

## FOREWORD

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- Volume I - Observations by Electron Microscopy of Dislocations in Graphite, by R. Sprague.
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- Volume XXV - Lamellar Compounds of Nongraphitized Petroleum Cokes, by H. F. Volk.
- Volume XXVI - Physical Properties of Some Newly-Developed Graphite Grades, by R. B. Dull.
- Volume XXVII - Carbonization Studies of Aromatic Hydrocarbons, by I. C. Lewis and T. Edstrom.
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Volume XXIX - Evaluation of Graphite Materials in a Subscale Solid-Propellant Rocket Motor, by D. C. Hiler and R. B. Dull.

Supplement - Evaluation of Graphite Materials in a Subscale Solid-Propellant Rocket Motor, by S. O. Johnson and R. B. Dull.

Volume XXX - Oxidation-Resistant Graphite-Base Composites, by K. J. Zeitsch and J. Criscione.

## ABSTRACT

This report discusses the impregnation of carbon and graphite materials with carbonaceous liquids and the subsequent heat treatment required to convert these liquids to coke and graphite in the pores of the base materials. The purpose of the impregnation process is to increase the strength and density and decrease the porosity of the finished articles. Impregnation procedures, the natures of the impregnants, and base stock structure affect the physical properties of impregnated graphite. Mercury porosimetry is used to define the pore structure of the bodies to be impregnated and aid in selection of impregnant and impregnating procedure. The physical properties of the impregnated graphite are related to the performance of nozzle inserts in a sub-scale solid propellant rocket motor.

This technical documentary report has been reviewed and is approved.



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## 1. INTRODUCTION

Impregnation of carbon and graphite bodies with liquids which will deposit a carbonaceous residue upon heat treatment has been used to improve the density, strength and other physical properties of the finished articles. The process of impregnation is well known in the graphite industry; pitch impregnation of carbon articles prior to graphitization was patented in 1909, <sup>(1)</sup> only 14 years after Dr. E. G. Acheson patented the process of manufacturing graphite. <sup>(2)</sup> This procedure quickly became a standard practice in the graphite industry, and today many of the current commercial graphite grades, such as ATL, AGSX, ATJ, and RVA, <sup>(3)</sup> have had one or more impregnations prior to the final graphitizing heat treatment.

Manufactured bulk graphite, even those grades whose processing history includes pitch impregnation, are still quite porous and permeable materials. Considerable attention has been given recently to the impregnation of graphite for the purpose of rendering it impermeable to gases at high temperatures. This work has been accelerated by various high temperature gas-cooled nuclear reactor concepts in which an impermeable or nearly impermeable graphite is a prime requirement. The investigation and development of methods for attaining low permeability and measuring minute gas flow through graphite has been the subject of numerous reports and papers, <sup>(4-11)</sup> showing considerable progress in this field.

Low permeability graphite can be obtained by several routes, the most common of which are: (a) impregnation with a carbonaceous liquid followed by a carbonizing heating treatment; (b) deposition of carbon by the pyrolysis of a hydrocarbon gas in the pores or on the surface of the graphite; the use of starting materials which themselves shrink during carbonization and graphitization, thereby producing compact, shaped bodies with closed pores, <sup>(12)</sup> and (d) the hot working of graphite shapes. <sup>(13)</sup>

This report will discuss the impregnation of graphite with carbonaceous liquids and the subsequent heat treatment to convert these liquids to coke and/or graphite in situ. The effect of impregnation process conditions on the resultant physical properties of the impregnated graphite will be discussed, and these physical properties will be correlated with performance of the graphites as nozzles in solid propellant rocket motors.

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## 2. LIQUID IMPREGNATION OF CARBON AND GRAPHITE

Graphites are impregnated to improve the physical properties of the material. Past experience in graphite processing enables the prediction of the effect of carbonaceous impregnants on the physical properties of graphite. Table 1 lists some of the common physical properties normally determined for graphite and how they are affected by impregnation with a carbonaceous liquid which is subsequently carbonized. The change in these properties effected by impregnation varies, depending upon the initial properties of the graphite grade employed, and ranges from an almost immeasurable change for some of the high density grades, such as ZTA, to the factors of 2 to 10 for the lower density fibrous graphite grades.<sup>(14)</sup> The purpose of the work discussed in this report is to show how the improvements in physical properties can be effected by close control of the impregnation process.

Table 1. Effect of Impregnation on Some Physical Properties of Graphite

<u>Physical Property</u>	<u>Change in Property Value</u>
Bulk Density	+
Electrical Resistivity	-
Strength, Tensile	+
Strength, Flexural	+
Strength, Compressive	+
Young's Modulus	+
Permeability Porosity	-
Thermal Expansion	+
Thermal Conductivity	+

In order to realize the maximum benefit from the impregnation of graphite, it is necessary to understand the materials and processes involved. The materials involved are (a) the porous solid (graphite) to be impregnated, and (b) the impregnant. The processes are (a) the impregnation, and (b) the subsequent heat treatment. The following sections will discuss these materials and processes in some detail.

### 2.1. The Porous Solid

In order to attain the goals of impregnation, as much as possible should be known about the structure of the material to be impregnated. Of primary concern is the porosity or, more specifically, the open porosity. The total porosity may be calculated from two physical properties

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which are easily determined. These properties are the bulk density of the body to be impregnated, determined by dividing its weight by its bulk volume, and the real density as determined by its crystal structure. From these two values, the total porosity may be calculated as follows:

$$\text{Total Porosity (per cent)} = 1 - \frac{\text{Bulk Density}}{\text{Real Density}} \times 100 \quad (1)$$

The open porosity, or the accessible volume which can be reached through minimum pore diameter  $D$ , cannot be calculated but must be measured. This measurement involves the immersion of a graphite sample (or other porous solid) in a non-wetting fluid, in the present case mercury, and driving the mercury into the graphite by increasing hydrostatic pressure. For any given pressure, mercury will be forced into pore diameters, or more correctly, pore entrances, of a minimum size as determined by the following equation:<sup>(15)</sup>

$$D = \frac{-.58 \sigma \text{ Cos } \theta}{P} \quad (2)$$

$D$  = pore diameter, microns

$\sigma$  = surface tension of fluid at room temperature  
(for Hg,  $\sigma = 480$  dynes/cm)

$\theta$  = contact angle between fluid and sample  
(for Hg with carbon and graphite,  $\theta = 140^\circ$ )

$P$  = hydrostatic pressure, lbs/in<sup>2</sup> absolute

Changes in the apparent volume of the mercury bath can be attributed to accessible volume  $\Delta V$  reached through pores of minimum diameter  $D$ . The volume of mercury forced into the sample is measured at increasing pressures (decreasing pore diameter) and corrected for a sample volume of one cubic centimeter. The cumulative volume of the sample filled with mercury (cc/cc) is plotted versus decreasing pore diameter as shown in Figure 1.

It is apparent from the highly irregular nature of the pores in any consolidated compact that the pore diameter defined above is qualitative and, in general, the pores have the characteristic of a large volume with a relatively large cross section entered through a small opening. This geometry is not only obvious from photomicroscopy but is evidenced in porosimetry measurements by the fact that on

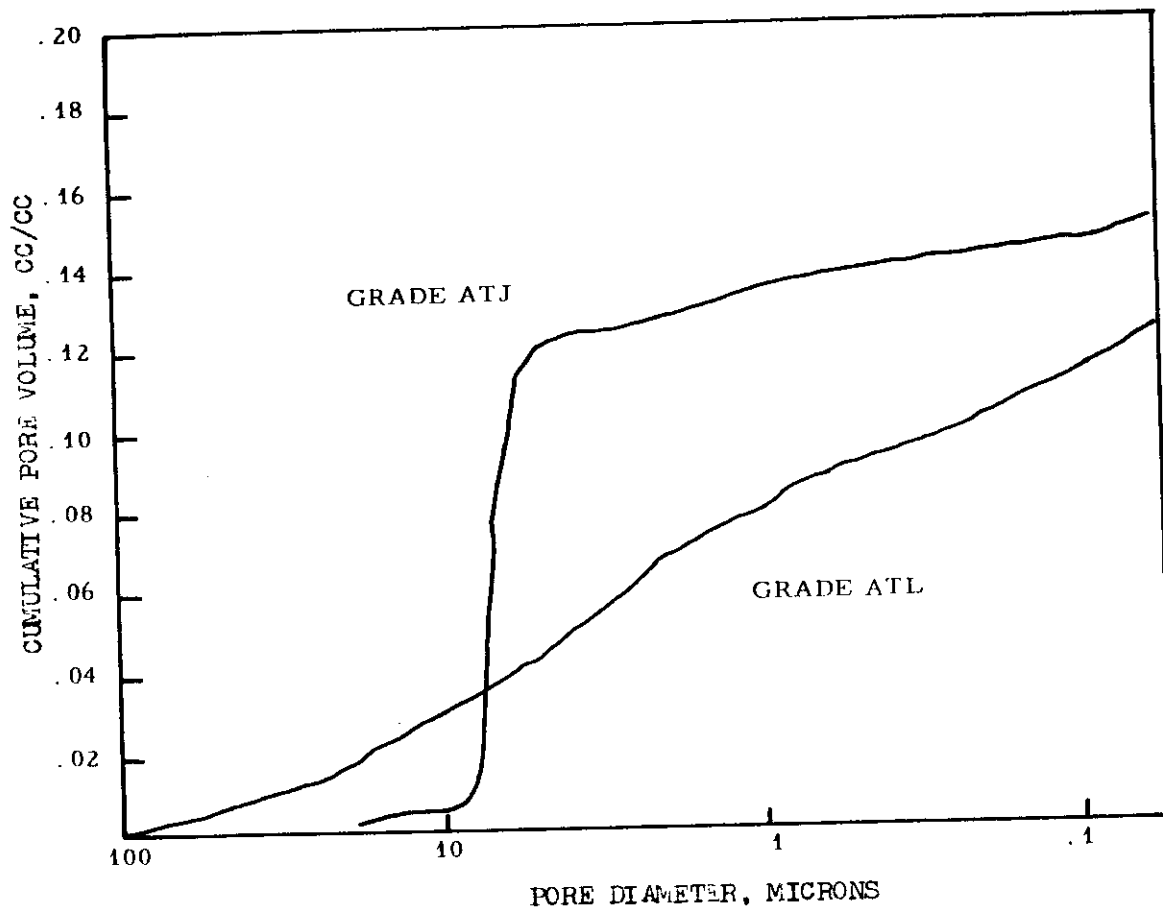


Figure 1. Plot of Accessible Pore Volume vs. Pore Diameter Grades ATJ and ATL Graphite

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releasing the pressure, virtually none (< 5 per cent) of the mercury is normally released from the sample. (4)

Determination of the minimum pore diameter a given liquid impregnant will penetrate permits one to read directly from the curves such as in Figure 1 the maximum volume of the impregnant which can be introduced into the porous solid. The theoretical weight gain upon impregnation is then calculated by <sup>(16)</sup>

$$\text{Weight Gain (per cent)} = \frac{\left( \sum_{d_i}^{\infty} \Delta V \right) (\text{Sp. Gr. of Impregnant})(100)}{\quad} \quad (3)$$

where:  $\sum_{d_i}^{\infty} \Delta V$  = void fraction of porous solid composed  
of pores larger than  $d_i$  diameter,

and  $d_i$  = minimum pore diameter which  
impregnant will penetrate

Since the flow of an impregnant into the pores of graphite is primarily a viscous flow, the required time and pressure for complete penetration is dependent on the square of the effective diameter of the pore openings. Therefore a root mean square diameter would be a measure of the effective pore size for penetration of a viscous fluid. The root mean square diameter ( $D_{rms}$ ) is defined as the square root of the sum of the squares of the pore diameter intervals weighted by the pore volume in each diameter interval ( $\sum_{d_i}^{\infty} \Delta V \cdot D^2$ ) and considered over pores of all possible sizes ( $\sum_{d_i}^{\infty} \Delta V$ ). The latter was previously described as the void fraction (porosity) calculated from the bulk and real densities. The mean diameter would be that which controlled the capillary action and diffusive flow. Table 2 shows the data used and calculated values of the average diameter and root mean square diameter for several graphite materials.

Table 2. Pore Properties of Several Graphite Grades

Material	Bulk Density g/cc	Real Density g/cc	$\sum_0^{\infty} \Delta V$ cc/cc	$\sum_0^{\infty} \Delta V \cdot D$ microns	$\sum_0^{\infty} \Delta V \cdot D^2$ microns <sup>2</sup>	$\bar{D}$ microns	$D_{rms}$ microns
ATL	1.780	2.26	0.212	0.7768	16.5177	3.66	8.83
ATJ	1.754	2.26	0.224	0.8649	6.1124	3.86	5.22
TS-392	1.802	2.26	0.203	0.2491	1.1931	1.23	2.42
RVA	1.850	2.26	0.181	0.2308	1.7830	1.28	3.14
ZT-6012	2.062	2.26	0.088	0.0020	0.0006	0.02	0.08

Figure 2 shows a plot of the porosimetry data and the location of both  $\bar{D}$  and  $D_{rms}$  for each material listed in Table 2.

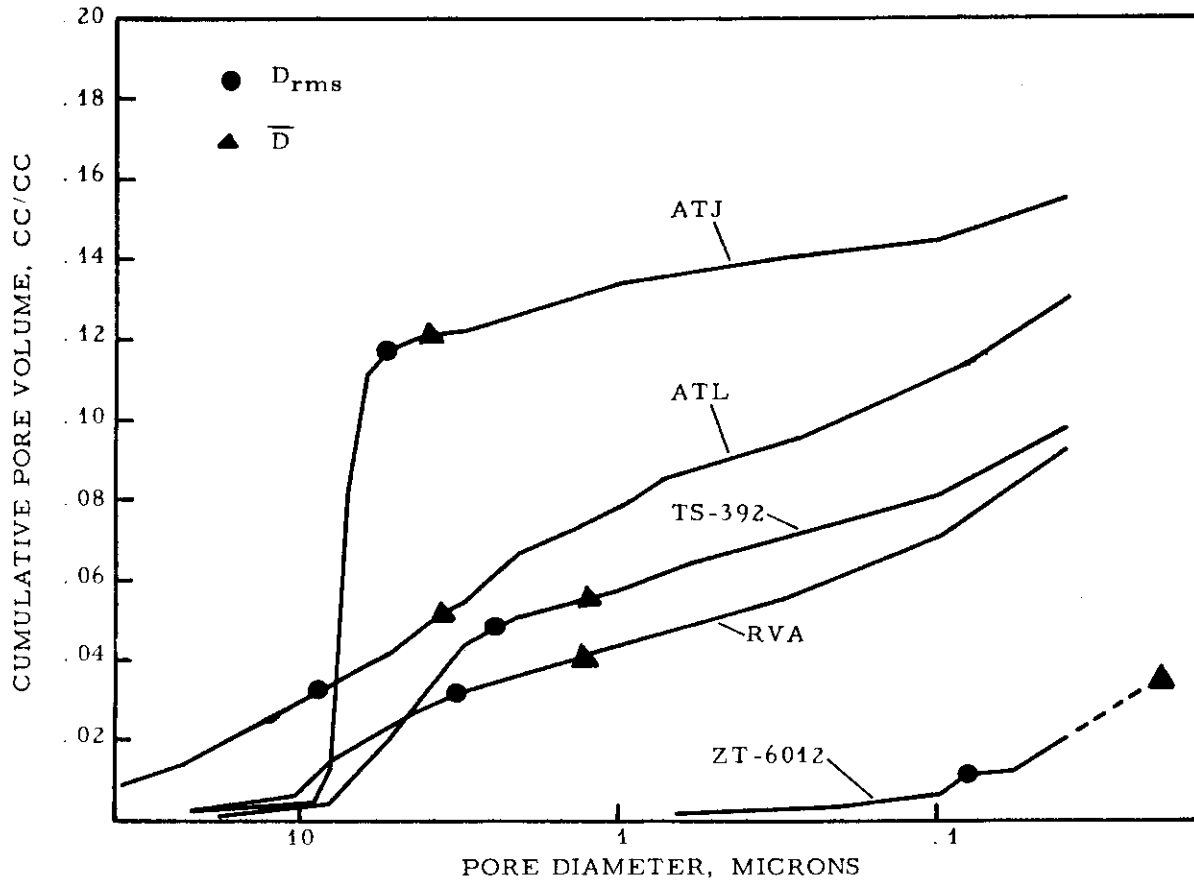


Figure 2. Cumulative Pore Volume vs. Pore Diameter for Various Graphites



As the effective pore size becomes smaller, the limitations of the mercury porosimeter prevent accurate measurements, and below a certain point, no measurements at all. The porosimeter employed for this work<sup>(17)</sup> permits the measurement of pores down to 0.04 micron diameter.

## 2.2. The Impregnant

With the porous solid now defined, the properties of possible impregnants are now considered. Theoretically any material can be used as an impregnant that is a liquid and is compatible with the porous solid.

The most important physical properties of an impregnant for graphite are (a) specific gravity, (b) viscosity, (c) surface tension, (d) contact angle between it and the porous solid, (e) size and shape of suspended solids, (f) reactivity upon heat treatment, and (g) coking value. In dealing with porous solids containing extremely small pores, it is also useful to know the mean molecular diameter of the impregnant, particularly when large organic molecules are involved.

Specific gravity data are necessary for calculating the theoretical weight gain upon impregnation according to equation (3), Section 2.1. It is important to know the specific gravity of the impregnant at the temperature of impregnation. The effect of temperature on specific gravity is also useful in determining whether or not volume changes upon heating or cooling would be of sufficient magnitude to adversely affect the impregnated material. Figure 3 shows the specific gravity-

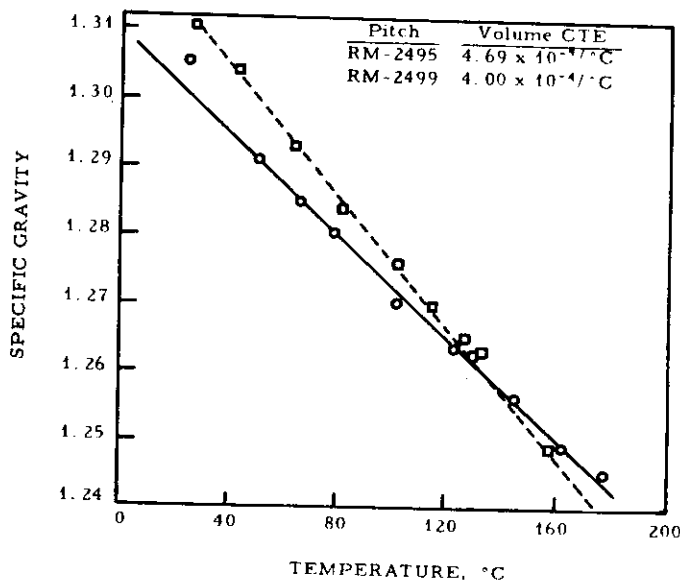


Figure 3. Specific Gravity versus Temperature for Coal Tar Pitches

temperature relationship for two coal tar pitches employed as binders and impregnants for carbon and graphite. (18) Similar data on resins and other liquids suitable for impregnants are available in the literature or from the manufacturer.

Viscosity is probably the most important single property affecting a liquid impregnation process because pressure and time for impregnation can be reduced considerably by use of a lower viscosity impregnant. An impregnant of lower viscosity will also penetrate smaller pores more readily. For thermoplastic impregnants, such as coal tar pitch, the use of heat is the most common, and most simple method of reducing viscosity. Figure 4 shows the viscosity-temperature relationship for typical coal tar pitches. Thermosetting impregnants cannot be subjected to elevated temperatures for viscosity reduction and, therefore, must have low viscosity at room temperature.

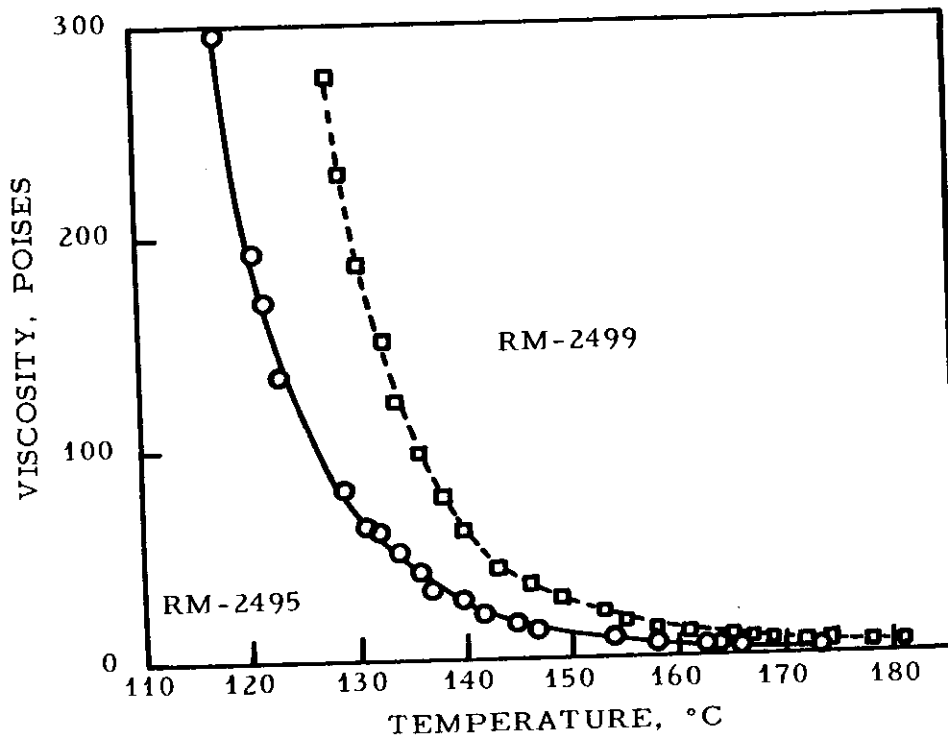


Figure 4. Viscosity versus Temperature for Coal Tar Pitches

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Data on surface tension and contact angle between impregnant and solid material are available or easily determined for most impregnant materials and graphite. Since all carbonaceous, or coking, impregnants wet carbon and graphite, the contact angle is less than 90°. Contact angles of 70° and 82° have been reported between coal tar pitch and graphite at 200°C. <sup>(18)</sup> Surface tension values for the same two pitches were 55 and 102 dynes/cm. Organic liquids suitable for impregnants exhibit slightly lower contact angles and surface tensions; however, compared to such properties as viscosity and coking value, these two are not decisive in impregnant selection.

Suspended solids in the liquid impregnant can hinder impregnation, particularly in the case of fine pore bodies. A solid particle which is of sufficient size to block a pore entrance will thereby prevent the impregnant from entering this pore. If the suspended solids are of sufficient size to cause incomplete impregnation, they may be removed by filtration prior to the impregnation process.

Since one purpose of impregnating graphite is to produce a low porosity, low permeability material for high temperature applications, heat treatment to carbonize the impregnant is the next step in the process. The thermal reactivity of the impregnant upon such a heat treatment is therefore of utmost importance. Differential thermal analysis (DTA) is an excellent tool for determining the thermal reactivity of materials, and detailed studies of pure organic compounds have been made by this method. <sup>(19)</sup> As an example of how the information obtained from DTA can be applied to the impregnation process, consider the reactivity of two typical impregnant materials - coal tar pitch and furfuryl alcohol + catalyst. Figure 5 shows thermograms of these two materials. The thermogram for coal tar pitch was determined by the National Carbon Research Laboratory <sup>(20)</sup> and furfuryl alcohol polymer by subcontract to Armour Research Foundation. <sup>(21)</sup> The thermogram for coal tar pitch is characterized by the absence of sharp exothermic and endothermic peaks, whereas furfuryl alcohol shows strong exotherms and endotherms over rather narrow temperature ranges. These exotherms and endotherms define the critical ranges during heat treatment. How the heat treatment schedules are adjusted to compensate for this reactivity will be discussed more fully in Section 2.4.

In order for a material to be useful as an impregnant for carbon or graphite, it should have a reasonable coking value. Coking value is defined as the per cent carbon residue after a carbonizing heat treatment (usually >800°C). Coking values have been published for a large number of organic materials, many of which are suitable as impregnants for carbon and graphite. <sup>(21,22,23)</sup> In general, a coking value of over 50 per

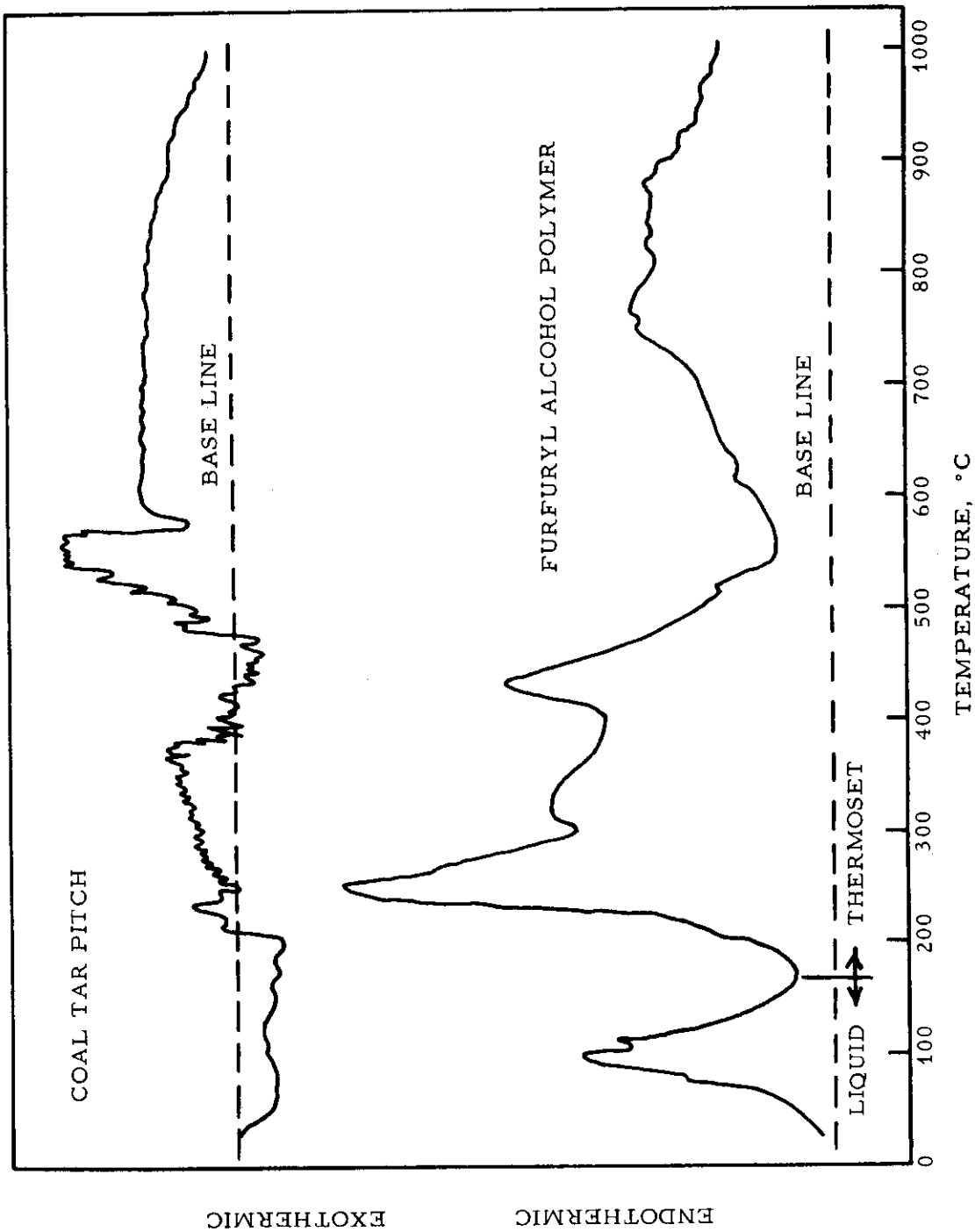


Figure 5. DTA Thermograms for Coal Tar Pitch and Furfuryl Alcohol Polymer

cent is desirable for carbonaceous impregnant; however, excellent results have been obtained from impregnation with sugar solutions having coking values of less than 20 per cent. (24, 25) A high coking value is still desirable, giving material with higher density and strength and providing a greater factor of safety in case of partial loss of impregnant by drainage, evaporation, or oxidation. More important, high coking value decreases the tendency for spalling because of the smaller volume of volatiles which must escape through the pores during heat treatment.

After considering the properties of possible impregnants in general, the problem now arises as to which impregnant will be the most effective for a given carbon or graphite material. For relatively porous materials, and this includes most of the commercial graphite grades, impregnation with a coal tar pitch is the most effective means for increasing density and strength. If permeability reduction is the primary goal, pitch impregnation should be followed by a resin impregnation. For very fine pore graphites, coal tar pitch is relatively ineffective and a lower viscosity impregnant must be employed. Such an impregnant could be a pure organic liquid or a coal tar pitch thinned with a solvent or plasticizer. The most widely used organic liquids are the furans, either singly or as admixtures.

Various impregnants which were made available through research or other means have been evaluated. These evaluations included five impregnants with particular emphasis given to (a) the physical properties of the impregnants, and (b) the performance of the resins on specific graphite grades. The impregnants were all solids which were thinned with furfural. Three of the impregnants contained pitches. The physical properties of the pitches are presented in Table 3. The pitches, after thinning, were used in impregnating a molded fine grain graphite. The results of the impregnation are presented in Table 4.

Table 3. Physical Properties of Thermoplastic-Pitches

Pitch	Quinoline Insoluble	Softening Point	Conradson* Carbon
Acenaphthylene	0.50 per cent	117.5 °C	
Kopper's	1.88 per cent	109 °C	39.4 per cent
Petroleum	0.20 per cent	115 °C	47.0 per cent

\*Note: Conradson Carbon is a rapid ASTM method for differentiating between coking residues for different hydrocarbons. The Conradson value is not necessarily indicative of the coke yield after impregnating and baking.

Table 4. Per Cent Weight Gain of Fine Grain Graphite for Various Impregnants

Impregnant	Original Density g/cc	Weight Gain per cent	250°C Cured Gain per cent	750°C Baked Gain per cent	Coke Yield per cent	Final Density g/cc	Remarks
50 per cent Petroleum Pitch	1.720	8.73	5.88	4.25	48.7	1.788	
50 per cent Furfural	1.742	7.57	5.10	3.56	47.0	1.802	
50 per cent Kopper's Pitch	1.751	7.40	6.00	-----	-----	-----	Spalled during the baking cycle
50 per cent Kopper's Pitch	1.724	8.88	6.06	-----	-----	-----	Spalled during the baking cycle
50 per cent Furfural							Too viscous for impregnating
50 per cent Acenaphthylene Pitch	1.726	0.0	-----	-----	-----	-----	Too viscous for impregnating
50 per cent Acenaphthylene Pitch	1.745	0.0	-----	-----	-----	-----	Loss of impregnant due to drainage
50 per cent Furfural	1.748	7.49	0.43	0.32	4.3	1.753	
10 per cent Acenaphthylene Pitch							
90 per cent Furfural	1.734	6.41	0.40	0.36	5.6	1.739	
90 per cent Furfural	1.735	9.6	5.77	3.85	40.1	1.807	
Code 88*							

\* National Carbon Company Plasticized Pitch Impregnant


A solution of acenaphthylene pitch and furfural was too viscous to penetrate the graphite matrix. It was necessary to reduce the amount of acenaphthylene to 10 per cent before any appreciable weight gain could be attained. However, excessive drainage of the thinned impregnant from the body rendered this approach ineffective. The use of acenaphthylene dissolved in furfural thus appears to have no value as a graphite impregnant. Acenaphthylene pitch is thermoplastic; consequently, it could be used as an impregnant without the use of an organic solvent. Time did not permit evaluating acenaphthylene pitch in this manner.

A solution of Kopper's pitch and furfural produced severe spalling in the baking cycle. The spalling was a consequence of excessive volatile evolution through the pores during the heat treatment. The relatively lower coking values for this pitch would account for the large volume of volatiles expelled.

Petroleum pitch dissolved in furfural appeared to be a good impregnant. The weight gain and per cent weight retained after baking was very similar to Code 88. The low quinoline insoluble (available free carbon) for petroleum pitch should reduce the amount of free carbon filtering out during the impregnation, thus increasing the impregnant penetration. Unfortunately, this impregnant had a short "pot-life" at room temperature. After seven days the impregnant solidified rendering it useless.

Two additional resins were evaluated as possible impregnants for RVA.<sup>(26)</sup> Grade RVA was selected because it is a premium quality graphite capable of being formed in large sizes. An impregnation of RVA with Code 88 impregnant produces grade CFZ, which is very uniform in physical properties and which has low permeability. CFZ, with its low porosity, low permeability, and high strength is an excellent candidate for rocket nozzles. A description of the resins is presented in Table 5.

Table 5. Description of Impregnating Resins

Manufacturer	Common Name	Composition	Generalized Chemical Structure	Physical State
Pennsylvania Industrial Chemical Company	Transphalt	Aromatic Polymer Residue		Solid
Velsicol Corporation	GE - 9	Same	Same	Solid

# Contrails

The physical properties of the resins diluted with furfural are presented in Table 6. Code 88 is also listed for a direct comparison.

Table 6. Physical Properties of Impregnating Resins

Resin*	Density g/cc	Viscosity cp	Conradson Carbon per cent
50 per cent GE-9			
50 per cent Furfural	1.136	130	29.2
50 per cent Transphalt			
50 per cent Furfural	1.142	1,130	17.6
Code 88	1.195	215	30.5

\* Note: All of the resins were catalyzed.

Velsicol GE-9 was dissolved in furfural in a 1:1 ratio by weight. The furfural dissolved the resin easily and rapidly. The results of impregnation trials made with this resin are shown in Table 7. RVA impregnated with resin had an initial bulk density of 1.878 g/cc. The per cent weight gain caused by the resin was 3.98, which is approximately 0.6 weight per cent below the maximum theoretical weight gain for this particular RVA sample. The resin impregnated 70 to 80 per cent of total pores and penetrated pores down to and including 0.10 micron diameter. The maximum theoretical weight gain, per cent pores impregnated, and penetration are calculated from the pore distribution of the sample, impregnation data, bulk densities of the resin and sample, and equation (2) Section 2.1.

Table 7. Weight Gain for Impregnated RVA

Resin	Original Density g/cc	Weight Gain per cent	300°C Cured Gain per cent	750°C Baked Gain per cent	Coke Yield per cent	Final Density g/cc
50 per cent GE-9						
50 per cent Furfural	1.878	3.98	2.84	2.27	57.2	1.913
Code 88	1.878	4.01	----	2.61	56.4	1.920
50 per cent Transphalt						
50 per cent Furfural	1.878	0.0	----	----	----	1.878



An impregnation comparison between this resin and Code 88 is presented in Table 8.

Table 8. Impregnation Results for Two Resins

Resin	Per Cent of Maximum Theoretical Weight Gain	Smallest Diameter Pores Penetrated
50 per cent GE-9		
50 per cent Furfural	88.4	0.10 Micron
Code 88	72.9	0.10 Micron

The per cent weight gain for this resin was nearer the maximum theoretical value than for Code 88. The per cent pores filled were slightly greater for the resin. The size of pores impregnated were the same for both impregnants. The per cent weight loss during the curing cycle (25°C to 300°C) is presented graphically in Figure 6, which clearly shows that the

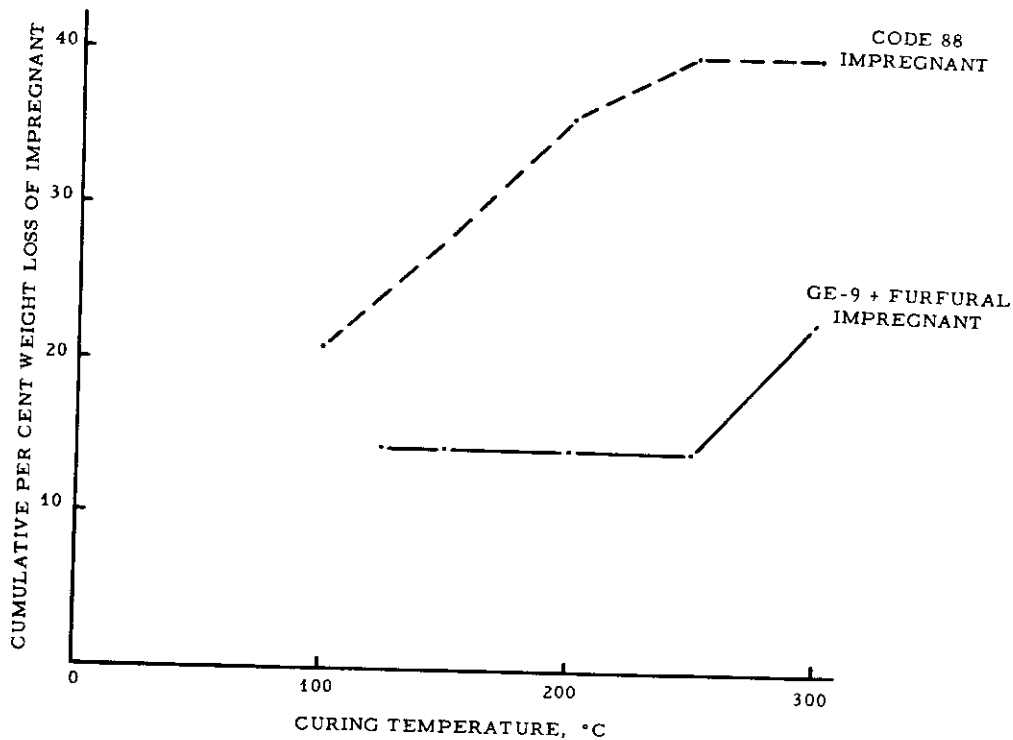


Figure 6. Cumulative Per Cent Weight Loss for Impregnants versus Curing Temperature

GE-9 resin produces less volatile evolution at the lower temperatures. A low volatile evolution during the curing cycle is a desired characteristic for impregnants, because it allows the impregnant to shrink, thereby providing pores for gas evolution at higher temperatures. The per cent coke yield after baking to 750°C was 57.2 per cent. The sample impregnated with Code 88 retained 56.4 per cent of the impregnant. A more typical coke yield for Code 88, however, is nearer 50 per cent. The bulk density for the sample containing GE-9 was 1.913 g/cc, which is an increase of about 2 per cent. The density of the sample impregnated with Code 88 was 1.920 g/cc or an increase of 2.2 per cent. No cracks or spalled portions were experienced on the samples containing GE-9 or Code 88.

GE-9 diluted with furfural appears to be at least as good an impregnant as Code 88. The possibility of this resin as an RVA impregnant looks encouraging.

No measurable weight gain was experienced with a solution of Transphalt and furfural. The stock impregnated was RVA with a bulk density of 1.878 g/cc. Three additional trials with this resin were also unsuccessful. The relatively higher viscosity of this resin would account for this behavior.

### 2.3. The Impregnation Process

The impregnation of carbon bodies with a coal tar pitch prior to graphitization is a process well known and used by all manufacturers of graphite. (27) The description of the process which follows applies primarily to the impregnation of graphite bodies for the purpose of substantially reducing the porosity and permeability below that attainable by pitch impregnation. Most of the factors affecting the success of this type of impregnation also apply to the initial pitch impregnation.

The impregnation process consists of the following steps:

- 1) The material to be impregnated is placed in an autoclave and subjected to a vacuum (usually  $\sim 0.5$  lbs/in<sup>2</sup> absolute for 2 - 3 hours) to remove gas from within the pores and adsorbed on the surface.
- 2) While maintaining the vacuum, the liquid impregnant is introduced into the autoclave, completely surrounding and covering the material to be impregnated.

- 3) A pressure ( $\sim 100 - 200$  lbs/in<sup>2</sup> gauge) is applied to drive the impregnant into the pores.
- 4) After a prescribed pressure period, as determined by the size and shape of the material being impregnated, the excess impregnant material is removed for additional processing.

Following this process, the actual impregnant pickup is compared to the theoretical pickup calculated from the available pore volume according to equation (3), Section 2.1. If these two values are not in close agreement, complete impregnation has not been achieved. Incomplete impregnation can result from a number of factors, the most common of which are (a) insufficient vacuum or non-removal of gas from the pores of the solid, (b) insufficient impregnation time or pressure for complete penetration, (c) suspended solids in the impregnant which can form a filter cake blocking flow into the porous material, and (d) chemical or physical degradation of the impregnant, such as increased viscosity, which would hinder flow.

#### 2.4. Heat Treatment After Impregnation

After impregnation with a carbonaceous material, the next step in the process is to heat treat the impregnated body to a temperature which will carbonize and/or graphitize the impregnant in the porous solid. Heat treatment is usually accomplished by covering the impregnated article with a granular packing material to protect it from oxidation and heating to carbonization and/or graphitization temperatures.

Upon heat treatment, thermoplastic impregnants of which coal tar pitch is a typical example, will decompose on the walls of the pores laying down a film of relatively low temperature carbon. A photomicrograph of a graphite impregnated with this type of material is shown in Figure 7. There is evidence of a refluxing action in the pores as the liquid phase is formed on the walls. The net effect of impregnation with a thermoplastic material is to decrease the size of the pores, and to increase the strength of the binder carbon. The time-temperature schedule for heating thermoplastic impregnants to carbonization temperatures may be constant over the range of volatile evolutions since there are no sharp exothermic or endothermic reactions occurring (see Figure 5.) The rate of temperature rise is adjusted only to permit the volatile gas to escape through the pores slowly enough to prevent disruption of the graphite.

Most of the coking impregnants useful for reducing the permeability of graphite are thermosetting resins. The effectiveness of such materials is due to the conversion of the hardened resin to coke without an inter-

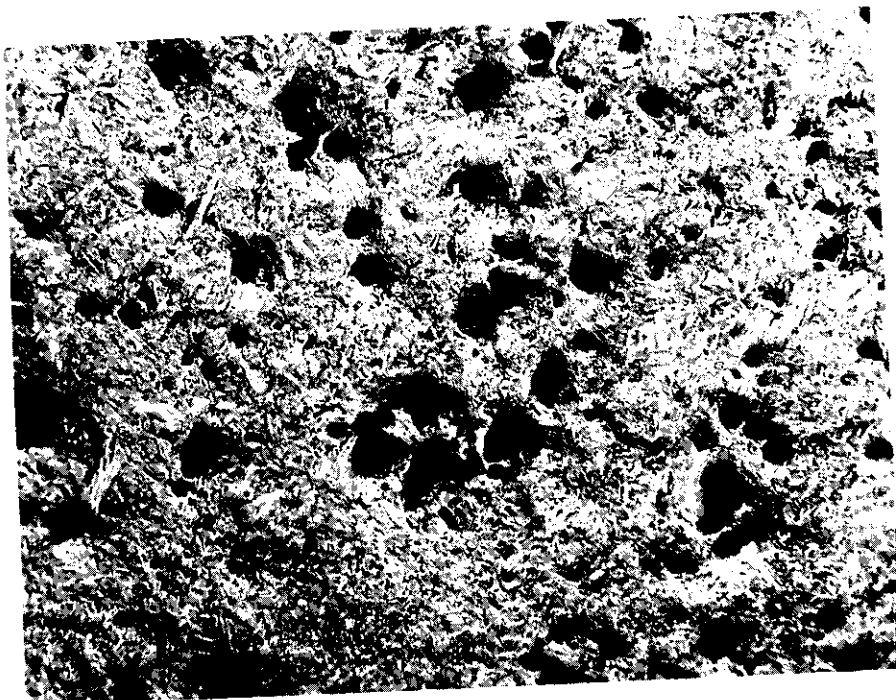


Figure 7. Photomicrograph of Pitch Impregnated Graphite, 100X

mediate softening or liquefaction. The mass of coke produced, therefore, has about the same shape as the thermoset resin from which it was made, and should be almost as effective as this resin in plugging up the pores, except for the shrinkage that it undergoes during coking. As a result, thermosetting impregnants are more effective in blocking pores as opposed to thermoplastics which tend to line pores. An example of this type impregnant is a coal tar pitch-furfural catalyst mixture that forms a non-graphitizable resin upon heat treatment. A photomicrograph of a graphite impregnated with this type of material and subjected to a carbonizing heat treatment is shown in Figure 8.

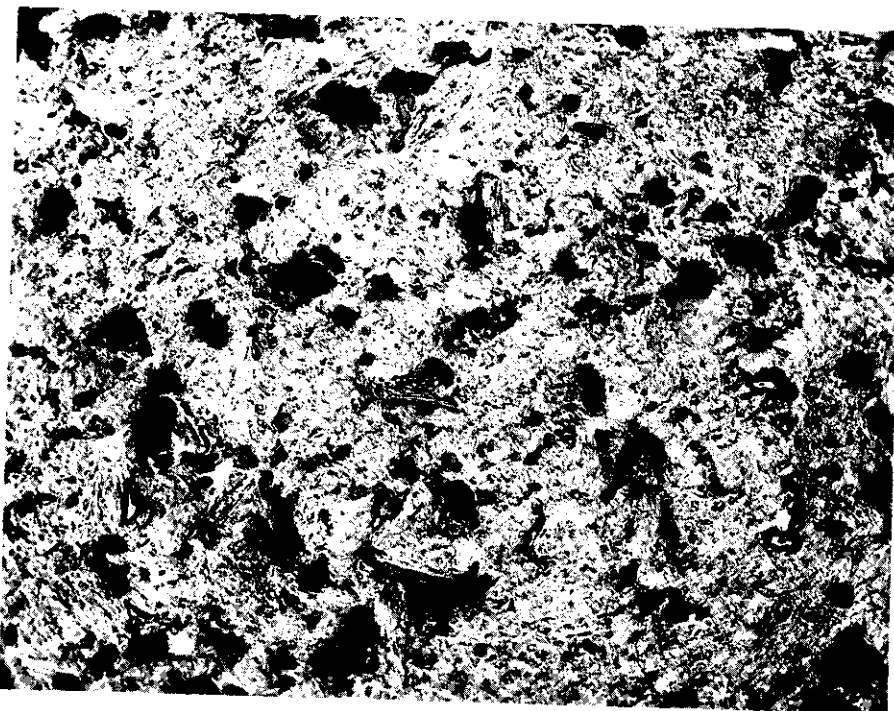


Figure 8. Photomicrograph of Graphite Impregnated with a Thermosetting Resin, 100X

Since the mass of thermoset impregnant may obstruct the pore opening, problems during heat treatment can arise due to pressure build-up in the closed pores upon volatilization of the lighter fractions of the impregnant. The gas evolution problem in heat treating thermosetting impregnants can be described by the following general observations.

At the beginning of the initial heat treating step; i. e., the thermosetting of the resin in the impregnated material, some impregnant will exude from the surface pores. This results in a "varnish" on the surface

of the graphite. Upon further polymerization, reaction products must diffuse through the partially blocked pores. If the rate of gas evolution is not controlled, excessive pressure within the pores can cause disruption of the impregnated material.

Normally in the heat treatment schedule for furan type resins, there is a hold period at approximately 100°C to allow water from the initial condensation reaction to escape slowly. The temperature is then increased slowly to a second exothermic peak when additional water and CO<sub>2</sub> is released from the breaking of the heterocyclic ring. This reaction occurs at 200° - 275°C, at which temperature another hold period is dictated. After this hold period the resultant polymer can be carbonized on a relatively fast temperature schedule without danger of disruption.

The tendency for disruption in any given temperature region of the heat treatment will depend not only on the amount of gas to be vented, but also on the ease with which it can escape. The permeability of the impregnated material is lowest after the impregnant has just thermoset, and gradually increases with temperature. The magnitudes involved are shown in Table 9. In this comparison grade CS graphite was impregnated with a coal tar pitch-furfural resin and heat treated at 100°C to thermoset the resin. This material was then baked and rebaked to successively higher temperatures, holding overnight at each temperature, and measuring weight loss and permeability after each bake.<sup>(28)</sup> Weight loss between room temperature and 100°C was not considered. Note that during the temperature range in which most of the volatile escape must take place, the material shows very low permeability; i.e., offers the greatest resistance to gas flow.

Table 9. Effect of Heat-Treatment Temperature on Weight Loss and Permeability of Impregnated CS Graphite.

Temperature °C	Cumulative Weight Loss, per cent	Relative Permeability to Air at 23°C
150	0.25	1
200	1.03	10
300	2.01	47
400	3.43	80
500	4.28	140
900	5.04	640

# *Contrails*

In summary, the principal factors which affect disruption of impregnated graphite during heat treatment are (a) the volume of gas generated during decomposition of the impregnant, (b) the resistance offered by the impregnated stock to the escape of the gas, and (c) the mechanical strength of the graphite matrix.

### 3. PHYSICAL PROPERTIES OF IMPREGNATED GRAPHITES

#### 3.1. Properties of Typical Single Pitch Impregnated Graphites

The physical properties of commercial graphite grades have been tabulated in available publications. (3, 4, 27) However, since it is not always clear from manufacturers' literature which grades are impregnated, the physical properties of grades AGSR and AGSX are given in Table 10 for direct comparison. These grades are identical except that grade AGSX has been pitch impregnated. These data clearly show the effect of a single pitch impregnation on the physical properties of graphite of different grain sizes. An improvement in properties (higher density, higher strength, etc.) is evident in all cases.

Table 10. Room Temperature Physical Properties of Grades AGSR and AGSX

Size	1-2 <sup>3</sup> / <sub>4</sub> in. Dia.		3-5 <sup>3</sup> / <sub>4</sub> in. Dia.		6 - 12 in. Dia.	
Grade	AGSR	AGSX	AGSR	AGSX	AGSR	AGSX
Max. Grain Size, in.	0.016	0.016	0.03	0.03	0.06	0.06
Bulk Density, g/cc	1.58	1.67	1.58	1.69	1.57	1.71
Specific Resistance, 10 <sup>-4</sup> ohm-cm	w. g. 8.39	7.99	8.64	8.21	8.85	8.20
	a. g. 15.00	13.30	12.80	13.90	11.10	10.10
Flexural Strength, lbs/in <sup>2</sup>	w. g. 2620	3100	2220	2710	1680	2370
	a. g. 980	1310	1430	1820	1250	1830
Tensile Strength, lbs/in <sup>2</sup>	w. g. 1090	1360	1100	1350	880	1320
	a. g. ----	----	760	1010	810	1170
Compressive Strength, lbs/in <sup>2</sup>	w. g. ----	----	4360	5640	3720	5180
	a. g. ----	----	3960	5260	3750	5180
Young's Modulus, 10 <sup>6</sup> lbs/in <sup>2</sup>	w. g. 1.45	1.75	1.57	1.62	1.16	1.53
	a. g. 0.65	0.79	0.77	0.93	0.76	1.02
Coefficient of Thermal Expansion, 10 <sup>-6</sup> /°C	w. g. 1.06	0.95	1.38	1.62	1.88	1.97
	a. g. ----	----	----	----	2.97	3.39
Thermal Conductivity, cal-cm/sec cm <sup>2</sup> °K	w. g. 0.370	0.388	0.357	0.377	0.351	0.378
	a. g. 0.207	0.233	0.243	0.223	0.279	0.306
Permeability, darcy's	w. g. ----	----	0.255	0.153	0.438	0.204
	a. g. ----	----	0.118	0.083	0.319	0.166

w. g. = with the grain  
a. g. = across the grain



## 3.2. Properties of Reimpregnated Graphites

It has been demonstrated in various tests, and will be discussed in Section 6 of this report, that the erosion rate of a graphite nozzle may be related to the porosity and permeability of the graphite. Grade ZTA graphite, one of the first grades developed specifically for application in rocket nozzles, has low porosity and permeability as a result of its processing; however, the present state of the art limits the size of ZTA to relatively small diameters (24 inches). In view of the fact that there is also a need for large graphite sections which exhibit low porosity, low permeability, and high strength for application in large, solid propellant rocket motors, attention has been given to grades ATL and RVA as base materials for impregnation. Grade ATL is molded graphite, currently available in sizes up to 60 inches in diameter and its properties and uniformity are typical of commercial graphites in this size range. Grade RVA is a premium quality molded graphite, currently available in sizes up to 30-inch diameter and its properties and uniformity are superior to any known graphite in this size range. Both grades are capable of being scaled up to larger sizes as the needs arise. Out of the work on the impregnation of these materials, two new grades - CFW and CFZ - have been developed, primarily for large rocket nozzle applications.

Grade CFW is processed by impregnating grade ATL with plasticized pitch impregnant and carbonizing the impregnant as described in the preceding sections. Grade CFZ is the impregnated version of grade RVA, processed in the same manner. The advantages of grade CFZ are greater uniformity of physical properties and lower permeability. Table 11 gives typical physical properties of grades CFW and CFZ along with those of grades ATL and RVA for comparison.

Table 11. Typical Room Temperature Physical Properties of Grades ATL, CFW, RVA and CFZ

Grade		ATL	CFW	RVA	CFZ
Bulk Density, g/cc		1.78	1.88	1.85	1.91
Specific Resistance, $10^{-4}$ ohm-cm	w. g.	11.30	11.60	12.00	12.00
	a. g.	11.80	12.30	15.00	15.00
Flexural Strength, lbs/in <sup>2</sup>	w. g.	2190	2750	3500	3800
	a. g.	2410	2740	2900	3300
Young's Modulus, $10^6$ lbs/in <sup>2</sup>	w. g.	1.28	1.55	1.67	1.75
	a. g.	1.24	1.41	1.28	1.40
Coefficient of Thermal Expansion, $10^{-6}/^{\circ}\text{C}$ Mean 30-100 $^{\circ}\text{C}$	w. g.	2.3	2.6	1.9	2.0
	a. g.	2.4	2.8	2.7	2.8
Permeability, darcy's	w. g.	0.068	0.004	0.0005	0.00001
	a. g.	0.064	0.004	0.0004	0.00001

w. g. = with the grain  
a. g. = across the grain

Figure 9 shows the porosimetry of the above four grades. The lower pore volume and the smaller pores of CFZ compared to CFW are evident from the curves in Figure 9 and from photomicrographs of the two materials. Figure 10 shows the microstructure of these grades at 100X. It is evident in both photomicrographs that the impregnant carbon has shrunk away from the pore walls. The impregnant carbon is the white material in the dark areas (pores).

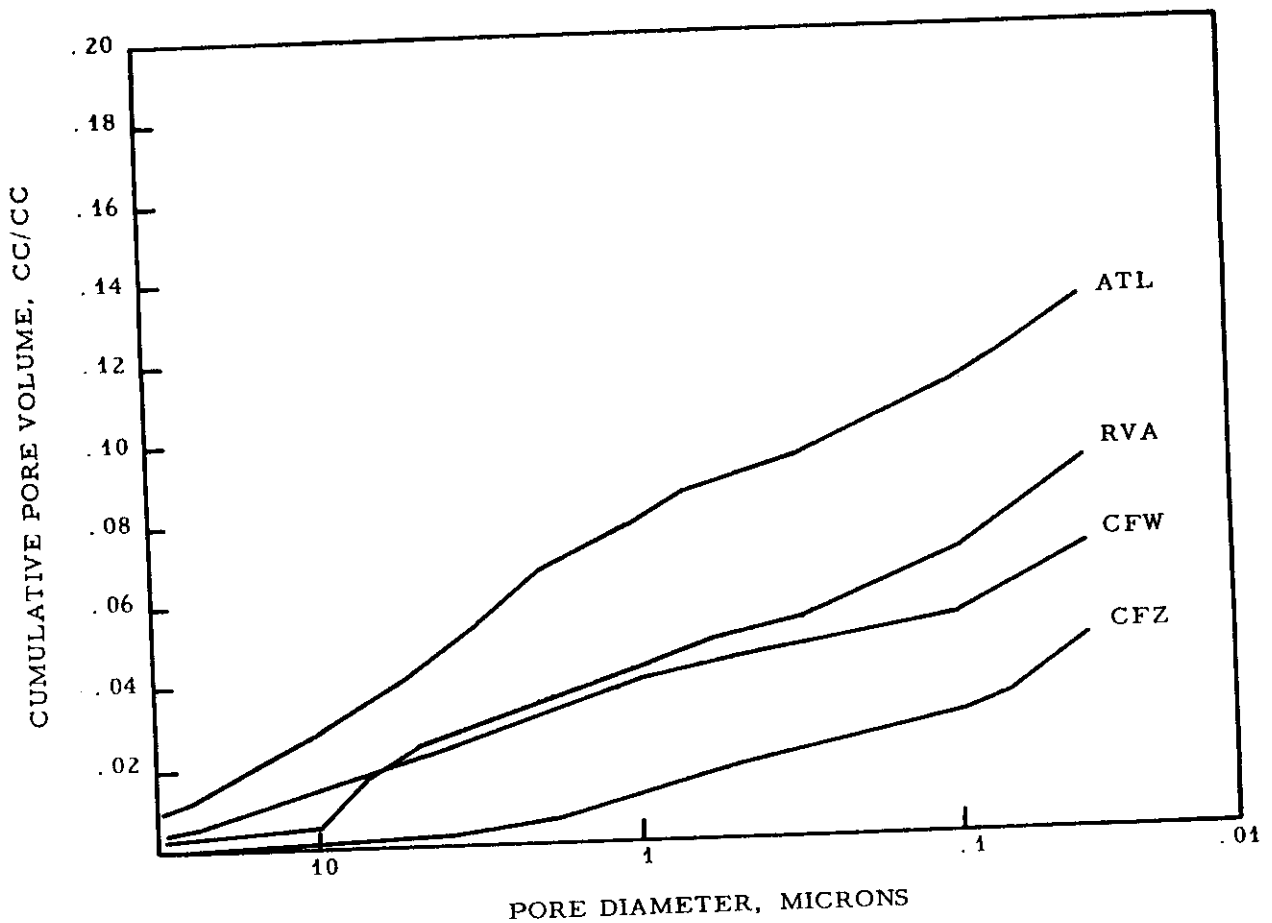


Figure 9. Cumulative Pore Volume versus Pore Diameter for Grades ATL, CFW, RVA and CFZ



Grade CFW



Grade CFZ

Figure 10. Photomicrographs of Grades CFW and CFZ, 100X

## 4. THE EFFECTS OF PRIOR BAKING TEMPERATURE ON SUBSEQUENT IMPREGNATIONS

In a conventional processing sequence for molded stock, the article is formed, baked to approximately 650°C, impregnated with coal tar, rebaked to 900°C, reimpregnated with coal tar, and graphitized (2800°C). The goal of the effort herein reported was to determine what effect baking temperatures and subsequent impregnation would have on the structural integrity of the green formed article. For purposes of this report, the material under investigation is identified as NS-4.

A number of samples were cut from NS-4 stock, to approximately 1 inch by 1 inch by 4 inches in length. These samples were baked at 10°/hr to 1000°C. At 100°C intervals, beginning at a temperature above the forming temperature (85°C) a specimen was removed and the change in volume and weight measured. The purpose of this baking series was to study what effect baking temperatures had on the pore distribution and volume changes for NS-4. From this data the optimum temperature could be determined for subsequent impregnations with a solution of coal tar pitch and furfural.

Percentage weight and volume change versus baking temperature is plotted in Figure 11. The curves in this plot were constructed from

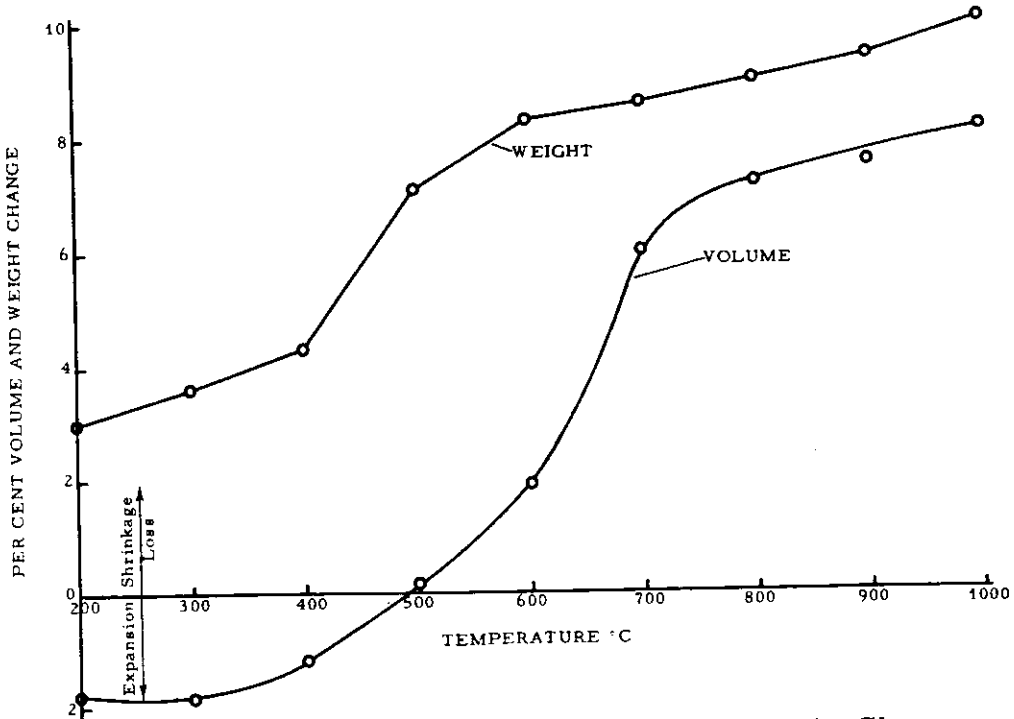


Figure 11. NS-4, Per Cent Volume and Weight Change versus Baking Temperature

the values in Tables 12 and 13. The volume expansion at the lower temperatures would account for poor baking yields. If the temperature gradients within a piece of graphite are great, the volume expansion at these low temperatures will in all probability result in cracks. The shape of this suggests that a lower formed density (lower molding pressure) might be advantageous. High molding pressures will cause the formed piece to spring back or expand upon annealing.

Table 12. NS-4, Volume Change at Various Baking Temperatures

Sample No.	Baking Temp. °C	Initial Vol. cc	Final Vol. cc	Per Cent $\Delta V$
Y-3	200	109.81	111.81	+ 1.82
Y-5	300	106.43	108.43	+ 1.87
Y-12	400	111.43	109.85	+ 1.24
Y-10	500	114.68	114.51	- 0.15
Y-7	600	111.60	109.53	- 1.85
Y-14	700	109.34	102.00	- 6.09
Y-16	800	103.90	93.66	- 7.08
Y-9	900	108.63	100.37	- 7.60
Y-2	1000	109.10	100.80	- 8.24

Table 13. NS-4, Weight Loss at Various Baking Temperatures

Sample No.	Baking Temp. °C	Initial Wt. cc	Final Wt. g/cc	Per Cent $\Delta W$
Y-3	200	178.60	173.29	2.97
Y-5	300	175.01	168.02	3.65
Y-12	400	175.98	168.30	4.36
Y-10	500	188.08	174.72	7.10
Y-7	600	186.31	170.90	8.27
Y-14	700	177.32	161.94	8.67
Y-16	800	159.75	147.51	9.19
Y-9	900	178.63	161.75	9.45
Y-2	1000	177.15	159.35	10.05

It might, therefore, be more desirable to form the piece with a lower green (unbaked) bulk density. This would have the effect of moving the whole volume curve in Figure 11 above the horizontal axis while still maintaining the general shape.

The percentages of weight gained following impregnation of the samples are tabulated in Table 14. The per cent weight gain for the 500°C baked samples was very similar to that of the 700°C baked sample. It was postulated at this time, since both samples had the same weight gain, that the increase in strength would be appreciable if the stock was initially baked to 500°C, impregnated and rebaked to 950°C as opposed to a 700°C first bake. The advantage being that the stock and impregnant would shrink simultaneously.

Table 14. Impregnated NS-4, Weight Gain and Density

Sample No.	Baking Temp. °C	R. T. Weight Gain Per Cent	250°C Weight Gain Per Cent	950°C Rebake Density
Y-3	200	10.13	5.72	Cracked
Y-5	300	10.82	6.24	Cracked
Y-12	400	12.52	7.16	Cracked
Y-10	500	14.78	10.94	1.760
Y-7	600	14.21	11.10	1.760
Y-14	700	14.80	10.84	1.743
Y-16	800	16.51	12.93	1.752
Y-9	900	13.90	10.78	1.745

The volumes after impregnating and rebaking to 950°C are plotted in Figure 12 as per cent volume shrinkage versus initial baking temperatures. The samples which were subjected to the lowest initial bake experienced the greatest shrinkage as expected from the plot of Figure 11.

The pore distribution curves for the five samples are plotted in Figure 13. The data used in plotting the curves were also used to determine the available porosity of the samples. The available porosity is significant, because of a subsequent second impregnation. It was therefore necessary to determine whether the most promising baking temperature; i. e., 500°C, would have an available porosity at least as good as the other four samples. The available porosity is actually the quotient of the displaced volume (as measured by mercury porosimetry) divided by the geometrical volume. The available porosity is expressed as a percentage of the sample volume in Table 15. Fortunately, the 500°C sample had an available porosity nearly equal to the maximum porosity measured; consequently, this particular sample should be as susceptible to subsequent impregnations as the samples baked to higher initial

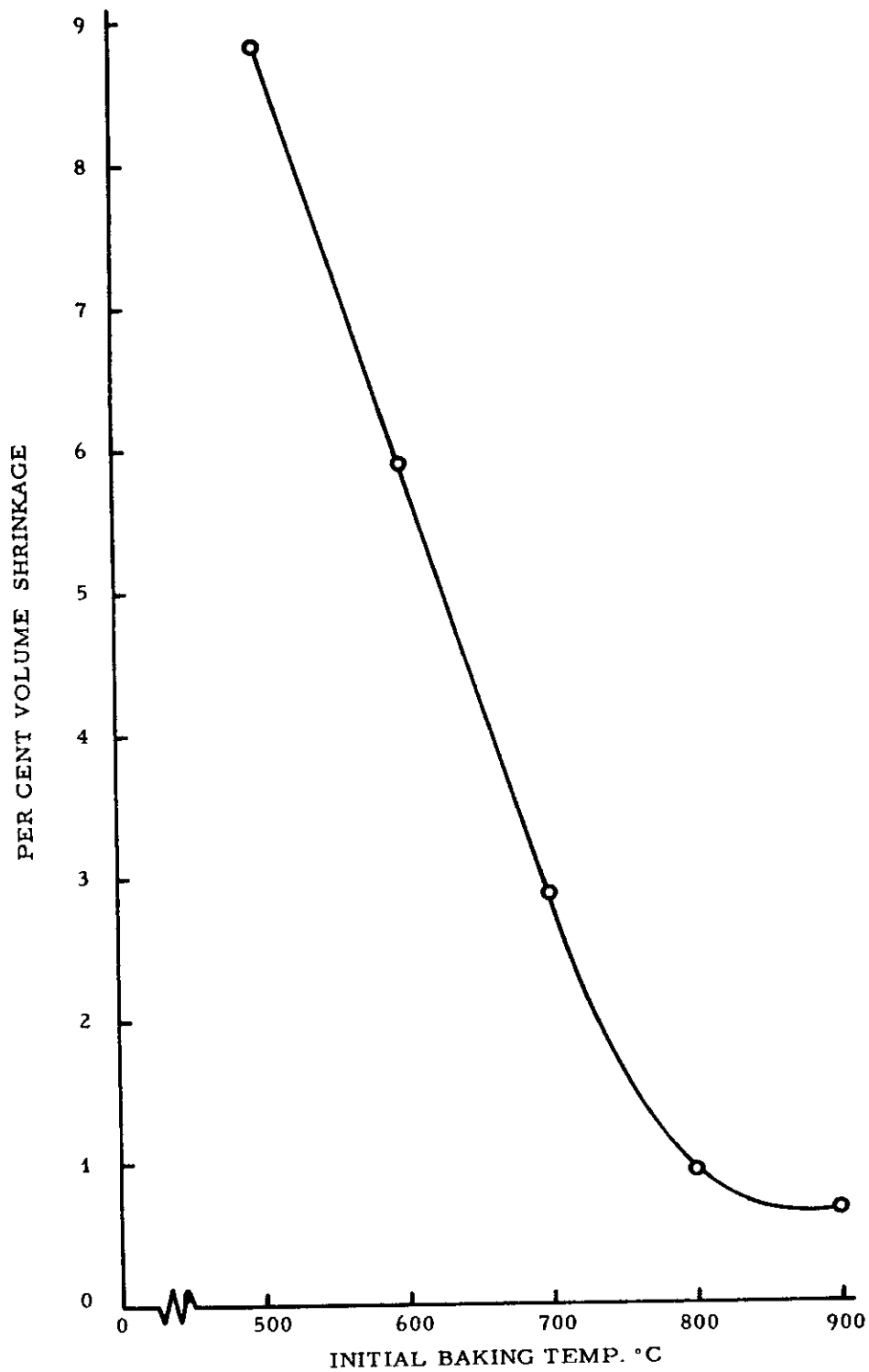


Figure 12. Impregnated NS-4, Per Cent Volume Shrinkage versus Initial Baking Temperature

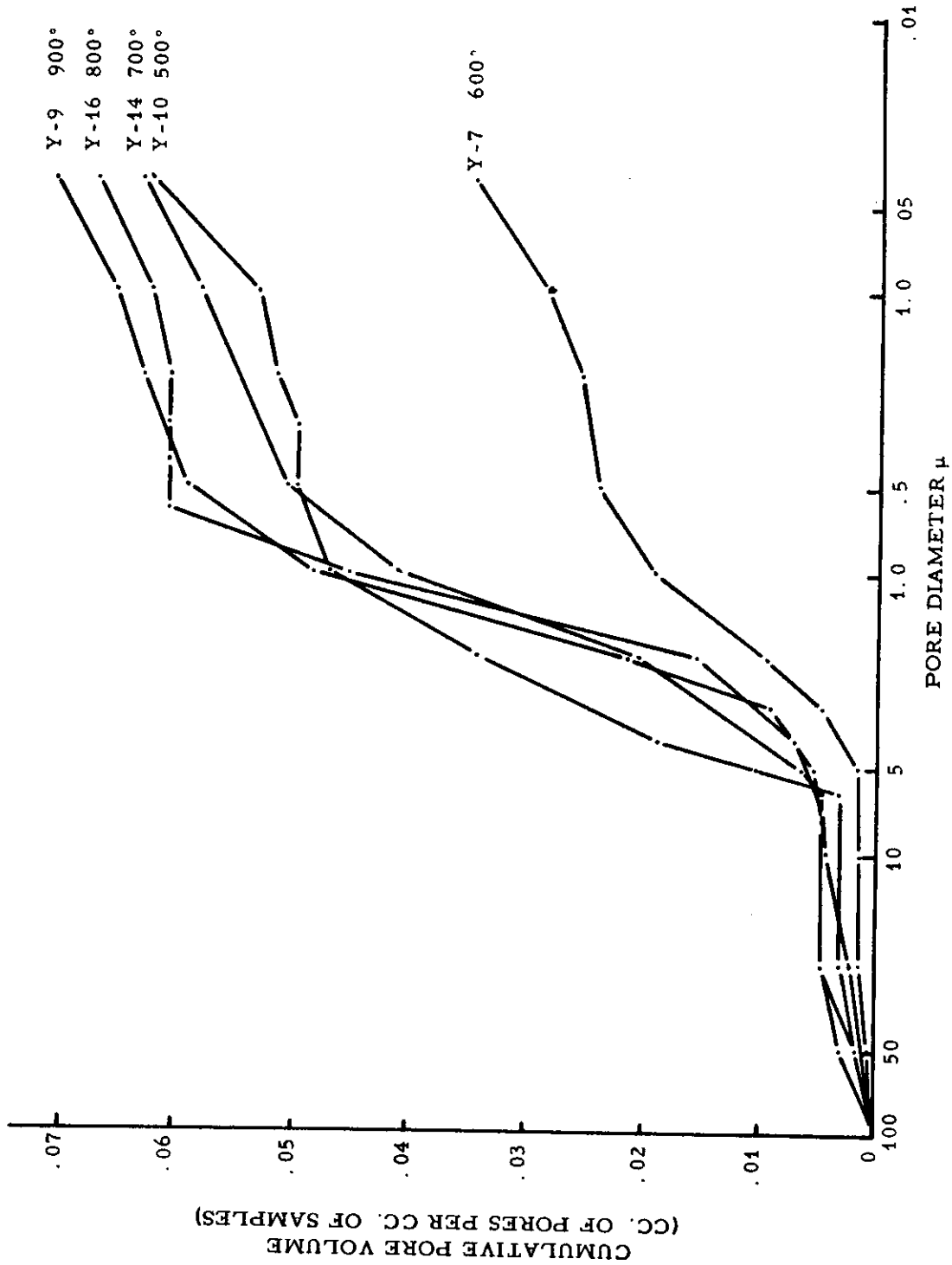


Figure 13. Pore Distribution for Impregnated and Rebaked NS-4



temperatures.

Table 15. Percentage Available Porosity of Impregnated NS-4

Sample No.	Baking Temp. °C	No. of Treats	Rebake Temp. °C	Per Cent Available Porosity/cc of Sample
Y-10	500	1	950	15.50
Y-7	600	1	950	9.00
Y-14	700	1	950	16.00
Y-16	800	1	950	16.50
Y-9	900	1	950	16.50

Flexural strengths for the samples were encouraging. Table 16 lists the results for the 500°C baked sample and the 900°C baked sample. The sample which was baked to the lower initial temperature experienced a much greater strength as was predicted.

Table 16. Flexural Strengths for Impregnated NS-4

Sample No.	N	Initial Baking Temp. °C	No. of Treats	Flexural* Strength lbs/in <sup>2</sup>
Y-9	1	900°C	1	7703
Y-10	1	500°C	1	9690

\* Note: Sample size 3/8 inch by 3/8 inch by 3 inches, 3rd point loading; 2/1 span

These encouraging results prompted an investigation with larger sizes; specifically, two 6-inch cubes. Both pieces were baked to 500°C, Code 88 impregnated and rebaked to 950°C. The baked bulk density, per cent volume shrinkage and per cent weight loss were measured following the 500°C bake and are tabulated in Tables 17 and 18. Each piece underwent essentially the same weight loss and volume change after baking as the smaller size samples previously discussed.

Table 17. Bulk Density for NS-4 Baked to 500°C

Sample No.	Initial Baking Temp. °C	Formed B. D. g/cc	Baked B. D. g/cc
1	500	1.57	1.41
4	500	1.59	1.43

Table 18. Per Cent Volume and Weight Change, NS-4 Baked to 500°C

Sample No.	Volume Shrinkage Per Cent	Weight Loss Per Cent
1	0.07	10.18
4	0.38	9.98

The densities and flexural strengths for the two pieces following a Code 88 impregnation and rebake are recorded in Tables 19 and 20, respectively. The fact that Sample 4 had a higher strength can be explained by the higher density for this sample. The strengths are not as great as those reported earlier in the report for the smaller size samples, but this is due to the difference in size of the specimen during testing. It is probable, from data taken on the smaller size samples, that these high strengths are the result of the impregnant and stock shrinking simultaneously. Another possible explanation as to why the strengths were so high can be given by examining photomicrographs of the impregnated pieces. A thermosetting resin will polymerize upon heating and leave

Table 19. Bulk Density for Impregnated NS-4

Sample No.	Initial Baking Temp. °C	No. of Treats	Rebake Temp. °C	B. D. g/cc
1	500	1	950	1.68
4	500	1	950	1.75

a residue of coke, which is commonly called "coking-out". However, past experience in impregnating with a thermosetting resin has shown the resin to "coke-out" in the graphite matrix while shrinking away from the surface. Figure 14 is a 250X magnification of graphite after two impregnations with a thermosetting resin. Notice that the impregnant,

Table 20. Flexural Strengths for Impregnated NS-4

Sample No.	Flexural Strength* lbs/in <sup>2</sup>	
1	6009	
2	5075	
3	4308	
4	5436	
5	5461	
6	5351	
7	5293	Sample Cut from Piece No. 1
8	5750	
9	5723	
10	5184	
11	5573	
12	5127	
13	5144	
14	5078	
	Average	
	Std. Dev.	
	±393	
1	6422	
2	6171	
3	6050	
4	6476	
5	5763	
6	6465	
7	6299	Sample Cut from Piece No. 4
8	6358	
9	6325	
10	6685	
11	6145	
12	6461	
13	5337	
14	6219	
	Average	
	Std. Dev.	
	±328	

\* Note: Sample size 1/2 by 1/2 by 5 inches; Single point loading  
3-inch span

the smooth light gray portions, is not attached to the graphite, except at a very few points. However, a 250X magnification of NS-4, which had a 500°C bake, Code 88 impregnation and 950°C rebake, produced quite a different picture. The impregnant has actually attached itself to the carbon surfaces. Whether or not the impregnant can actually bond itself to a carbon surface (NS-4, Figure 15), but not to graphite (Figure 14) is not known, but this phenomenon could certainly account for the high strengths. Additional photomicrographs (Figures 16 and 17) of impregnated NS-4 eliminates any chance of this phenomenon being coincidental.

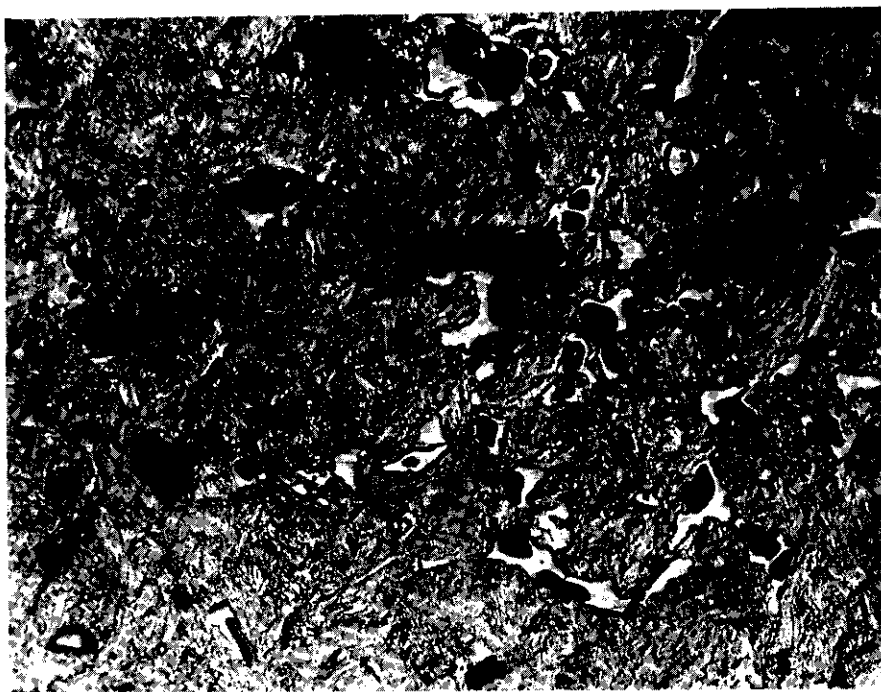


Figure 14. Graphite after Two Impregnations with Thermosetting Resin, 250X

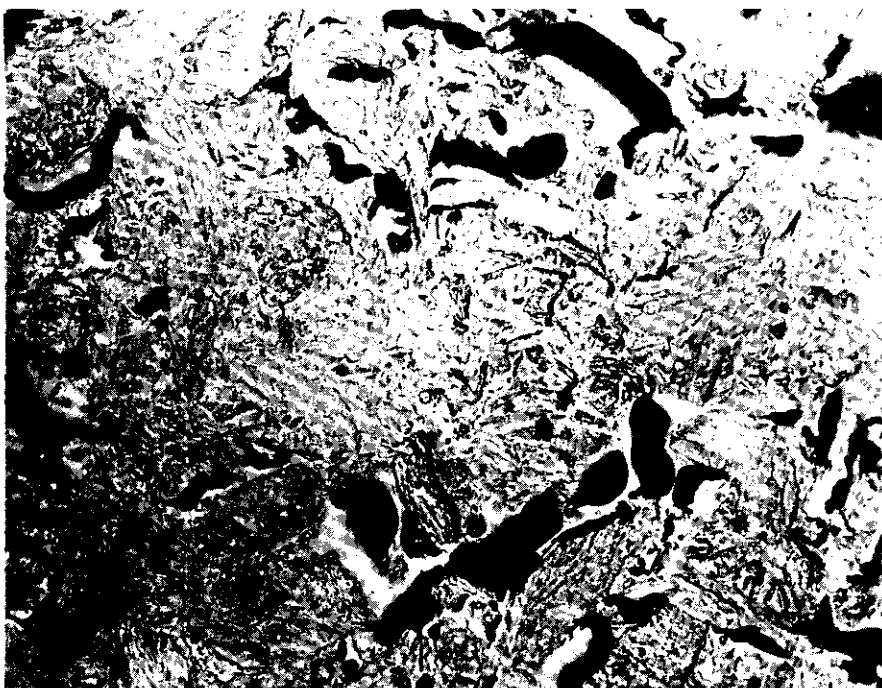


Figure 15. NS-4 after One Impregnation with Thermosetting Resin, 250X

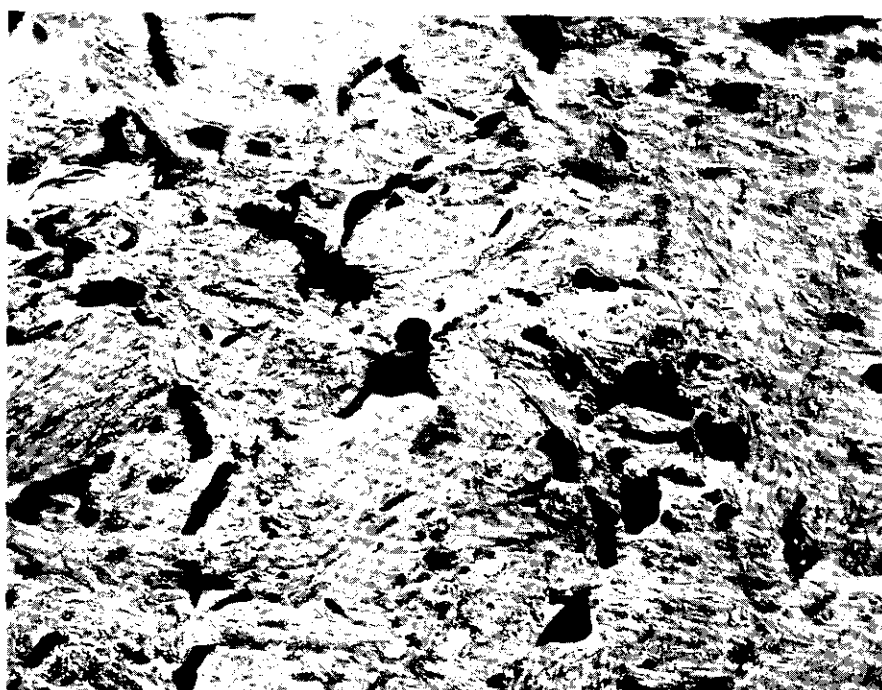


Figure 16. NS-4, Block 1, after One Impregnation with Thermosetting Resin, 250X

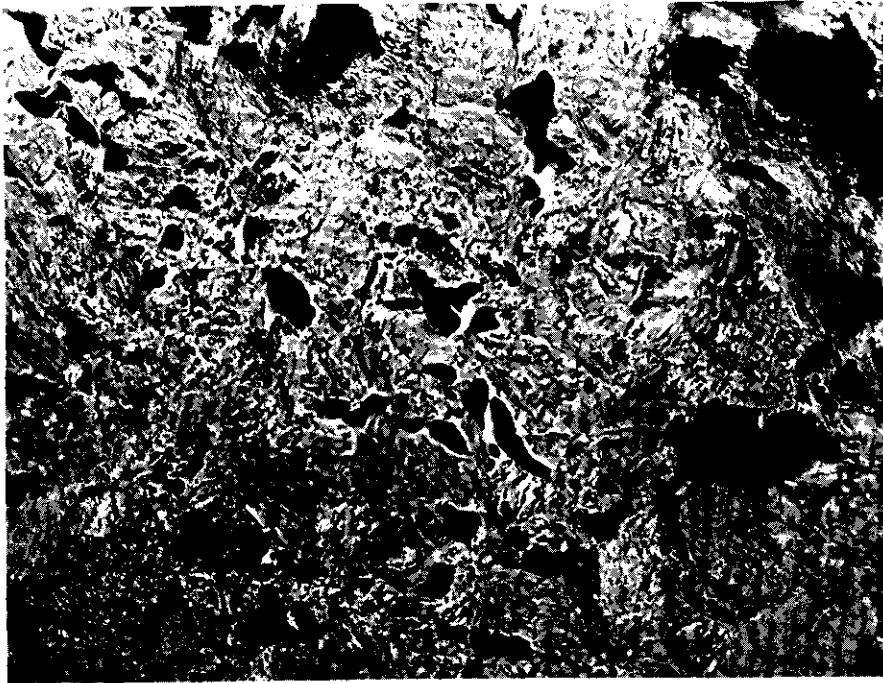


Figure 17. NS-4, Block 2, after One Impregnation with Thermosetting Resin, 250X

The results of this development program supports the theory of an existing threshold density level reported for certain molded grades. Also, from the data collected, an initial baking temperature of 500°C, followed by an impregnation and a 950°C rebake would improve flexural strengths.

## 5. IMPREGNATION OF RVA GRAPHITE WITH CODE 88

An impregnation of RVA with Code 88 produced grade CFZ graphite which performed favorably as a rocket nozzle. The erosion rate for the nozzle was 0.53 mils/second. Only the ZT grades and TS-391 had lower erosion rates when fired under the same conditions as the CFZ graphite. (29)

Conventional impregnating procedures were initially tried when impregnating RVA; however, numerous Code 88 impregnations on RVA using this method met with little success. The maximum RVA size which could be successfully impregnated was about 4 inches in diameter.

Therefore, a series of impregnating trials was performed to determine a method for successfully impregnating RVA with Code 88.

One piece of RVA with a density of 1.87 g/cc was machined to 15 inches in diameter by 35 inches in length and conventionally Code 88 impregnated. The weight gain was 3.8 per cent. The heat treatment (250°C) of the impregnant was performed in a heater which utilizes forced air. The heater is commonly called a preheater. The curing cycle once again produced scrap, as evidenced in Figure 18. A density



Figure 18. Code 88 Impregnated and Cured (250°C) RVA

traverse, Table 21, of a salvaged sample dismissed any possibility of the stock cracking due to a "dry core" which is the term used to describe incomplete impregnant penetration. A dry core can cause stress gradients to develop during heat treatment.

Table 21. Density Traverse of Code 88 Impregnated RVA

Specimen No.	Location of Specimen	Density, g/cc
1	Edge	1.93
2		1.94
3		1.92
4		1.93
5		1.92
6		1.92
7		1.91
8	Center	1.91
9		1.91
10		1.91
11		1.92
12		1.92
13		1.94
14	Edge	1.92
15	Edge	1.92
16		1.93
17		1.93
18		1.91
19		1.92
20		1.92
21	Center	1.91
22		1.92
23		1.92
24		1.91
25		1.92
26	Edge	1.90

Another 15-inch diameter by 35-inch length piece of RVA was Code 88 impregnated. This particular piece was machined from the same piece as the 15-inch diameter piece previously mentioned. The stock, following the impregnation, was cut radially in half. Both pieces were then cured to a maximum temperature of 250°C, but in the absence of air. Both pieces came out of the cure in good condition. This was encouraging, because it was the first time that impregnated RVA of this



size had survived the cure. One of the two was then baked at 10°/hr to 850°C and the one remaining at 5°/hr to 850°C. The one subjected to the higher heating rate cracked as shown in Figure 19. The other piece was in good condition. The bulk density was 1.915 g/cc, which is within the range desired for grade CFZ.

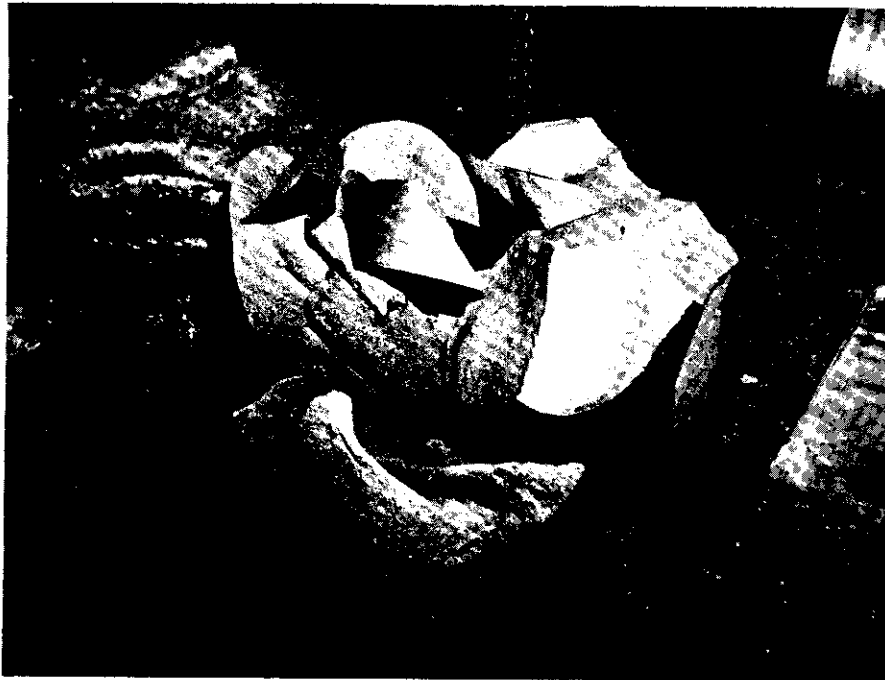


Figure 19. Code 88 Impregnated and Baked (750°C) RVA

Curing in the absence of air was done because low temperature (250°C) oxidation of the impregnant was suspected. Oxidation will have the effect of producing a greater coking value at the surface and thus increase the shrinkage at this point. It was this variance in shrinkage, from the surface of the stock to the center, that was suspected of causing the curing and baking cracks.

A piece of RVA 31 inches in diameter was secured for additional impregnation trials. Three separate approaches were tried on pieces cut from the 31-inch diameter RVA. The piece was cut as presented in Figure 20. Piece No. 1 was pitch impregnated. Number 2-A was impregnated with Code 88, cured in the absence of air and baked at 5°/hr to 850°C. Number 2-B was impregnated with an impregnant made from coal tar pitch, furfural, and dead oil.

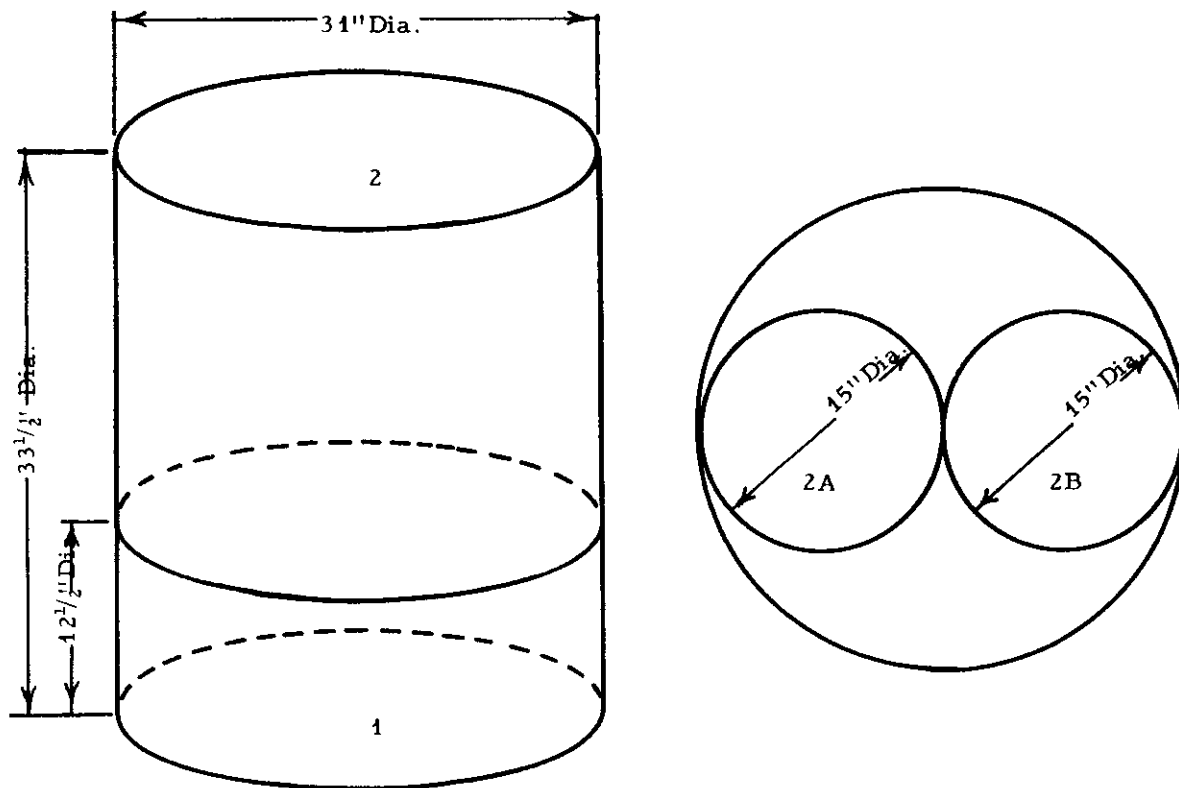


Figure 20. Sectioning 31-Inch Diameter RVA for Impregnation

The pitch impregnation was unsuccessful. The pitch raised the overall bulk density from 1.870 g/cc to 1.898 g/cc, but the increase in density was the result of a dense region on the outer four inches of the piece. In other words, a dry core was experienced. The density traverse is presented in Table 22. The high viscosity and free carbon (carbon

particles suspended in the pitch) content of the pitch prevents it from penetrating fine grain, high density material such as grade RVA graphite.

Table 22. Density Traverse of Pitch Impregnated RVA

Specimen No.	Location of Specimen	Bulk Density, g/cc
1	Edge	1.90
2		1.90
3		1.89
4		1.87
5		1.87
6		1.88
7		1.88
8	Center	1.88
85		1.88
86		1.88
87		1.88
88		1.88
89		1.88
90		1.88
91		1.90
92	Edge	1.92

Piece 2-A was a follow-up on the assumption that curing in the presence of oxygen was responsible for the difficulty in producing CFZ. This particular piece was Code 88 impregnated and cured in a sagger packed with soft charcoal and coke. The charcoal was used because it is an excellent oxygen scavenger.

The curing schedule was as follows:

R. T. to 125°C at 100°/hr; hold 24 hours.  
125°C to 175°C at 100°/hr; hold 48 hours.  
175°C to 200°C at 100°/hr; hold 24 hours.  
200°C to 225°C at 100°/hr; hold 24 hours.  
225°C to 250°C at 100°/hr; hold 24 hours.  
250°C to R. T.

A visual examination of the piece at this time showed it to be in good condition. The piece was again packed as before and baked 5°/hr. to 850°C. The structure of the stock was excellent following the bake. The bulk density was 1.910 g/cc.

# Contrails

Piece 2-B was impregnated with the coal tar pitch, furfural and dead oil mixture. Dead oil is a residual by-product of manufacturing tar. The ratio of pitch to dead oil to furfural was 1:1:2 by weight. Dead oil has no coking value; i. e. , no coke residue will be formed by heating to elevated temperatures. Dead oil will boil at 200°C, consequently, the oil will volatilize completely during the curing cycle, leaving pores within the stock and increasing bakeability.

After impregnating, the impregnant was cured in a preheater using the exact heating schedule as piece 2-A. The curing produced very severe spalling as evidenced by Figure 21. Because of the extent of the spalling, it was postulated that the impregnant resin had partially polymerized before the dead oil had completely volatilized. Five additional trials were made using impregnants diluted with dead oil. This time the amount of dead oil was reduced to 20 per cent by weight of the pitch-furfural. The curing was performed in an inert atmosphere. However, severe spalling still existed and no further trials were made with dead oil.



Figure 21. Cured (125°C) RVA Impregnated with Pitch, Furfural, and Dead Oil

# Contrails

Every effort failed to produce CFZ, except the method of curing Code 88 in an inert atmosphere. This method has been tried three times on 15-inch diameter stock and was successful each time. It was now obvious that the curing of Code 88 impregnated RVA would need to be done in a non-oxidizing atmosphere and that the curing and baking cycles would need to be closely controlled.

A piece of RVA 27 inches in diameter, the largest diameter the available impregnating facilities could conveniently handle, was Code 88 impregnated. The piece was cured according to the previously given heating rate, but the protective pack contained coke only. The piece cracked as evidenced by Figure 22. Ensuing trials using charcoal in the pack and as an oxygen scavenger resulted in the successful processing of two pieces.

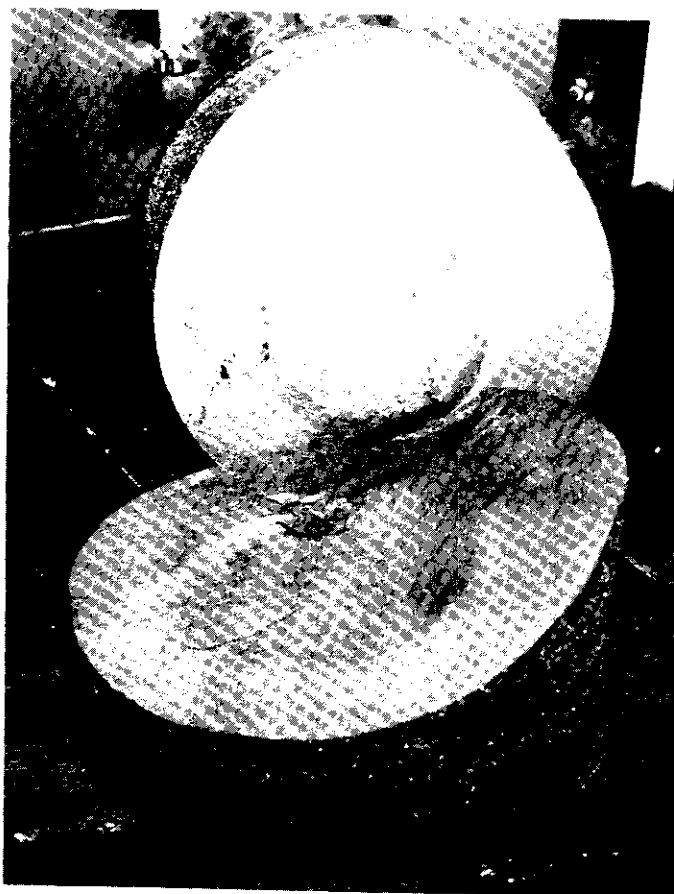


Figure 22. Code 88 Impregnated and Baked RVA

6. RELATIONSHIP OF PROPERTIES TO PERFORMANCE  
IN SOLID PROPELLANT TEST MOTORS

Evaluation of impregnated graphite materials includes testing as nozzle inserts in a subscale static rocket motor. Parameters affecting performance of an insert other than properties of the insert material, are (a) type of propellant, (b) chamber pressure, (c) nozzle design, and (d) back-up material. These parameters were held constant so that performance as a function of material properties could be evaluated.

A solid propellant manufactured by Atlantic Research Corporation, Arcite 373D, was used throughout the evaluation. This is a slightly oxidizing propellant having a theoretical flame temperature of 5600°F.

Figure 23 shows the design of the insert and exit cone, and Figure 24 the entire nozzle assembly. A throat diameter of 0.535

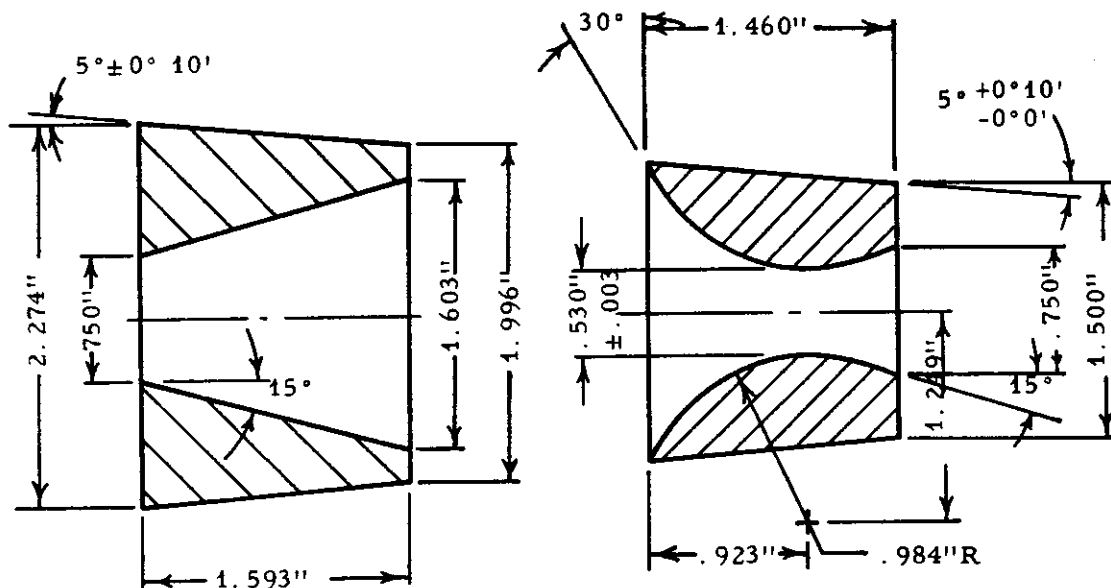


Figure 23. Graphite Nozzle Insert and Expansion Cone for National Carbon Company Test Motor

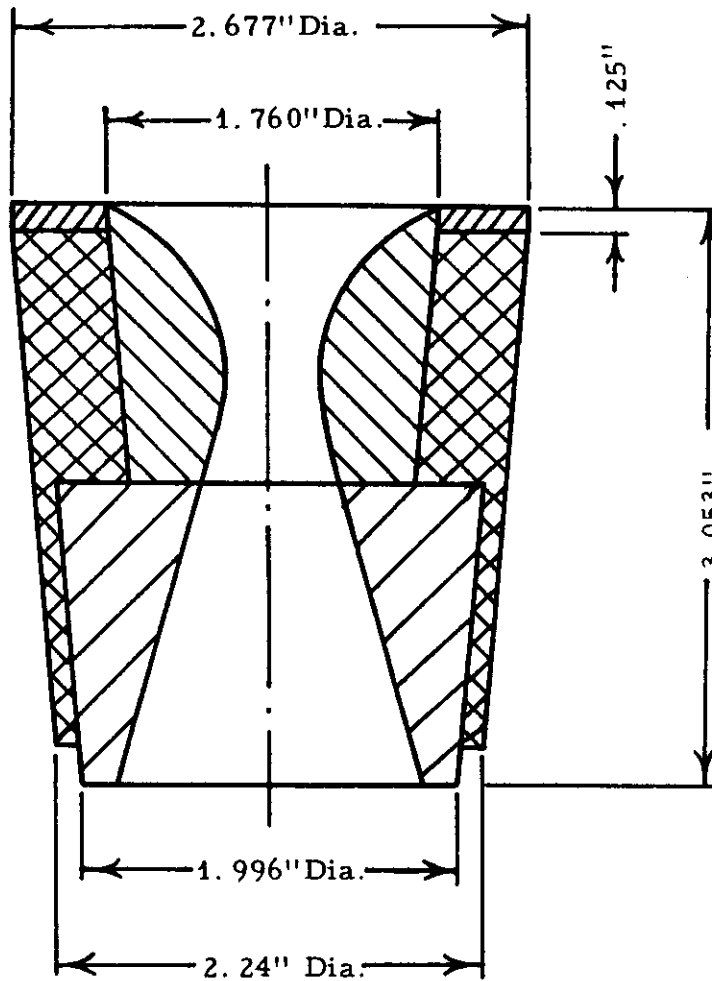


Figure 24. Graphite Nozzle Insert and Back-up Assembly for Test Motor

inch was used with all cured propellant grains, and a diameter of 0.485 inch with all uncured propellant grains in order to obtain a maximum equilibrium chamber pressure of approximately 1000 lbs/in<sup>2</sup>. Under this condition a thrust of approximately 300 lbs/sec was produced. The nozzle insert back-up material was zirconium oxide (ZrO<sub>2</sub>) for all tests.

Criteria for determining the suitability of a graphite grade as a nozzle insert material are (a) the erosion rate of the material, and (b) the ability of the material to withstand thermal shock during firing. Firings of 12 to 75 seconds duration were used for the materials evaluation. Figure 25 shows the general shape of the chamber pressure-time curve with the height of the curve exaggerated. In Figure 25,  $t_c$  is the time at which the propellant ignites,  $t_e$  the time at which the

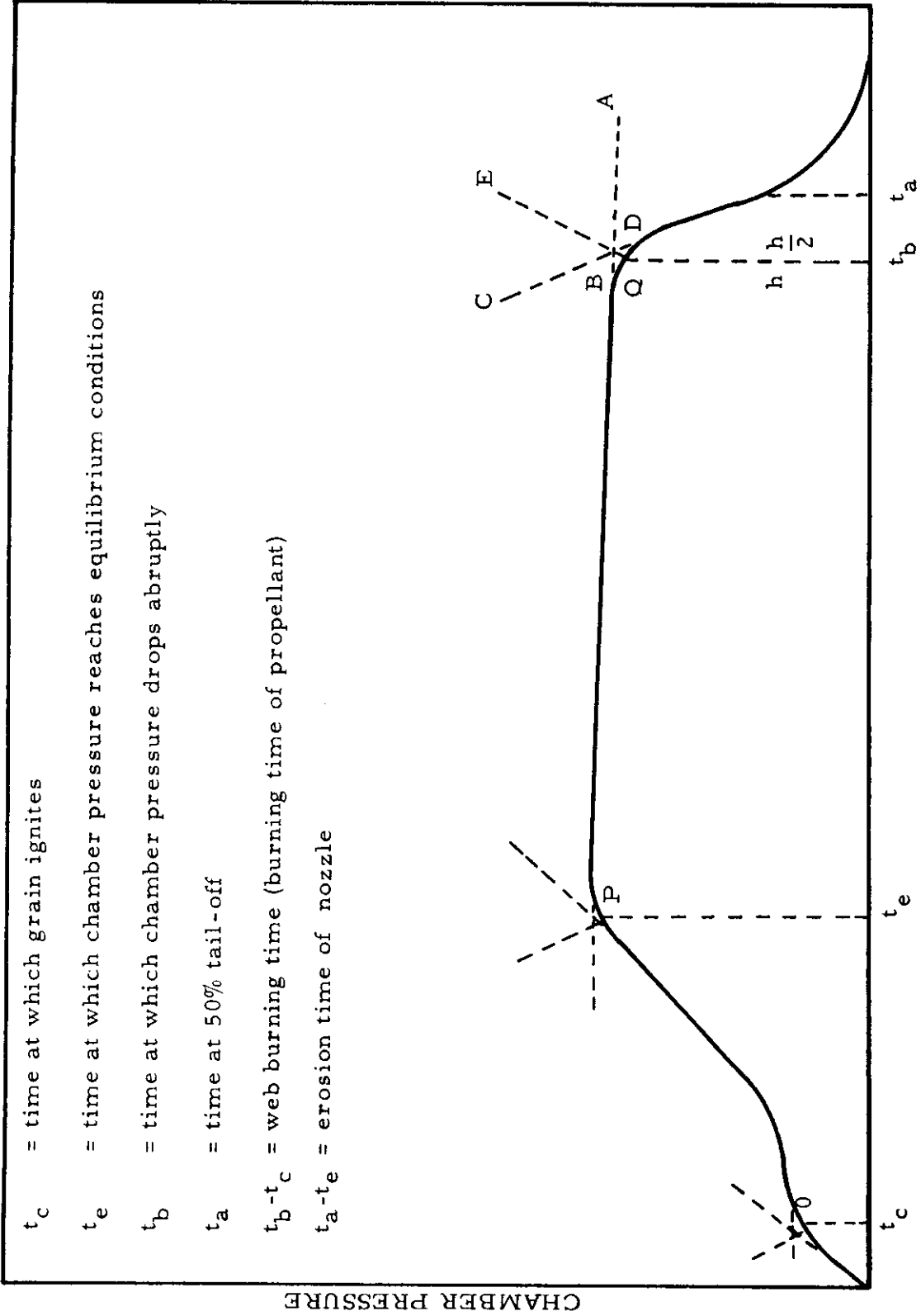


Figure 25. Chamber Pressure versus Time, Solid Propellant Rocket Test Motor



the chamber pressure reaches equilibrium,  $t_b$  the time at which the chamber pressure begins to drop abruptly, and  $t_a$  the time at 50 per cent tail-off; i. e., the time at which the chamber pressure becomes 50 per cent of the pressure at  $t_b$ .

When calculating erosion rates it is customary to use  $t_a - t_c$  as the time during which the nozzle insert undergoes erosion. This is satisfactory as long as  $t_e - t_c$  is small compared to  $t_a - t_c$ . In the motor employed for this work  $t_e - t_c$  is approximately 3 to 4 seconds. This amounts to 20 to 30 per cent of  $t_a - t_e$  for a 12 second firing. In order to compare erosion rates for 12, 30 and 60 second firings  $t_a - t_e$  is taken as the erosion time.

Table 23 shows the performance of impregnated graphite nozzle inserts during static subscale rocket motor tests, with the performance of grades ZTA, ATJ, and RVA as base lines with which the impregnated graphites may be compared. The base grade of CFW is ATL; however, ATL has not been considered as a nozzle material, therefore, it was not evaluated in the motor.

Table 23. Static Subscale Rocket Motor Firing Data

	Bulk Density g/cc	Porosity Factor	Ave. Chamber Pressure lbs/in <sup>2</sup>	Web Burning Time sec.	Ave. Mass Flow lbs/sec.	Ave. Radial Erosion Rate mils/sec.
		$\sum \Delta V_i D_i^2$ · 10 <sup>4</sup> Microns <sup>2</sup>				
1. Grade ZTA	1.94	-----	960	12.3	----	0.25
2. Grade ZTA (segmented)	1.96	0.0345	933	63.6	1.49	0.26
3. Grade ZTA (segmented)	1.91	0.165	780	66.7	1.42	0.32
4. Grade ZTA with one impregnation	1.96	0.0358	786	72.1	1.22	0.24
5. Grade ZT-6012	2.08	0.0006	746	74.9	1.27	0.12
6. Grade ATJ	----	-----	806	12.8	----	0.73
7. Grade ATJ	1.72	6.096	712	44.8	1.09	0.70
8. Grade TS-392 (specially impregnated ATJ type graphite)	1.82	1.326	828	32.5	1.24	0.62
9. Grade TS-360 (grade ATJ with one impregnation)	1.84	0.587	669	75.7	1.03	0.62
10. Grade TS-391 (grade ATJ with three impregnations)	1.89	0.0717	783	67.4	1.41	0.28
11. Grade RVA	1.88	0.0919	658	69.1	1.11	0.88
12. Grade CFZ	1.93	0.111	857	32.2	1.25	0.77
13. Grade CFZ	1.93	0.0896	825	44.2	1.28	0.53
14. Grade CFZ (regraphitized)	1.92	0.105	742	47.6	1.06	0.51
15. Grade CFW	1.9f	1.640	627	75.2	1.05	0.64

The porosity factor  $\frac{\sum_{i=1}^{\infty} \Delta V_i D_i^2}{.04}$  has been previously described in Section 2.1. This factor can be shown to be a function of the viscous flow permeability coefficient of the graphite material. It is the viscous flow portion of the total permeability that predominates under the conditions which exist in the throat of a rocket nozzle during firing. The porosity factor was determined for each insert after firing because the pores of impregnated graphites tend to open up during firing except when the material has been regraphitized to approximately 2800°C after impregnation. Porosity data were not obtained on the first ZTA and ATJ graphite inserts fired, because the importance of this property was not recognized at the time. The average mass flow rate was calculated by dividing the propellant weight by the web burning time.

Figure 26 is a plot of the average erosion rate  $\bar{E}$  versus the

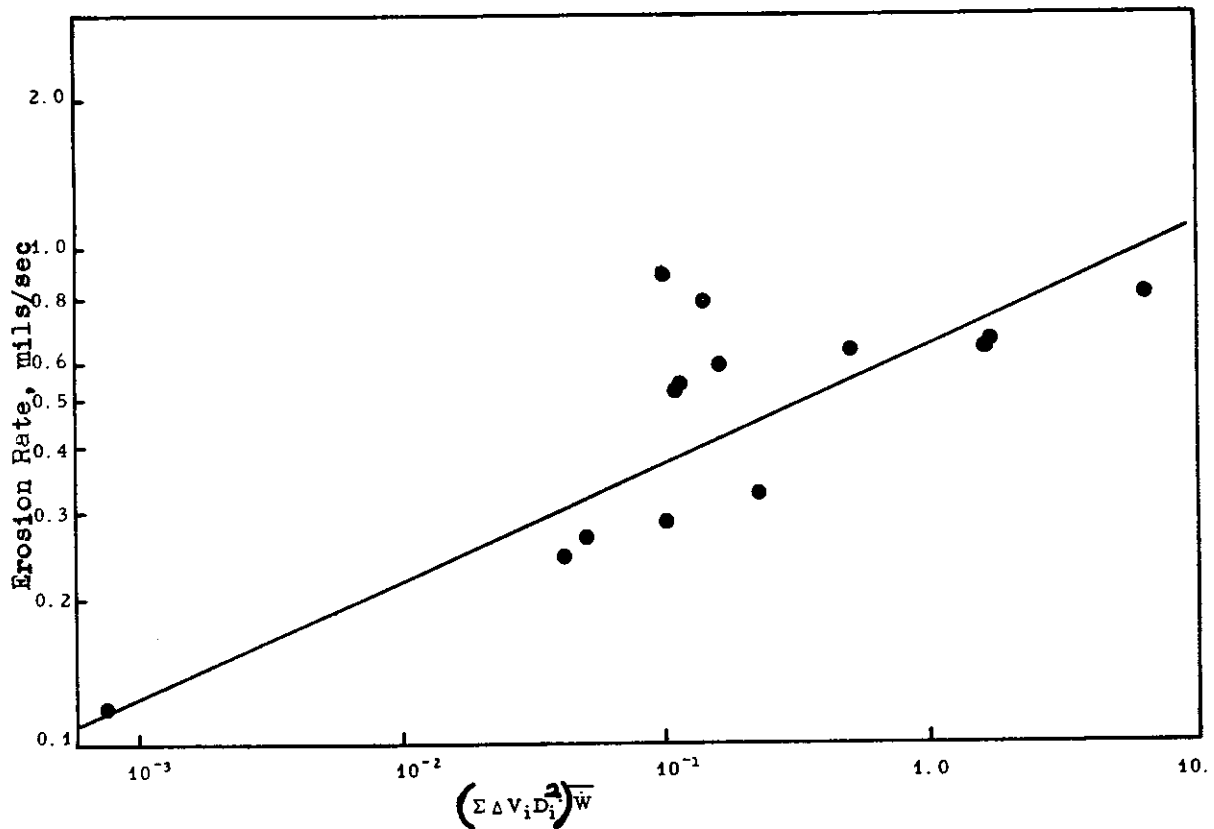


Figure 26. Average Erosion Rates of Graphite Nozzle Materials versus Mass Flow Rate-Porosity Factors

# Contrails

product of the porosity factor of the graphite insert and the average mass flow rate  $\bar{E}$  vs.  $(\sum_{i=0}^{\infty} \Delta V_i D_i^2) \bar{W}$  on a log-log scale. Although some correlation is shown, there is too much scatter to attach any significance to this relationship. In studying the data further, it became apparent that even small variations in the chamber pressure of the motor must be taken into consideration. The best correlation worked

out was a plot of  $\log \frac{\text{Erosion Rate}}{(\text{Chamber Pressure})^4} \times 10^{13}$  versus bulk density of the nozzle insert. Figure 27 shows this relationship for three types of

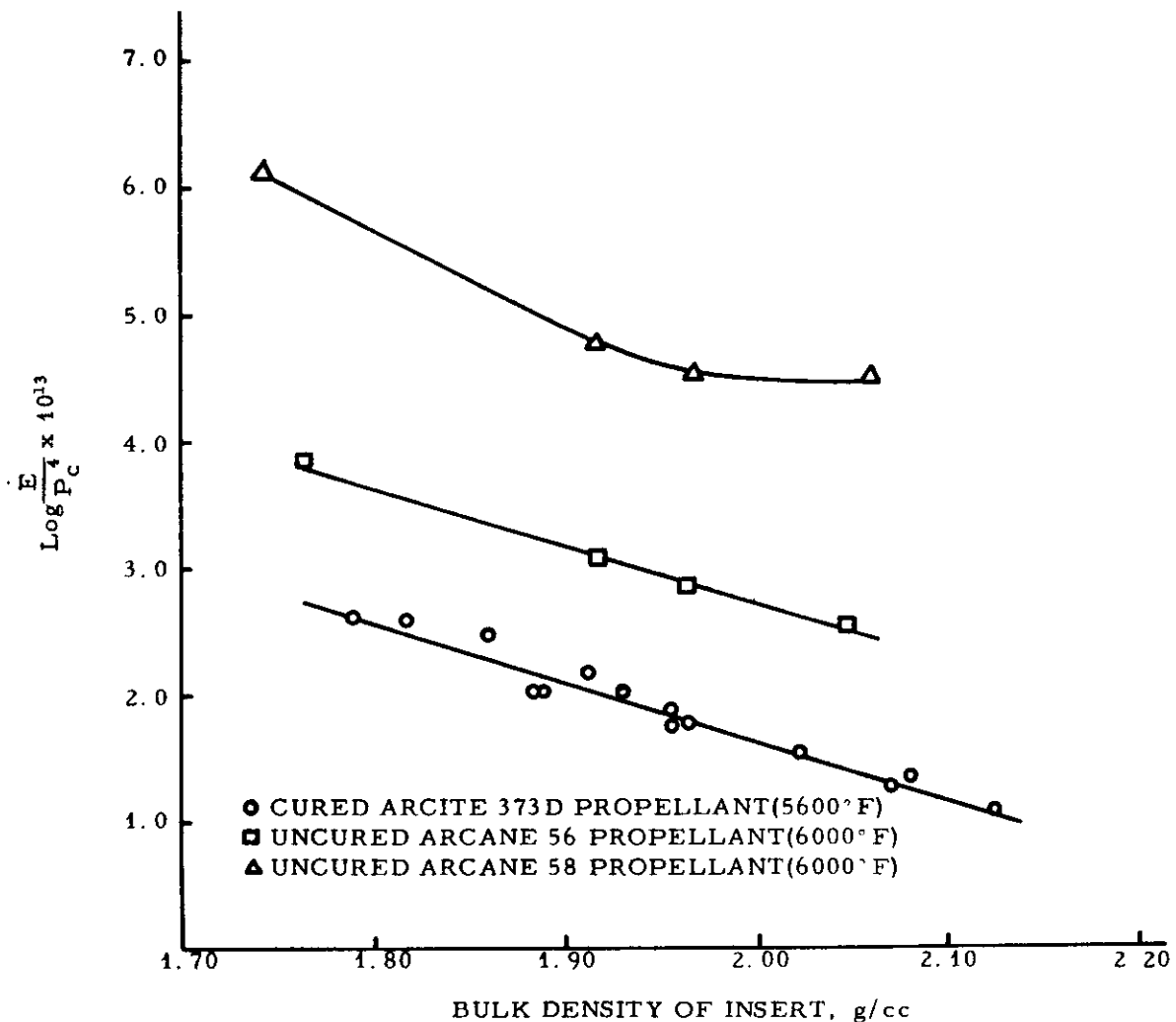


Figure 27.  $\log \frac{\text{Erosion Rate}}{(\text{Chamber Pressure})^4}$  versus Bulk Density of Insert

# *Contrails*

propellant. In all cases the tests fit this correlation quite closely. The physical significance, if any, of the fourth power exponent of pressure is not known. However, concentration of the oxidizing components of the gas, gas boundary layer characteristics and velocity, mass flow rate and temperature of the gas all are functions of chamber pressure to some extent.

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