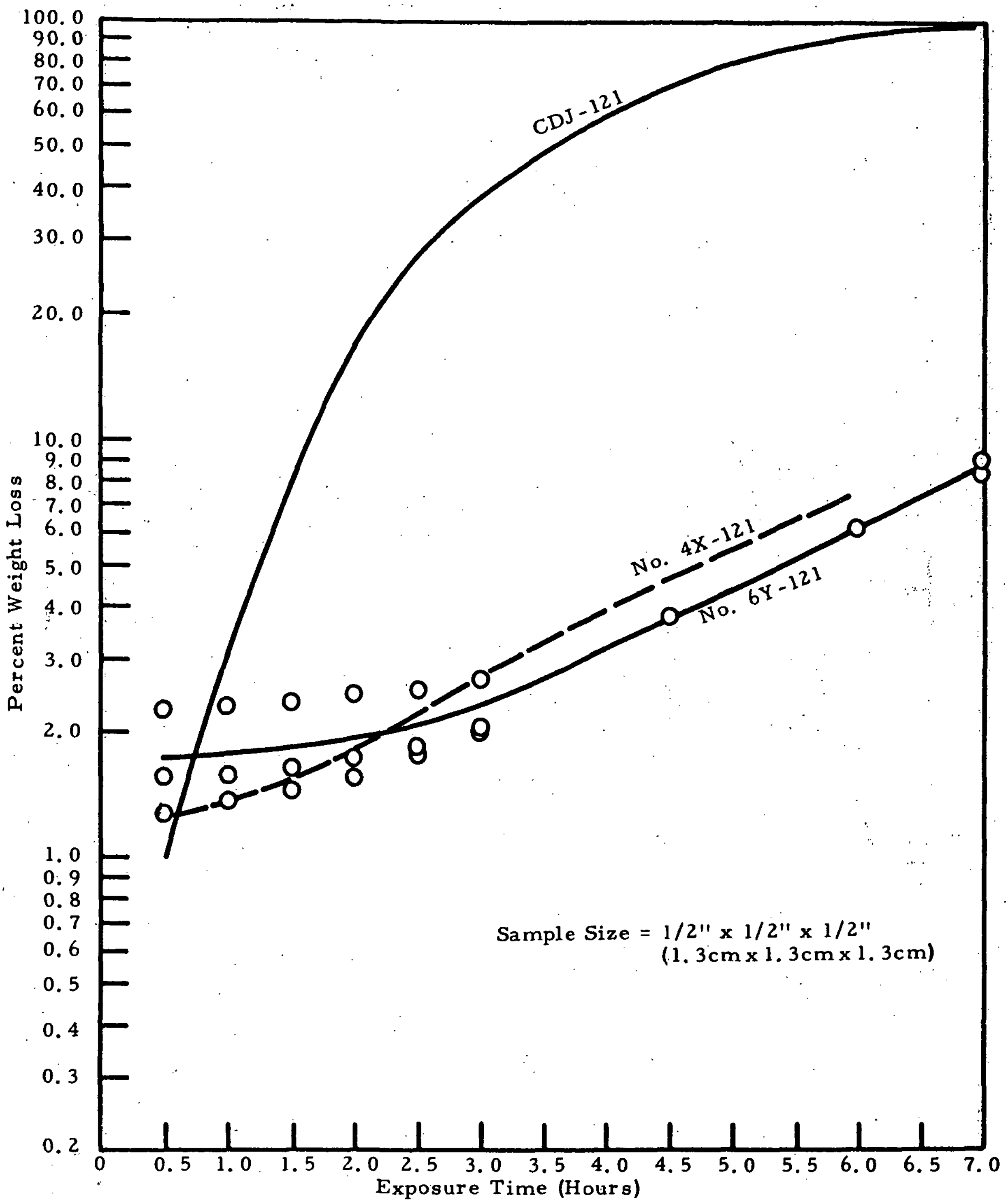

Figure 16. Percent Weight Loss Versus Exposure Time at 1300°F (704°C) - Formulation No. 6Y-121 Material.

G720397

Figure 15 is a plot of the 1300°F (704°C) oxidation rate determined for the formulation No. 5-121 material. The initial weight losses measured for the formulation No. 5-121 material were considerably larger than those determined during Task IV(10) for the similar formulation No. 3-121 material. The weight pickups measured after impregnation with the No. 121 oxidation-inhibiting treatment indicated that the formulation No. 5 material was more porous and considerably less uniform than the material manufactured from formulation No. 3. The greater porosity of the formulation No. 5 material and the resultant higher treat pickup probably increased the amount of adsorbed moisture removed during the initial one-half hour of exposure. This expulsion of moisture may account for the higher initial oxidation rate of the formulation No. 5 material as compared with that of the formulation No. 3 material. Although their initial weight losses were different, both the formulation No. 5-121 material and the formulation No. 3-121 material experienced a 5-percent weight loss after approximately six hours of exposure to the 1300°F (704°C) ambient air.

The oxidation curve for the formulation No. 6Y-121 material is presented in Figure 16. Comparison of this oxidation curve with that determined for the similar formulation No. 4X-121 material during Task IV(10) shows that the two materials have comparable oxidation resistance. The formulation No. 6Y-121 material experienced a 5-percent loss in weight after 5.4 hours of exposure and the formulation No. 4X-121 material required only 4.7 hours to achieve this weight loss.

The difference between the oxidation rates of the materials manufactured from formulations Nos. 1X-121, 1Z-121, 3-121, 5-121, 4X-121, and 6Y-121 were relatively small. A statistical analysis of these oxidation data was conducted to determine whether the observed differences were significant. Table XXV lists the differences in percent weight loss measured after 1/2 hour and three hours of exposure to the oxidizing conditions. This procedure for specifying oxidation losses was adopted during Task I(9) when the evaporation of absorbed moisture was found to distort the incremental weight losses measured after the first 1/2 hour of exposure.

TABLE XXV

Oxidation Test Data for Materials Impregnated with No. 121 Oxidation-Inhibiting Treatment

Δ Percent Weight Loss 1/2 - 3 Hours

	Formulation No. 1Z-121	Formulation* No. 1X-121	Formulation No. 5-121	Formulation* No. 3-121	Formulation No. 6Y-121	Formulation* No. 4X-121
Maximum	0.84	2.06	0.77	0.87	0.73	2.61
Minimum	0.59	0.72	0.48	0.29	0.39	0.83
Average	0.76	1.27	0.67	0.64	0.53	1.51
Standard Deviation	0.15	0.70	0.16	0.31	0.17	0.96
n	3	3	3	3	3	3

Statistical Analysis of Oxidation Test Data

Materials	F Distribution			Student's t Distribution				
	F Calculated	F** From Tables	Differences In Variances	t Calculated	Probability	Degrees of Freedom	t*** From Tables	Difference Between Oxidation Results
No. 1Z-121 vs. No. 5-121	1.5	69.0	Not Significant	0.70	0.05	4	2.78	Not Significant
No. 1Z-121 vs. No. 6Y-121	1.5	69.0	Not Significant	1.69	0.05	4	2.78	Not Significant
No. 1Z-121 vs. No. 1X-121	24.5	69.0	Not Significant	1.23	0.05	4	2.78	Not Significant
No. 1Z-121 vs. No. 3-121	5.0	69.0	Not Significant	1.08	0.05	4	2.78	Not Significant
No. 1Z-121 vs. No. 4X-121	46.0	69.0	Not Significant	1.34	0.05	4	2.78	Not Significant
No. 5-121 vs. No. 6Y-121	1.0	69.0	Not Significant	1.02	0.05	4	2.78	Not Significant
No. 5-121 vs. No. 1X-121	16.3	69.0	Not Significant	1.45	0.05	4	2.78	Not Significant
No. 5-121 vs. No. 3-121	3.3	69.0	Not Significant	0.15	0.05	4	2.78	Not Significant
No. 5-121 vs. No. 4X-121	30.7	69.0	Not Significant	1.49	0.05	4	2.78	Not Significant
No. 6Y-121 vs. No. 1X-121	16.3	69.0	Not Significant	1.78	0.05	4	2.78	Not Significant
No. 6Y-121 vs. No. 3-121	3.3	69.0	Not Significant	0.34	0.05	4	2.78	Not Significant
No. 6Y-121 vs. No. 4X-121	30.7	69.0	Not Significant	1.74	0.05	4	2.78	Not Significant
No. 1X-121 vs. No. 3-121	5.2	69.0	Not Significant	1.42	0.05	4	2.78	Not Significant
No. 1X-121 vs. No. 4X-121	1.9	69.0	Not Significant	0.35	0.05	4	2.78	Not Significant
No. 3-121 vs. No. 4X-121	9.7	69.0	Not Significant	1.50	0.05	4	2.78	Not Significant

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* Measured during Task IV

** Hoel, Paul G., Introduction to Mathematical Statistics, John Wiley & Sons, Inc., New York-London, Pages 404 to 407, C1962.

*** Brownlee, K. A., Industrial Experimentation, Chemical Publishing Co., Inc., New York, Page 144, C1947.

Note: See Appendix III for explanation of F and Student's t Distribution.

Table XXV also displays the results of the Student's t distribution(15,16) used to compare the weight losses (Δ Percent Weight Loss 1/2-3 hours) determined for the six materials. The statistical analysis indicates that the apparent difference in the oxidation rate of formulations No. 1X-121 material and that of the formulation No. 1Z-121 material is not significant. No significant differences were indicated in the oxidation rates of the materials manufactured from formulations Nos. 1X-121, 1Z-121, 3-121, 5-121, 4X-121, and 6Y-121.

The oxidation rates determined for the samples of the materials manufactured from formulations Nos. 1X-121, 5-121, and 6Y-121 indicate that the three materials are potentially good carbon-graphite seal ring materials.The materials manufactured from formulations Nos. 1Z-121 and 6Y-121 showed oxidation resistances at least comparable with those of the similar materials manufactured during Task III.(6)

SECTION VII

DISCUSSION OF THE RESULTS

An overall comparison of the material properties measured for the seal ring bodies of formulations Nos. 1Z, 5, and 6Y is needed to determine which materials are best suited for use as self-acting seals which will be exposed to ambient air temperatures up to 1300°F (704°C). The results of Task VII have shown that the materials manufactured from formulations Nos. 1Z-121 and 6Y-121 are potentially better seal ring materials for high temperature use than commercial Grade CDJ-121. Although the two materials are not so strong and hard as Grade CDJ-121, they have much better thermal properties. The high thermal conductivities of the seal ring bodies of formulations Nos. 1Z and 6Y will provide rapid transfer of the deleterious frictional heat which can develop during periods of sliding contact. After they have been impregnated with the No. 121 oxidation-inhibiting treatment, the two materials have significantly better oxidation resistance than Grade CDJ-121. The seal life of the two materials, therefore, should surpass that of Grade CDJ-121 under high ambient air temperature conditions where oxidation is the limiting performance factor. Both of the materials have the further advantage of being much more machinable than Grade CDJ. Good machinability is very desirable for a seal ring material, since seal dam widths as small as 0.02 inches (.05 cm) often are necessary in seal design.

The material properties determined for the seal ring bodies of formulation No. 1Z indicate that it is a potentially good material for meeting the goal of the Contract. In some respects, the formulation No. 1Z material is a better seal ring material than that manufactured from the similar formulation No. 1X during Task III.(6) The formulation No. 1X material had been judged during Task IV(6) to be the best material manufactured during Task III(6) for meeting the goal of this Contract. After impregnation with the No. 121 oxidation-inhibiting treatment, the formulation No. 1Z-121 material had an oxidation rate at least as low as that of the material manufactured from formulation No. 1X-121. The narrow spread in the No. 121 treat pickups measured for the compacts of formulation No. 1Z-121 indicates that it was the most uniform material manufactured thus far. Formulations Nos. 1X and 1Z yielded carbon-graphite materials with similar thermal and mechanical properties.

Formulation No. 1Z was not among the three material formulations originally selected for the manufacturing of carbon-graphite seal ring bodies during Task VI. Formulation No. 1Z was substituted for formulation No. 1Y after processing problems prevented the manufacture of the latter material. Although a sufficient quantity of the formulation No. 1Z material was successfully produced to fulfill the testing and delivery requirements prescribed by the Contract, a processing problem also was encountered during its manufacture. This problem consisted of the chipping of the resin-impregnated 2800°C baked compacts during rebaking to 1000°C. The chipping problem was attributed to the furfuryl alcohol (50 pbw)-Bakelite BRP-5095 resin (35 pbw) impregnant. The resin solution apparently filled the open porosity of the large compacts so completely that, during pyrolysis, volatiles could not escape without disrupting the stock. Although this resin impregnant was successfully used during Task V to produce small (4-inch x 0.5-inch x 0.25-inch (10.2 cm x 1.3 cm x 0.6 cm)) 1000°C baked samples of formulation No. 1Y, it is not a good impregnant for manufacturing large (5-inch (12.7 cm) diameter x 1.4-inch (3.6 cm) thick) compacts. The disruption of the large resin impregnated compacts during rebaking to 1000°C prevented the manufacture of the formulation No. 1Y material and the formulation No. 6Y ring blanks during Task VI. The chipping of the formulation No. 1Z material was reduced to a tolerable level by using a very slow firing schedule to rebake the resin impregnated compacts to 1000°C. No further damage was sustained by the formulation No. 1Z compacts during final baking to 2800°C.

Formulation No. 5 was the base material for one of the three formulations (No. 5Y) originally selected for the manufacture of seal ring bodies during Task VI. The formulation No. 5 material was the same as that manufactured from formulation No. 3 during Task III(6) except that formulation No. 5 included pressure curing and pressure baking as a part of its processing. The two baking procedures had been found during the Task V screening studies to be good ways to improve the mechanical properties. Major processing problems were encountered during the manufacture of the formulation No. 5 material. These processing problems most probably resulted from the use of the one-year-old formulation No. 3 mix remaining from Task III.(6) The Bakelite BRP-5095 resin binder in this mix apparently had deteriorated with age. The apparent deterioration of the resin binder had first been noted during the Task V screening study. The 1000°C baked density (1.427 g/cc) of the compacts prepared during Task V from the one-year-old mix was considerably lower than that (1.519 g/cc) of the formulation No. 3 compacts produced during Task III.(6) In view of the processing difficulties experienced, only a few of the formulation No. 5 compacts were completely processed during Task V through baking to 2800°C. The formulation No. 5 compacts were not resin-impregnated prior to final baking to 2800°C, since the Contractor wanted to avoid any further processing problems which might result from the use of the furfuryl alcohol-Bakelite BRP-5095 resin-impregnating solution.

The formulation No. 5 material was not completely characterized during Task VII, since the apparent deterioration of the resin binder had prevented the material from gaining the full benefit of pressure baking. Only the mechanical properties and oxidation rate of the formulation No. 5 material were determined. The oxidation testing was carried out by using samples impregnated with the No. 121 oxidation-inhibiting treatment. The material properties measured for the pressure baked formulation No. 5 material were approximately the same as those measured during Task IV(6) for the similar formulation No. 3 material.

The material properties determined for the formulation No. 6Y material indicate that it is a potentially better seal ring material than that manufactured from the similar formulation No. 4X during Task III.(6) Formulation No. 6Y resulted in a material with mechanical properties approximately the same as those determined for the formulation No. 4X material. However, the formulation No. 6Y material had a higher thermal conductivity than that measured for the formulation No. 4X material and a considerably lower coefficient of thermal expansion. The higher thermal conductivity indicates that the formulation No. 6Y material will more rapidly dissipate the frictional heat generated during limited periods of sliding contact. The lower coefficient of thermal expansion measured for the formulation No. 6Y material is beneficial from a thermal deformation standpoint. The formulation No. 6Y-121 material and that manufactured from formulation No. 4X-121 oxidized at approximately the same rate.

No manufacturing problems were encountered during the processing of the solid plugs of formulation No. 6Y through final baking to 2800°C. Formulation No. 6Y specified the impregnation of 1000°C baked formulation No. 6 compacts with the furfuryl alcohol (50 pbw)-Bakelite BRP-5095 resin (35 pbw) solution prior to final baking to 2800°C. However, the apparent formation of a low porosity surface on the solid plugs during processing impeded the penetration of the resin impregnant. Due to the low resin pickup (1.1-percent), very little carbonaceous material was gained from the resin impregnant after rebaking the solid plugs. Since the solid plugs of formulation No. 6Y experienced such a small resin pickup, the material properties determined for the formulation No. 6Y material during Task VII should be, for all practical purposes, the same as those which would be measured for the non-resin-impregnated formulation No. 6 base material.

Ring blanks were manufactured from formulation No. 6 after processing problems prevented the manufacture of the resin-impregnated formulation No. 6Y ring blanks. The processing problems resulted from the large resin pickup (11.1%) obtained for the formulation No. 6Y ring blanks. Unlike the solid plugs of the formulation No. 6Y material, the ring blanks apparently did not form the low porosity surface during processing; a result which accounted for the large resin pickup. The larger surface-to-volume ratio of the ring blanks, as compared with that of the solid plugs, was probably in some way responsible for preventing the low porosity surface condition from developing. Due to the large resin pickup, the formulation No. 6Y ring blanks broke apart during rebaking to 1000°C.

The processing experience and material properties determined for the seal ring bodies of formulations Nos. 1X-121, 1Z-121, 4X-121, and 6Y-121 have been examined and the materials ranked as to their suitability for fulfilling the goal of this Contract. These four materials were the best of all the materials manufactured during Tasks III(6) and VI for use as self-acting seal rings. The four materials can be ranked in the following order of decreasing suitability. This comparison is exclusive of wear effects, since the materials manufactured from formulations Nos. 1Z-121 and 6Y-121 were not wear-performance tested.

1. Formulation No. 1Z-121.
2. Formulation No. 1X-121.
3. Formulation No. 6Y-121.
4. Formulation No. 4X-121.

The materials manufactured from formulations Nos. 1Z-121 and 1X-121 are listed first and second, since they are approximately twice as hard as the materials manufactured from formulations Nos. 6Y-121 and 4X-121. Due to their increased hardness, the first two materials should be more erosion- and wear-resistant than the other two materials. The formulation No. 1Z-121 material is listed first, since it is more uniform and at least as oxidation-resistant as the formulation No. 1X-121 material. Of the two materials, however, the formulation No. 1Z-121 was found to be the more difficult to manufacture. Formulation No. 6Y-121 is listed third, since it produced a material with better thermal properties than that of the material manufactured from formulation No. 4X-121; the oxidation-resistance was equal to that of formulation No. 4X-121. The materials manufactured from formulations Nos. 4X-121 and 6Y-121 have approximately the same mechanical properties.

Further improvements in the strength, uniformity, hardness, and oxidation resistance of the materials developed during Tasks I through VII would enable broader application of these materials. The use of finer particulate filler materials might be one method of obtaining the required improvements. Intensive mixing may also be beneficial, and, when used in combination with warm molding, might allow for a reduction in the binder level required for processing with attendant improvements in properties. Pressure baking also warrants further study. The pressure-baked formulation No. 5 material might have been one of the best materials manufactured thus far if it had been produced with a "fresh" batch of the Bakelite BRP-5095 resin as the binder material.

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

PROCEDURES USED TO MEASURE MATERIAL PROPERTIES

Bulk Density-	Determined by direct physical measurement of mass and volume.
Helium Density-	Measured with Beckman pycnometer.
Flexural Strength-	ASTM C651-70 through use of a 4.5-inch x 1.0-inch x 0.5-inch (11.4 cm x 2.5 cm x 1.3 cm) ground sample.
Elastic Modulus-	Determined by a sonic resonance method by utilizing a variable frequency oscillator, amplifier, frequency counter, oscilloscope, filter, and transmitting and receiving transducers. Measured at room temperature by using a 4.5-inch x 1.0-inch x 0.5-inch (11.4 cm x 2.5 cm x 1.3 cm) ground sample.
Hardness-	Measured with a Rockwell Hardness Tester by using a 0.5-inch (1.3 cm) diameter ball, a 100 Kg major load, and the R_s scale.
Thermal Conductivity-	Calculated from a measured thermal diffusivity by using a sample of known density and specific heat. Thermal diffusivity is measured by a laser flash method by using a pulsed ruby laser with associated mirrors, filters, thermocouples, oscilloscopes, and camera. Measured at room temperature by using a 0.5-inch (1.3 cm) diameter x 0.080-inch (.20 cm) thick sample.
Coefficient of Thermal Expansion-	Measured by an elongation method by using a tube furnace, twin telescopes, thermocouples and optical pyrometers. This measurement was carried out from room temperature to 1000°C in an argon atmosphere by using a 0.5-inch x 0.5-inch x 2.5-inch (1.3 cm x 1.3 cm x 6.4 cm) ground sample.

APPENDIX II (Cont'd)

Pore Volume and Distribution by Mercury Intrusion-	The sample is placed in a chamber and evacuated. Mercury from an external reservoir is induced into the sealed chamber as the system is allowed to come back up to atmospheric pressure. When equilibrium is reached, increasing amounts of pressure are applied to the mercury in the reservoir and the corresponding changes in the volume of the mercury in the reservoir are recorded as the mercury is intruded into the sample. Knowing the corresponding reservoir volume and pressure changes allows one to calculate the pore volume and distribution of the sample, since the size of the pores filled by mercury is inversely proportional to the applied pressure. Mercury does not wet carbon-graphite material.
Pore Volume by Nitrogen Desorption-	The volume of pores smaller than 600Å in diameter was determined from the nitrogen desorption isotherm by using the exact form of the equation attributed to Barrett, Joyner, and Halenda(17, 18) with no simplifying assumptions.

APPENDIX III

DEFINITION OF STATISTICAL TERMS

F Distribution (16)

$$F_{\text{calculated}} = \frac{\hat{\sigma}_x^2}{\hat{\sigma}_y^2}$$

Where $\hat{\sigma}_x^2$ and $\hat{\sigma}_y^2$ are unbiased estimates of the two sample variances. $\hat{\sigma}_x^2$ will always denote the larger of the two estimates.

$$\hat{\sigma}_x^2 = \frac{\sum_{i=1}^{n_x} (x_i - \bar{x})^2}{n_x - 1}$$

Where $\bar{x} = \frac{\sum_{i=1}^{n_x} x_i}{n_x}$; n_x is the size of the random samples.

Similarly:

$$\hat{\sigma}_y^2 = \frac{\sum_{i=1}^{n_y} (y_i - \bar{y})^2}{n_y - 1}$$

After calculating the value of F, it is compared to the 2.5% critical value of F obtained from a statistical F distribution table. To determine the 2.5% critical value of F from the table, the two degrees of freedom are necessary. The two degrees of freedom are calculated as follows:

$$\nu_1 = n_x - 1,$$
$$\nu_2 = n_y - 1.$$

The 2.5% critical value of F is for a double tail analysis at a 95% confidence level. If the calculated value of F is less than the 2.5% critical value of F obtained from the statistical table, then the Student's t distribution can be used to compare the means of the two samples as follows.

Student's t Distribution (15, 16)

The Student's t distribution is used to determine whether the mean of one sample is significantly different from the mean of a second sample, or whether the two sample means can be regarded as drawn from one population.

$$\bar{x} = \frac{\sum_{i=1}^{n_x} x_i}{n_x}, \quad \bar{y} = \frac{\sum_{i=1}^{n_y} y_i}{n_y}$$

Where $\bar{x}$ is the larger of the two sample means.

$$\sigma^2 = \frac{\left[\sum_{i=1}^{n_y} (y_i^2) - \frac{\left(\sum_{i=1}^{n_y} (y_i)\right)^2}{n_y} + \sum_{i=1}^{n_x} (x_i^2) - \frac{\left(\sum_{i=1}^{n_x} (x_i)\right)^2}{n_x}\right.}{(n_x + n_y - 2)}$$

$$t_{\text{calculated}} = \frac{\bar{x} - \bar{y}}{\sigma} \sqrt{\frac{n_x \cdot n_y}{n_x + n_y}}$$

After calculating the value of t, it is compared to the value of t obtained from a statistical t distribution table. To obtain the value of t from the table, the degrees of freedom must be calculated using the following equation:

Degrees of freedom $= n_x + n_y - 2$.

After calculating the degrees of-freedom, the corresponding value of t can be found in the table using a value of P (probability) equal to 0.05 for a single tail analysis at a 95% confidence level. The difference between the means of the two sample populations is significant only if the calculated value of t is greater than the value of t from the table. That is:

$t_{\text{calculated}} > t_{\text{table}}$ = significant

$t_{\text{calculated}} < t_{\text{table}}$ = not significant

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