NASA CR-72986

①

DEVELOPMENT OF SEAL RING CARBON-GRAPHITE MATERIALS
(TASKS III and IV)

by

N.J. Fechter and P.S. Petrunich

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

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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

NASA-CR-72986

Send to
John Glave

UNION CARBIDE

UNION CARBIDE CORPORATION

CARBON PRODUCTS DIVISION

12900 SNOW ROAD, PARMA, OHIO · AREA CODE: 216-433-8600

MAIL ADDRESS: P. O. BOX 6116, CLEVELAND, OHIO 44101

PARMA TECHNICAL
CENTER

Roger

October 11, 1971

Dear Sir:

We are pleased to enclose your copy of a Topical Report entitled, "Development of Seal Ring Carbon-Graphite Materials (Tasks III and IV)" by N. J. Fechter and P. S. Petrunich. This work was performed under Contract NAS 3-13211.

This report is being sent to your attention at the request of Mr. Lawrence P. Ludwig, Project Manager, NASA-Lewis Research Center.

Very truly yours,

L. D. Stoughton

L. D. Stoughton
Contract Administrator

LDS/jlp

N71-36910

1. Report No.
CR-72986

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
DEVELOPMENT OF SEAL RING CARBON-GRAPHITE MATERIALS (TASKS III AND IV)

5. Report Date
August 31, 1971

6. Performing Organization Code

7. Author(s)
N. J. Fechter and P. S. Petrunich

8. Performing Organization Report No.

9. Performing Organization Name and Address
Union Carbide Corporation
Carbon Products Division
12900 Snow Road
Parma, Ohio 44130

10. Work Unit No.

11. Contract or Grant No.
NAS-3-13211

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington D. C. 20546

13. Type of Report and Period Covered
Contractor Report

14. Sponsoring Agency Code

15. Supplementary Notes
Project Manager, Lawrence P. Ludwig, Fluid System Components Division, NASA Lewis Research Center, Cleveland, Ohio

16. Abstract

Carbon-graphite seal ring bodies for operation at air temperatures to 1300°F were manufactured from the four formulations developed during Task I and from resin impregnated versions of three of the four formulations. Thermal, chemical, and wear properties of four selected materials were characterized. The results have shown:

(1) The porosities, oxidation resistances, and thermal conductivities of the four materials are significantly greater than those of a typical commercial grade. The mechanical and wear properties, although inferior to those of the commercial grade, were judged acceptable for self-acting seal applications.

(2) The mechanical properties of carbon-graphite seal ring materials are improved through impregnation with a phenolic resin prior to heat treatment at 2800°C.

(3) Materials bonded with the phenolic resin can be more difficult to process than those bonded with the coal tar pitch.

(4) Substitution of graphite fibers for carbon black as the minor filler component improves the processibility and strength-to-weight ratio of a material.

(5) Addition of small quantities of particulate glassy carbon to one of the materials degraded oxidation resistance without improving wear resistance.

17. Key Words (Suggested by Author(s))
seal ring materials
carbon-graphite

18. Distribution Statement
Unclassified-unlimited

19. Security Classif. (of this report)
Unclassified

20. Security Classif. (of this page)
Unclassified

21. No. of Pages
113

22. Price*
$3.00

*For sale by the National Technical Information Service, Springfield, Virginia 22151

FOREWORD

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

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

LIST OF TABLES

LIST OF TABLES (Cont'd)

LIST OF FIGURES

LIST OF FIGURES (Cont'd)

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 temperatures up to 1300°F (704°C). The carbon-graphite material is being developed for use as 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.

This Topical Report covers Tasks III and IV of the Contract and is the follow up to Topical Report NASA CR-72799 which covers Tasks I and II. Task I included the screen testing of 12 material systems that had been developed and optimized through a literature search and bench-scale testing. The results of Task I were used to select four approaches to the manufacture of carbon-graphite seal ring bodies under Task II. Carbon-graphite seal ring bodies were manufactured from the selected formulations during Task III, and certain properties of the manufactured materials were determined during Task IV. Samples of the four materials were delivered to the NASA Lewis Research Center for evaluation.

Seven carbon-graphite seal ring materials were actually manufactured during Task III. The seven materials included the four formulations selected during Task II and resin impregnated versions of three of these formulations. Formulation No. 1 filler system consisted of 80 pbw (parts by weight) Union Carbide Corporation Grade CHP artificial graphite and 20 pbw Commercial Solvents Corporation Thermax furnace black. The material was bonded with Barrett No. 30 medium coal tar pitch by using a binder level of 60 pph (parts by weight of binder per one hundred parts by weight of filler).

Formulation No. 2 had the same composition as that of formulation No. 1 except for the addition of 5 pbw Lockheed Company LMSC glassy carbon. Formulations Nos. 3 and 4 both included CHP graphite as the major filler component (80 pbw) with Thermax (20 pbw) and fibers prepared from Union Carbide Corporation Grade WCA graphite cloth (20 pbw) as the minor filler constituents, respectively. Both materials were bonded with Bakelite BRP-5095 phenolic resin (58 pph for formulation No. 3 and 67.5 pph for formulation No. 4). For all four formulations, a final baking temperature of 2800°C was used to yield carbon-graphite materials which had a high degree of crystallinity. Although an increase in the degree of crystallinity of carbon-graphite material results in an increase in oxidation resistance, it tends to degrade the mechanical and wear properties of the material. The resin impregnated versions of formulations Nos. 1, 2, and 4 were prepared in an attempt to reduce the porosities and improve the mechanical and wear properties of these relatively highly-crystalline materials. Improvements in oxidation resistance were anticipated from the porosity reductions. These seal ring bodies were prepared by impregnating the 1000°C baked compacts of formulations Nos.1, 2, and 4 with a BRP-5095 resin and acetone solution prior to heat treatment at 2800°C. All the resin impregnated materials were identified by the formulation number followed by the letter "X" (e.g., formulation No. 1X.) Processing problems precluded the production of a resin impregnated version of formulation No. 3.

The scale-up in both the quantity of materials processed and the size of the compacts manufactured during Task III resulted in a few processing problems which had not been encountered during Task I. Formulation No. 3 proved to be the most difficult to process. The acetone used to dissolve the resin binder during mixing was very difficult to remove. Baking the large 8.6 inch (21.8 cm) diameter green ring blanks of formulation No. 3 also proved to be a problem, since the large shrinkage of the material caused the ring blanks to crack and/or laminate during baking to 1000°C. A change in baking rate reduced this problem to a tolerable level.

The specified properties of four of the seven materials manufactured during Task III were measured during Task IV. Selection of the four materials was based on preliminary mechanical property measurements which indicated that the resin impregnation resulted in increased flexural strength, hardness, and elastic modulus. The four materials chosen were manufactured from formulations Nos. 1X, 2X, 3, and 4X. After these materials were impregnated with the No. 121 oxidation inhibiting treatment, their relative oxidation resistances were between 2.5 and 5.0 times greater than that of commercial seal ring Grade CDJ which had been subjected to the same treatment. The relative oxidation resistance of the carbon-graphite materials is defined as the length of time required for the materials to experience a 5 percent weight loss when exposed to 1300°F (704°C) air. The 5 pbw addition of glassy carbon in formulation No. 2X was found to significantly degrade the oxidation resistance of the material. As expected, the mechanical properties of the materials manufactured during Task III were inferior to those of commercial seal ring Grade CDJ. The average flexural strengths of the four materials ranged between 3500 psi (2400 N/cm^2) and 4800 psi (3300 N/cm^2) as compared with 8800 psi (6060 N/cm^2) for Grade CDJ. All four of the materials characterized during Task IV had significantly higher thermal conductivities and lower coefficients of thermal expansion than those of Grade CDJ. High thermal conductivity and low thermal expansion are desirable seal ring properties from a thermal deformation standpoint.

Seal ring materials impregnated with the No. 121 oxidation inhibiting treatment were wear tested under nominal test conditions. Frictional heat maintained the ambient air temperature at approximately 200°F (93°C) during this operation. The average wear rates of the four materials ranged between 0.60 and 1.00 mils (.0015 and .0025 cm)per hour as compared with 0.28 mils (.00071 cm) per hour for the No. 121 treated Grade CDJ. The addition of 5 pbw glassy carbon in formulation No. 2X did not improve wear resistance.

Analyses of the materials showed that formulations Nos. 1X-121, 3-121 and 4X-121 each had the following properties that are desirable for primary rings for self-acting seals:

a. Oxidation resistance better than a typical commercial grade that was selected for comparison because of its wide use.

b. Significantly greater thermal conductivity and lower thermal expansion than the typical commercial grade.

The flexural strengths of materials prepared from formulations Nos. 1X, 3 and 4X were about one half that of the commercial grade selected for comparison; but this was judged to be sufficient strength since self-acting carbon rings are retained by a metal band. The hardness of these materials were generally lower (because of the highly graphitic state) than that of the commercial grade selected for comparison. Thus, erosion resistance may not be adequate. The seal life of the three materials should surpass that of the commercial grade under high ambient air temperature conditions where oxidation is the limiting performance factor. The addition of 5 pbw of glassy carbon in formulation No. 2X-121 either had no effect or had damaging effects on the material properties.

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 are the result of larger engines. Contact type seals with carbon-graphite seal rings are used in many current gas turbine engines; however, the limited pressure, speed, and temperature capability of the contact seal restricts this use to operation below 125 psi (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 produced 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 can 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.

---

* 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 materials systems. Forty-seven material/process subsystems were produced and evaluated to optimize the selected 12 material systems. Small compacts 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, hardnesses, and 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. The oxidation tests indicated 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.

This Topical Report covers Tasks III and IV of the Contract. The scope of work for Task III consists of the manufacture of carbon-graphite seal ring bodies from the selected four formulations. 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 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.

SECTION III

CONCLUSIONS

1. The oxidation resistances and thermal properties of the four materials manufactured from formulations Nos. 1X-121, 2X-121, 3-121, and 4X-121 are significantly better than those of commercial seal ring Grade CDJ. Grade CDJ is widely used as a seal ring material in turbine engines used to power commercial aircraft. The mechanical and wear properties of the four materials are not so good as those of CDJ but should be satisfactory for self-acting seals.

2. The density, strength, elastic modulus, and hardness of three of the carbon-graphite materials were improved by impregnating the 1000°C baked compacts with Bakelite BRP-5095 resin prior to heat treatment at 2800°C.

3. The addition of 5 pbw of glassy carbon to one of the carbon-graphite seal ring materials degraded the oxidation resistance and resulted in no improvement in mechanical, thermal, or wear properties. (The use of glassy carbon was investigated as an additive for increasing seal life.)

4. Substitution of fibers prepared from Grade WCA graphite cloth for Thermax as a minor filler component results in carbon-graphite material with improved processibility, because the material containing the graphite fibers experiences considerably less shrinkage during baking. The structural uniformity of the material prepared with the graphite fiber was poorer than that of the similar material which contained Thermax.

5. The material containing 80 pbw Grade CHP artificial graphite and 20 pbw Thermax as fillers is more difficult to process when Bakelite BRP-5095 phenolic resin is substituted for No. 30 medium pitch as the binder. The resin-bonded material is more difficult to process because it undergoes significantly greater shrinkage during baking than the pitch-bonded material. The resin-bonded material also requires the extra processing step of removing the acetone used to dissolve the resin during mixing. Removal of the entrapped acetone from this material was very difficult.

SECTION IV

MANUFACTURING OF CARBON-GRAPHITE MATERIALS (TASK III)

A. Identification of the Material Formulations

The four process approaches developed during Task I(5) and selected during Task II(5) were employed to manufacture carbon-graphite seal ring bodies during Task III. The four basic formulations and their impregnated versions are displayed in Table I. Resin impregnation was directed to improving the strength and hardness of the base materials and reducing their total porosities. An increase in hardness obtained by this impregnation should improve the wear resistance of a carbon-graphite body, since its load carrying capacity would be increased. Reducing porosity should help to improve the oxidation resistance of a carbon-graphite body, since the permeability of the material to the oxidizing gas would be reduced. To produce the resin-impregnated versions, the 1000°C baked compacts of the base materials were impregnated with Bakelite BRP-5095 phenolic resin and then rebaked to 1000°C prior to final heat treatment at 2800°C.

Of the seven materials manufactured during Task III from formulations Nos. 1, 2, 3, 4, 1X, 2X, and 4X, four were selected for the material property characterization prescribed in Task IV. The selection was based on the processing experience and on a preliminary mechanical property evaluation. The number, size, and shape of the carbon-graphite bodies manufactured were determined by testing requirements described in a following section. Finished sizes of the specimens which were to be tested for wear or oxidation performance were impregnated with the No. 121 oxidation-inhibiting treatment. The specimens impregnated with this oxidation-inhibiting treatment were identified by the formulation number followed by a dash and the Number 121 (e. g. Formulation No. 1X-121).

TABLE I

Identification of the Four Basic Material Formulations and Their Impregnated Versions

Formulation No.	Base Material			Impregnants	
	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

---

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.

The carbon-graphite seal ring bodies produced during Task III were manufactured from particulate and binder raw materials which were characterized during Task I.(5) The remainder of this section presents the results for the characterization tests of the raw materials. All the test procedures used to characterize the raw materials are described in Appendix I.

1. CHP Artificial Graphite

Helium Density = 2.22 g/cc

Surface Area = 6.7 m^2/g

Screen Analysis

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

Chemical Analysis

% Ash = 0.066
% Moisture = 0.039

Emission Spectrographic Analysis (Semi-Quantitative)

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

2. 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

---

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

3. Ground Glassy Carbon

Helium Density = 1.91 g/cc*

Surface Area = 5.6 m^2/g

Screen Analysis

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

Chemical Analysis

% Ash = 0.92
% Moisture = 0.85

Emission Spectrographic Analysis (Qualitative)**

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

---

* Sample drifted considerably and, therefore, the results are questionable.
** No standards available to run semi-quantitative analysis.

4. WCA Graphite Fibers

Helium Density = 1.43 g/cc*

Surface Area = 1.3 m^2/g

Chemical Analysis

% Ash = 0.04
% Moisture = 0.03

Emission Spectrographic Analysis
Semi-Quantitative

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

---

* Sample drifted considerably; therefore, results are questionable.

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**

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

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

---

* 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**

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

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

---

* No standards available to run semi-quantitative analysis.

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

B. Processing of the Material Formulations

The same basic processing techniques used to develop the four material formulations during Task I(5) were applied to the manufacture of the materials produced during Task III. The scale-up in both the quantity of material and the size of the compacts manufactured during Task III produced a few problems which had not been encountered during the previous work under Task I(5); these problems, corrected by adjusting the processing procedures, are discussed along with detailed descriptions of the processing techniques used to manufacture the carbon-graphite seal ring bodies. The procedure used to impregnate the compacts with Bakelite BRP-5095 resin was developed during Task III by using bench-scale testing.

Two different types of compacts were prepared for each of the seven material formulations: 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 rectangular and rod specimens submitted to the NASA Project Manager were machined from the solid plugs.

A series of test bakes were conducted to determine the best molding conditions for each of the materials manufactured during Task III. Small compacts of each material were molded at 5000 psi (3450 N/cm^2) 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 a sound internal structure was selected as the molding condition for each material. The processing techniques employed to manufacture compacts from the seven materials produced in Task III are as follows:

1. Formulation No. 1 - CHP Artificial Graphite (80 pbw) - Thermax (20 pbw) - No. 30 Medium Pitch (60 pph):

a) Blend filler raw materials for one hour.

b) Preheat filler and mixer to 150°C, add pitch, and mix filler and binder in 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) 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.

A problem was encountered when the green compacts of formulations Nos. 1 and 2 were baked from room temperature to 1000°C, Fifteen 5-inch (12. 7 cm) diameter solid plugs and three ring blanks of each of the formulations Nos. 1 and 2 were packed in a large, square sagger with coke as the packing medium. The compacts were packed in six layers with their diameters parallel with the bottom of the sagger. Each of the top three layers consisted of two ring blanks and two 5-inch (12. 7 cm) diameter plugs; the bottom three layers each contained eight 5-inch (12. 7 cm) diameter plugs. An X-ray analysis of the 1000°C baked compacts showed that several of the solid plugs packed in the bottom three layers had cracked during baking. Apparently, the compacts shifted in the pack as they shrunk during baking, and the weight of the pack nonuniformily stressed the lower compacts, causing the cracking to occur. The problem was remedied by reducing the size of the subsequent packs to three parallel layers of compacts. The smaller packs reduced the amount of weight applied on the compacts located at the bottom of the pack.

2. Formulation No. 1X-CHP Artificial Graphite (80 pbw) - Thermax (20 pbw) - No. 30 Medium Pitch (60 pph) - 1000°C Baked Compacts Impregnated with Bakelite BRP-5095 Resin:

a) Through baking of the green compacts to 1000°C, use the same processing as that used for formulation No. 1.

b) Impregnate 1000°C baked compacts with a Bakelite BRP-5095 resin and acetone solution by using the following procedure:

1. Place compacts in autoclave and evacuate for 1 hour at 27-29-inch (9.1-9.8 N/cm^2) Hg vacuum.
2. Impregnate compacts with solution consisting of 50 pbw Bakelite BRP-5095 resin and 50 pbw acetone.
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, heat to 150°C, and hold temperature for 2 hours. Remove compacts from autoclave and place them in a 150°C circulating air oven for 2 hours to complete resin cure.

c) Pack resin impregnated compacts with coke in a sagger and bake impregnated compacts 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.

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

A six-layer pack discussed previously, was used to rebake (1000°C, Step C) the resin impregnated compacts of formulation No. 1X. The larger pack could be used without cracking the compacts, since they had been previously baked to 1000°C. The compacts were thus strong enough to support the weight of the expanded pack without cracking. Six-layer packs also were used when the resin impregnated compacts of formulations Nos. 2X and 4X were rebaked to 1000°C.

3. Formulation No. 2-CHP Artificial Graphite (80 pbw) - Thermax (20 pbw) - Glassy Carbon (5 pbw) - No. 30 Medium Pitch (60 pph):

a) Blend filler raw materials in small batches for one hour. Primary blending should be carried out in small batches to obtain good dispersion of the glassy carbon.

b) Blend together all the smaller preblended filler batches for one hour.

c) The other processing steps are the same as those listed for formulation No. 1, starting at mixing (Step b).

4. Formulation No. 2X-CHP Artificial Graphite (80 pbw) - Thermax (20 pbw) - Glassy Carbon (5 pbw) - No. 30 Medium Pitch (60 pph) - 1000°C Baked Compacts Impregnated with Bakelite BRP-5095 Resin:

a) Through the baking of the green compacts to 1000°C, the processing is the same as that used for formulation No. 2

b) The other processing steps are the same as those listed for formulation No. 1X, starting at the impregnation of the 1000°C baked compacts (Step b).

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

a) Blend filler raw materials for one hour.

b) Dissolve BRP-5095 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. This step will remove the residual acetone.

f. Crush material again by using a hammer pulverizer. This 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. Pack green compacts with coke in a sagger, place a layer of charcoal on the top of the pack, and bake green compacts 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. For very large compacts such as the 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, slow the baking schedule to 5°C per hour between 150°C and 1000°C to reduce laminating and cracking.

k. 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. 1 compacts.

Of the seven materials manufactured during Task III, formulation No. 3 was the most difficult to process. One problem, which was not encounterd during Task I(5), was the difficulty of removing all of the acetone from the mixed material. This problem was not encountered during Task I(5) since, only a small quantity (10 lbs) of material was processed, the volume of acetone to be removed was relatively small. Approximately 160 lbs (73 Kg.) of mix was prepared during Task III, which required the removal of a large volume of acetone. Heating the 160 lbs (73 Kg.) of mixed material, which was actually a liquid with the particulate material dispersed in it, for 16 hours at 75°C evolved most of the acetone, leaving a soft, pliable mass. However, some residual acetone was trapped in the mix when a relatively impervious crust formed on top of the material during heating. The residual acetone caused the material to be soft and pliable at room temperature. Removal of the crust followed by an additional 24-hour exposure to the 75°C temperature did not remove all the entrapped acetone, since the crust reformed. To evolve all the residual acetone by the continuous process of removing the crust followed by heating would be very time consuming and could cause partial polymerization of the resin.

Partial polymerization of the resin could degrade the physical properties of the 2800°C baked compacts as was noted during Task I.(5) The Contractor had to crush the material to expose more surface area and vacuum evacuate it for 16 hours while maintaining a temperature of 50°C to remove all the acetone without partially polymerizing the resin. The material had to be hardened by chilling at -20°C before it could be crushed. Since all the acetone must be removed from the mix before molding to prevent lamination of the compacts during baking, the Contractor included Step e as part of the required processing for formulation No. 3.

The fact that formulation No. 3 is such a high shrinkage material produced a problem when the large green ring blanks were baked at 10°C per hour between 150°C and 1000°C. Resin-bonded formulation No. 3 has a volume ratio (1000°C baked volume/green volume) of 0.704 as compared with the 0.871 value measured for the pitch bonded formulation No. 1. The large shrinkage caused the formulation No. 3 ring blanks to crack and/or laminate when baked at the 10°C per hour rate. The problem was minimized by reducing the baking rate to 5°C per hour between 150°C and 1000°C to reduce the rate at which the ring blanks shrink.

6. Formulation No. 4 - CHP Artificial Graphite (80 pbw) - WCA Fibers (20 pbw) - Bakelite BRP-5095 Resin (67.5 pph):

a. Blend shredded WCA graphite cloth with CHP graphite for one hour.

b. Micromill the blended filler material.

c. Blend milled filler material for one hour.

d. The other processing steps are the same as those listed for formulation No. 3, starting at mixing (Step b). All the green compacts for formulation No. 4 processed during Task III were baked at 10°C per hour between 150°C and 1000°C.

7. Formulation No. 4X-CHP Artificial Graphite (80 pbw) - WCA Fibers (20 pbw) - Bakelite BRP-5095 Resin (67.5 pph) - 1000°C Baked Compacts Impregnated with Bakelite BRP-5095 Resin:

a. Through the baking of the green compacts to 1000°C, the processing is the same as that used for formulation No. 4.

b. The other processing steps are the same as those listed for formulation No. 1X, starting at the impregnation of the 1000°C baked compacts (Step b).

SECTION V

MATERIAL PROPERTIES
(TASK IV)

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 air 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. 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 the seven formulations during Task III were all found to be very machinable as compared with commercial seal ring Grade CDJ. The good machinability of the carbon-graphite articles manufactured during Task III 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 IV, the Contractor determined the following material properties for the carbon-graphite seal ring bodies manufactured during Task III.

1. Mechanical Properties
    a. Density before and after impregnation with 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 relative to a carbon-graphite seal material typical of current practice.
    b. Total porosity, pore size and size distribution, uniformity of impregnation, and structural uniformity.
4. Wear Properties Relative to a Reference Material at Nominal Environment conditions

This section of the report is divided into subsections. The next subsection discusses the mechanical properties determined for the compacts of all seven of the material formulations manufactured during Task III. The remaining subsections cover the thermal and wear properties, the porosities, and the oxidation rates determined for the compacts of the selected four formulations.

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. 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 consistent with high oxidation resistance.

Under the scope of this Contract, the Contractor was required to fully characterize the material properties of the carbon-graphite seal ring bodies manufactured from the four formulations selected during Task II(5) and described in Table I. A total of seven materials (formulations Nos. 1, 2, 3, 4, 1X, 2X, and 4X) were manufactured during Task III. This total excludes the materials impregnated with the No. 121 oxidation inhibiting treatment. The Contractor thus had to select the four formulations which had produced seal ring bodies warranting full material characterization: Nos. 1X, 2X, 3, and 4X were chosen. The decision as to which four materials warranted full characterization was based on the results of mechanical property measurements made on the compacts of all seven formulations. Since only one version of formulation No. 3 was manufactured during Task III, the selection of the remaining three materials to be fully characterized was restricted to choosing between the resin-impregnated and nonresin-impregnated versions of formulations Nos. 1, 2, and 4.

Tables II through VIII 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 the seven material formulations. Except for the hardness measurement, these mechanical properties were the ones which the Contractor was required to determine. 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 at the end of this report describes the procedures used to determine the material properties. The ASTM methods were used where applicable.

Formulation No. 1X material was selected for detailed property examination rather than formulation No. 1 material, since impregnation with the Bakelite BRP-5095 resin produced a relatively large improvement in mechanical properties. The resin impregnation resulted in an average improvement of 1.5% in density, 18% in flexural strength, 12% in elastic modulus, and 6.3% in hardness. Similarly, formulation No. 2X was chosen rather than formulation No. 2, since the resin impregnation produced an average increase of 1.9% in density, 22% in flexural strength, 14% in elastic modulus, and 10% in hardness.

TABLE II

Mechanical Properties - Formulation No. 1 Material

Bulk Density*	Green Density(g/cc)	1000°C Density(g/cc)	2800°C Density(g/cc)
5" Dia. Plugs			
Maximum	1.602	1.669	1.711
Minimum	1.593	1.660	1.701
Average	1.597	1.664	1.707
Standard Deviation	0.003	0.003	0.005
n	5	5	5
Ring Blanks			
Maximum	1.593	1.666	1.705
Minimum	1.592	1.657	1.702
Average	1.593	1.662	1.704
n	2	2	2

Flexural Strength**	(psi)	(N/cm^2)	Rockwell "S" Hardness***	
Maximum	4060	2800	Maximum	86
Minimum	3530	2430	Minimum	76
Average	3810	2630	Average	80
Standard Deviation	242	167	Standard Deviation	5
n	6	6	n	6

Elastic Modulus**	(10^{6}psi)	(10^{5}N/cm^2)
Maximum	1.35	9.30
Minimum	1.27	8.75
Average	1.31	9.03
Standard Deviation	0.03	0.21
n	6	6

---

*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 C 651-70.

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

TABLE III

Mechanical Properties - Formulation No. 1X Material

Bulk Density*

	Green Density(g/cc)	1000°C Density(g/cc)	2800°C Density(g/cc)
5" Dia. Plugs			
Maximum	1.594	1.696	1.737
Minimum	1.591	1.690	1.728
Average	1.592	1.694	1.733
Standard Deviation	0.003	<0.001	0.003
n	4	4	4
Ring Blank			
Measured	1.593	1.694	1.739
n	1	1	1

Flexural Strength**

	(psi)	(N/cm^2)	Rockwell "S" Hardness***	
Maximum	4870	3360	Maximum	87
Minimum	4270	2940	Minimum	82
Average	4480	3090	Average	85
Standard Deviation	220	152	Standard Deviation	2
n	6	6	n	6

Elastic Modulus**

	(10^6 psi)	(10^5 N/cm^2)
Maximum	1.50	10.34
Minimum	1.43	9.85
Average	1.47	10.13
Standard Deviation	0.03	0.21
n	6	6

---

* Calculated from physical dimensions and weights measured for compacts.

** Measured using a 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 C 651-70

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

TABLE IV

Mechanical Properties - Formulation No. 2 Material

Bulk Density*	Green Density(g/cc)	1000°C Density(g/cc)	2800°C Density(g/cc)
5" Dia. Plugs			
Maximum	1.564	1.627	1.670
Mini mum	1.562	1.617	1.660
Average	1.563	1.619	1.664
Standard Deviation	< 0.001	0.003	0.004
n	4	4	4
Ring Blanks			
Maximum	1.560	1.624	1.664
Minimum	1.559	1.617	1.663
Average	1.560	1.621	1.664
n	2	2	2

Flexural Strength**	(psi)	(N/cm²)	Rockwell "S" Hardness***	
Maximum	4030	2780	Maximum	84
Minimum	3770	2600	Minimum	78
Average	3880	2670	Average	80
Standard Deviation	86	59	Standard Deviation	2
n	6	6	n	6

Elastic Modulus**	(10^6 psi)	(10^5 N/cm²)
Maximum	1.34	9.23
Minimum	1.31	9.03
Average	1.32	9.09
Standard Deviation	0.01	0.07
n	6	6

---

*Calculated from physical dimensions and weights measured for compacts.

**Measured using 4.5" x 1.0" x 0.5" samples (11.4 cm x 2.5 cm x 1.3 cm). Flexural samples broken on a 3.0" (7.6 cm) span per ASTM Procedure C 651-70.

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

TABLE V

Mechanical Properties - Formulation No. 2X Material

Bulk Density*

	Green Density (g/cc)	1000°C Density (g/cc)	2800°C Density (g/cc)
5" Dia. Plugs			
Maximum	1.561	1.663	1.706
Minimum	1.551	1.650	1.688
Average	1.556	1.658	1.696
Standard Deviation	0.004	0.005	0.008
n	4	4	4
Ring Blank			
Measured	1.561	1.653	1.695
n	1	1	1

Flexural Strength**

	(psi)	(N/cm^2)	Rockwell "S" Hardness***	
Maximum	4990	3440	Maximum	91
Minimum	4500	3100	Minimum	86
Average	4750	3270	Average	88
Standard Deviation	172	119	Standard Deviation	3
n	6	6	n	6

Elastic Modulus**

	(10^6 psi)	($10^5 N/cm^2$)
Maximum	1.52	10.47
Minimum	1.44	9.92
Average	1.50	10.34
Standard Deviation	0.03	0.21
n	6	6

---

* 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 C 651-70.

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

TABLE VI

Mechanical Properties - Formulation No. 3 Material

Bulk Density*

	Green Density(g/cc)	1000°C Density(g/cc)	2800°C Density(g/cc)
5" Dia. Plugs			
Maximum	1.410	1.523	1.651
Minimum	1.405	1.514	1.633
Average	1.407	1.519	1.644
Standard Deviation	<0.001	0.006	0.005
n	6	6	6
Ring Blanks			
Maximum	1.410	1.540	1.656
Minimum	1.407	1.536	1.642
Average	1.409	1.538	1.649
n	2	2	2

Flexural Strength**

	(psi)	(N/cm²)	Rockwell "S" Hardness***	
Maximum	3610	2490	Maximum	60
Minimum	3310	2280	Minimum	54
Average	3480	2400	Average	58
Standard Deviation	118	81	Standard Deviation	2
n	6	6	n	6

Elastic Modulus**

	(10^6 psi)	(10^5 N/cm²)
Maximum	1.17	8.06
Minimum	1.12	7.72
Average	1.15	7.92
Standard Deviation	0.02	0.14
n	6	6

---

* 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 C 651-70.

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

TABLE VII

Mechanical Properties - Formulation No. 4 Material

Bulk Density*

	Green Density(g/cc)	1000°C Density(g/cc)	2800°C Density(g/cc)
5" Dia. Plugs			
Maximum	1.440	1.354	1.452
Minimum	1.429	1.340	1.431
Average	1.434	1.346	1.441
Standard Deviation	0.005	0.005	0.008
n	6	6	6
Ring Blanks			
Maximum	1.437	1.377	1.437
Minimum	1.433	1.364	1.435
Average	1.435	1.371	1.436
n	2	2	2

Flexural Strength**

	(psi)	(N/cm²)	Rockwell "S" Hardness***	
Maximum	4240	2920	Maximum	30
Minimum	3600	2480	Minimum	22
Average	3880	2670	Average	26
Standard Deviation	244	168	Standard Deviation	2
n	6	6	n	6

Elastic Modulus**

	(10^6 psi)	(10^5 N/cm²)
Maximum	1.20	8.27
Minimum	1.17	8.06
Average	1.19	8.20
Standard Deviation	0.01	0.07
n	6	6

---

* Calculated from physical dimensions and weights measured 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 C 651-70.

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

TABLE VIII

Mechanical Properties - Formulation No. 4X Material

Bulk Density*

	Green Density(g/cc)	1000°C Density(g/cc)	2800°C Density(g/cc)
5" Dia. Plugs			
Maximum	1.437	1.426	1.474
Minimum	1.427	1.389	1.441
Average	1.430	1.413	1.457
Standard Deviation	0.004	0.015	0.012
n	5	5	5
Ring Blank			
Measured	1.437	1.420	1.488
n	1	1	1

Flexural Strength**

	(psi)	(N/cm²)	Rockwell "S" Hardness***	
Maximum	4800	3310	Maximum	79
Minimum	4020	2770	Minimum	41
Average	4470	3080	Average	59
Standard Deviation	313	216	Standard Deviation	12
n	6	6	n	6

Elastic Modulus**

	(10^6 psi)	(10^5 N/cm²)
Maximum	1.60	11.02
Minimum	1.35	9.30
Average	1.49	10.27
Standard Deviation	0.11	0.76
n	6	6

---

* Calculated from physical dimensions and weights measured 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 C 651-70.

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

The relatively large improvement in mechanical properties measured for the compacts after impregnation with the Bakelite resin resulted from rather small resin pickups. The measured resin pickups were the same for the compacts of formulations Nos. 1X and 2X; 9% (by weight) after impregnation, 4% after curing, and 1.6% after rebaking the compacts to 1000°C. Driving off the acetone used to dissolve the Bakelite resin accounts for the cured resin pickup being lower than that measured after impregnation. Carbonization of the resin accounts for the resin pickup being still lower after rebaking the compacts to 1000°C. The internal instructures of the compacts manufactured from formulations Nos. 1 and 2 are apparently very uniform, since little variation was noted in the measured resin pickups.

Formulation No. 3 was selected as the third material warranting complete material property evaluation. The difficulties encountered during manufacturing of the compacts of formulation No. 3 (discussed in the previous section) delayed the processing of the material. The delay in processing prohibited the manufacturing of a Bakelite BRP-5095 resin-impregnated version of the material.

Formulation No. 4X was selected as the fourth material warranting full property evaluation because, once again, the resin impregnation produced an improvement in the mechanical properties as compared with those of the formulation No. 4 compacts. Unlike the two versions of formulations Nos. 1 and 2, there was some overlap in the maximum and minimum density and flexural strength values determined for the compacts of formulations Nos. 4 and 4X. However, the Contractor believed that the average increases in mechanical properties were sufficient to warrant the selection of formulation No. 4X. The resin impregnation produced an average increase of 1.1% in density, 15% in flexural strength, 25% in elastic modulus, and 127% in hardness; there is some question as to the significance of the large increase in hardness.

A rather large range of resin pickups was measured for the compacts of formulation No. 4X which indicates a relatively large compact-to-compact variation in the internal structure of the formulation No. 4 material. The measured resin pickups for the compacts of formulation No. 4X ranged between 6.7% and 18.9% after impregnation, 5.2% and 13.4% after curing, and 2.3% and 5.7% after rebaking the compacts to 1000°C. A nonuniform internal structure accounts for the overlapping in the mechanical properties measured for the compacts of formulations Nos. 4 and 4X.

The mechanical properties determined for the carbon-graphite seal ring bodies manufactured from the seven formulations were all lower than the corresponding values specified for commercial seal ring Grade CDJ-83. 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 3.2×10^6 psi (2.2×10^6 N/cm^2), and a Rockwell "E" hardness of 105. As discussed in Topical Report NASA CR-72799, some sacrifice in strength and hardness was found to be necessary when developing the oxidation resistant, carbon-graphite materials. The decrease in mechanical properties resulted from the baking to 2800°C of the compacts containing a high purity graphite as a major filler constitutent. The mechanical properties determined for the seven materials manufactured during Task III are, however, adequate for their use as seal ring materials. Formulations Nos. 1X, 2X, and 4X resulted in carbon-graphite articles having flexural strengths and elastic moduli similar to those of commercial seal ring Grade AUT. Grade AUT, which is manufactured by the Union Carbide Corporation, has a flexural strength of 4900 psi (3400 N/cm^2) and an elastic modulus of 1.3×10^6 psi (9.0×10^5 N/cm^2).

C. Thermal Properties

As a part of the material characterization program, the Contractor was required to determine the thermal conductivities and the coefficients of thermal expansion of the selected four materials manufactured during Task III. Both of the thermal properties affect the performance of a carbon-graphite seal ring material. Since self-acting seals experience limited periods of sliding contact, they require a carbon-graphite material having a high thermal conductivity so that the frictional heat generated during sliding contact will be rapidly dissipated. Low thermal deformation also can be important with this type of seal since the proper interfacial geometry must be maintained to prevent high speed rubbing contact.(6) 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 IX lists the thermal conductivities measured for the carbon-graphite seal ring bodies of formulations Nos. 1X, 2X, 3 and 4X. The determination of the thermal conductivities was carried out at room temperature by using the laser flash method (Appendix II). All the values measured 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. The thermal conductivity of a carbon-graphite material is directly related to its degree of crystallinity. Since Grade CDJ is not baked to a final temperature of 2800°C, it is not so crystalline as the four materials manufactured during Task III. The results presented in Table IX also show that the compacts of formulations Nos. 1X and 2X have higher thermal conductivities than those determined for the carbon-graphite materials of formulations Nos. 3 and 4X, a result which is probably due to a difference in the porosity of the compacts or the degree of crystallinity of the binder materials. Information gained during the literature search portion of Task I(5) indicated that the phenolic resin may not be so crystalline as coal tar pitch after baking to 2800°C. The fact the compacts of formulations Nos. 1X and 2X had practically the same thermal conductivities shows that the addition of 5 pbw of glassy carbon in the formulation No. 2X material had little effect on thermal conductivity.

TABLE IX

Thermal Conductivities-Formulations Nos. 1X, 2X, 3 and 4X Material

Formulation*	Thermal Conductivity Cal/cm-sec-°C	BTU-ft/ft^2-hr-°F	Joule/meter-sec-°K
No. 1X w.g.	0.181	43.80	75.8
No. 1X a.g.	0.149	36.06	62.3
No. 2X w.g.	0.177	42.83	74.2
No. 2X a.g.	0.146	35.33	61.2
No. 3 w.g.	0.143	34.61	59.7
No. 3 a.g.	0.122	29.52	50.9
No. 4X w.g.	0.145	35.09	60.7
No. 4X a.g.	0.082	19.84	34.3

Formulation	Anisotropy Ratio**
No. 1X	1.21
No. 2X	1.21
No. 3	1.17
No. 4X	1.77

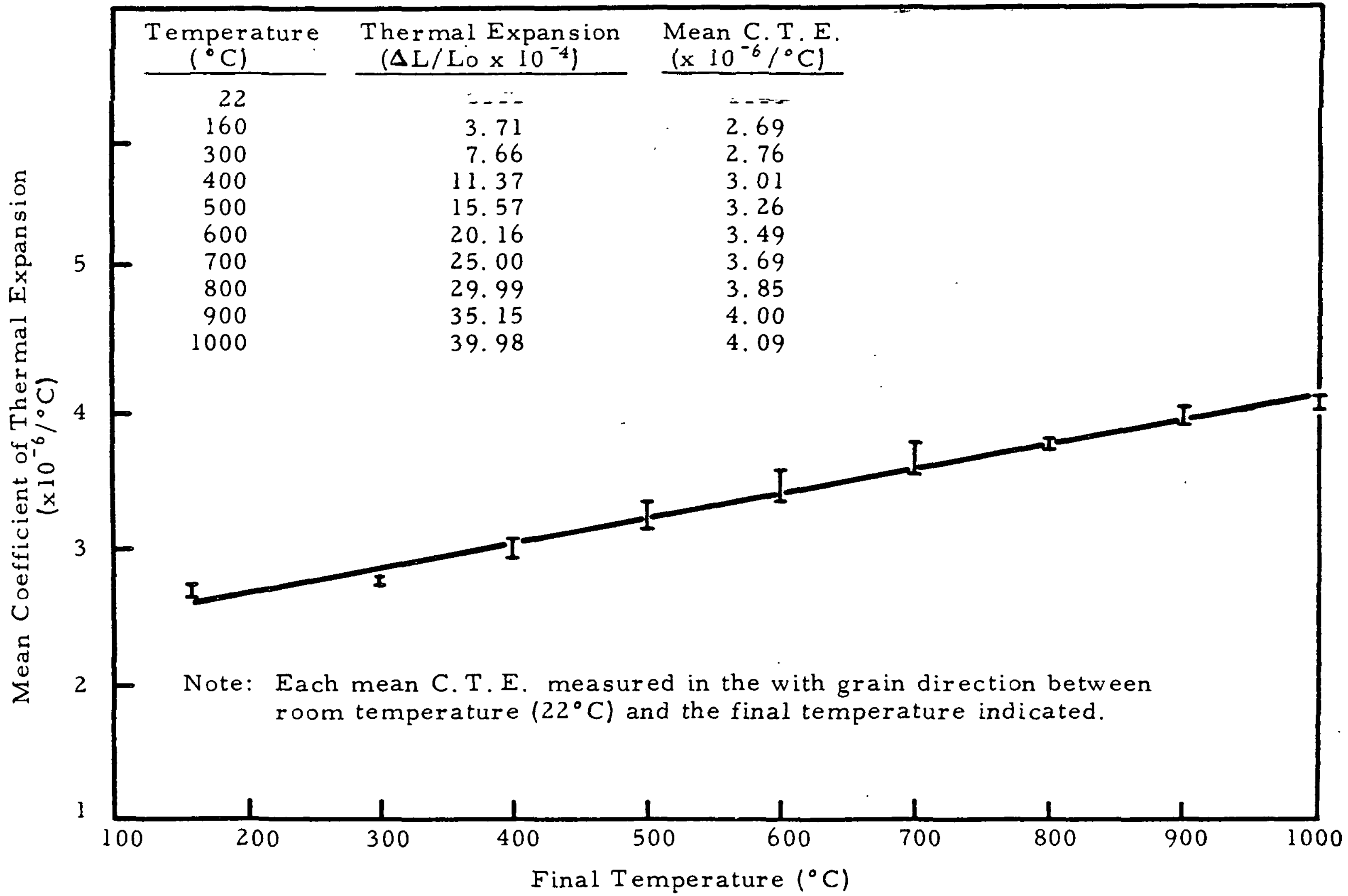
---

* w.g. - with grain
a.g. - across grain

** Anisotropy Ratio = Thermal Conductivity (w.g.)/Thermal Conductivity (a.g.)

The sample configuration, 0.5 inch (1.3 cm) diameter x 0.080 inch (.20 cm) thick, for the thermal conductivity measurement was small enough to permit machining of samples in both grain directions from the plugs produced during Task III. Except for density, all the previously reported mechanical properties were determined on samples machined in the with-grain direction. As expected, all four of the materials manufactured during Task III displayed higher thermal conductivities in the with-grain direction. The anisotropy ratios presented in Table IX were calculated by using the measured with-grain and across-grain thermal conductivities. The carbon-graphite seal ring bodies of formulations Nos. 1X, 2X, and 3 are isotropic, whereas, the compacts of formulation No. 4 are slightly more anisotropic. All four of the materials showed considerably greater isotropy than those of the hot-molded anisotropic graphites produced by Group CMF-13 of the Los Alamos Scientific Laboratory (LASL)(7). The LASL materials, in which pyrolytic and natural graphites were used as the primary particulate fillers, had thermal conductivity anisotropy ratios ranging between 3.0 and 7.2. The use of artificial graphite as the primary particulate filler accounts for the greater isotropy of the compacts of formulations Nos. 1X, 2X, 3, and 4X as compared with the LASL materials.

Figures 1 through 4 are plots of the coefficients of thermal expansion determined for the compacts of formulations Nos. 1X, 2X, 3 and 4X. Each plot represents the average of two tests conducted on samples machined in the with-grain direction. Figure 5 is a plot of the coefficient of thermal expansion of seal ring Grade CDJ-83, which has been included for purposes of comparison. All five materials 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 four materials tested. A comparison of Figures 1 and 2 shows that the addition of 5 pbw of glassy carbon to the formulation No. 1X composition had a negligible effect on the coefficient of thermal expansion. Of the four materials manufactured during Task III, the seal ring bodies of formulation No. 4X had the lowest overall coefficient of thermal expansion, especially at the higher temperatures. Similarly, the formulation No. 3 compacts displayed the highest overall coefficient of thermal expansion, especially at the lower temperatures.

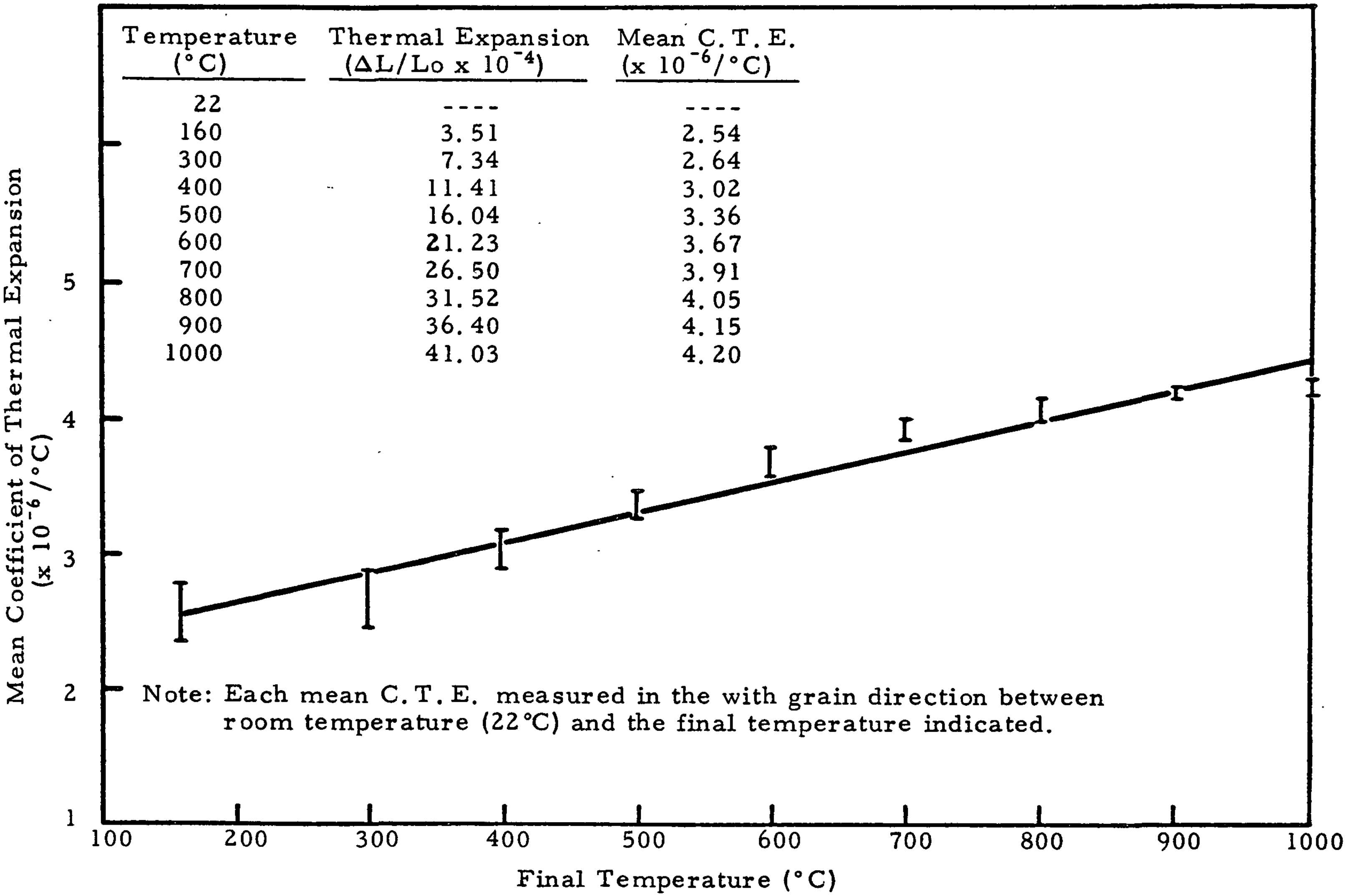


Temperature (°C)	Thermal Expansion ($\Delta L/Lo \times 10^{-4}$)	Mean C.T.E. ($\times 10^{-6}/°C$)
22	----	----
160	3.71	2.69
300	7.66	2.76
400	11.37	3.01
500	15.57	3.26
600	20.16	3.49
700	25.00	3.69
800	29.99	3.85
900	35.15	4.00
1000	39.98	4.09

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. 1X Material.

G 710428

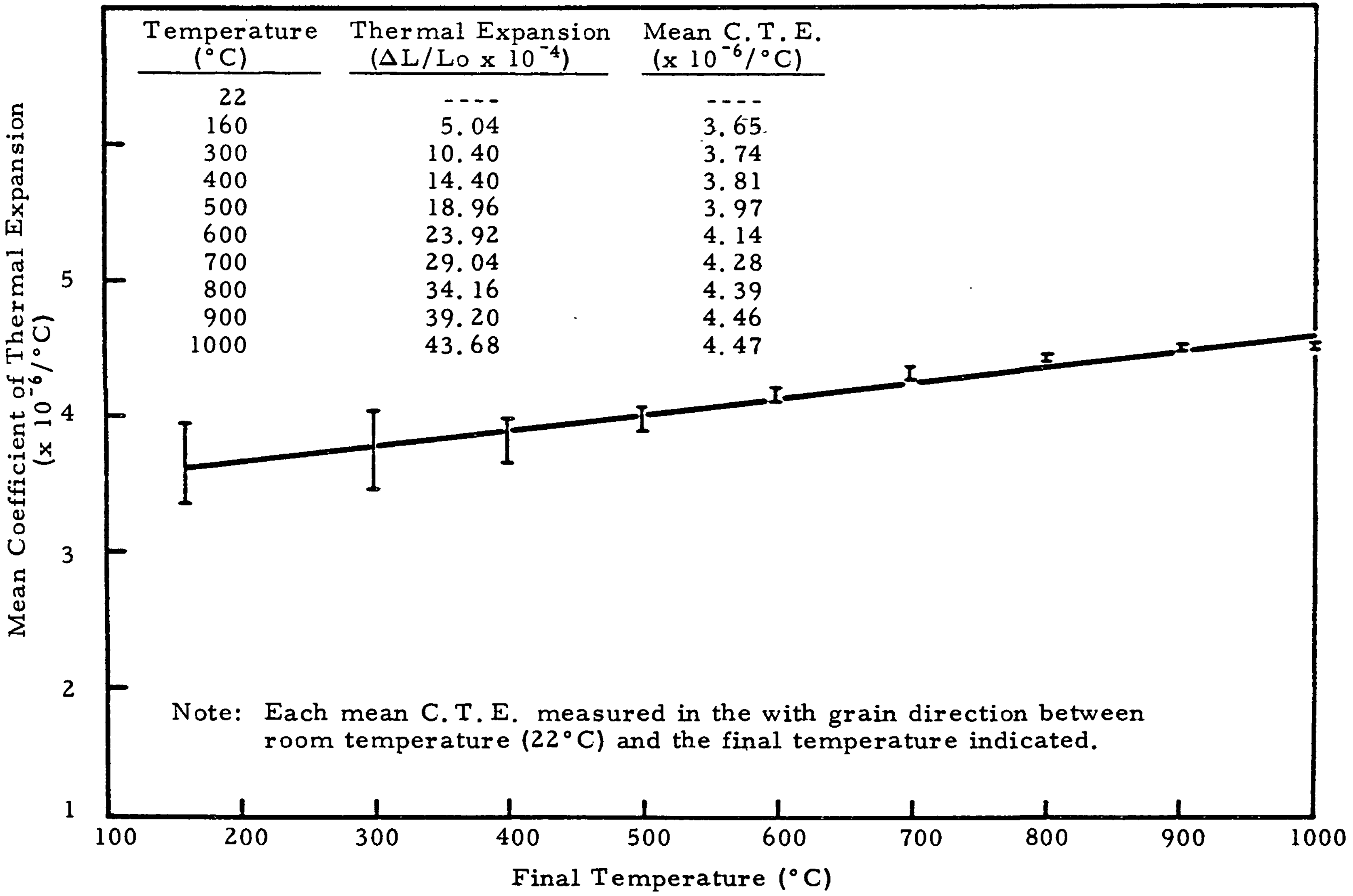


Temperature (°C)	Thermal Expansion ($\Delta L/Lo \times 10^{-4}$)	Mean C.T.E. ($\times 10^{-6}/°C$)
22	----	----
160	3.51	2.54
300	7.34	2.64
400	11.41	3.02
500	16.04	3.36
600	21.23	3.67
700	26.50	3.91
800	31.52	4.05
900	36.40	4.15
1000	41.03	4.20

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. 2X Material.

G 710429

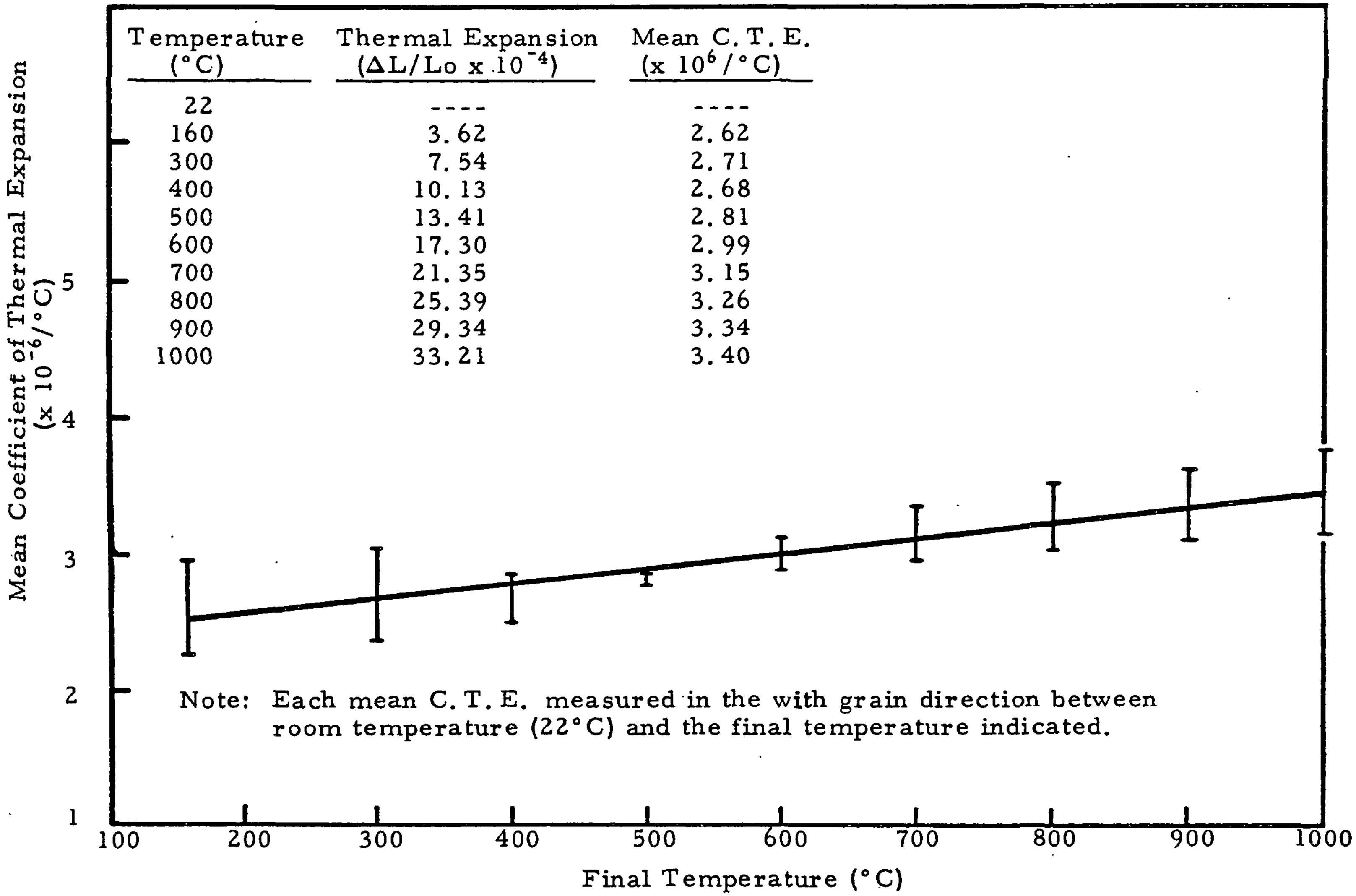


Temperature (°C)	Thermal Expansion ($\Delta L/Lo \times 10^{-4}$)	Mean C.T.E. ($\times 10^{-6}/°C$)
22	----	----
160	5.04	3.65
300	10.40	3.74
400	14.40	3.81
500	18.96	3.97
600	23.92	4.14
700	29.04	4.28
800	34.16	4.39
900	39.20	4.46
1000	43.68	4.47

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-Formulation No. 3 Material.

G 710430



Temperature (°C)	Thermal Expansion ($\Delta L/Lo \times 10^{-4}$)	Mean C. T. E. ($\times 10^6$/°C)
22	----	----
160	3.62	2.62
300	7.54	2.71
400	10.13	2.68
500	13.41	2.81
600	17.30	2.99
700	21.35	3.15
800	25.39	3.26
900	29.34	3.34
1000	33.21	3.40

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

Figure 4. Mean Coefficient of Thermal Expansion - Formulation No. 4X Material

G 710431

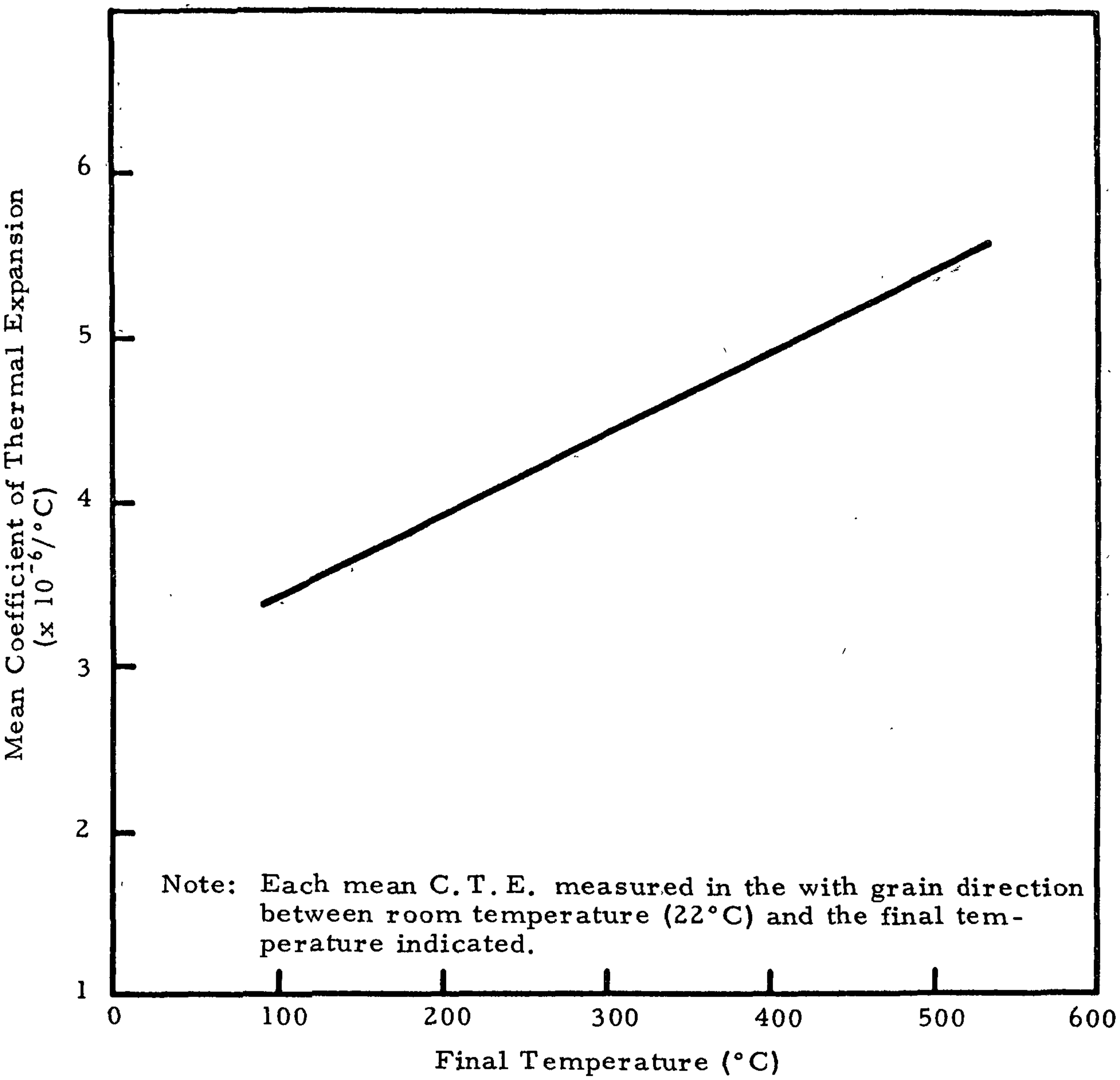


Figure 5. Mean Coefficient of Thermal Expansion - Grade CDJ-83.

G 710432

The thermal properties determined for the compacts of formulations Nos. 1X, 2X, 3, and 4X indicate that all four are potentially good carbon-graphite seal ring materials. A low coefficient of thermal expansion 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) then thermal deformation is mitigated by using high thermal conductivity and low thermal expansion carbon-graphite materials.

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 its 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 wetting tend to block the pores, as well as the larger open volumes. (8) 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 X presents the percent total porosities calculated for the compacts of formulation Nos. 1X, 2X, 3, and 4X, and 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 pore volume to the volume occupied by the pores and the carbonaceous material in the compact being analyzed.

TABLE X

Percent Total Porosities of Formulations Nos. 1X, 2X, 3, and 4X Material

Formulation	Helium Density (g/cc)	Bulk Density (g/cc)	Percent Total Porosity
No. 1X	1.940	1.730	10.8
No. 2X	1.890	1.700	10.1
No. 3	1.900	1.650	13.2
No. 4X	1.765	1.466	16.9
Grade CDJ	1.841	1.756	4.6

Impregnation with the Bakelite BRP-5095 resin reduced the total porosity from 16.6% for the formulation No. 1 compacts to 10.8% for the formulation No. 1X compacts. Similarly, the resin impregnation of the seal ring bodies of formulations Nos. 2X and 4X reduced their total porosities from 16.0% (formulation No. 2) and 22.1% (formulation No. 4) to 10.1% and 16.9%, respectively. As previously reported, mechanical properties were improved by the resin impregnation. The fact that the total porosity of Grade CDJ is approximately one-half that determined for the compacts of formulations Nos. 1X and 2X contributes to Grade CDJ-83 having a significantly higher flexural strength and elastic modulus.

The total porosity also may influence the thermal conductivities of the seal ring bodies of formulations Nos. 1X, 2X, 3, and 4X. As mentioned in Section V-C, the thermal conductivities of the formulations Nos. 1X and 2X compacts were higher than those of the compacts of formulations Nos. 3 and 4X. The difference in thermal conductivities may have resulted from the lower total porosities of the compacts of formulations Nos. 1X and 2X, or it may have been caused by a difference in the degree of crystallinity of the filler and the binder materials after carbonization. The No. 30 medium pitch used to bond formulations Nos. 1X and 2X may have been more crystalline after it was baked to 2800°C than the Bakelite BRP-5095 resin used to bond formulations Nos. 3 and 4X. The "graphite" fibers used in formulation 4X also probably have a lower degree of crystallinity than the Thermax carbon black used in the other formulations.

The lower porosity seal ring bodies of formulations Nos. 1X, 2X, and 4X should have better oxidation resistance than the compacts of formulations Nos. 1, 2, and 4. The mechanism controlling the oxidation rate of a carbon-graphite seal ring operating at temperatures up to 1300°F (704°C) consists of the chemisorption of the oxidizing gas at an active site, rearrangement of the chemisorbed gas on the surface to a desorbable product, and desorption of the products from the surface. Reducing the porosity of a carbon-graphite compact may retard oxidation rate, by decreasing its permeability to the oxidizing gas. The possibility exists, however, that the resin-impregnated compacts of formulations Nos. 1X, 2X, and 4X may experience higher oxidation rates than their nonresin-impregnated counterparts. After the carbonized resin impregnant has been baked to 2800°C, it may not be so crystalline as the carbon-graphite base material. Since the degree of crystallinity greatly affects the rate at which a carbon-graphite material oxidizes, the carbonized resin impregnant could oxidize at a faster rate than that of the more crystalline base material.

Tables XI to XIV present the results of the pore volume and pore size distribution measurements made on compacts of formulations Nos. 1X, 2X, 3, and 4X by using mercury intrusion. Figures 6 to 13 are the corresponding plots of the pore volume and cumulative pore volume versus pore diameter for the four 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 seal ring bodies of formulations Nos. 1X, and 2X were found to have smaller pores and less total pore volume than the compacts of formulations Nos. 3 and 4X. The formulation No. 2X compact had the smallest average pore diameter (3.9μ). The average pore diameters of the other three materials were 4.4μ for formulation No. 1X, 8.7μ for formulation No. 3, and 5.6μ for formulation No. 4X. The intruded pore volumes of the compacts of formulations Nos. 1X and 2X were the same (0.076 cc/g). Formulation No. 4X produced a seal ring body having the largest intruded pore volume, 1.8 times that measured for the compacts of formulations Nos. 1X and 2X. The intruded pore volume of the formulation No. 3 compact was approximately 1.3 times that of the formulations Nos. 1X and 2X compacts.

TABLE XI

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

SAMPLE WEIGHT = 7.9956 GRAMS.
SAMPLE VOLUME = 4.7060 CC.
SURFACE AREA = 2.219 SQUARE METERS PER GRAM.
TOTAL VOLUME INTRUDED = 0.6043 CC.
AVERAGE PORE RADIUS = 2.213 MICRONS.

BULK DENSITY AT 100 MICRONS = 1.6990 G/CC.
BULK DENSITY AT 0.02 MICRONS = 1.9493 G/CC.
HELIUM DENSITY = 1.9400 G/CC.
APPARENT DENSITY = 1.7300 G/CC.
VOLUME OF PORES BETWEEN 100 MICRONS AND 0.020 MICRONS = 0.0755 CC/G.
VOID FRACTION = 0.127

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	0.00001	0.00001	0.01	0.00000	0.0000	0.0755
50.000- 25.000	37.5000	0.00000	0.00001	0.01	0.00000	0.0000	0.0755
25.000- 20.000	22.5000	0.00000	0.00001	0.01	0.00000	0.0000	0.0755
20.000- 15.000	17.5000	0.00087	0.00089	0.68	0.00017	0.0005	0.0755
15.000- 10.000	12.5000	0.01096	0.01185	9.06	0.00219	0.0063	0.0750
10.000- 5.000	7.5000	0.03587	0.04773	36.50	0.00717	0.0207	0.0637
5.000- 4.000	4.5000	0.01700	0.06473	49.50	0.01700	0.0098	0.0479
4.000- 3.000	3.5000	0.01258	0.07731	59.12	0.01258	0.0072	0.0381
3.000- 2.000	2.5000	0.00870	0.08602	65.78	0.00870	0.0050	0.0308
2.000- 1.000	1.5000	0.00564	0.09166	70.10	0.00564	0.0032	0.0258
1.000- 0.800	0.9000	0.00131	0.09297	71.10	0.00657	0.0007	0.0225
0.800- 0.600	0.7000	0.00129	0.09427	72.09	0.00646	0.0007	0.0218
0.600- 0.500	0.5500	0.00067	0.09494	72.61	0.00676	0.0003	0.0210
0.500- 0.400	0.4500	0.00123	0.09618	73.55	0.01232	0.0007	0.0206
0.400- 0.350	0.3750	0.00051	0.09669	73.94	0.01021	0.0002	0.0199
0.350- 0.300	0.3250	0.00038	0.09708	74.24	0.00779	0.0002	0.0196
0.300- 0.280	0.2900	0.00033	0.09741	74.50	0.01689	0.0001	0.0194
0.280- 0.260	0.2700	0.00033	0.09775	74.76	0.01682	0.0001	0.0192
0.260- 0.240	0.2500	0.00035	0.09811	75.03	0.01778	0.0002	0.0190
0.240- 0.220	0.2300	0.00034	0.09845	75.30	0.01738	0.0002	0.0188
0.220- 0.200	0.2100	0.00034	0.09880	75.56	0.01725	0.0001	0.0186
0.200- 0.180	0.1900	0.00023	0.09904	75.74	0.01198	0.0001	0.0184
0.180- 0.160	0.1700	0.00036	0.09940	76.02	0.01812	0.0002	0.0183
0.160- 0.140	0.1500	0.00056	0.09996	76.45	0.02810	0.0003	0.0181
0.140- 0.120	0.1300	0.00083	0.10080	77.09	0.04164	0.0004	0.0177
0.120- 0.100	0.1100	0.00065	0.10145	77.59	0.03285	0.0003	0.0173
0.100- 0.080	0.0900	0.00181	0.10327	78.97	0.09059	0.0010	0.0169
0.080- 0.060	0.0700	0.00261	0.10588	80.98	0.13088	0.0015	0.0158
0.060- 0.050	0.0550	0.00215	0.10804	82.62	0.21550	0.0012	0.0143
0.050- 0.040	0.0450	0.00452	0.11256	86.08	0.45231	0.0026	0.0131
0.040- 0.030	0.0350	0.00653	0.11910	91.08	0.65345	0.0037	0.0105
0.030- 0.020	0.0250	0.01165	0.13075	99.99	1.16549	0.0067	0.0067

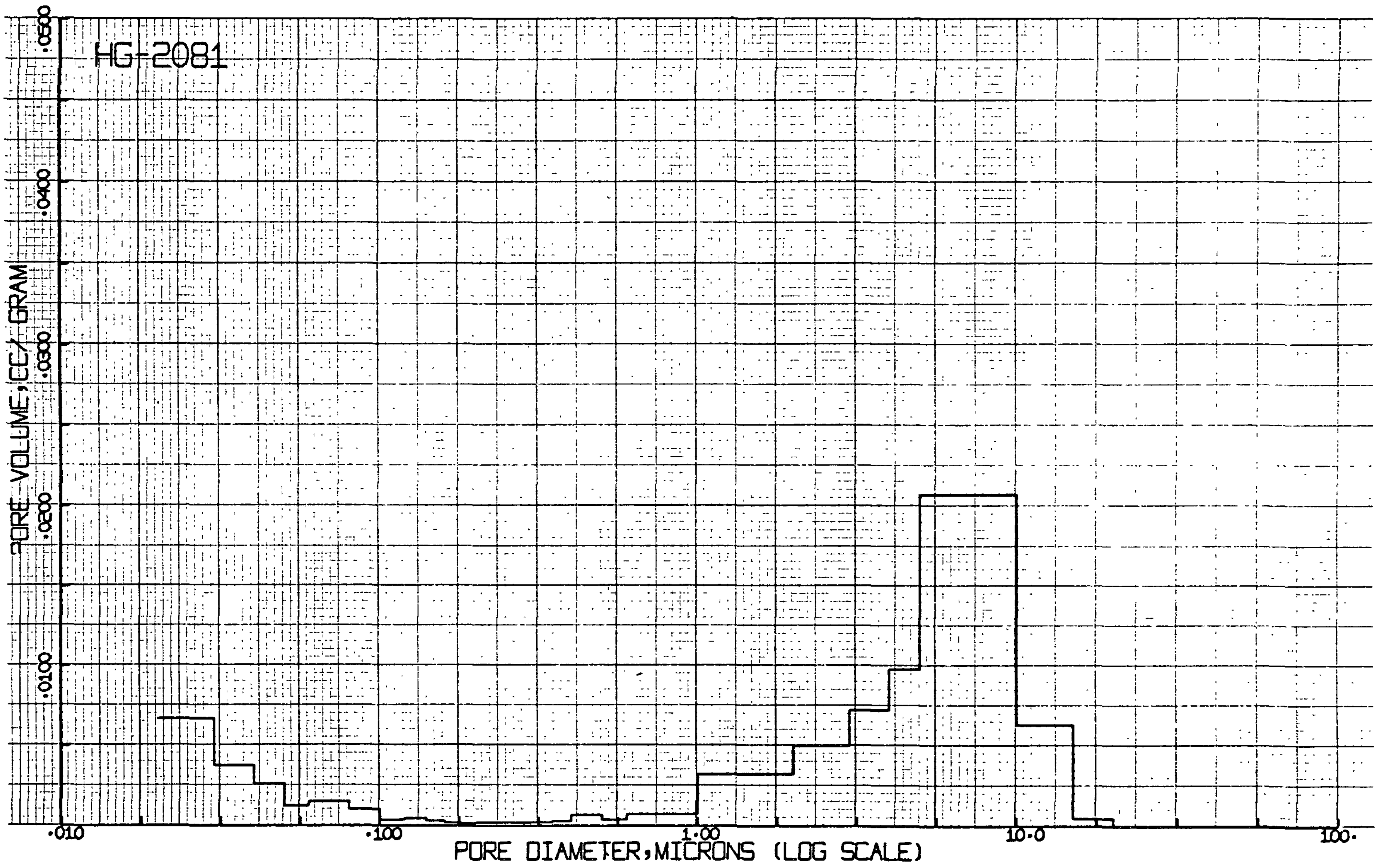


Figure 6. Pore Volume versus Pore Diameter by Mercury Intrusion - Formulation No. 1X Material.

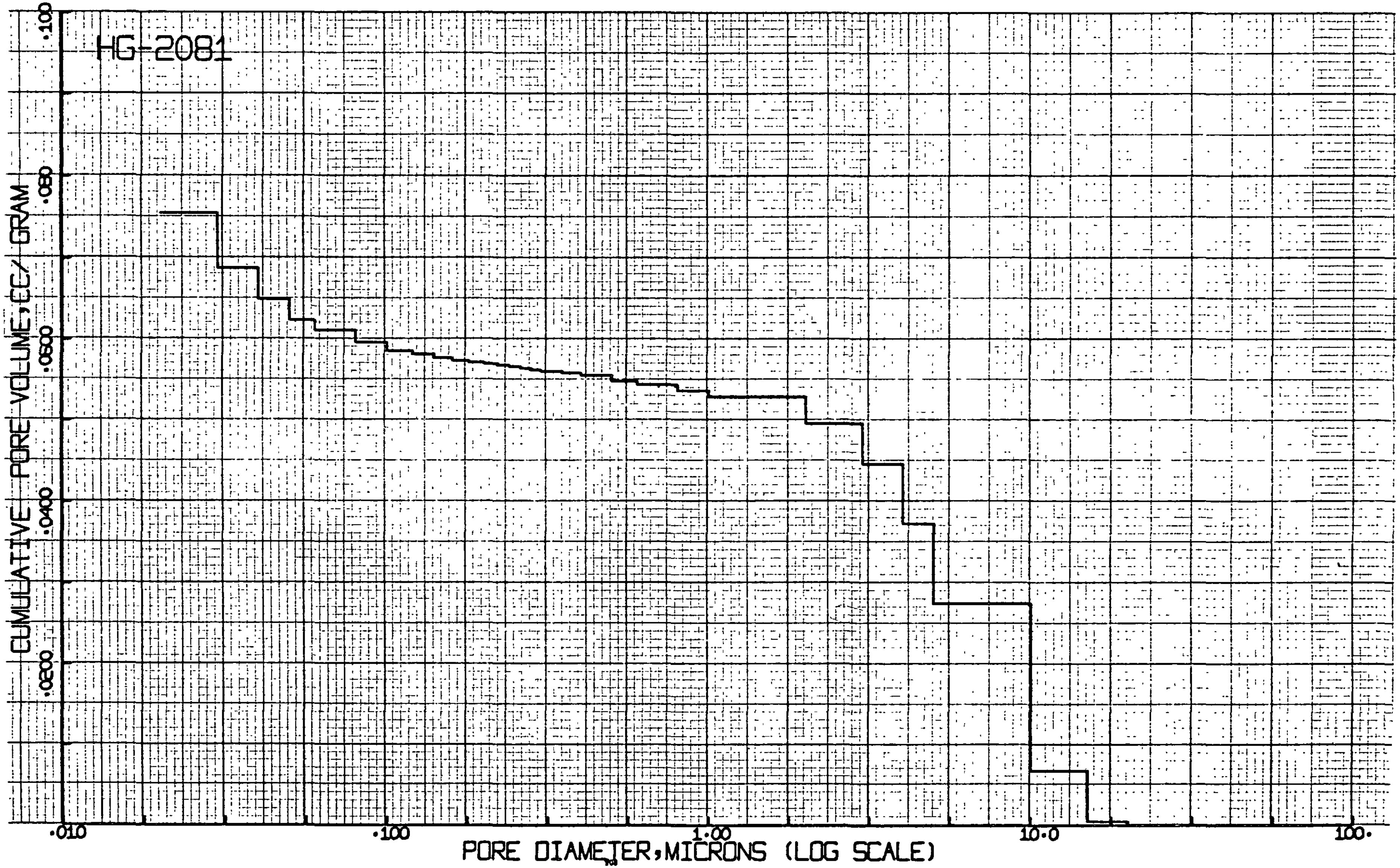


Figure 7. Cumulative Pore Volume versus Pore Diameter by Mercury Intrustion - Formulation No. 1X Material.

TABLE XII

Pore Volume and Distribution by Mercury Intrusion-Formulation No. 2X Material

SAMPLE WEIGHT = 5.8978 GRAMS.
SAMPLE VOLUME = 3.5556 CC.
SURFACE AREA = 2.488 SQUARE METERS PER GRAM.
TOTAL VOLUME INTRUDED = 0.4494 CC.
AVERAGE PORE RADIUS = 1.964 MICRONS.

BULK DENSITY AT 100 MICRONS = 1.6587 G/CC.
BULK DENSITY AT 0.02 MICRONS = 1.8987 G/CC.
HELIUM DENSITY = 1.8900 G/CC.
APPARENT DENSITY = 1.7000 G/CC.
VOLUME OF PORES BETWEEN 100 MICRONS AND 0.020 MICRONS = 0.0762 CC/G.
VOID FRACTION = 0.125

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	0.00021	0.00021	0.16	0.00000	0.0001	0.0762
50.000- 25.000	37.5000	0.00037	0.00058	0.45	0.00001	0.0002	0.0760
25.000- 20.000	22.5000	0.00018	0.00076	0.59	0.00003	0.0001	0.0758
20.000- 15.000	17.5000	0.00076	0.00153	1.18	0.00015	0.0004	0.0757
15.000- 10.000	12.5000	0.00622	0.00775	5.99	0.00124	0.0036	0.0753
10.000- 5.000	7.5000	0.02652	0.03428	26.46	0.00530	0.0155	0.0716
5.000- 4.000	4.5000	0.01549	0.04978	38.43	0.01549	0.0091	0.0560
4.000- 3.000	3.5000	0.02021	0.06999	54.03	0.02021	0.0118	0.0469
3.000- 2.000	2.5000	0.01206	0.08205	63.34	0.01206	0.0070	0.0350
2.000- 1.000	1.5000	0.00581	0.08787	67.83	0.00581	0.0034	0.0279
1.000- 0.800	0.9000	0.00103	0.08890	68.63	0.00516	0.0006	0.0245
0.800- 0.600	0.7000	0.00134	0.09025	69.66	0.00672	0.0007	0.0239
0.600- 0.500	0.5500	0.00091	0.09116	70.37	0.00913	0.0005	0.0231
0.500- 0.400	0.4500	0.00103	0.09219	71.17	0.01031	0.0005	0.0225
0.400- 0.350	0.3750	0.00039	0.09258	71.47	0.00784	0.0002	0.0219
0.350- 0.300	0.3250	0.00115	0.09374	72.36	0.02302	0.0006	0.0217
0.300- 0.280	0.2900	0.00072	0.09446	72.92	0.03625	0.0004	0.0210
0.280- 0.260	0.2700	0.00097	0.09544	73.67	0.04876	0.0005	0.0206
0.260- 0.240	0.2500	0.00000	0.09544	73.67	0.00000	0.0000	0.0200
0.240- 0.220	0.2300	0.00000	0.09544	73.67	0.00000	0.0000	0.0200
0.220- 0.200	0.2100	0.00000	0.09544	73.67	0.00000	0.0000	0.0200
0.200- 0.180	0.1900	0.00000	0.09544	73.67	0.00000	0.0000	0.0200
0.180- 0.160	0.1700	0.00005	0.09549	73.71	0.00258	0.0000	0.0200
0.160- 0.140	0.1500	0.00062	0.09611	74.19	0.03115	0.0003	0.0200
0.140- 0.120	0.1300	0.00084	0.09696	74.85	0.04242	0.0004	0.0196
0.120- 0.100	0.1100	0.00073	0.09770	75.41	0.03682	0.0004	0.0191
0.100- 0.080	0.0900	0.00173	0.09943	76.75	0.08659	0.0010	0.0187
0.080- 0.060	0.0700	0.00265	0.10209	78.80	0.13291	0.0015	0.0177
0.060- 0.050	0.0550	0.00220	0.10429	80.51	0.22063	0.0012	0.0161
0.050- 0.040	0.0450	0.00493	0.10922	84.31	0.49320	0.0029	0.0148
0.040- 0.030	0.0350	0.00685	0.11607	89.60	0.68501	0.0040	0.0119
0.030- 0.020	0.0250	0.01346	0.12954	99.99	1.34635	0.0079	0.0079

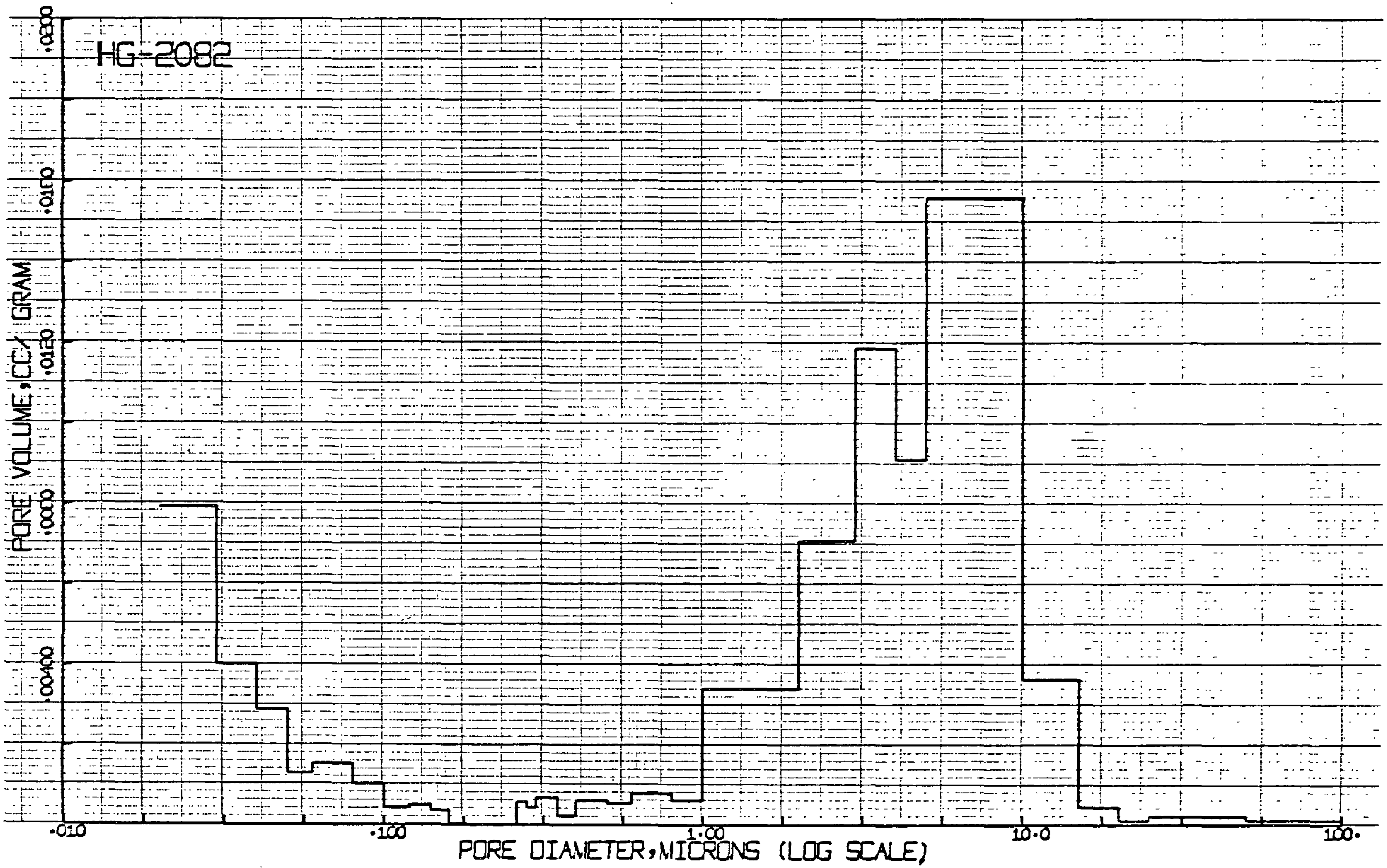


Figure 8. Pore Volume versus Pore Diameter by Mercury Intrusion - Formulation No. 2X Material.

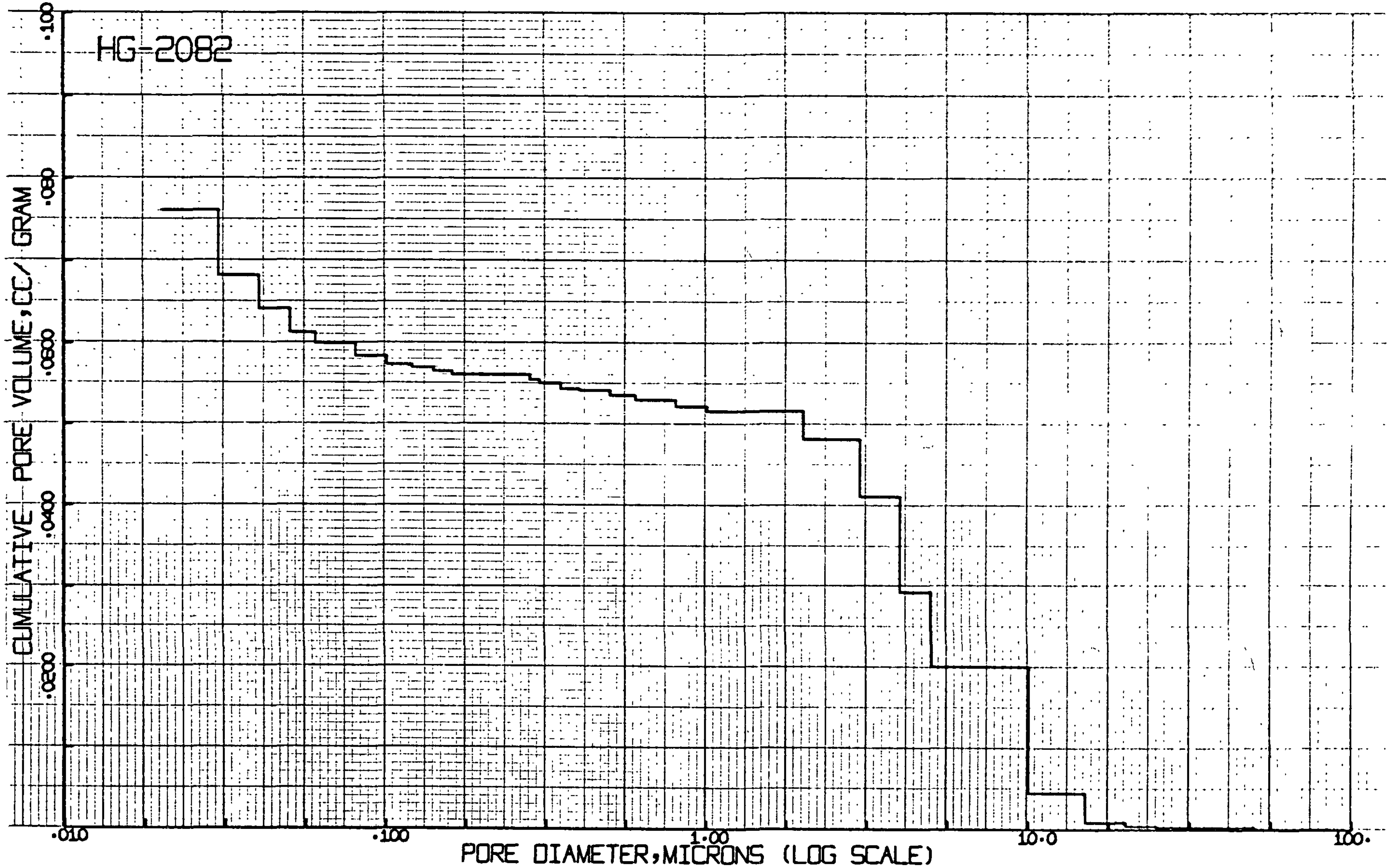


Figure 9. Cumulative Pore Volume versus Pore Diameter by Mercury Intrusion - Formulation No. 2X Material.

TABLE XIII

Pore Volume and Distribution by Mercury Intrusion-Formulation No. 3 Material

SAMPLE WEIGHT = 7.5131 GRAMS.
SAMPLE VOLUME = 4.5559 CC.
SURFACE AREA = 2.078 SQUARE METERS PER GRAM.
TOTAL VOLUME INTRUDED = 0.7275 CC.
AVERAGE PORE RADIUS = 4.337 MICRONS.

BULK DENSITY AT 100 MICRONS = 1.6490 G/CC.
BULK DENSITY AT 0.02 MICRONS = 1.9624 G/CC.
HELIUM DENSITY = 1.9000 G/CC.
APPARENT DENSITY = 1.9500 G/CC.
VOLUME OF PORES BETWEEN 100 MICRONS AND 0.020 MICRONS = 0.0968 CC/G.
VOID FRACTION = 0.155

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	0.00015	0.00015	0.09	0.00000	0.0000	0.0968
50.000- 25.000	37.5000	0.00023	0.00039	0.24	0.00000	0.0001	0.0967
25.000- 20.000	22.5000	0.00000	0.00039	0.24	0.00000	0.0000	0.0965
20.000- 15.000	17.5000	0.02047	0.02086	13.05	0.00409	0.0124	0.0965
15.000- 10.000	12.5000	0.05059	0.07145	44.72	0.01011	0.0306	0.0841
10.000- 5.000	7.5000	0.04593	0.11738	73.40	0.00919	0.0278	0.0535
5.000- 4.000	4.5000	0.00157	0.11896	74.45	0.00157	0.0009	0.0256
4.000- 3.000	3.5000	0.00170	0.12066	75.52	0.00170	0.0010	0.0247
3.000- 2.000	2.5000	0.00326	0.12392	77.56	0.00326	0.0019	0.0237
2.000- 1.000	1.5000	0.00348	0.12741	79.74	0.00348	0.0021	0.0217
1.000- 0.800	0.9000	0.00072	0.12814	80.19	0.00363	0.0004	0.0196
0.800- 0.600	0.7000	0.00107	0.12921	80.88	0.00535	0.0006	0.0191
0.600- 0.500	0.5500	0.00051	0.12972	81.19	0.00515	0.0003	0.0186
0.500- 0.400	0.4500	0.00081	0.13053	81.70	0.00812	0.0004	0.0182
0.400- 0.350	0.3750	0.00044	0.13098	81.97	0.00884	0.0002	0.0177
0.350- 0.300	0.3250	0.00040	0.13138	82.22	0.00804	0.0002	0.0174
0.300- 0.280	0.2900	0.00022	0.13160	82.36	0.01129	0.0001	0.0172
0.280- 0.260	0.2700	0.00031	0.13192	82.57	0.01599	0.0001	0.0170
0.260- 0.240	0.2500	0.00021	0.13214	82.70	0.01091	0.0001	0.0168
0.240- 0.220	0.2300	0.00021	0.13235	82.83	0.01053	0.0001	0.0167
0.220- 0.200	0.2100	0.00023	0.13258	82.98	0.01157	0.0001	0.0165
0.200- 0.180	0.1900	0.00029	0.13288	83.16	0.01460	0.0001	0.0164
0.180- 0.160	0.1700	0.00041	0.13330	83.42	0.02099	0.0002	0.0163
0.160- 0.140	0.1500	0.00063	0.13393	83.82	0.03169	0.0003	0.0158
0.140- 0.120	0.1300	0.00061	0.13455	84.21	0.03079	0.0003	0.0155
0.120- 0.100	0.1100	0.00055	0.13510	84.55	0.02753	0.0003	0.0152
0.100- 0.080	0.0900	0.00107	0.13617	85.22	0.05360	0.0006	0.0149
0.080- 0.060	0.0700	0.00160	0.13777	86.23	0.08019	0.0009	0.0143
0.060- 0.050	0.0550	0.00139	0.13916	87.10	0.13909	0.0008	0.0133
0.050- 0.040	0.0450	0.00347	0.14264	89.27	0.34779	0.0021	0.0124
0.040- 0.030	0.0350	0.00530	0.14794	92.59	0.53029	0.0032	0.0103
0.030- 0.020	0.0250	0.01182	0.15977	99.99	1.18261	0.0071	0.0071

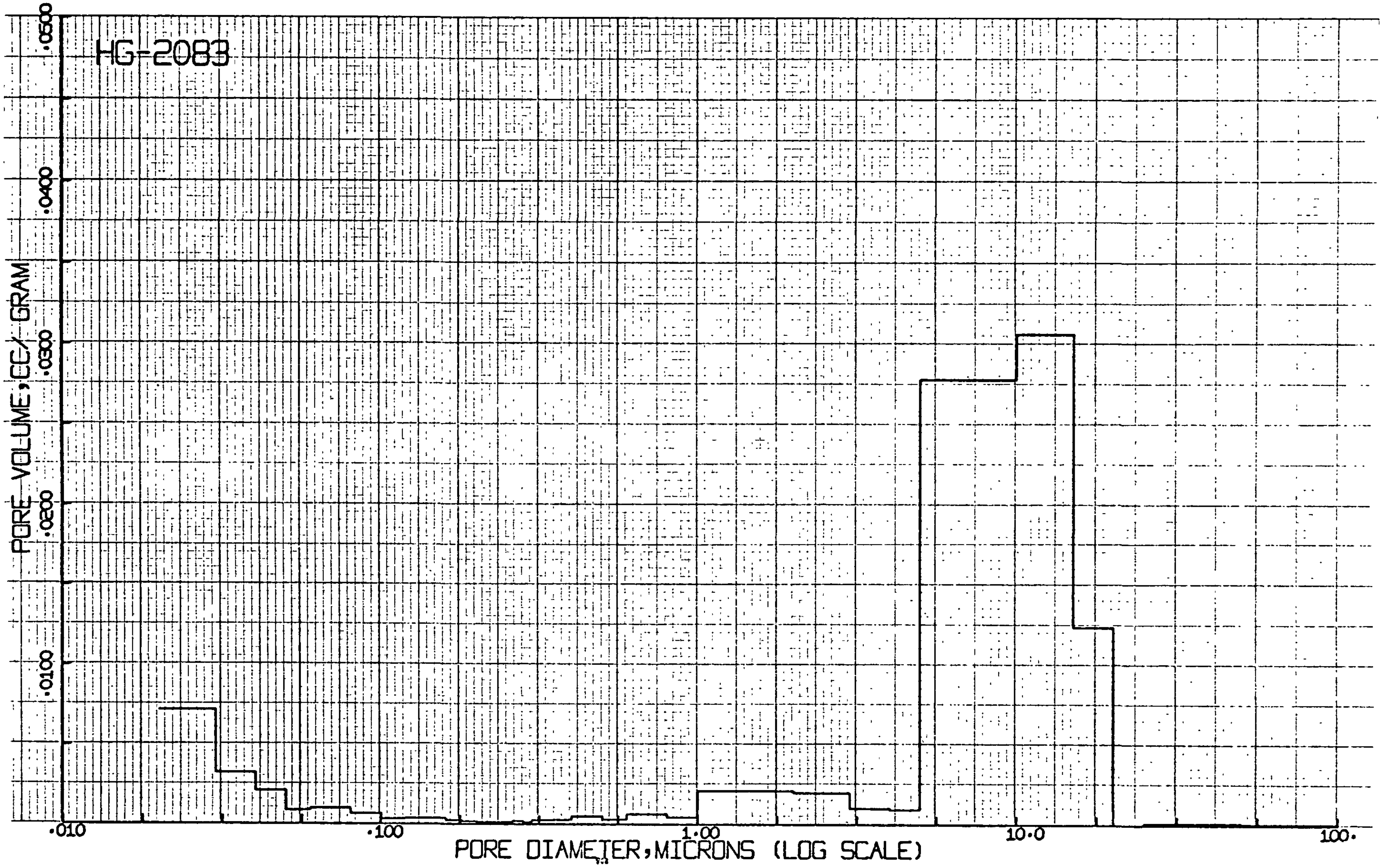


Figure 10. Pore Volume versus Pore Diameter by Mercury Intrusion - Formulation No. 3 Material.

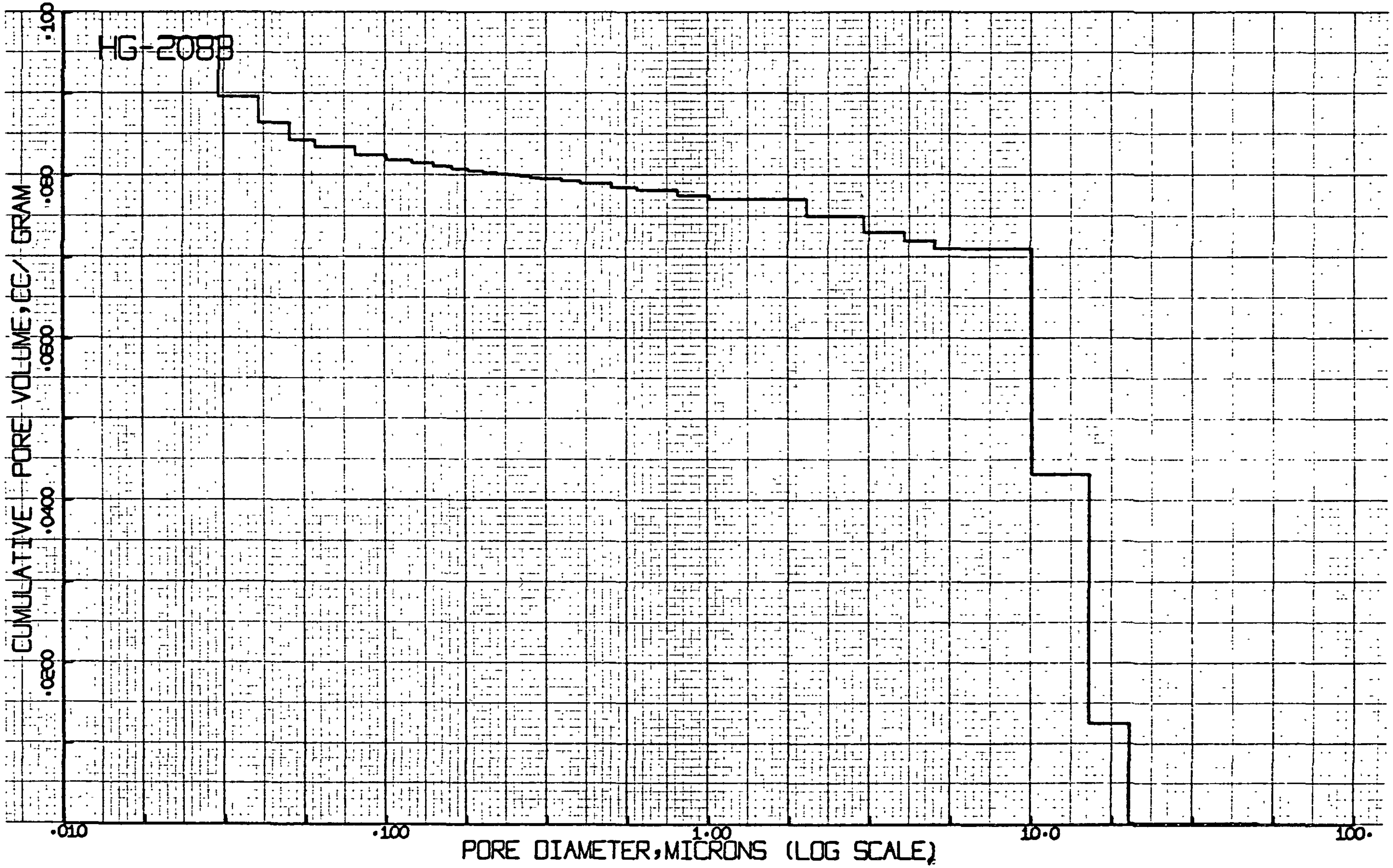


Figure 11. Cumulative Pore Volume versus Pore Diameter by Mercury Intrusion - Formulation No. 3 Material.

TABLE XIV

Pore Volume and Distribution by Mercury Intrusion-Formulation No. 4X Material

SAMPLE WEIGHT = 7.0444 GRAMS.
SAMPLE VOLUME = 4.8186 CC.
SURFACE AREA = 2.994 SQUARE METERS PER GRAM.
TOTAL VOLUME INTRUDED = 0.9760 CC.
AVERAGE PORE RADIUS = 2.824 MICRONS.

BULK DENSITY AT 100 MICRONS = 1.4619 G/CC.
BULK DENSITY AT 0.02 MICRONS = 1.8332 G/CC.
HELIUM DENSITY = 1.7650 G/CC.
APPARENT DENSITY = 1.4660 G/CC.
VOLUME OF PORES BETWEEN 100 MICRONS AND 0.020 MICRONS = 0.1385 CC/G.
VOID FRACTION = 0.196

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	0.00067	0.00067	0.33	0.00001	0.0004	0.1385
50.000- 25.000	37.5000	0.00107	0.00175	0.86	0.00004	0.0007	0.1380
25.000- 20.000	22.5000	0.00000	0.00175	0.86	0.00000	0.0000	0.1373
20.000- 15.000	17.5000	0.01087	0.01262	6.21	0.00217	0.0074	0.1373
15.000- 10.000	12.5000	0.03126	0.04388	21.60	0.00625	0.0213	0.1299
10.000- 5.000	7.5000	0.04313	0.08701	42.84	0.00862	0.0294	0.1086
5.000- 4.000	4.5000	0.01103	0.09804	48.27	0.01103	0.0075	0.0791
4.000- 3.000	3.5000	0.00965	0.10770	53.02	0.00965	0.0065	0.0716
3.000- 2.000	2.5000	0.01173	0.11943	58.80	0.01173	0.0080	0.0650
2.000- 1.000	1.5000	0.01516	0.13460	66.26	0.01516	0.0103	0.0570
1.000- 0.800	0.9000	0.00455	0.13915	68.50	0.02276	0.0031	0.0467
0.800- 0.600	0.7000	0.00489	0.14405	70.92	0.02449	0.0033	0.0436
0.600- 0.500	0.5500	0.00285	0.14691	72.32	0.02858	0.0019	0.0402
0.500- 0.400	0.4500	0.00354	0.15046	74.07	0.03545	0.0024	0.0383
0.400- 0.350	0.3750	0.00163	0.15209	74.87	0.03274	0.0011	0.0359
0.350- 0.300	0.3250	0.00183	0.15393	75.78	0.03679	0.0012	0.0348
0.300- 0.280	0.2900	0.00083	0.15477	76.19	0.04177	0.0005	0.0335
0.280- 0.260	0.2700	0.00080	0.15558	76.59	0.04038	0.0005	0.0329
0.260- 0.240	0.2500	0.00112	0.15670	77.14	0.05631	0.0007	0.0324
0.240- 0.220	0.2300	0.00141	0.15812	77.84	0.07077	0.0009	0.0316
0.220- 0.200	0.2100	0.00131	0.15943	78.49	0.06570	0.0008	0.0306
0.200- 0.180	0.1900	0.00166	0.16110	79.31	0.08340	0.0011	0.0298
0.180- 0.160	0.1700	0.00177	0.16288	80.18	0.08882	0.0012	0.0286
0.160- 0.140	0.1500	0.00259	0.16547	81.46	0.12958	0.0017	0.0274
0.140- 0.120	0.1300	0.00261	0.16808	82.74	0.13056	0.0017	0.0256
0.120- 0.100	0.1100	0.00238	0.17047	83.92	0.11947	0.0016	0.0239
0.100- 0.080	0.0900	0.00380	0.17428	85.79	0.19032	0.0025	0.0222
0.080- 0.060	0.0700	0.00450	0.17878	88.01	0.22532	0.0030	0.0195
0.060- 0.050	0.0550	0.00313	0.18192	89.56	0.31396	0.0021	0.0166
0.050- 0.040	0.0450	0.00417	0.18610	91.61	0.41743	0.0028	0.0144
0.040- 0.030	0.0350	0.00548	0.19158	94.31	0.54808	0.0037	0.0116
0.030- 0.020	0.0250	0.01154	0.20312	99.99	1.15428	0.0078	0.0078

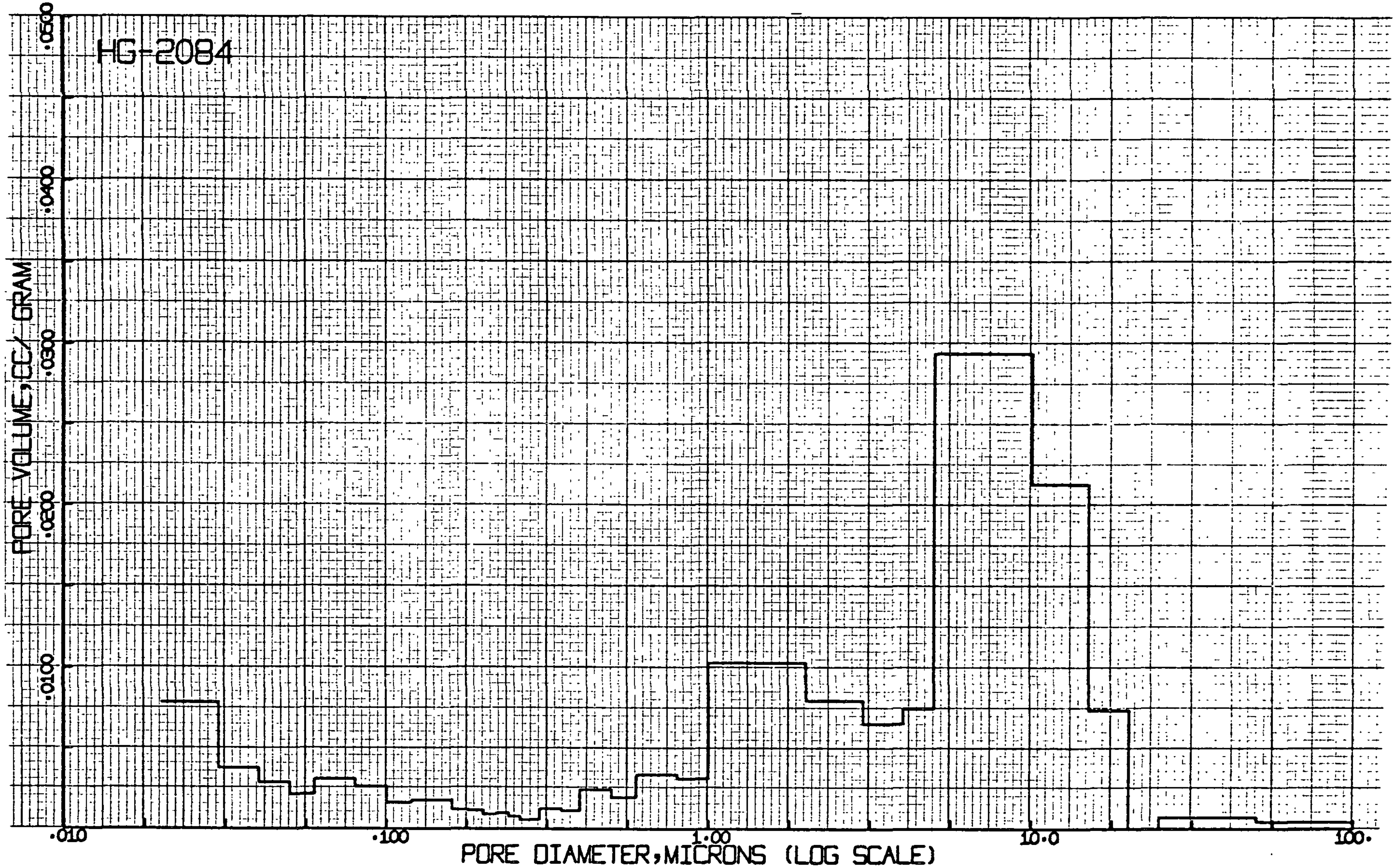


Figure 12. Pore Volume versus Pore Diameter by Mercury Intrusion - Formulation No. 4X Material.

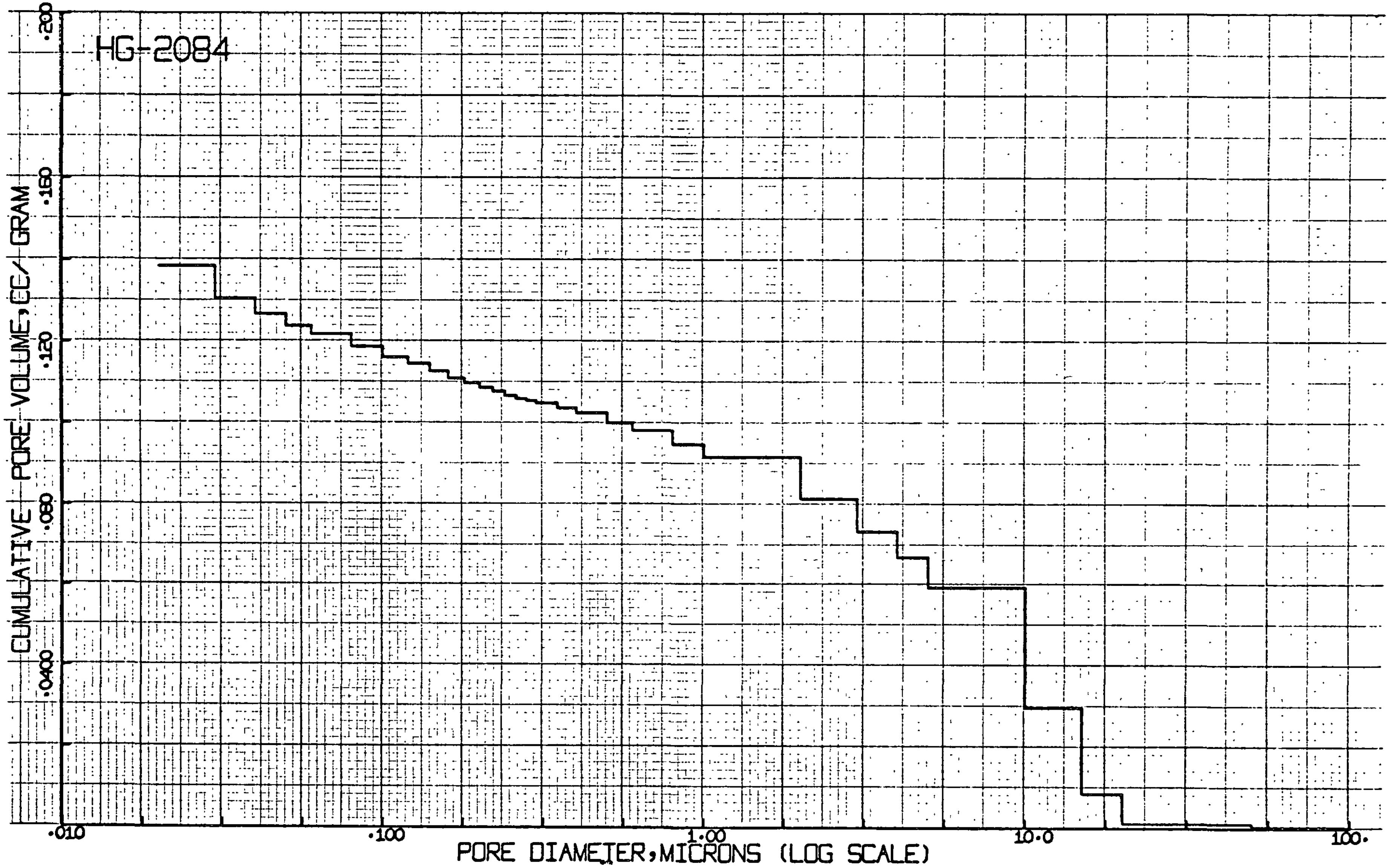


Figure 13. Cumulative Pore Volume versus Pore Diameter by Mercury Intrusion - Formulation No. 4X Material

For purposes of comparison, Table XV displays the pore volume and pore size distribution determined by mercury intrusion for Grade CDJ. Figures 14 and 15 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 for the seal ring bodies of formulations Nos. 1X, 2X, 3, and 4X.

Tables XVI and XIX display the results of nitrogen pore volume measurements made on compacts of the four material formulations. Figures 16 through 19 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 20-600Å. For the range of pore sizes measured by nitrogen desorption (too small in diameter to be accurately measured by mercury intrusion), the compacts of formulations Nos. 1X and 2X were found to have larger pores and greater pore volume than the seal ring bodies of formulations Nos. 3 and 4X. The compact of formulation No. 2X had the largest pores occupying the greatest volume (average pore diameter = 450Å, total pore volume = 0.0084 cc/g). Formulation No. 1X was found to produce a carbon-graphite article having an average pore diameter of 240Å and a total pore volume of 0.0014 cc/g. The total pore volumes determined for the compacts of formulations Nos. 3 and 4X were 0.00064 cc/g and 0.00099 cc/g, respectively. The average pore diameters of the compacts of formulations Nos. 3 and 4X were significantly smaller than those of the seal ring bodies manufactured from formulations Nos. 1X and 2X: 110Å for the formulation No. 3 compact and 50Å for the formulation No. 4X compact. The fact that phenolic resins result in chars having some closed microporosity may explain why the resin bonded formulations Nos. 3 and 4X produce compacts of smaller average pore diameters and volumes in the nitrogen desorption range than those of the two pitch bonded materials. Table XX presents the results of the nitrogen pore volume measurement made on a sample of Grade CDJ. Figure 20 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.

TABLE XV

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

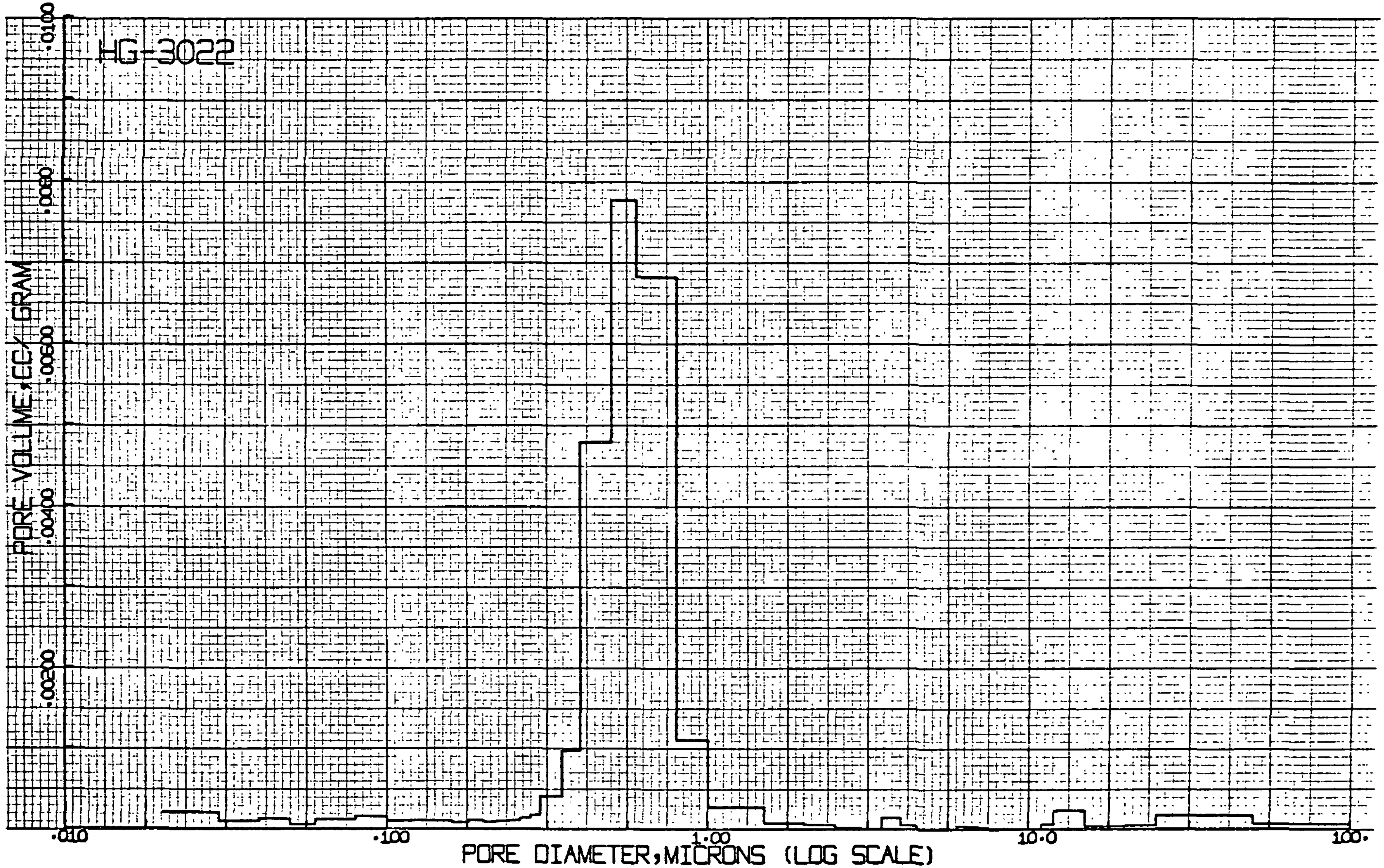


Figure 14. Pore Volume versus Pore Diameter by Mercury Intrusion - Grade CDJ.

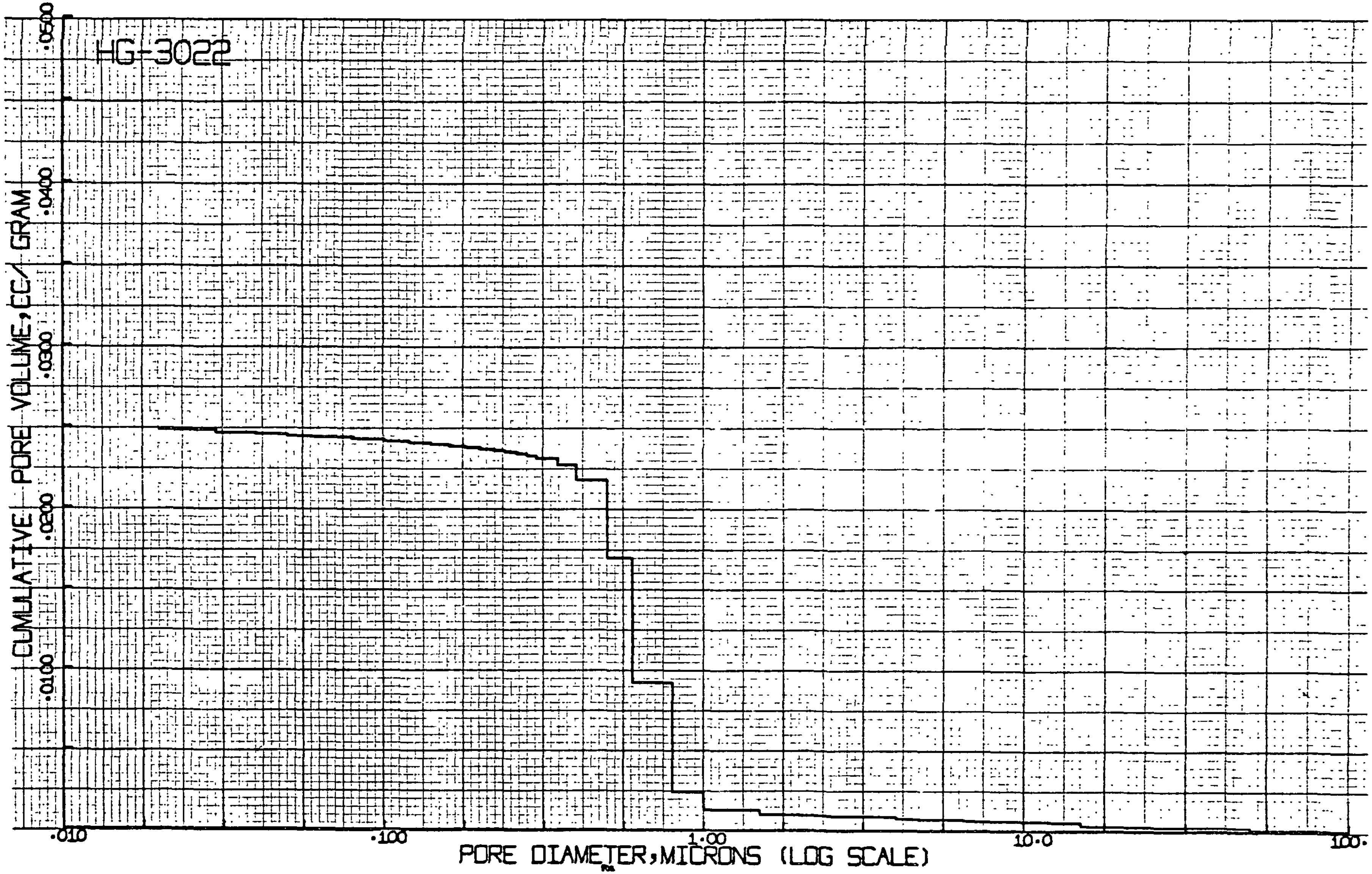


Figure 15. Cumulative Pore Volume versus Pore Diameter by Mercury Intrusion - Grade CDJ.

TABLE XVI

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

SAMPLE WEIGHT = 23.87720 GRAMS.

BET SURFACE AREA = 1.0 SQUARE METERS PER GRAM.
TOTAL PORE VOLUME = 0.00140 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	19.847	0.1984	19.847
500- 450	475.0	7.542	0.1508	27.389
450- 400	425.0	6.345	0.1269	33.735
400- 350	375.0	5.339	0.1067	39.074
350- 300	325.0	4.649	0.0929	43.723
300- 280	290.0	1.868	0.0934	45.592
280- 260	270.0	1.912	0.0956	47.504
260- 240	250.0	1.999	0.0999	49.504
240- 220	230.0	1.960	0.0980	51.464
220- 200	210.0	2.111	0.1055	53.576
200- 180	190.0	2.204	0.1102	55.780
180- 160	170.0	2.794	0.1397	58.575
160- 150	155.0	1.373	0.1373	59.949
150- 140	145.0	1.496	0.1496	61.445
140- 130	135.0	1.597	0.1597	63.042
130- 120	125.0	1.546	0.1546	64.588
120- 110	115.0	1.776	0.1776	66.365
110- 100	105.0	2.127	0.2127	68.492
100- 95	97.5	1.080	0.2161	69.573
95- 90	92.5	1.397	0.2794	70.970
90- 85	87.5	1.275	0.2550	72.245
85- 80	82.5	1.535	0.3071	73.781
80- 75	77.5	1.534	0.3069	75.316
75- 70	72.5	1.839	0.3678	77.155
70- 65	67.5	2.111	0.4223	79.267
65- 60	62.5	2.265	0.4530	81.532
60- 55	57.5	2.695	0.5390	84.227
55- 50	52.5	2.090	0.4181	86.318
50- 45	47.5	3.097	0.6195	89.416
45- 40	42.5	2.862	0.5724	92.278
40- 35	37.5	1.958	0.3917	94.237
35- 30	32.5	4.398	0.8797	98.636
30- 25	27.5	1.363	0.2727	100.000
25- 20	22.5	0.000	0.0000	100.000
BELOW 20	10.0	0.000	0.0000	100.000

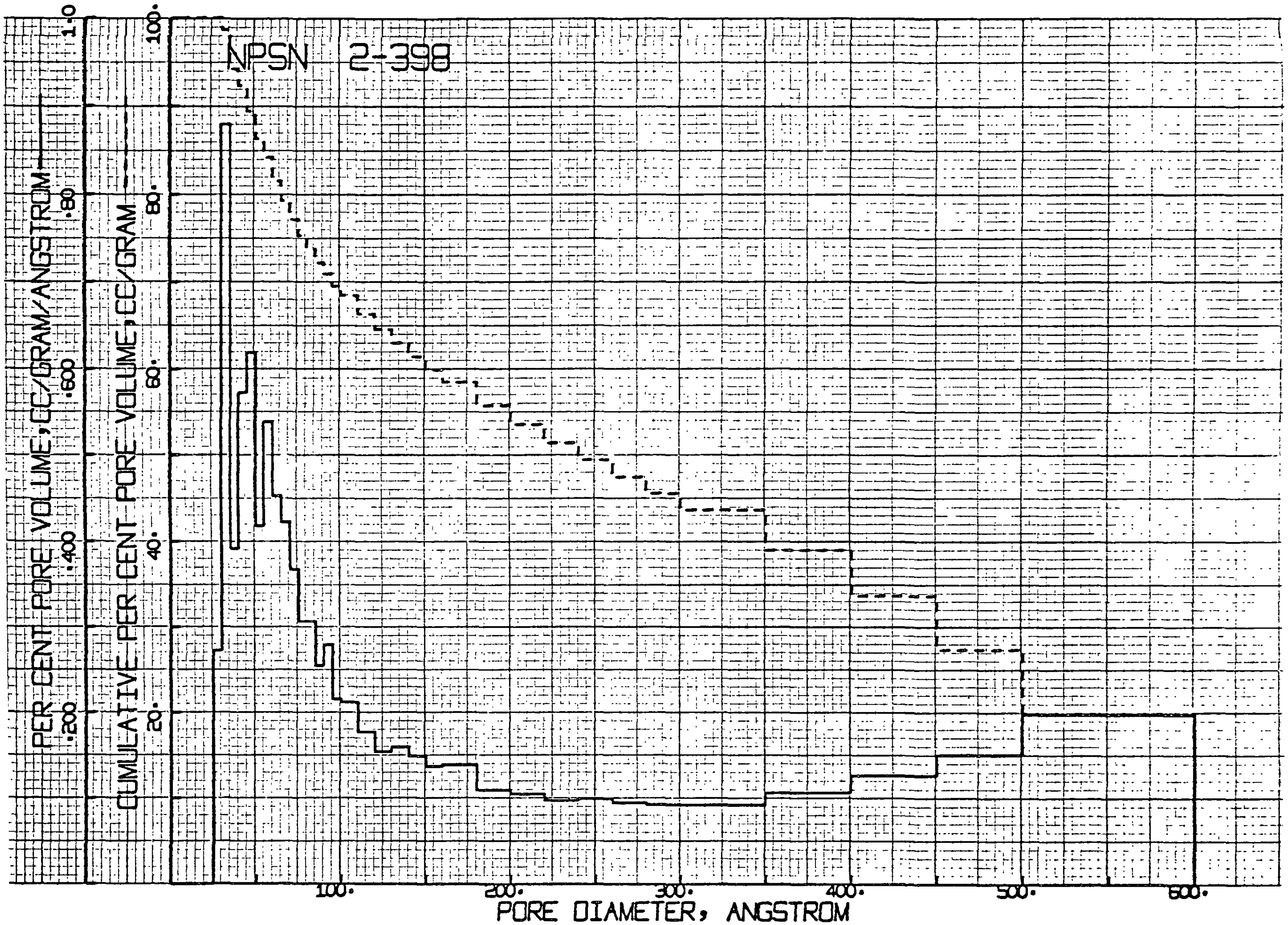


Figure 16. Percent Pore Volume and Cumulative Percent Pore Volume versus Pore Diameter by Nitrogen Desorption Formulation No. 1X Material.

TABLE XVII

Pore Volume and Distribution by Nitrogen Desorption-Formulation No. 2X Material

SAMPLE WEIGHT = 23.48140 GRAMS.

BET SURFACE AREA = 0.1 SQUARE METERS PER GRAM.
TOTAL PORE VOLUME = 0.00835 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	29.302	0.2930	29.302
500- 450	475.0	18.163	0.3632	47.465
450- 400	425.0	14.560	0.2912	62.026
400- 350	375.0	9.167	0.1833	71.194
350- 300	325.0	7.847	0.1569	79.041
300- 280	290.0	3.624	0.1812	82.666
280- 260	270.0	3.332	0.1666	85.998
260- 240	250.0	2.705	0.1352	88.704
240- 220	230.0	2.543	0.1271	91.247
220- 200	210.0	2.065	0.1032	93.312
200- 180	190.0	1.688	0.0844	95.000
180- 160	170.0	1.547	0.0773	96.548
160- 150	155.0	0.632	0.0632	97.181
150- 140	145.0	0.580	0.0580	97.761
140- 130	135.0	0.523	0.0523	98.284
130- 120	125.0	0.429	0.0429	98.713
120- 110	115.0	0.398	0.0398	99.112
110- 100	105.0	0.328	0.0328	99.440
100- 95	97.5	0.154	0.0308	99.595
95- 90	92.5	0.162	0.0325	99.757
90- 85	87.5	0.101	0.0202	99.858
85- 80	82.5	0.062	0.0125	99.921
80- 75	77.5	0.026	0.0052	99.948
75- 70	72.5	0.013	0.0027	99.961
70- 65	67.5	0.038	0.0076	99.999
65- 60	62.5	0.000	0.0000	99.999
60- 55	57.5	0.000	0.0000	99.999
55- 50	52.5	0.000	0.0000	99.999
50- 45	47.5	0.000	0.0000	99.999
45- 40	42.5	0.000	0.0000	99.999
40- 35	37.5	0.000	0.0000	99.999
35- 30	32.5	0.000	0.0000	99.999
30- 25	27.5	0.000	0.0000	99.999
25- 20	22.5	0.000	0.0000	99.999
BELOW 20	10.0	0.000	0.0000	99.999

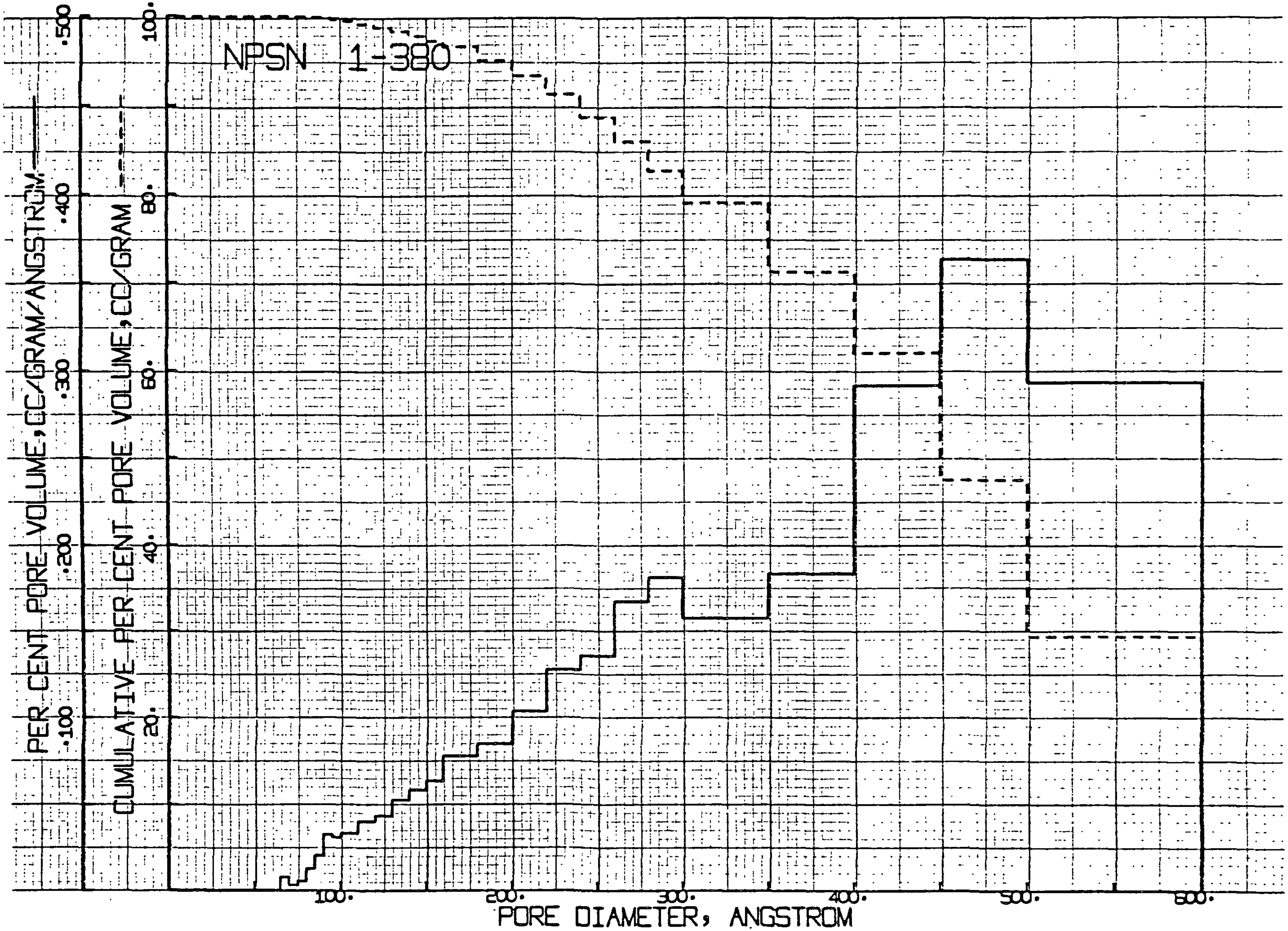


Figure 17. Percent Pore Volume and Cumulative Percent Pore Volume versus Pore Diameter by Nitrogen Desorption-Formulation No. 2X Material.

TABLE XVIII

Pore Volume and Distribution by Nitrogen Desorption-Formulation No. 3 Material

SAMPLE WEIGHT = 22.58520 GRAMS.

BET SURFACE AREA = 0.4 SQUARE METERS PER GRAM.
TOTAL PORE VOLUME = 0.00064 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	6.943	0.0694	6.943
500- 450	475.0	3.982	0.0796	10.926
450- 400	425.0	3.799	0.0759	14.726
400- 350	375.0	4.397	0.0879	19.123
350- 300	325.0	4.255	0.0851	23.379
300- 280	290.0	1.821	0.0910	25.200
280- 260	270.0	1.951	0.0975	27.151
260- 240	250.0	2.218	0.1109	29.370
240- 220	230.0	2.157	0.1078	31.528
220- 200	210.0	2.336	0.1168	33.864
200- 180	190.0	2.665	0.1332	36.530
180- 160	170.0	2.874	0.1437	39.404
160- 150	155.0	1.616	0.1616	41.021
150- 140	145.0	1.717	0.1717	42.739
140- 130	135.0	2.013	0.2013	44.753
130- 120	125.0	2.265	0.2266	47.021
120- 110	115.0	2.444	0.2444	49.465
110- 100	105.0	2.980	0.2980	52.446
100- 95	97.5	1.592	0.3164	54.038
95- 90	92.5	1.511	0.3023	55.550
90- 85	87.5	1.541	0.3083	57.092
85- 80	82.5	1.533	0.3066	58.625
80- 75	77.5	1.165	0.2331	59.791
75- 70	72.5	1.865	0.3730	61.656
70- 65	67.5	2.110	0.4220	63.766
65- 60	62.5	3.349	0.6698	67.116
60- 55	57.5	2.441	0.4882	69.557
55- 50	52.5	2.553	0.5106	72.110
50- 45	47.5	2.629	0.5259	74.740
45- 40	42.5	3.531	0.7062	78.271
40- 35	37.5	4.126	0.8253	82.398
35- 30	32.5	2.718	0.5437	85.117
30- 25	27.5	3.164	0.6328	88.281
25- 20	22.5	5.134	1.0269	93.416
BELOW 20	10.0	6.583	0.3291	99.999

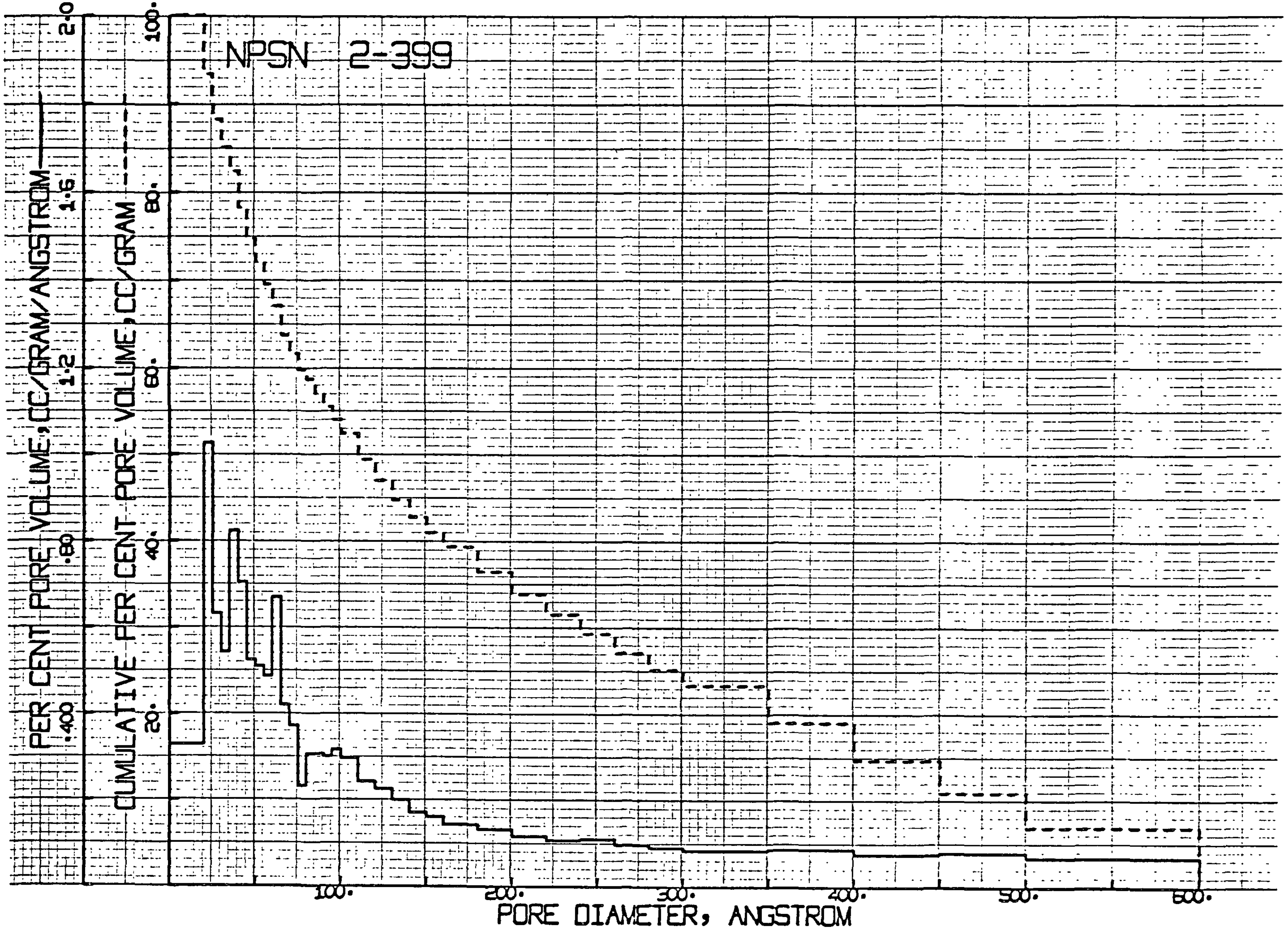


Figure 18. Percent Pore Volume and Cumulative Percent Pore Volume versus Pore Diameter by Nitrogen Desorption-Formulation No. 3 Material.

TABLE XIX

Pore Volume and Distribution by Nitrogen Desorption-Formulation No. 4X Material

SAMPLE WEIGHT = 20.19930 GRAMS.

BET SURFACE AREA = 0.4 SQUARE METERS PER GRAM.
TOTAL PORE VOLUME = 0.00099 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	4.470	0.0447	4.470
500- 450	475.0	2.273	0.0454	6.743
450- 400	425.0	2.685	0.0537	9.429
400- 350	375.0	2.878	0.0575	12.307
350- 300	325.0	3.117	0.0623	15.424
300- 280	290.0	1.400	0.0700	16.824
280- 260	270.0	1.416	0.0708	18.241
260- 240	250.0	1.629	0.0814	19.871
240- 220	230.0	1.834	0.0917	21.706
220- 200	210.0	1.771	0.0885	23.477
200- 180	190.0	2.021	0.1010	25.499
180- 160	170.0	2.215	0.1107	27.714
160- 150	155.0	1.196	0.1196	28.911
150- 140	145.0	1.303	0.1303	30.214
140- 130	135.0	1.422	0.1422	31.636
130- 120	125.0	0.090	0.0090	31.727
120- 110	115.0	1.188	0.1188	32.916
110- 100	105.0	2.196	0.2196	35.112
100- 95	97.5	3.524	0.7049	38.637
95- 90	92.5	0.901	0.1803	39.538
90- 85	87.5	0.976	0.1952	40.515
85- 80	82.5	1.206	0.2412	41.721
80- 75	77.5	1.107	0.2214	42.828
75- 70	72.5	1.638	0.3276	44.466
70- 65	67.5	1.490	0.2980	45.957
65- 60	62.5	0.573	0.1146	46.530
60- 55	57.5	1.171	0.2342	47.701
55- 50	52.5	2.544	0.5088	50.245
50- 45	47.5	1.982	0.3965	52.228
45- 40	42.5	1.916	0.3833	54.145
40- 35	37.5	3.559	0.7119	57.704
35- 30	32.5	1.487	0.2975	59.192
30- 25	27.5	2.351	0.4702	61.543
25- 20	22.5	15.981	3.1963	77.525
BELOW 20	10.0	22.474	1.1237	100.000

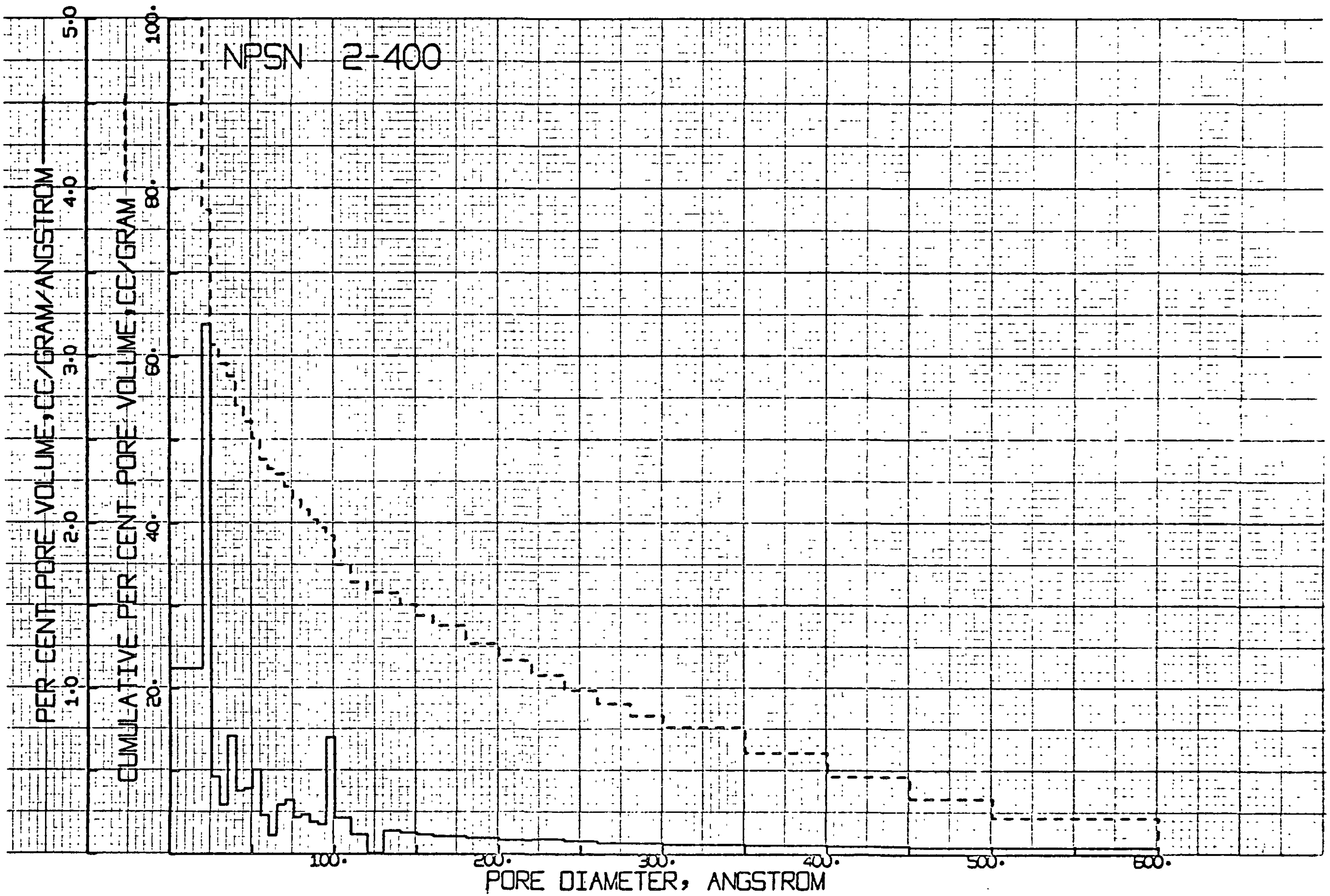


Figure 19. Percent Pore Volume and Cumulative Percent Pore Volume versus Pore Diameter by Nitrogen Desorption-Formulation No. 4X Material.

TABLE XX

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, 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	13.880	0.1388	13.880
500- 450	475.0	6.957	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	68.725
110- 100	105.0	2.456	0.2456	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	74.809
85- 80	82.5	1.516	0.3033	76.325
80- 75	77.5	1.563	0.3127	77.888
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

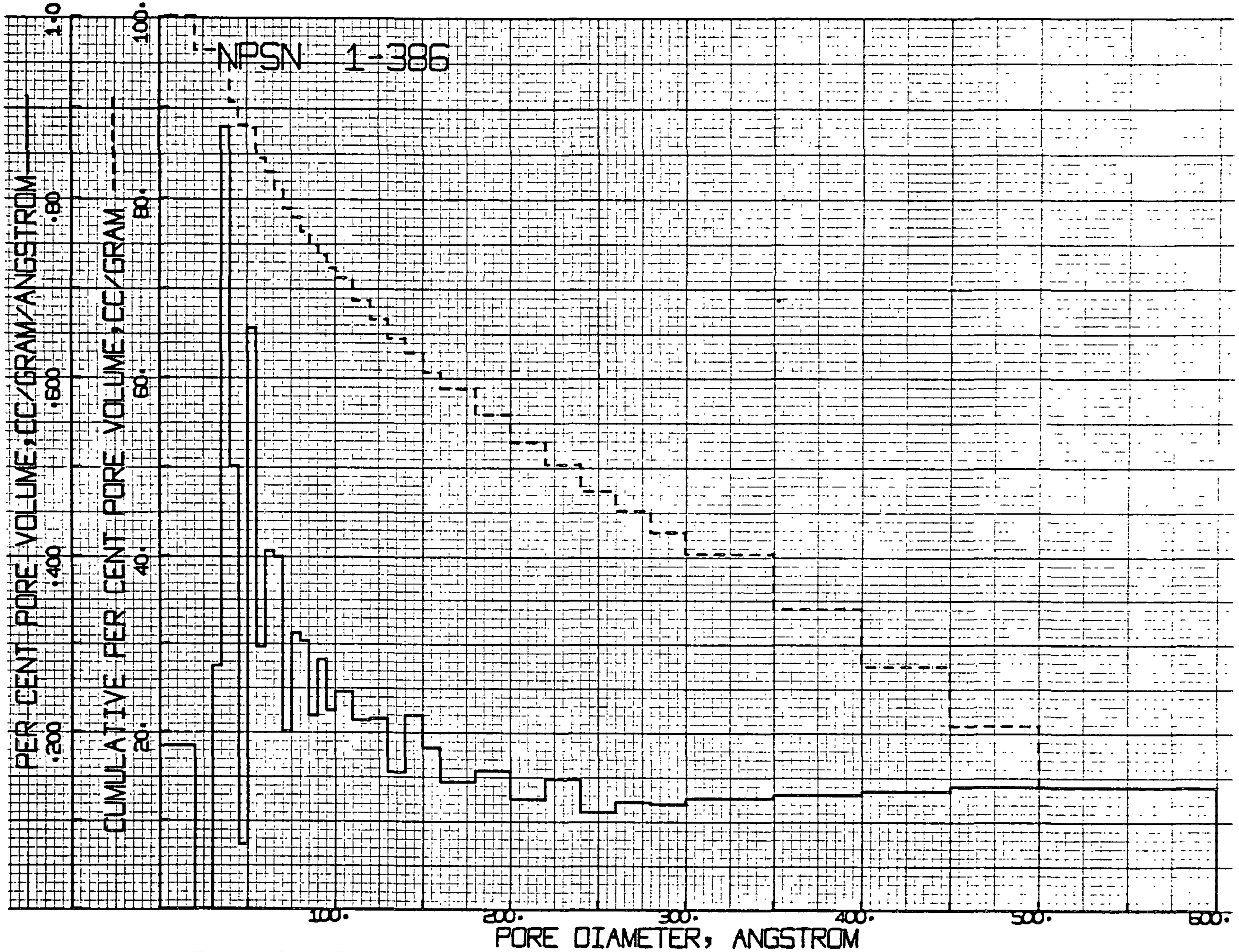


Figure 20. Percent Pore Volume and Cumulative Percent Pore Volume versus Pore Diameter by Nitrogen Desorption-Grade CDJ.

The internal structures of the carbon-graphite seal ring bodies manufactured from formulations Nos. 1X, 2X, 3, and 4X appeared by visual examination to be very homogeneous and fine-grained. No large pores or voids were noted in the compacts examined. 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 XXI lists the treat pickups measured for 1/2-inch (1.3 cm) cubes of formulations Nos. 1X, 2X, 3, and 4X after impregnation with the No. 121 oxidation-inhibiting treatment. The impregnated 1/2-inch (1.3 cm) cubes were used later for measuring the oxidation resistance of the four materials. The oxidation-inhibiting treat pickups for the samples of formulations Nos. 1X, 2X, and 3 indicate that all three of the materials have uniform internal structures. The greater coefficient of variation in treat pickup ("V" in Table XXI) determined for the impregnated samples for formulation No. 4X shows that the compacts of formulation No. 4X are not so internally uniform as those of formulations Nos. 1X, 2X, and 3.

Comparison of the pore volume data determined by mercury intrusion (Table XXI) with that of the No. 121 oxidation-inhibiting treat pickups shows the expected trend of increasing treat pickup with increasing pore volume. Normalization of the data presented in Table XXI with respect to the formulation No. 2X material shows that the formulation No. 4X compacts experienced a disproportionately high treat pickup as compared with that of the other three materials. The treat pickups for the compacts of formulations Nos. 1X, 2X, and 3 were directly proportional to pore volumes determined by mercury intrusion (e.g., the formulation No. 3 material had a normalized intruded pore volume of 1.28 and a normalized treat pickup of 1.24). The formulation No. 4X material, however, had a normalized intruded pore volume of 1.83 and a disproportionately high normalized treat pickup of 2.73. This phenomenon had been observed previously during Task I of this Contract.(9)

TABLE XXI

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

	Formulation No. 1X	Formulation No. 2X	Formulation No. 3	Formulation No. 4X
Weight Percent Treat Pickup*				
Maximum	1.68	1.80	2.19	5.52
Minimum	1.41	1.50	1.97	4.07
Average	1.59	1.67	2.07	4.56
Standard Deviation	0.10	0.12	0.09	0.62
V**	6.2	7.4	4.5	13.6
n ***	6	6	6	6
By Mercury Intrusion:				
Average Pore Diameter (μ)	4.462	3.928	8.674	5.628
Intruded Pore Volume (cc/g)	0.076	0.076	0.097	0.139
Normalized Data				
Average No. 121 Treat Pickup	0.95	1.00	1.24	2.73
Average Pore Diameter	1.14	1.00	2.21	1.43
Intruded Pore Volume	1.00	1.00	1.28	1.83

---

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

** V = coefficient of variation = $100 \times \sigma / \text{average}$

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

Correlation of the No. 121 oxidation-inhibiting treat pickup to the pore structure of a carbon-graphite seal ring body is difficult, since the size range of pores penetrated by and filled with the treatment after impregnation is not known. Some pores will be too small for the treatment to penetrate them and some will be too large to retain the treat after impregnation, in which case they will not be completely filled with the No. 121 treatment. Two possible explanations may account for the disproportionate treat pickup measured for the seal ring bodies of formulation No. 4X. The compacts of formulation No. 4X may have a greater proportion of their pore volume concentrated in the range of pore sizes which are penetrated by and filled with the No. 121 treatment. For example, suppose the No. 121 treatment penetrates and fills only pores ranging between 5μ and 15μ in diameter. In that range of pore diameters, the compacts of formulation No. 2X have a measured pore volume of 0.019 cc/g as compared with a value of 0.051 cc/g for the formulation No. 4X material. The resulting treat pickup of the formulation No. 4X compacts, thus, would be 2.68 times that of the seal ring bodies of formulation No. 2X. The value of 2.68 is similar to that for the normalized No. 121 treat pickup presented for the formulation No. 4X material in Table XXI. A second possible explanation for the disproportionate pickup may be that the formulation No. 4X material, which contains 20 pbw WCA graphite fibers, is wetted to a greater extent by the No. 121 treatment than are the other three materials, which contain 20 pbw of Thermax furnace black. If the formulation No. 4X material is more wettable, its disproportionately high pickup would result from its greater ability to accept and retain the No. 121 treatment in its pore structure.

During Tasks III and IV, the materials impregnated with the No. 121 oxidation-inhibiting treatment were identified (Table I) by the formulation number followed by the number 121 (e.g., formulation No. 1X-121). The data listed in Table XXII show that the impregnation of the samples with the No. 121 treatment did increase the final densities of the four formulations. However, the impregnation with the No. 121 treatment probably had little effect on increasing the strengths and hardnesses of the materials, since the pickups were relatively low and since no additional carbonaceous material was added to the compacts as was the case when the seal ring bodies of formulations Nos. 1, 2, and 4 were impregnated with the Bakelite BRP-5095 resin prior to final baking to 2800°C.

TABLE XXII

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

	Formulation No. 1X	Formulation No. 1X-121
Maximum	1.739	1.767
Minimum	1.729	1.756
Average	1.735	1.762
Standard Deviation	0.006	0.003
n	6	6
	Formulation No. 2X	Formulation No. 2X-121
Maximum	1.705	1.735
Minimum	1.687	1.715
Average	1.695	1.725
Standard Deviation	0.009	0.011
n	6	6
	Formulation No. 3	Formulation No. 3-121
Maximum	1.661	1.698
Minimum	1.648	1.681
Average	1.654	1.688
Standard Deviation	0.006	0.008
n	6	6
	Formulation No. 4X	Formulation No. 4X-121
Maximum	1.478	1.560
Minimum	1.466	1.531
Average	1.473	1.540
Standard Deviation	0.006	0.011
n	6	6

The pore structures determined for the seal ring bodies of formulations Nos. 1X, 2X, 3, and 4X indicate that all four are potentially good carbon-graphite seal ring materials. All four of the formulations resulted in fine-grain materials with relatively low porosity.

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. Formulations Nos. 1X, 2X, 3, and 4X 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. As a requirement for Task IV, oxidation tests were conducted at 1300°F (704°C) with 1/2-inch (1.3 cm) cubes prepared from the seal ring bodies of formulations Nos. 1X, 2X, 3, and 4X. 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 XXI.

The oxidation test procedure and equipment employed during Task IV were the same as those used during the Task I oxidation studies.(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 21 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 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 21.

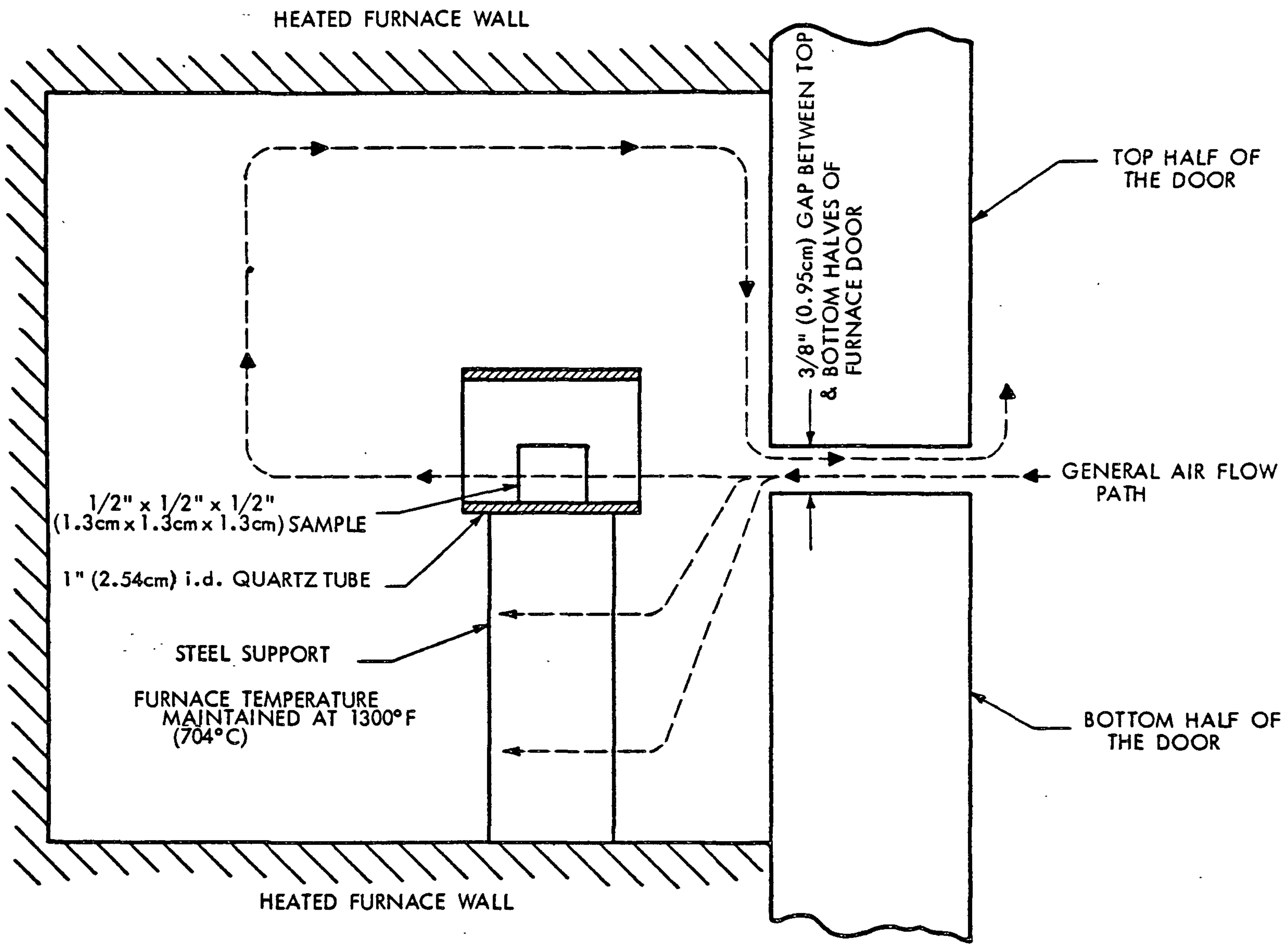


Figure 21. Oxidation Testing Apparatus

N-23865

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 conditions, the quartz tubes containing the samples were removed from the furnace, cooled to room temperature, weighed, and placed back inside the furnace for another 1/2-hour period. The 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.

Three oxidation tests were conducted during Task IV using the No. 121 treated samples. During each test, one sample of each of the formulations Nos. 1X-121, 2X-121, 3-121, and 4X-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 five materials in the furnace were changed for each test to avoid any possible position-to-position variation in oxidizing conditions. One of the tests was extended to include a weight measurement after four and one-half hours' exposure, and a second test was extended to include a six-hour reading. During the time interval between the Task I and Task IV oxidation studies, the furnace used for these tests was damaged. The controller malfunctioned, causing the furnace temperature to rise above the designed temperature limit. All the heating elements and the inside ceramic walls had to be replaced. A new controller was installed on the furnace for the Task IV oxidation studies. The required rebuilding of the furnace and the installation of a new controller may have produced a slight change in the temperature distribution and air flow present in the furnace. At elevated temperatures (e.g., 1300°F (704°C), small changes in the temperature distribution and/or air flow can have a rather large effect on the oxidation results. Therefore, direct comparison between the Task I(10) and Task IV oxidation results should not be made. The oxidation tests were designed to give a relative measure of the oxidation rates of materials tested at the same time. The oxidation data for all the individual materials tested during Task IV can be directly compared.

Figures 22 to 25 are semi-logarithmic plots of the average percent weight loss versus exposure time at 1300°F (704°C) for the samples of formulations Nos. 1X-121, 2X-121, 3-121, and 4X-121. Each figure includes the control Grade CDJ-121 oxidation curve. The oxidation rates for all four of the No. 121 treated samples manufactured during Task III were significantly lower than that of Grade CDJ-121. A 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. Grade CDJ-121 experienced a 5-percent weight loss after being exposed to the 1300°F (704°C) ambient air for 1.3 hours. A 5-percent loss in weight at 1300°F (704°C) was recorded after 4.7 hours for the samples from formulations Nos. 1X-121 and 4X-121, 3.3 hours for the formulation No. 2X-121 samples, and 5.9 hours for the formulation No. 3-121 samples.

The differences between the oxidation rates of the four materials manufactured from formulations Nos. 1X-121, 2X-121, 3-121 and 4X-121 were relatively small. A statistical analysis of these oxidation data was conducted to determine whether the observed differences were significant. Table XXIII lists the differences in percent weight loss measured after 1/2 hour and three hours' exposure to the oxidizing conditions. This procedure for specifying oxidation losses was adopted during Task I when the evaporation of absorbed moisture was found to distort the incremental weight losses measured after the first 1/2-hour exposure period.(10) Table XXIII also displays the results of the Student's t distribution(11, 12) used to compare the weight losses (Δ Percent Weight Loss 1/2-3 hours) determined for the four materials.

The statistical analysis showed that no significant differences existed in the oxidation rates determined for the samples of formulations Nos. 1X-121, 3-121, and 4X-121. However, the oxidation rate of the formulation No. 2X-121 samples was found to be significantly greater than those of the other three materials.

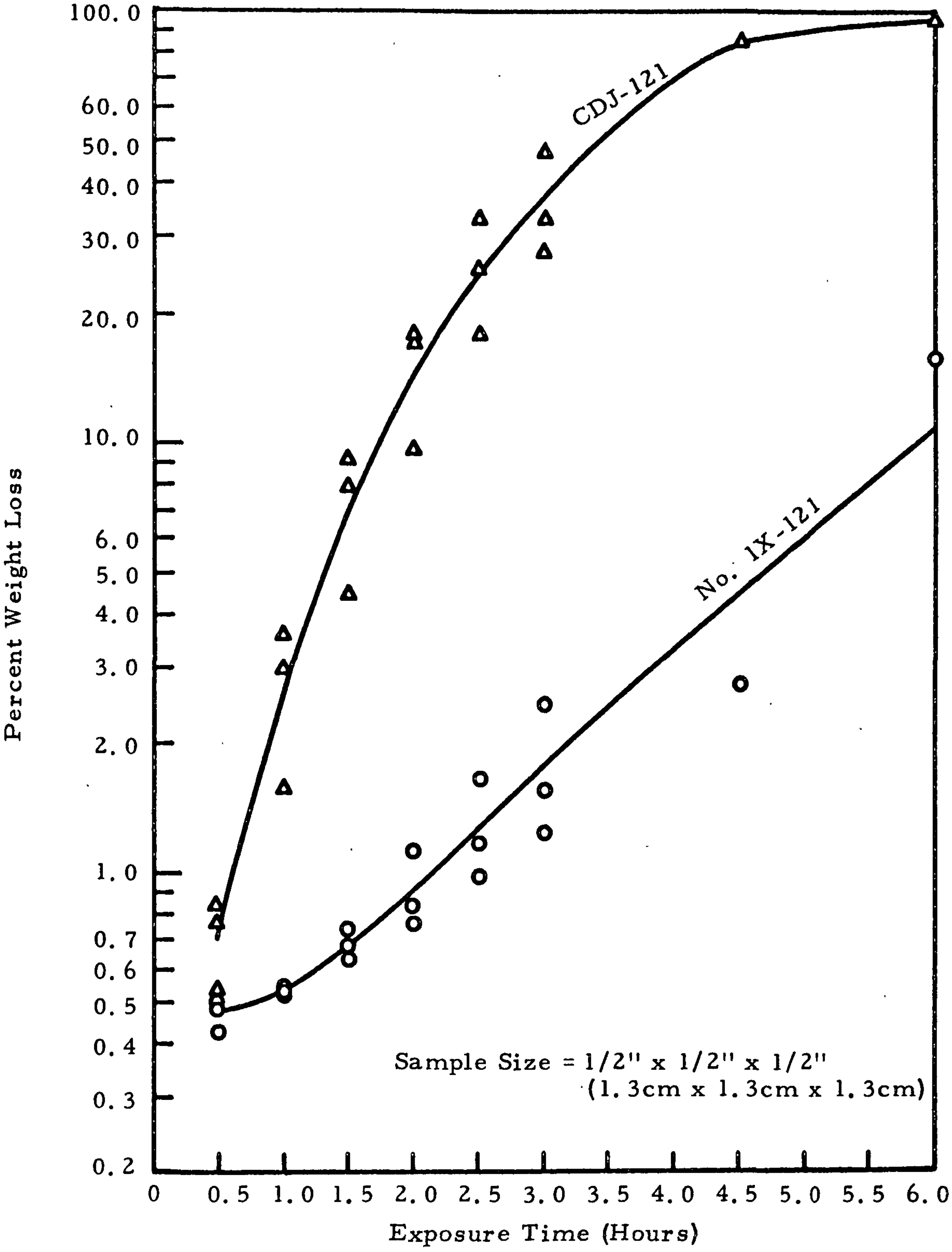


Figure 22. Percent Weight Loss versus Exposure Time at 1300°F (704°C)-Formulation No. 1X-121 Material.

G 710433

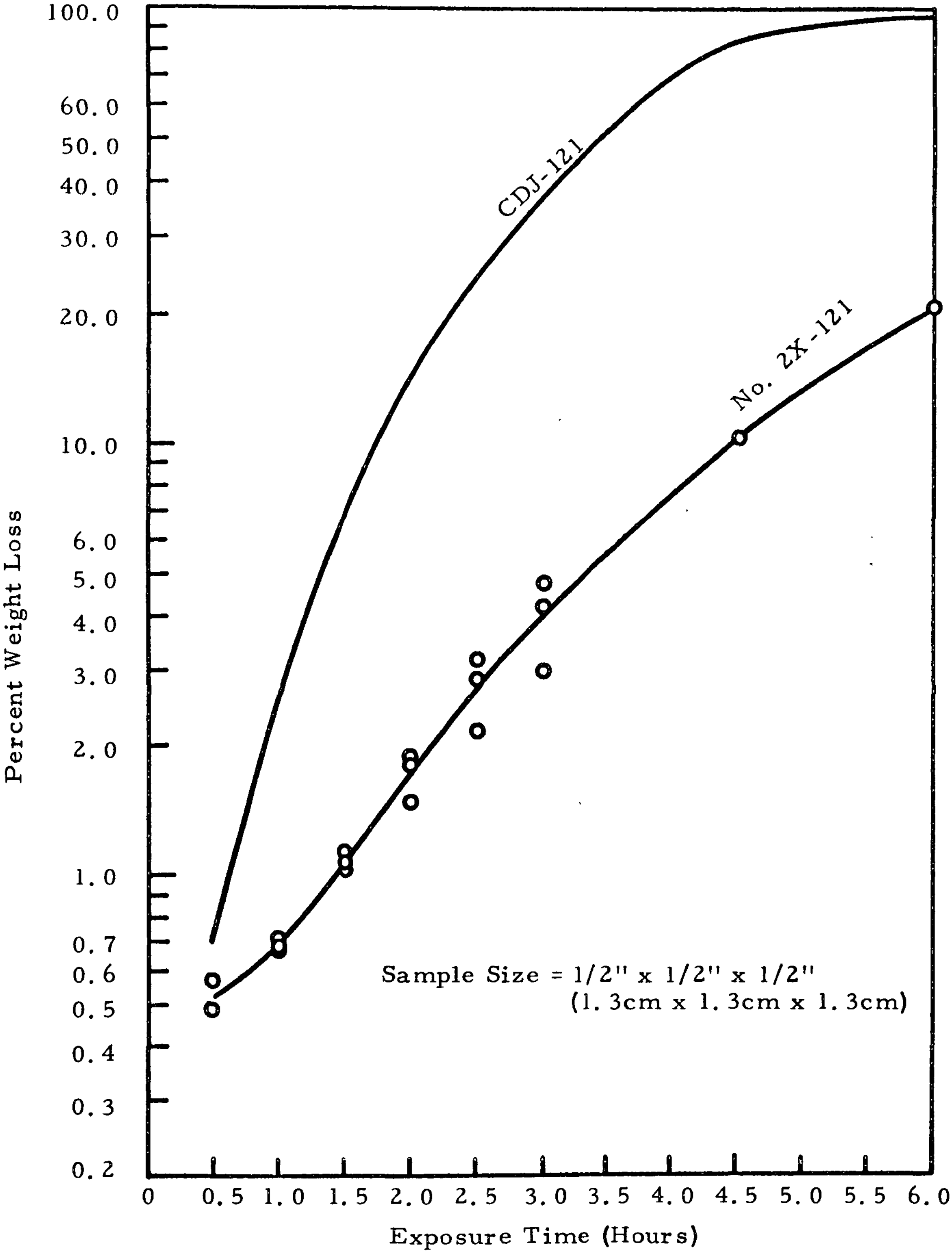


Figure 23. Percent Weight Loss versus Exposure Time at 1300°F (704°C)-Formulation No. 2X-121 Material.

G 710434

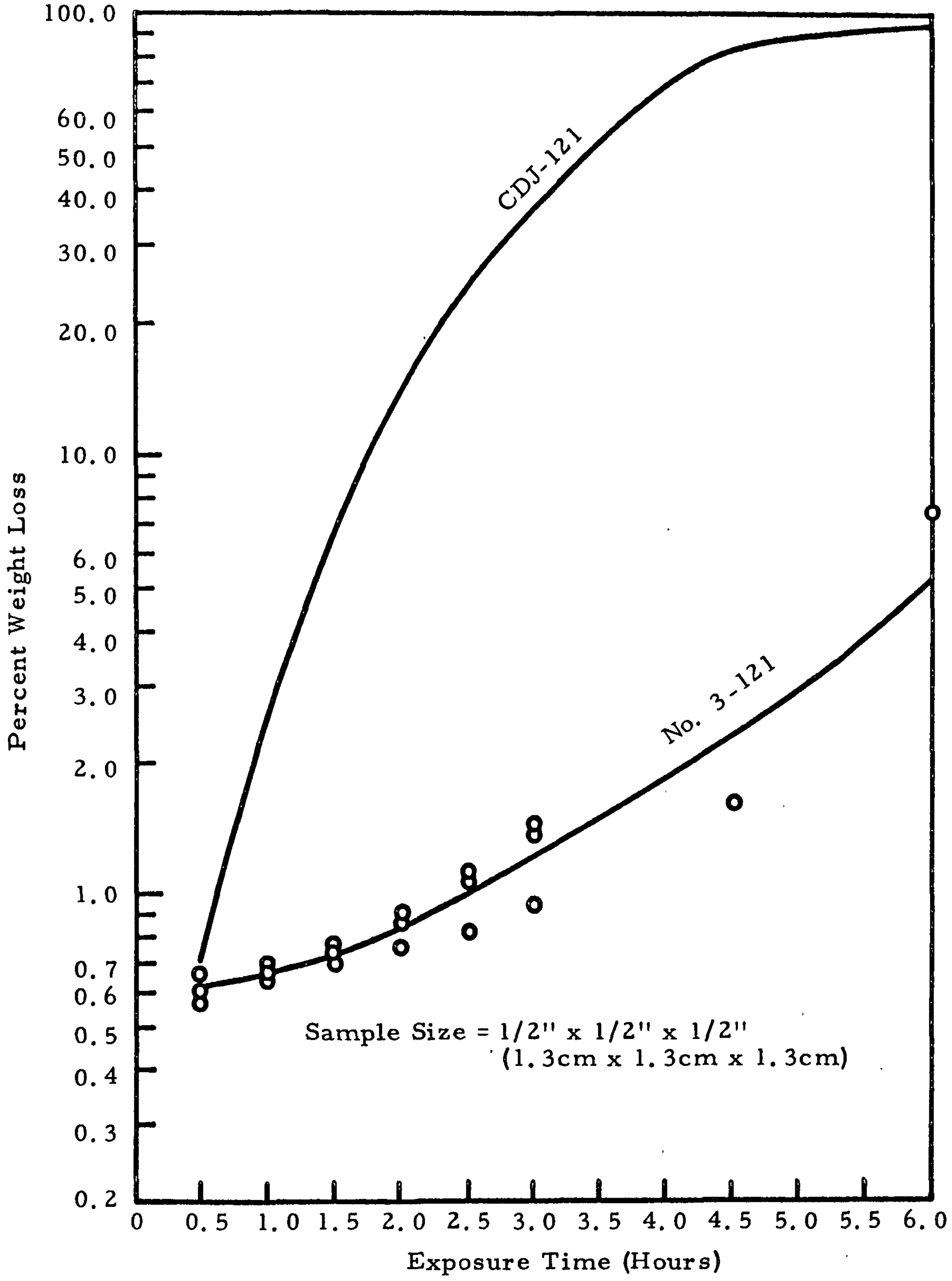


Figure 24. Percent Weight Loss versus Exposure Time at 1300°F (704°C)-Formulation No. 3-121 Material.

G 710435

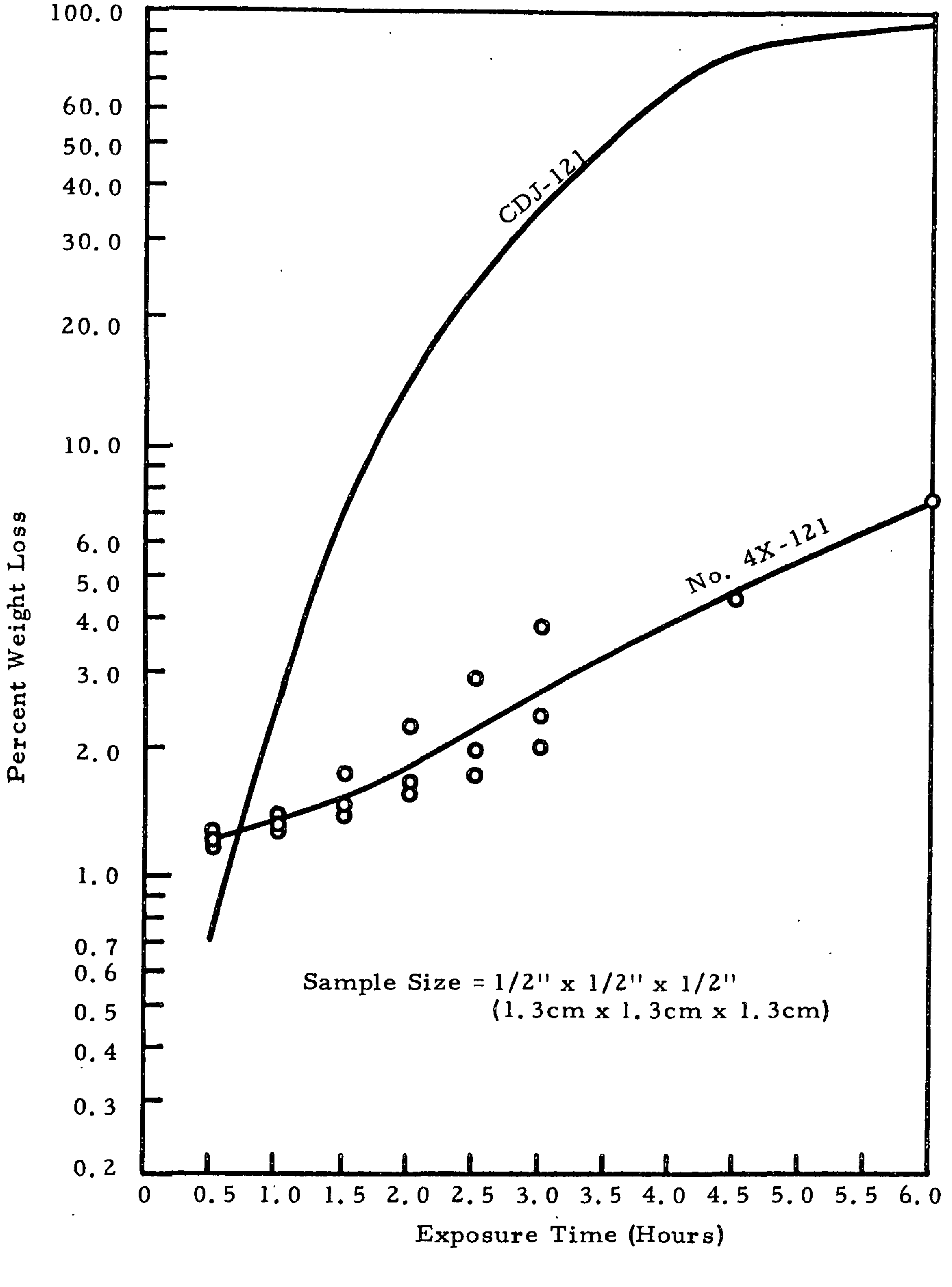


Figure 25. Percent Weight Loss versus Exposure Time at 1300°F (704°C)-Formulation No. 4X-121 Material.

G 710436

TABLE XXIII

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

Δ Percent Weight Loss 1/2 - 3 Hours

	Formulation No. 1X-121	Formulation No. 2X-121	Formulation No.3-121	Formulation No. 4X-121	Grade CDJ-121
Maximum	2.06	4.20	0.87	2.61	46.45
Minimum	0.72	2.41	0.29	0.83	26.79
Average	1.27	3.44	0.64	1.51	35.18
Standard Deviation	0.70	0.92	0.31	0.96	10.14
n	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.1X-121 vs. No. 2X-121	1.7	69.0	Not Significant	4.08	0.05	4	2.78	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. 2X-121 vs. No. 3 -121	9.0	69.0	Not Significant	7.17	0.05	4	2.78	Significant
No. 2X-121 vs. No. 4X-121	1.1	69.0	Not Significant	2.95	0.05	4	2.78	Significant
No. 3 -121 vs. No. 4X-121	9.7	69.0	Not Significant	1.50	0.05	4	2.78	Not Significant

---

* Hoel, Paul G., Introduction to Mathematical Statistics, John Wiley & Sons, Inc., New York-London, pages 404 to 407, C 1962.

** Brownlee, K. A., Industrial Experimentation, Chemical Publishing Co., Inc., New York, page 144, C 1947.

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

These oxidation studies showed that the addition of 5 pbw of glassy carbon in the formulation No. 2X material results in a decrease in oxidation resistance. Material formulation No. 2X is identical to formulation No. 1X except for the addition of glassy carbon. Both materials gained about the same percentage in weight after impregnation with the No. 121 oxidation-inhibiting treatment. The significant difference between the oxidation rates of the two materials probably resulted from a difference in their degree of crystallinity and/or microporosity. Formulation No. 2X contains a larger proportion of less-crystalline filler materials. Since the oxidation rate of a carbon-graphite material is greatly affected by its crystallinity, the formulation No. 2X compacts would oxidize faster than the compacts of formulation No. 1X. The difference in oxidation rates also may have resulted from the difference in the microporosity of the two materials. In the range of pore sizes measured by nitrogen desorption (600Å to 20Å in diameter), the formulation No. 2X material had an average pore diameter of 450Å and a pore volume of 0.0084 cc/g. The formulation No. 1X material had an average pore diameter of 240Å and a pore volume of 0.0014 cc/g. The pores ranging between 600Å to 20Å in diameter are probably too small to be penetrated by the No. 121 oxidation-inhibiting treatment, but not too small to be penetrated by oxygen. The formulation No. 2X-121 material, thus, would oxidize at a faster rate, since it is more permeable to the oxidizing gas.

No significant differences were noted in the oxidation rates for the samples of formulations Nos. 1X-121, 3-121, and 4X-121, since the effects on oxidation rates of differences in the porosities of the three materials were counteracted by the differences in the amount of the No. 121 oxidation-inhibiting treatment gained after impregnation. For example, the formulation No. 4X material would be expected to oxidize considerably faster than the formulation No. 1X material, since the compacts of formulation No. 4X have a greater total porosity. However, no significant differences were noted in the oxidation rates of the No. 121 treated samples of the two materials, since the No. 121 treat pickup determined for the formulation No. 4X samples was approximately 2.5 times that measured for the samples of formulation No. 1X.

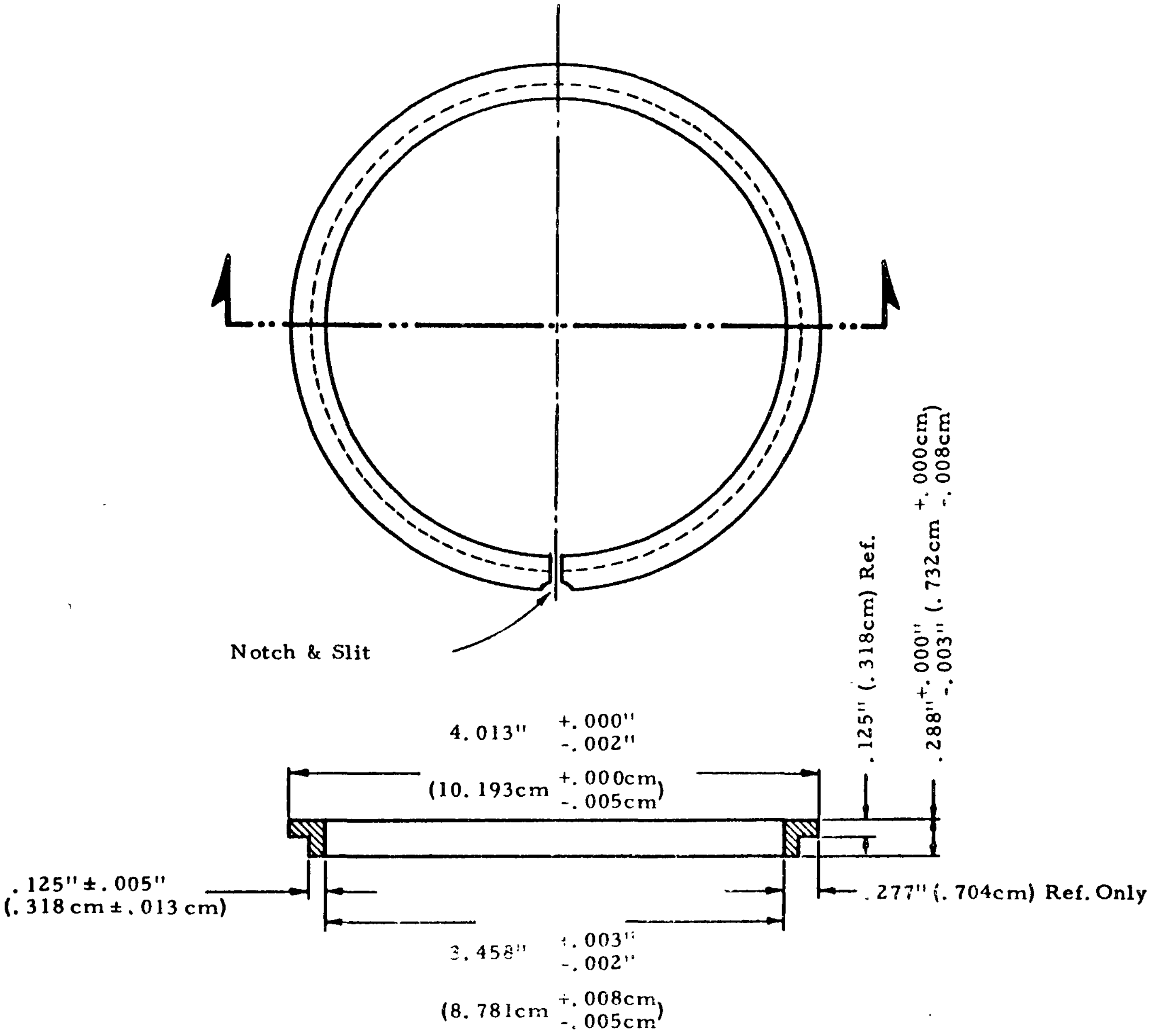
The fact that the samples of formulation No. 4X-121 contained a greater amount of the oxidation-inhibiting treatment apparently reduced the negative effects on oxidation resistance resulting from the materials greater total porosity.

The oxidation rates for samples of the materials manufactured from formulations Nos. 1X-121, 2X-121, 3-121, and 4X-121 indicate that all four are potentially good carbon-graphite seal ring materials. The formulation No. 2X-121 material, however, would not be so good a seal ring material as the other three at ambient air temperatures as high as 1300°F (704°C).

F. Wear Tests

A seal with self-acting lift augmentation experiences mechanical wear during start-up and shut-down of the engine and during momentary periods of high-speed sliding contact. The momentary periods of high-speed sliding contact result from the close dimensional tolerance associated with the thin gas films. The importance of wear resistance, therefore, cannot be neglected when a carbon-graphite material is developed for use as a self-acting seal ring material. Task IV included the determination of the wear properties of the selected four materials manufactured during Task III. Wear testing was to be carried out under oil lubricated conditions. The results of these tests were to be compared with those of a reference material, such as commercial seal ring Grade CDJ-121.

Seal rings were machined from the compacts of formulations Nos. 1X, 2X, 3, and 4X, impregnated with the No. 121 oxidation-inhibiting treatment, and wear tested. Figure 26 is a drawing of the seal ring configuration used by the Contractor for measuring wear properties. A drawing of the test chamber used for wear testing is presented in Figure 27. Two rings are tested at one time. Compressed air is used to load the rings against the outside housing and against the mating faces which are locked on the rotating arbor by two spacers. The notch in each ring fits over a key in the outside housing so that the rings are held stationary relative to the housing.



Note: (1) Flat sides to be parallel within .001" (.003cm)

(2) Lap to .288" $^{+.000''}_{-.003''}$ (.732cm $^{+.000\text{cm}}_{-.008\text{cm}}$)

(3) Lap to 3 lightbands

Figure 26. Configuration of Seal Ring used for Wear Testing.

G 710437

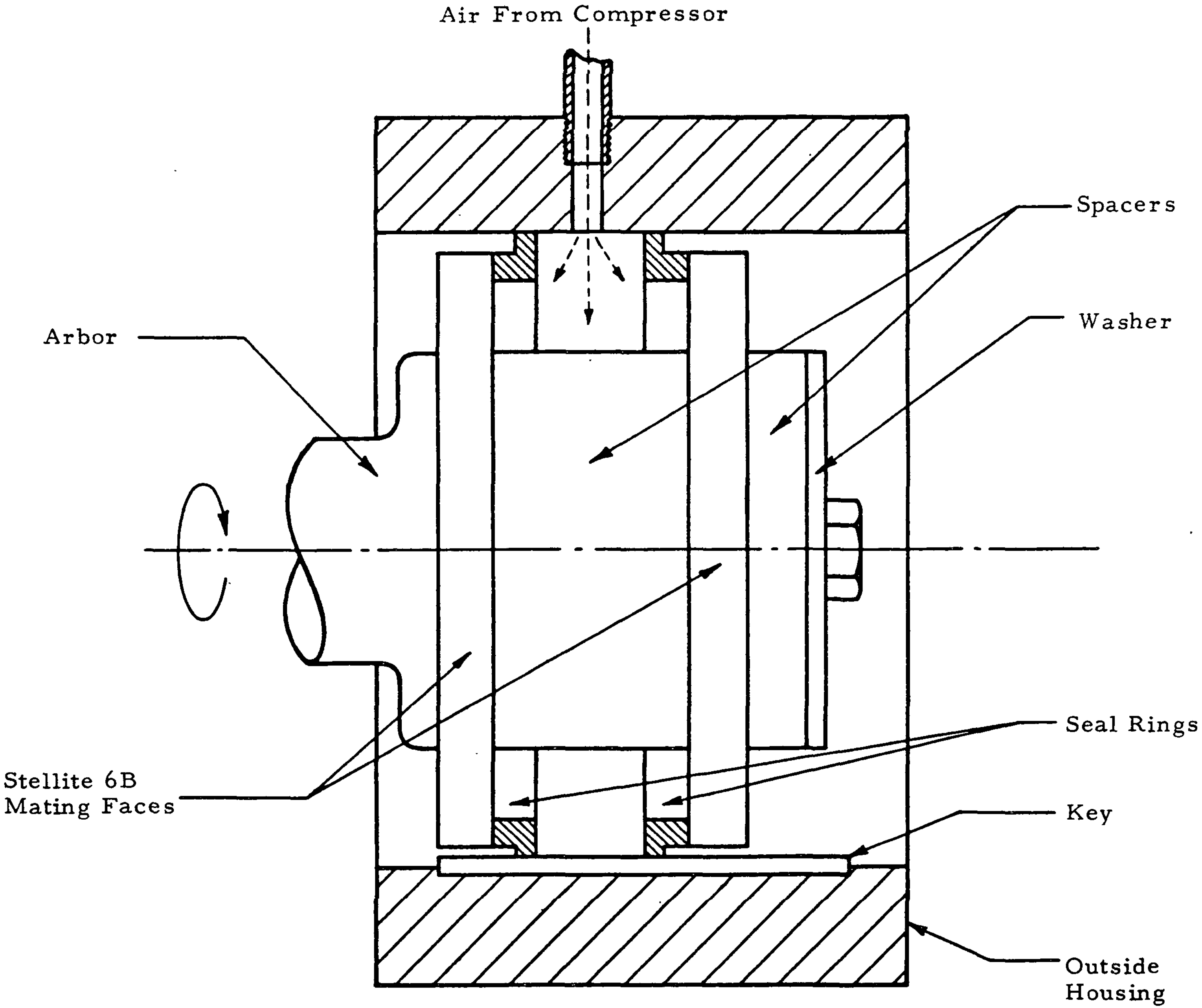


Figure 27. Test Chamber used for Wear Testing.

G 710441

The test chamber is coupled to the motor drive in such a way that a moment arm attached to the test chamber and connected to a spring scale may be used to measure the frictional torque during operation. The compressed air is conditioned by removing oil vapor, water vapor, and solid contaminants from the air flow. The air then passes through a series of pressure regulators, and through an oil mist lubricator into the test chamber. Most, if not all, of the air escaping from the test chamber passes between the notches in the carbon-graphite rings and the key in the housing (see Figures 26 and 27).

All the wear tests conducted during Task IV were run for 7 hours at a speed of 8400 rpm and at a face pressure of 40 psig (27.6 N/cm^2). The test chamber was not heated externally, but frictional heat generated during operation maintained the air inside the test chamber at approximately 200°F (93°C). The air flow was maintained at 8 SCFM (0.23 m^3/min.), and 4 drops per minute of No. 1 type 11 oil (ESSO 2380) were induced into the air flow through the oil mist lubricator located in the air line. The thickness of the untested rings was measured at four locations before and after each test. Dividing the average measured change in thickness by the test duration yielded a wear rate in mils per hour.

The wear rate data determined for the seal rings of formulations Nos. 1X-121, 2X-121, 3-121, and 4X-121 are displayed in Table XXIV. The results for Grade CDJ-121 are included in the table for purposes of comparison. Table XXV presents the results of a statistical analysis of the measured wear rates. All four formulations resulted in carbon-graphite materials which had significantly greater wear rates than that of Grade CDJ-121, a result which would be expected at the 200°F (93°C) test temperature used, since all four of the materials are considerably softer and weaker than Grade CDJ-121. The seal life of the four materials manufactured from formulations Nos. 1X-121, 2X-121, 3-121, and 4X-121 should surpass that of Grade CDJ-121 under high ambient air temperature conditions where oxidation is the limiting performance factor. Except for the difference between the wear rates of the seal rings of formulations Nos. 1X-121 and 3-121, no statistically significant differences were noted between the wear rates of the materials manufactured during Task III.

TABLE XXIV

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

	Formulation No. 1X-121		Formulation No. 2X-121		Formulation No. 3 -121		Formulation No. 4X-121		Grade CDJ-121	
Wear Rate	mils/hr	10^{-3} cm/hr	mils/hr	10^{-3} cm/hr	mils/hr	10^{-3} cm/hr	mils/hr	10^{-3} cm/hr	mils/hr	10^{-3} cm/hr
Maximum	0.70	1.78	0.95	2.41	1.21	3.07	1.13	2.87	0.87	2.21
Minimum	0.46	1.17	0.52	1.32	0.77	1.96	0.68	1.60	0.01	0.03
Average	0.60	1.52	0.70	1.78	1.00	2.54	0.87	2.21	0.28	0.71
Standard Deviation	0.11	0.28	0.19	0.48	0.19	0.48	0.24	0.61	0.28	0.71
n*	4	4	4	4	4	4	4	4	17	17
Coefficient of Friction										
Average	0.088		0.079		0.080		0.077		0.056	
n*	2		2		2		2		16	

---

* n Denotes number of rings used for analysis

Test Conditions	
Speed	8400 RPM
Face Pressure	40 psig (27.6 N/cm^2)
Mating Material	Stellite 6B
Test Duration	7 Hours
Air Temperature	Approximately 200°F (93°C) resulting from frictional heat.
Lubrication	4 Drops per minute of No. 1 type 11 oil (Esso 2380) through oil mist lubricator in air line.
Air Flow	8 SCFM (0.23 m^3/min)
Moisture In Air	185 to 195 ppm by volume.

TABLE XXV

Statistical Analysis of Wear Rate Data

Materials	F Distribution			Student's t Distribution				
	F Calculated	F* From Tables	Difference In Variances	t Calculated	Probability	Degrees of Freedom	t** from Tables	Difference Between Wear Rates
CDJ-121 vs. No. 1X-121	6.3	20.0	Not Significant	7.11	0.05	19	2.09	Significant
CDJ-121 vs. No. 2X-121	2.2	20.0	Not Significant	9.11	0.05	19	2.09	Significant
CDJ-121 vs. No. 3 -121	2.1	20.0	Not Significant	15.61	0.05	19	2.09	Significant
CDJ-121 vs. No. 4X-121	1.3	20.0	Not Significant	12.35	0.05	19	2.09	Significant
No. 1X-121 vs. No. 2X-121	2.9	21.9	Not Significant	0.96	0.05	6	2.45	Not Significant
No. 1X-121 vs. No. 3 -121	3.0	21.9	Not Significant	3.82	0.05	6	2.45	Significant
No. 1X-121 vs. No. 4X-121	5.0	21.9	Not Significant	2.04	0.05	6	2.45	Not Significant
No. 2X-121 vs. No. 3 -121	1.0	21.9	Not Significant	2.33	0.05	6	2.45	Not Significant
No. 2X-121 vs. No. 4X-121	1.7	21.9	Not Significant	1.11	0.05	6	2.45	Not Significant
No. 3 -121 vs. No. 4X-121	1.7	21.9	Not Significant	0.85	0.05	6	2.45	Not Significant

---

* Hoel, Paul G., Introduction to Mathematical Statistics, John Wiley & Sons, Inc., New York - London, pages 404 to 407, C 1962.

** Brownlee, K. A., Industrial Experimentation, Chemical Publishing Co., Inc., New York, page 144, C 1947.

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

A correlation can be drawn between the wear rates and mechanical properties of the materials manufactured from the four formulations. The stronger, harder materials generally had the lower wear rates. However, the presence of 5 pbw glassy carbon in formulation No. 2X-121 did not increase the seal life of this material as had been initially anticipated.

Table XXIV also lists the coefficients of friction calculated from the frictional torques measured during wear testing. The frictional torques used for the calculations were measured during the tests when the rings of the same formulations occupied both seal positions in the test chamber. The coefficients of friction determined for the four materials manufactured from formulations Nos, 1X-121, 2X-121, 3-121, and 4X-121 were all greater than that recorded for Grade CDJ-121. All wear testing was done with oil induced into the system. If the rings had not been run in the presence of oil, the coefficients of friction for all five materials would probably be different from those presented in Table XXIV.

All four of the carbon-graphite materials manufactured from formulations Nos. 1X-121, 2X-121, 3-121, and 4X-121 appear to have sufficient wear resistance for use as self-acting seals.

SECTION VI

DISCUSSION OF THE RESULTS

An overall comparison of the material properties measured for the seal ring bodies of formulations Nos. 1X, 2X, 3, and 4X 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 IV have shown that the materials manufactured from formulations Nos. 1X-121, 2X-121, 3-121, and 4X-121 are potentially better seal ring materials for high temperature use than commercial Grade CDJ. Although the four materials are not so strong and hard as Grade CDJ, they have much better thermal properties. The high thermal conductivities of the seal ring bodies of formulations Nos. 1X, 2X, 3, and 4X 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 four materials all have significantly better oxidation resistance than that of Grade CDJ-121. The seal life of the four materials, therefore, should surpass that of Grade CDJ-121 under high ambient air temperature conditions where oxidation is the limiting performance factor. All four 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. 1X indicate that it is the best formulation of those manufactured during Task III for meeting the goal of this Contract. Formulation No. 1X resulted in one of the strongest and hardest materials manufactured during Task III. The material had the highest thermal conductivity recorded during Task IV, and its oxidation rate after impregnation with the No. 121 oxidation-inhibiting treatment was one of the lowest measured. The narrow spread in the No. 121 treat pickup measured for the compacts of formulation No. 1X indicates that the material has a very uniform internal structure. Wear testing at nominal environmental conditions showed the No. 121 treated seal rings of formulation No. 1X to have the longest seal life of the four formulations tested.

The fact that the seal ring bodies of formulation No. 1X had the highest thermal conductivity and were among the strongest and hardest compacts manufactured during Task III probably accounts for the material's lower wear rate.

Aside from its good material properties, formulation No. 1X was found to be one of the easiest materials to process during Task III. No major problems were encountered during the manufacture of the seal ring bodies from formulation No. 1X. A minor problem arose when the green compacts of formulation No. 1 were baked from room temperature to 1000°C. Apparently, too many compacts were packed in the same container the first time this material was baked. The weight of the pack that was concentrated on the seal ring bodies located at the bottom caused several of them to crack during baking. The cracking problem was remedied by reducing the number of compacts packed in the container. The Bakelite BRP-5095 resin impregnation improved the strength and hardness of the formulation No. 1 compacts.

Characterization of the properties of the formulation No. 2X material showed that the use of 5 pbw of glassy carbon significantly degraded the oxidation resistance without an improvement in any of the other material properties measured. Glassy carbon was included in formulation No. 2X as a possible means of increasing the wear resistance of the seal. Wear tests conducted during Task IV showed that the glassy carbon addition actually caused the seal rings of formulation No. 2X-121 to wear slightly faster than those of its nonadditive counterpart (formulation No. 1X-121). As with the formulation No. 1X material, impregnation of the compacts with the Bakelite resin prior to heat treatment at 2800°C resulted in the formulation No. 2X compacts being considerably harder and stronger than those of formulation No. 2.

Although the formulation No. 3-121 material experienced a slightly lower oxidation rate than those measured for the samples of formulations No. 1X-121 and 4X-121, its mechanical, thermal, and wear properties are not so good as those of the other three materials. Formulation No. 3 resulted in seal ring bodies which were considerably weaker than those manufactured from formulations Nos. 1X, 2X, and 4X. Thermal conductivity measurements also were found to be considerably lower than those of the materials from formulations Nos. 1X and 2X. The fact that the formulation No. 3 material had poorer mechanical and thermal properties probably accounts for the higher wear rate determined for the seal rings of formulation No. 3-121. A statistical analysis has shown that there is a significant difference between the wear rates of the seal rings of formulations Nos. 1X-121 and 3-121. It is actually somewhat unfair to compare the material properties of the formulation No. 3 material with those of the compacts of formulations Nos. 1X, 2X, and 4X, since formulation No. 3 did not include the Bakelite BRP-5095 resin impregnation as a processing step. Had a resin impregnated version of formulation No. 3 been produced, the resultant material probably would have had better mechanical, thermal, and wear properties than its nonresin-impregnated counterpart.

Of all the materials manufactured during Task III, formulation No. 3 proved to be the most difficult to process. A major problem was encountered when removing the acetone from the "mix". Due to the formation of an impervious crust, some of the acetone was trapped in the "mix" after it had been heated at 75°C for 16 hours. All the acetone must be removed from the "mix" before molding, or the rapid evolution of the acetone during baking will result in the cracking of the compacts. The residual acetone was finally removed after the material was frozen solid, crushed, and vacuum evacuated for 16 hours in an autoclave while the temperature was maintained at 50°C. Another problem was encountered when the large green ring blanks of formulation No. 3 were baked between room temperature and 1000°C. Localized stresses produced by the high shrinkage of the material caused all the ring blanks to crack and/or laminate while they were baked between 150°C and 1000°C at 10°C per hour. The temperature is rushed to 150°C to avoid sagging of the compacts during the period when the first stage of the Bakelite resin is soft. Reducing the baking rate to 5°C per hour between 150°C and 1000°C reduced the rate of shrinkage and reduce the cracking of the compacts. Although formulation No. 3 was difficult to process, the No. 121 oxidation-inhibiting treat pickups for the oxidation samples indicate that this material has a very uniform internal structure.

Formulation No. 4X is the most unconventional material manufactured during Task III, since it incorporates graphite fibers instead of Thermax furnace black in the filler system and a phenolic resin rather than pitch as the carbon binder raw material. Substitution of the graphite fibers for the furnace black resulted in a material with a higher strength-per-unit weight ratio than those of the other materials manufactured during Task III. Although the compacts of formulation No. 4X were considerably softer than those of formulation No. 1X, the strengths of the two materials were very similar. The Bakelite resin impregnation resulted in the compacts of formulation No. 4X being considerably stronger and harder than those of formulation No. 4. The thermal conductivity of the formulation No. 4X material is considerably lower than that of the sample of formulation No. 1X. The anisotropy ratios calculated from the measured with-grain and across-grain thermal conductivities show that the formulation No. 4X material is more anisotropic than the materials manufactured from formulations Nos. 1X, 2X, and 3. The greater anisotropy probably results from the use of the graphite fibers. The oxidation resistance of the formulation No. 4X-121material is about the same as that of the samples of formulation No. 1X-121. Both materials experienced a 5 percent loss in weight after 4.7 hours exposure to the 1300°F (704°C) ambient air. Material formulation No. 4X is apparently not as internally uniform as the materials manufactured from the other three formulations, since the spread in the No. 121 treat pickups of the samples of formulation No. 4X was considerably greater than that of the other three materials. The fact that the mechanical and thermal properties of the formulation No. 4X compacts were not so good as those of the seal ring bodies of formulation No. 1X probably accounts for the higher wear rate experienced by the seal rings of formulation No. 4X-121. Similarly, the wear rate of the formulation No. 4X-121 material was lower than that of the formulation No. 3-121 material, since the mechanical properties of the formulation No. 4X material were better than those of the formulation No. 3 material.

Only one significant problem was encountered during the manufacture of the formulation No. 4X material. The Contractor found it necessary to mill the filler system of formulation No. 4X through a larger screen than that used during Task I.(5) The larger screen size was needed to increase the rate at which the filler system could be milled. No apparent change in the size of the milled graphite fibers resulted from the use of the larger screen size.

After the material properties determined for the seal ring bodies of formulations Nos. 1X-121, 2X-121, 3-121, and 4X-121 have been examined, the materials may be ranked as to their suitability for fulfilling the goal of the Contract. Formulation No. 2X-121 has not been included in the ranking, since the Task IV results indicate that glassy carbon is not a good additive for carbon-graphite seal ring materials. The remaining three materials can be ranked in the following order of decreasing suitability.

1. Formulation No. 1X-121
2. Formulation No. 4X-121
3. Formulation No. 3-121

Since no significant differences were noted in the oxidation rates of the three materials, the ranking is based on the results of the other material property measurements. The formulation No. 1X-121 material is ranked first, since it possesses the best mechanical, thermal, and wear properties of the three materials listed. Formulation No. 4X-121 is ranked second, since it is a stronger and slightly more wear-resistant material than that of formulation No. 3-121. The with-grain thermal conductivities of the latter two materials are very similar.

Impregnation of the formulation No. 3 compacts with the Bakelite BRP-5095 resin will very likely result in an improvement in the mechanical and wear properties of the material. A screening study of various resins might yield a more suitable resin impregnant than the Bakelite BRP-5095 resin and acetone solution used to impregnate the compacts of formulations Nos. 1X and 4X. Adjustment of the proportions of the filler materials used in formulation No. 4X also might help to improve the properties and uniformity of the material. The binder level of formulation No. 4X probably can be increased, since no lamination point was determined when the material was developed during Task I.(5) Increasing the binder level would help to improve the material properties of formulation No. 4X.

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-inchx2.5-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 of 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(13, 14) with no simplifying assumptions.

APPENDIX III

DEFINITION OF STATISTICAL TERMS

F Distribution (12)

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

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.

APPENDIX III (Cont'd)

Student's t Distribution (11, 12)

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:

$$\text{Degrees of freedom} = n_x + n_y - 2.$$

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:

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

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

REFERENCES

1. Parks, A. J., McKibbin, R. H., and Ng, C. C. W., "Development of Main Shaft Seals for Advanced Air Breathing Propulsion Systems," NAS3-7609, Final Report Phase I (August, 1967), NASA CR 72338, page 49.
2. Johnson, Robert L., and Ludwig, Lawrence P., "Shaft Face Seal with Self-Acting Lift Augmentation for Advanced Gas Turbine Engines," NASA-TN-D-5170, NASA Lewis Research Center, Cleveland, Ohio, April, 1969.
3. Strom, Thomas N., Allen, Gordon P., and Johnson, Robert L., "Wear and Friction of Impregnated Mechanical Carbons at Temperatures to 1400°F (760°C) in Air or Nitrogen," NASA-TN-D-3958, page 2, NASA Lewis Research Center, Cleveland, Ohio, May, 1967.
4. Lauzau, W. R., Shelton, B. R., and Waldheger, R. A., "The Use of Carbon-Graphite in Mechanical Seals," Lubrication Engineering, Volume 19, pages 201-209, May, 1963.
5. Fechter, N. J., and Petrunich, P. S., "Development of Seal Ring Carbon-Graphite Materials (Tasks I and II)," Union Carbide Corporation, Topical Report NASA CR-72799 (Contract NAS3-13211), January, 1971.
6. Loc. cit., Reference 2, page 17.
7. Smith, Morton C., "CMF-13 Research on Carbon and Graphite," Los Alamos Scientific Laboratory, LA-4057 (W-7405-ENG. 36) (Report No. 7)(Summary of Progress from Aug. 1 to Oct. 31, 1968) pages 5-7, December 31, 1968.
8. <u>The Industrial Graphite Engineering Handbook,</u> Union Carbide Corporation, pages 5A.08.02-5A.08.03, C1969.
9. Loc. cit., Reference 5, pages 88 and 90.
10. <u>Ibid.</u>, pages 84-89.

REFERENCES (Cont'd)

11. Brownlee, K. A., Industrial Experimentation, Chemical Publishing Co., Inc., New York, pages 28-32, C1947.

12. Hoel, Paul G., Introduction to Mathematical Statistics, John Wiley & Sons, Inc., New York-London, pages 271 to 288, C1962.

13. Barrett, E. P., Joyner, L. G., and Halenda, P. B., The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms, Journal of the American Chemical Society, Volume 73, page 373, 1951.

14. Roberts, B. F., A Procedure for Estimating Pore Volume and Area Distributions by Sorption Isotherms, Journal of Colloid and Interface Science, Volume 23, pages 266-273, 1967.

DISTRIBUTION LIST

	Addressee	No. of Copies
1.	NASA Headquarters	
	Washington, D.C. 20546	
	Attention: N. F. Rekos (RLC)	1
	A. J. Evans (RA)	1
	J. Maltz (RWM)	1
	J. J. Gangler (RRM)	1
2.	NASA-Lewis Research Center	
	21000 Brookpark Road	
	Cleveland, Ohio 44135	
	Attention: A. Ginsburg, MS 5-3	1
	E. E. Bisson, MS 5-3	1
	R. L. Johnson, MS 23-2	1
	L. P. Ludwig, MS 23-2	10
	M. A. Swikert, MS 23-2	1
	C. H. Voit, MS 5-3	1
	H. E. Hinckley, MS 500-206	1
	Report Control Office, MS 5-5	1
	Library, MS 60-3	1
	Technology Utilization Office, MS 3-19	1
	Dr. B. Lubarsky, MS 3-3	1
3.	NASA-Scientific and Technical Information Facility	
	P. O. Box 33	
	College Park, Maryland 20740	
	Attention: NASA Representative	2
4.	NASA-Langley Research Center	
	Langley Station	
	Hampton, Virginia 23365	
	Attention: Mark R. Nichols, MS 403	1
5.	United States Air Force	
	Wright-Patterson Air Force Base	
	AF Systems Command USAF	
	Wright-Patterson AFB, Ohio 45433	
	Attention: AFAPL (APFL), K. L. Berkey	1
	AFAPL (AFTC), C. Simpson	1
	APTP, I. J. Gershon	1
	SEJDF, S. Prete	1
	MANE, R. Headrick	1
6.	U. S. Naval Air Development Center	
	Aeronautical Materials Department	
	Warminster, Pennsylvania 18974	
	Attention: A. L. Lockwood	1

Addressee No. of Copies

7. Commanding Officer
U. S. Navy Underwater Weapons
Research and Engineering Section
Newport, Rhode Island 02890
Attention: Technical Library (T12-A-183) 1

8. U. S. Navy Marine Engineering Laboratory
Friction and Wear Division
Naval Academy
Annapolis, Maryland 21490
Attention: R. B. Snapp 1

9. Department of the Army
U. S. Army Aviation Material Labs.
Fort Eustis, Virginia 23604
Attention: John W. White, Chief
Propulsion Division 1

10. AVCOM
AMSAVEGTT
Mart Building
405 South 12th Street
St. Louis, Missouri 63166
Attention: E. England 1

11. Aerojet-General Corporation
5100 W. 164th Street
Cleveland, Ohio 44142
Attention: W. L. Snapp 1

12. Advance Carbon Products, Inc.
Hampshire & Mariposa Sts.
San Francisco, California 94110
Attention: W. J. Crader 1

13. Avco Corporation
Lycoming Division
550 South Main Street
Stratford, Connecticut 06497
Attention: R. Cuny 1

14. Battelle Memorial Institute
505 King Avenue
Columbus, Ohio 43201
Attention: C. M. Allen 1

15. B. F. Goodrich Company
Aerospace & Defense-Products Division
Troy, Ohio 45373
Attention: L. S. Blalkowski 1

	Addressee	No. of Copies
16.	Boeing Aircraft Company P. O. Box 3399 Seattle, Washington 98124 Attention: W. S. Lambert 2-1100	1
17.	Borg-Warner Corporation Roy C. Ingersoll Research Center Wolf and Algonquin Roads Des Plaines, Illinois 60018	1
18.	Carborundum Company Graphite Products 2050 Corry Drive Sanborn, N. Y. 14132 Attention: R. M. Market	1
19.	Cartiseal Corporation 634 Glenn Avenue Wheeling, Illinois 60090 Attention: R. Voltik	1
20.	Chicago Rawhide Manufacturing Company 1311 Elston Avenue Chicago, Illinois 60622 Attention: R. Blair	1
21.	Clevite Corporation Cleveland Graphite Bronze Division 17000 St. Clair Avenue Cleveland, Ohio 44110 Attention: Thomas H. Koenig	1
22.	Continental Aviation & Engineering 12700 Kercheval Detroit, Michigan 48215 Attention: A. J. Follman	1
23.	Crane Packing Company 6400 W. Oakton Street Morton Grove, Illinois 60053 Attention: Harry Tankus	1
24.	Defense Ceramics Information Center Battelle Memorial Institute Columbus, Labs. Room 11-9021 505 King Avenue Columbus, Ohio 43201	1

Addressee   No. of Copies

25. McDonnell Douglas Corporation
333 West First Street
Dayton, Ohio 45402
Attention: R. G. Donmoyer 1

26. Durametallic Corporation
Kalamazoo, Michigan 49001
Attention: H. Hummer 1

27. Fairchild-Hiller Corporation
Republic Aviation Division
Farmingdale, Long Island
New York, 11735
Attention: C. Collis 1

28. Franklin Institute Laboratories
20th & Parkway
Philadelphia, Pennsylvania 19103
Attention: W. Shapiro 1

29. Garlock, Inc.
Palmyra, New York 14522
Attention: E. W. Fisher 1

30. Garrett Corporation
Air Research Mfg. Division
9851-9951 Sepulvelda Blvd.
Los Angeles, California 90009
Attention: A. Silver 1

31 General Dynamics Corporation
1025 Connecticut Avenue, N. W.
Washington, D. C. 20036
Attention: G. J. Vila 1

32. General Electric Company
Advanced Engine and Technology Department
Cincinnati, Ohio 45215
Attention: L. B. Venable 1
C. C. Moore H-25 1

33. General Motors Corporation
Allison Division
No. 3, Department 7339
Indianapolis, Indiana 46206
Attention: E. M. Deckman 1

Addressee		No. of Copies
34.	Great Lakes Carbon Corporation 299 Park Avenue New York, New York 10017 Attention: J. P. Sachs	1
35.	Gulf General Atomic Inc. P. O. Box 608 San Diego, California 92112 Attention: J. C. Bokros	1
36.	I. I. T. Research Foundation 10 West 35 Street Chicago, Illinois 60616 Attention: Dr. Strohmeier	1
37.	Kendall Refining Company Bradford, Pennsylvania 16701 Attention: F. I. I. Lawrence	1
38.	Keystone Carbon Corporation 1935 State St. Marys, Pennsylvania 15857 Attention: B. R. Reuscher	1
39.	Koppers Company, Inc. Metal Products Division Piston Ring and Seal Department P. O. Box 298 Baltimore, Maryland 21203 Attention: E. Taschenburg	1
40.	Lockheed Aircraft Company 118 West First Street Dayton, Ohio 45402 Attention: R. R. Witte	1
41.	Los Alamos Scientific Lab. University of California Los Alamos, New Mexico Attention: M. C. Smith	1
42.	Martin Marietta Corporation P. O. Box 14153 Dayton, Ohio 45414 Attention: Z. G. Horvath	1
43.	Mechanical Technology Incorporated 968 Albany-Shaker Road Latham, New York 12110 Attention: Donald F. Wilcock	1

Addressee	No. of Copies
44. Midwest Aero Industries Corporation 4834 Delemere Avenue Royal Oak, Michigan 48073 Attention: J. Sherlock	1
45. Midwest Research Institute 425 Volker Blvd. Kansas City, Missouri 64110 Attention: V. Hopkins	1
46. Morganite, Inc. 33-02 48th Avenue Long Island City, New York 10001 Attention: S. A. Rokaw	1
47. North American Rockwell Corporation 5100 W. 164th Street Cleveland, Ohio 44142 Attention: George Bremer	1
48. Northrop Corporation 1730 K Street, N. W. Suite 903-5 Washington, D. C. 20006 Attention: S. W. Fowler, Jr.	1
49. Poco Graphite Inc. P. O. Box 1524 Garland, Texas 75040 Attention: Dr. R. F. Wehrmann	1
50. Pure Carbon Company, Inc. 441 Hall Avenue St. Marys, Pennsylvania 15857 Attention: Dr. R. R. Paxton	1
51. Rocketdyne 6633 Canoga Avenue Canoga Park, California 91304 Attention: M. Butner	1
52. Sealol Inc. P. O. Box 2158 Providence, Rhode Island 02905 Attention: Justus Stevens	1
53. SKF Industries, Inc. 1100 First Avenue King of Prussia, Pennsylvania 19406 Attention: L. B. Sibley	1

Addressee		No. of Copies
54.	St. Marys Carbon Company 1939 State Road St. Marys, Pennsylvania 15857 Attention: J. E. Lanzel	1
55.	Southwest Research Institute P. O. Drawer 28510 San Antonio, Texas 78228 Attention: P. M. Ku	1
56.	Stanford Research Institute 333 Ravenwood Avenue Menlo Park, California 94025 Attention: R. C. Fey	1
57.	Stein Seal Company 20th Street & Indiana Avenue Philadelphia, Pennsylvania 19132 Attention: Dr. P. C. Stein	1
58.	Stackpole Carbon Company St. Marys, Pennsylvania 15857 Attention: Dr. E. I. Shobert	1
59.	Ultra Carbon Corporation 1300 N. Madison Avenue Bay City, Michigan 48706 Attention: Del Hughes	1
60.	United Aircraft Corporation Pratt & Whitney Aircraft Division East Hartford, Connecticut 06108 Engineering Building EBIM 2 Attention: R. Shevchenko	1
61.	United States Graphite Company 1621 Holland Saginaw, Michigan 48601 Attention: F. F. Ruhl	1
62.	Westinghouse Electric Corporation 5100 W. 164th Street Cleveland, Ohio 44142 Attention: Lynn Powers	1
63.	Wright Aeronautical Division Curtiss-Wright Corporation 333 W. 1st Street Dayton, Ohio 45402 Attention: D. Lombardo	1

Addressee	No. of Copies
64. The University of Tennessee Department of Mechanical & Aerospace Eng. Knoxville, Tennessee 37916 Attention: Professor W. K. Stair	1
65. Aerospace Corporation Building A-2 P. O. Box 95085 Los Angeles, California 90045 Attention: James Todd	1
66. Morganite Incorporated 401 N. Ashe Avenue P. O. Box 347 Dunn, N. Carolina 28334 Attention: S. A. Rokaw	1
67. National Technical Information Service Springfield, Virginia 22151	40

~~Joe Magyar E452/106^2/26751~~