FOREWORD

This volume is the thirty-second of the WADD Technical Report 61-72 series describing various phases of research and development on advanced graphite materials conducted by National Carbon Company, a Division of Union Carbide Corporation, under USAF Contract No. AF 33 (616)-6915.

The work covered in this report was conducted from September 1961 through December 1962 at the Research Laboratory at Parma, Ohio and the Advanced Materials Laboratory, Lawrenceburg, Tennessee of National Carbon Company under the management of R. M. Bushong, Director of the Advanced Materials Project, J. C. Bowman, Director of Research, W. P. Eatherly, Assistant Director of Research, and of R. C. Stroup, Manager of the Advanced Materials Laboratory.

The contract for this R&D program was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735002, "Refractory Inorganic Non-Metallic Materials: Graphitic;" Project No. 7381, "Materials Application," Task No. 738102, "Materials Processes;" and Project No. 7-817, "Process Development for Graphite Materials." The work was administrated by the Air Force Materials Laboratory, Aeronautical Systems Division, with Captain R. H. Wilson, L. J. Conlon, and W. P. Conrardy acting as Project Engineers.

Other volumes in this WADD Technical Report 61-72 series are:

Volume   I - Observations by Electron Microscopy of Dislocations in Graphite, by R. Sprague

Volume   II - Applications of Anisotropic Elastic Continuum Theory to Dislocations in Graphite, by G. B. Spence.

Volume   III - Decoration of Dislocations and Low Angle Grain Boundaries in Graphite Single Crystals, by R. Bacon and R. Sprague.

Volume   IV - Adaptation of Radiographic Principles to the Quality Control of Graphite, by R. W. Wallouch.

Volume   V - Analysis of Creep and Recovery Curves for ATJ Graphite, by E. J. Seldin.

Volume   VI - Creep of Carbons and Graphites in Flexure at High Temperature, by E. J. Seldin.

Volume   VII - High-Density, Recrystallized Graphite by Hot-Forming, by E. A. Neel, A. A. Kellar and K. J. Zeitsch.

ABSTRACT

Binder systems were investigated with respect to their thermosetting charactistics both to replace pitch-sulfur combinations presently used in the pressure-curing process and to provide binders for development of new graphite grades. The binder systems included: (a) prepolymerized furfural-alcohol resin; (b) pitch, furfural, furfuryl-alcohol combinations; (c) pitch with a ferric chloride catalyst; and (d) pitch with oxidizers such as inorganic persulfates, chlorates and oxides. Acenaphthylene pitch, a new binder, was investigated with regard to thermosetting properties when used in the pressure-curing process. These binder systems were used in the fabrication of graphite articles and property determinations were made on the finished graphites.

The binder modifications or systems investigated have produced no outstanding advantages over the pitch-sulfur system for use in the pressure-curing process. The most promising of the new systems was pitch combined with oxidizing agents other than sulfur, which produced a thermosetting binder of high coking value and which was comparable to the pitch-sulfur binder in other properties.

This technical documentary report has been reviewed and is approved.

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1. INTRODUCTION

Coal-tar pitch has been used as the principal binder material in the manufacture of artificial carbon and graphite since the inception of the carbon industry. It offers a combination of properties which have never been successfully met by any other material except for very special applications. Nevertheless, it has several major deficiencies which have led to a continuing effort to improve its utilization throughout the history of the industry. The two major problems encountered with coal-tar pitch binders are related to the evolution of volatile hydrocarbons (300° to 500°C) and to the thermoplastic nature of the pitch before the onset of carbonization. These characteristics of the pitch place severe limitations both on the processes used in making carbon and on the ultimate properties of the carbon product.

The pyrolysis reaction of pitch can be altered by addition of dehydrogenating agents, by oxidation, or by combination with other organic compounds. The purposes of modification are to increase the per cent of carbon remaining after pyrolysis (increase coking value), to decrease the quantity and control the rate of evolution of the volatile components, and to maintain the structural integrity of the carbon-matrix-deposited binder system. It is also necessary to provide sufficient plasticity or mobility in the system to enable the forming and retention of the shape of an article when the binder is combined with an aggregate. Several modified pitch systems have been studied and used extensively in the fabrication of carbon and graphite articles.[1, 2, 3] This particular study emphasizes the pitch-sulfur system and its analogs.

A basic approach toward achieving improved binder systems lies in the better understanding of the chemical and physical properties which influence binder action. Coal-tar pitch is a complex material consisting of a mixture of many different aromatic and heterocyclic compounds. Its actual composition and chemical reactivity is incompletely understood. A part of the current binder program has therefore included extensive physical and chemical studies of commercial coal-tar pitches. This work performed by the ERA Research Laboratories[4] has increased our understanding of the constitution of coal-tar pitch. A further activity of this general program concerned the investigations carried out by the Armour Research Foundation on binders derived from thermosetting furfuryl alcohol resins.[5]

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The present report describes an additional major effort involving the synthesis and characterization of a laboratory pitch binder from the pure aromatic hydrocarbon acenaphthylene. This binder product serves as a prototype for coal-tar pitch which can be prepared reproducibly and studied systematically for the purpose of better understanding of binders in general. The results of chemical and physical investigations of this synthetic pitch are presented and related to binder behavior.

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2. SUMMARY AND CONCLUSIONS

Various pitch-oxidizing agent combinations have been evaluated as improved replacements for the pitch-sulfur system. Additionally, pitches prepared from acenaphthylene and resins produced from furfuryl alcohol have been examined as thermosetting binders. The conclusions of these studies are summarized as follows.

1) The most promising binder system investigated was pitch and ammonium persulfate. The possible advantage gained would be in the area of reducing tooling and fume system costs as a result of eliminating the corrosive and poisonous sulfurous gases formed during the pressure curing of carbon plugs made with the pitch-sulfur binder.

2) The furfuryl alcohol resins studies and the addition of these resins to pitch generally resulted in a degradation of graphite physical properties when compared to the pitch-sulfur system.

3) Replacement of coal-tar pitch with acenaphthylene pitch in pressure-cured grade RVA stock resulted in a degradation of all graphite properties (except resistivity) as a consequence of an incomplete thermosetting reaction between acenaphthylene pitch and sulfur.

Synthetic pitch binders have been produced in the laboratory from the aromatic hydrocarbon acenaphthylene. These pitches have been subjected to detailed chemical and physical studies. Conclusions drawn from the results of these studies may be summarized as follows.

1) Acenaphthylene is a thermally reactive compound that will produce a high yield of a pitch-like product by a simple process of heating at atmospheric pressure in a reflux system and subsequent distillation of by-product acenaphthene.

2) The physical and thermal properties of this pitch product can be varied over a wide range by changing the process conditions. The most significant process variable appears to be the amount of acenaphthene distilled during the final stage. For example, the softening point of a pitch refluxed for 30 hours will vary from 50°C if no distillate is removed to about 250°C if essentially all of the acenaphthene is distilled off.

3) The chemical, physical and thermal properties of the synthetic acenaphthylene pitches are very similar to those of comparable coal-tar pitches. Notable exceptions are the absence of

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nitrogen and sulfur contaminants and the much reduced benzene and quinoline insoluble fractions in the acenaphthylene pitches.

4) Acenaphthylene pitch is an excellent binder material as determined in laboratory extrusion and baking trials. It is comparable to and in some respects superior to standard coal-tar binders. For example, in all of the laboratory trials graphites produced using the acenaphthylene pitch as the binder had lower electrical resistivities and lower coefficients of thermal expansion than those using coal-tar pitch.

5) Acenaphthylene pitch should be an excellent impregnant material for carbon based on the extremely low quinoline insolubles (Q. I.) found in these pitches.

6) Acenaphthylene pitch produces a high yield of coke capable of conversion to an excellent graphite as demonstrated by both X-ray diffraction and CTE measurements.

3. BINDER SYSTEMS BASED ON PITCH AND COKING OR OXIDIZING ADDITIVES

3.1. Pitch-Sulfur System

In the forming of large-diameter, fine-grain graphite sections by the pressure-curing process, inert filler material consisting of graphite particles, graphite flour and thermatomic black are bonded with a coal-tar pitch and sulfur binder system.[6] The binder system used in the pressure-curing process is of particular interest in this report.

The heating characteristics of a pitch are changed by the addition of powdered sulfur. Sulfur melts at 110°C and plasticizes high-melting-point pitches (e. g., 175°C-melting-point pitch) and renders the pitch fluid at the lower temperature. The sulfur begins to react with the hydrogen from the pitch at approximately 200°C to form H_2S which is evolved as a gas, and a thermally stable carbon residue is left behind. Reaction of the pitch-sulfur nears completion and the pitch is thermally set at about 325°C.

Use of the pitch-sulfur binder system presents several advantages over the use of pitch alone.

1) H_2S gas and carbon residue are the main reaction products from the heating of the pitch-sulfur mixture while, with pitch alone, hydrocarbons and carbon residue are the main reaction products. Consequently, a greater amount of carbon residue will be left from a given quantity of pitch in the pitch-sulfur binder than for pitch alone, because very little carbon is removed with the reaction gases from the pitch-sulfur system. This increase in residual carbon enhances the physical properties of carbon or graphite sections formed with the pitch-sulfur binder system.

2) Hydrogen sulfide from the pitch-sulfur reaction is a low-molecular-weight, noncondensible gas and is easily removed in the thermosetting of carbon sections under mechanical pressure. The low-temperature hydrocarbon gases formed during the heating of pitch in the absence of sulfur are higher in molecular weight than H_2S and are condensible, making them difficult to remove.

3) The plasticizing action as well as the thermosetting action of the sulfur at low temperatures (110° and 325°C, respectively) is used in the pressure-curing process for forming of high-density, fine-grain graphite. The plasticizing action permits precompacting at 110°C and the thermosetting action permits curing of the precompacted plugs,

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under mechanical pressure, at 325°C. Graphite sections, having been thermoset under mechanical pressure, attain relatively high density which is retained on subsequent processing.

4) Thermoset graphite sections can be baked unsupported and, consequently, can be baked in any type of furnace, provided an inert atmosphere is maintained. Graphite sections formed with a thermoplastic or pitch binder system must be supported in a coke-sand pack when baked at temperatures up to 500°C to prevent deformation of the piece. The pitch-sulfur system has the advantage of becoming thermally set at 325°C as compared to 500°C for the pitch alone, and the lower temperature makes for easier processing.

Disadvantages of using the pitch-sulfur binder system are:

1) Large quantities of the poisonous H_2S gas are produced on heating of pitch-sulfur.

2) Sulfur, H_2S, and SO_2 (formed from burning H_2S in air) are very corrosive to steels, so tooling life is short unless stainless steel is used.

3) Graphite sections formed with pitch-sulfur are more susceptible to low-temperature oxidation (650°C) than graphite sections formed with pitch alone.

A thermosetting binder system retaining the advantages but eliminating the disadvantages of the pitch-sulfur system might be obtained by replacing the sulfur with other pitch-coking or oxidizing agents. Such systems were investigated and the additives evaluated were benzoquinone, chloranil, hydroquinone, hydrochloric acid, trichloroethylene, ferric chloride and inorganic persulfates, chlorates and oxides.

3.2. Replacement of Sulfur in Pitch-Sulfur System

Modifications of the pitch-sulfur binder system were investigated in an attempt to provide a thermosetting binder without the disadvantages of sulfur. Two types of additives were studied as replacement for the sulfur: (a) chemicals to promote coking of the pitch without oxidation; (b) oxidizing agents other than sulfur.

3.2.1. Pitch Plus Coking Additives

The carbon-residue yields or coking values of pitches when heated to 800°C can be increased by the addition of various chemicals other

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than oxidizing agents. Some of these chemicals tested as possible substitutes for sulfur in the pitch-sulfur binder system are: (a) p-benzoquinone, (b) chloranil, (c) hydroquinone, (d) 5 per cent HCl solution, (e) trichloroethylene, and (f) ferric chloride.

Table 1 lists the results of attempts to thermoset plugs molded from mixes containing carbonaceous filler with binder consisting of pitch and the above-listed chemicals. All of the pitch-chemical binder systems tested were either too difficult to cure or failed to thermoset at temperatures up to 325°C. The ability of a binder to thermoset at low temperatures (325°C or below) is considered a prerequisite to obtaining high density and strength in the pressure-curing process[6] and, since none of the pitch-chemical systems listed above met this requirement, investigation of these systems was discontinued.

Table 1. Curing Results of Pitch-Plus-Coking Additive Binder Systems

Additive Tested	Additive Level, pph	Blend Type	Pitch Type	Pitch Level, pph	Curing Results (after heating to temperatures up to 325°C
p-Benzoquinone	1		175° mp	22	Plug softens upon reheating
	2		175° mp	22	Not thermoset
	3		175° mp	22	Not thermoset
	6	50 parts Graphite Particles, 50 parts Graphite Flour and 8 parts Thermatomic Black	175° mp	22	Not thermoset
Chloranil	2		175° mp	22	Not thermoset
Hydroquinone	6		175° mp	24	Not thermoset
5 Per Cent HCl Solution	8		175° mp	24	Piece exploded on ejection
Trichloroethylene	6		175° mp	24	Very difficult to cure (some gas blows* occurred on curing)
Ferric Chloride	5	100 parts Coke Flour	110°mp	40	Not cured in mold - heating to 300°C did not result in a thermoset plug

* Gas blows - condition where reaction gases escape from mold in spurts.

3.2.2. Pitch Plus Oxidizing Agents Other than Sulfur

Binder systems were investigated in which oxidizing agents or potential oxidizers were added to the pitch to react in the same manner as sulfur in the pitch-sulfur mixture. The oxidizing agents investigated were: (a) carbon tetrachloride (CCl_4), (b) ammonium persulfate ($[NH_4]_2S_2O_8$), (c) potassium persulfate ($K_2S_2O_8$), (d) potassium dichromate ($K_2Cr_2O_7$), (e) sodium chlorate ($NaClO_3$), (f) chromium trioxide (CrO_3), (g) zinc dioxide (ZnO_2), and (h) magnesium dioxide (MgO_2).

Carbon tetrachloride was eliminated early in the investigation because the evolution of chlorine and hydrogen chloride gas proved to be as undesirable as the hydrogen sulfide and sulfur dioxide gases driven off from the pitch-sulfur binder. The rest of the oxidizing agents in the list above generate oxygen at elevated temperatures (100° to 500°C) and have the potential of producing the same effect as sulfur with the advantage of producing relatively harmless gases (e.g., water vapor) when heated with pitch.

The initial step in the investigation of these oxidizing agents was to mold 2-inch diameter plugs consisting of 100 parts petroleum-coke flour, 40 parts 110°C-melting-point coal-tar pitch and 5 parts of the selected oxidizing agent. Plugs consisting of coke with pitch and sulfur and coke with pitch were formed for comparative purposes. All of the plugs were heated under controlled conditions to 300°C, held for one hour, and cooled. The thermosetting quality of the binders was evaluated by cutting $1/8$-inch thick discs from the "cured" plugs and determining whether or not the binder softened when the discs were heated over a Bunsen burner. Figure 1 shows photographs of the discs after they were subjected to the thermosetting test. Results of this test indicated that the pitch-sulfur, pitch-$(NH_4)_2S_2O_8$, pitch-$K_2S_2O_8$ and the pitch-$NaClO_3$ binder systems were completely or nearly thermoset after heating to 300°C.

Those binder systems showing promise as substitutes for the pitch-sulfur binder were evaluated further to determine: (a) quantitative analysis of water and carbon dioxide formed on heating to 300°C; (b) amount of pitch-coke residue at 800°C. Plugs 1 inch in diameter by 2 inches in length were formed from coke flour, 110°C-melting-point pitch and the oxidizing agents of particular interest; i.e., $(NH_4)_2S_2O_8$, $K_2S_2O_8$ and $NaClO_3$ with the pitch-sulfur system again included as a control. The gases formed upon heating the plugs were analyzed for water and carbon dioxide employing the apparatus sketched in Figure 2. Data from the CO_2 determinations were meaningless due to malfunction of the absorber.

Figure 1. Photograph of Carbon Discs Subjected to a Thermoset Test

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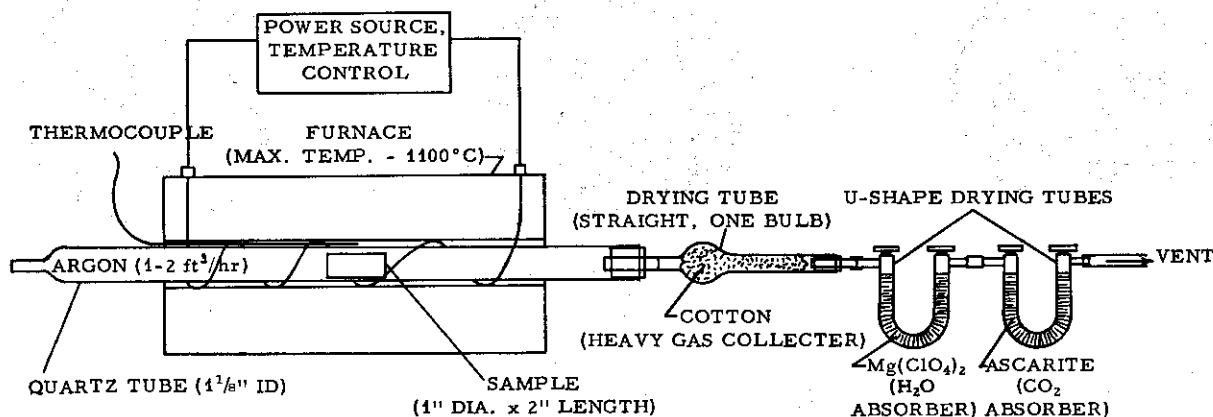
Figure 2. Schematic Diagram of Gas Analysis Apparatus
Used in Pitch-Oxidizing Agent Studies

The amount of water collected from the gases produced by heating plugs containing different types and levels of additives are listed in Table 2 and shown graphically in Figure 3. Large amounts of water

Table 2. Water of Reaction Determinations, Heating
of Pitch Plus Oxidizing Agents

Binder System	Additive Level, per cent of pitch	Weight of Water Collected Per Unit Weight of Pitch*, milligrams/gram	Results of Thermoset Test
Pitch	-	7	Not Thermoset
Pitch-$(NH_4)_2S_2O_8$	7.5	41	Thermoset
	12.5	59	Thermoset
	25.0	61	Thermoset
Pitch-$K_2S_2O_8$	7.5	18	Slightly Thermoset
	12.5	31	Slightly Thermoset
	25.0	39	Thermoset
	37.5	52	Thermoset
Pitch-$NaClO_3$	7.5	29	Slightly Thermoset
	12.5	44	Thermoset
	25.0	54	Thermoset

* Water collected at a test temperature of 300°C and test time of 3 hours
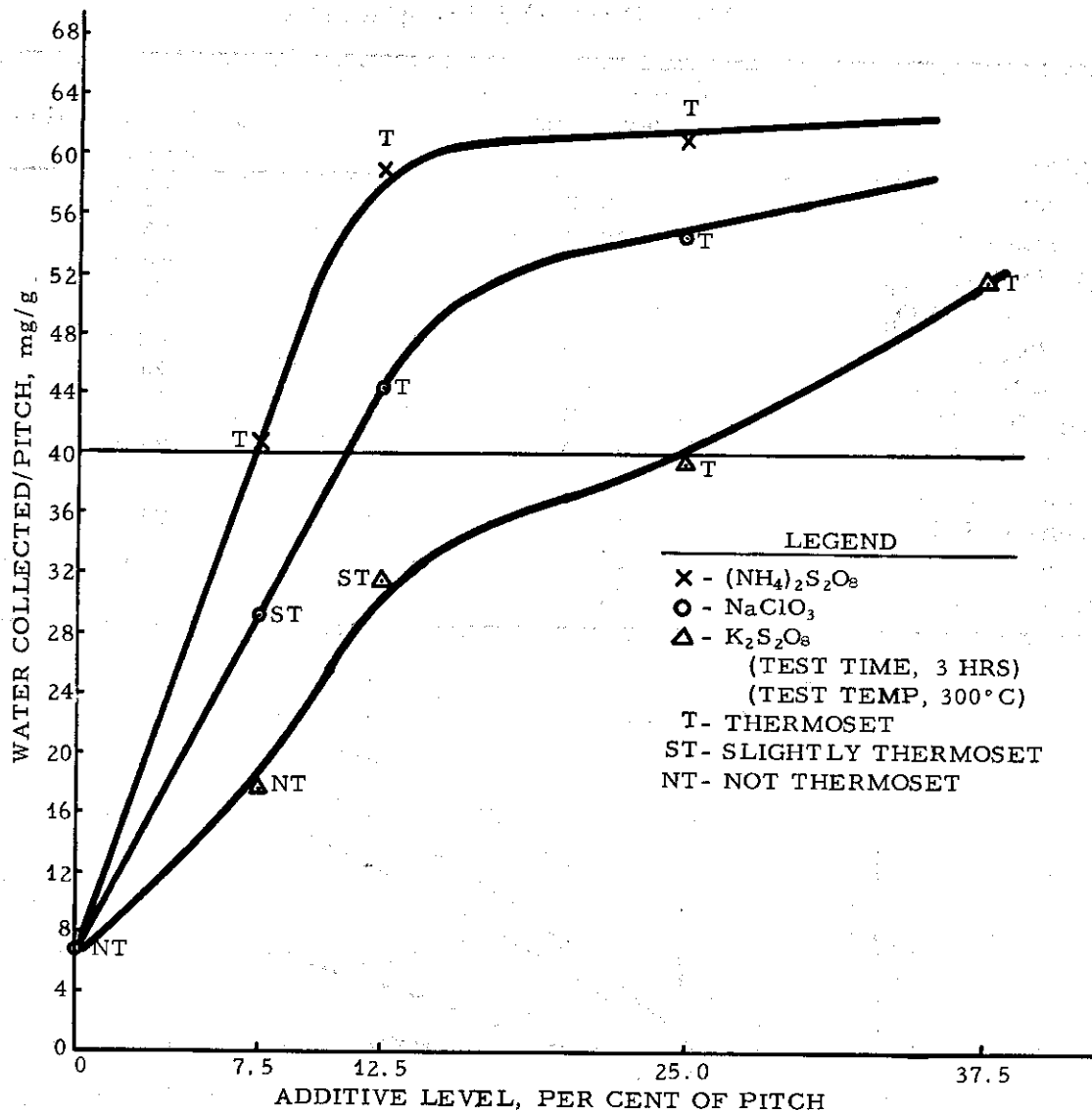
Figure 3. Water of Reaction as a Function of Additive Level,
Pitch-Plus-Oxidizing Agent Binder Systems

were obtained from heating the pitch-oxidizer systems with the pitch-
$(NH_4)_2S_2O_8$ giving off the greatest quantity. Thermosetting of the pitch
by these chemicals is then undoubtedly caused by stripping of the
hydrogen from the pitch by the oxygen released during heating of the
oxidizers. Pitch-coke yields upon baking the formed plugs to 800°C
are shown in Table 3 and Figure 4. The most promising of the oxidizing
agents investigated was $(NH_4)_2S_2O_8$ as evidenced by the thermosetting
test, the quantity of water formed on heating to 300°C and the pitch-coke
yields on baking to 800°C.

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Table 3. Per Cent Carbon-Residue Yield at
800°C, Pitch-Oxidizing Agents

Binder System	Additive Level, per cent of pitch	Carbon Residue, per cent
Pitch	0.0	63.7
Pitch-Sulfur	20.0	81.7
Pitch-$(NH_4)_2S_2O_8$	7.5	77.5
Pitch-$(NH_4)_2S_2O_8$	12.5	79.7
Pitch-$(NH_4)_2S_2O_8$	25.0	88.4
Pitch-$NaClO_3$	7.5	71.5
Pitch-$NaClO_3$	12.5	75.3
Pitch-$NaClO_3$	25.0	82.4
Pitch-$K_2S_2O_8$	7.5	71.8
Pitch-$K_2S_2O_8$	12.5	73.6
Pitch-$K_2S_2O_8$	25.0	77.1
Pitch-$K_2S_2O_8$	37.5	80.8
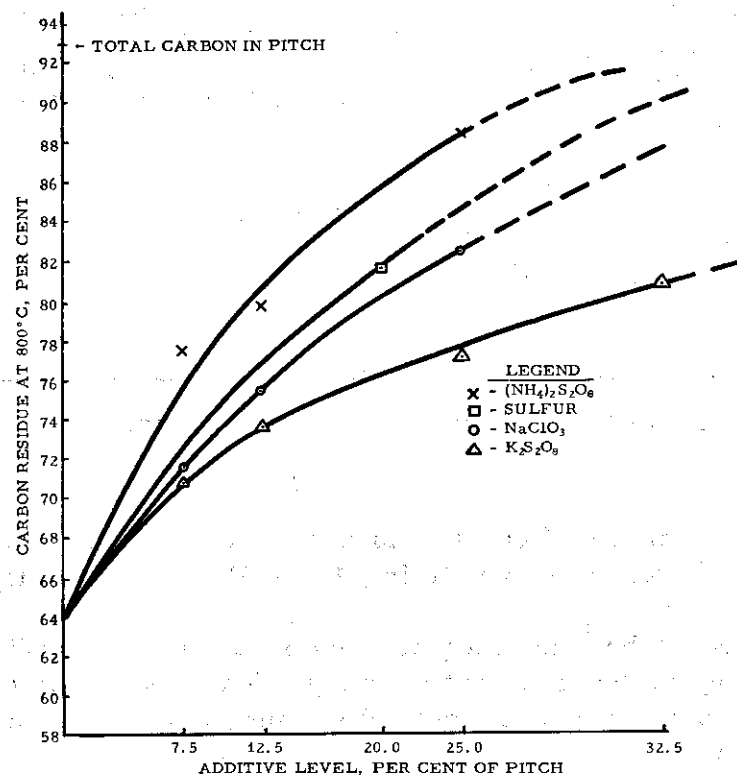
Figure 4. Per Cent Carbon-Residue Yields as a Function of Additive
Level, Pitch-Plus-Oxidizing Agent Binder Systems

The pitch-ammonium persulfate binder system was further evaluated by producing 10-inch diameter plugs from mixes containing graphite particles, graphite flour, thermatomic-black pitch and $(NH_4)_2S_2O_8$. These plugs were formed by the pressure-curing process, and room temperature properties of this material after graphitization were compared to room-temperature properties of pressure-cured, graphitized control samples processed with pitch-sulfur binder. Results of the property measurements given in Table 4 show that the pitch-ammonium persulfate material was very similar to the pitch-sulfur material.

Table 4. Room-Temperature Properties, Pitch-$(NH_4)_2S_2O_8$ Binder System Versus Pitch-Sulfur Binder System

Property	Pressure-Cured Graphite*, Pitch-$(NH_4)_2S_2O_8$ Binder, 10" Dia. by 10" Length	Pressure-Cured Graphite*, Pitch-Sulfur Binder, 10" Dia. by 10" Length
Number of Samples Tested		
w. g.	9	20
a. g.	11	20
Bulk Density, g/cc	1.79	1.82
Flexural Strength, ** lbs/in^2		
w. g.	3400	3530
a. g.	2370	2560
Young's Modulus, 10^6 lbs/in^2		
w. g.	1.60	1.70
a. g.	1.00	1.00
Resistivity, 10^{-4} ohm-cm		
w. g.	11.3	11.3
a. g.	15.9	16.5

* Impregnated prior to graphitization.
** Samples $1/2$" by $1/2$" cross section, third-point loading employed.
 w. g. = with grain, a. g. = across grain.

A primary disadvantage of the pitch-sulfur binder system is that graphite produced with this binder exhibits a higher than normal oxidation rate at low temperatures (650°C). It was important, therefore,

to determine the oxidation rate of plugs containing $(NH_4)_2S_2O_8$, $K_2S_2O_8$, and $NaClO_3$ to determine if an improvement in oxidation resistance of pressure-cured material had been obtained.

The oxidation weight losses at 650°C for graphite samples containing various binder systems are shown in Table 5 and Figure 5.

Table 5. Per Cent Oxidation Weight Loss of Pitch-
Oxidizing Agent Binder Systems*

Binder System	Additive Level, per cent of pitch	Test Temperature, °C	Test Time, min.	Weight Loss, per cent
Pitch	0.0	650	10	1.3
			30	3.2
			50	4.9
			70	6.6
Pitch-Sulfur	20.0	650	10	2.0
			30	5.9
			50	11.2
			70	17.6
Pitch-$(NH_4)_2S_2O_8$	12.5	650	10	2.1
			30	6.0
			50	11.0
			70	16.2
Pitch-$NaClO_3$	12.5	650	10	3.6
			30	9.5
			50	14.1
			70	18.9
Pitch-$K_2S_2O_8$	25.0	650	10	5.3
			30	18.9
			40	27.3

* Samples - 1 cm by 1 cm by 4 cm, Air Flow through furnace = 22.5 SCFH.
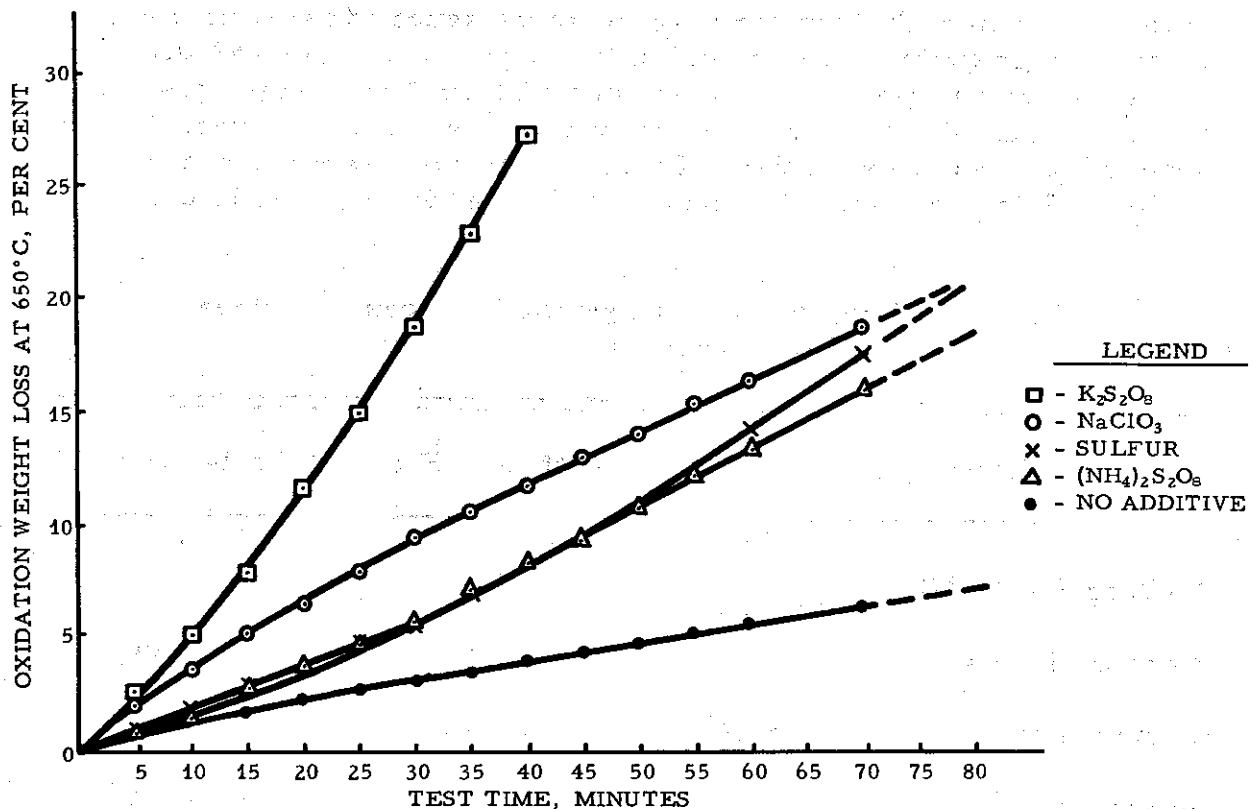
Figure 5. Per Cent Oxidation Weight Loss as a Function of
Time, Pitch-Plus-Oxidizing Agent Binder Systems

These data indicate that all of the chemicals investigated reduced
the oxidation resistance of the finished graphite and, from this respect,
there was no advantage in using any of the other oxidizing agents as a sub-
stitute for sulfur. However, these chemicals might still be considered as
substitutes for the sulfur to eliminate the problem of poisonous and cor-
rosive gases being generated during the pressure-curing operation. Fur-
ther testing is necessary to determine corrosive effects, if any, of the
reaction gases formed by heating the oxidizing agents with pitch. The
amount and toxicity of any poisonous gases formed from these chemicals
must also be checked.

3.3.   Evaluation of Acenaphthylene Pitch in Pressure-Cured Material

The substitution of acenaphthylene pitch for coal-tar pitch in
small-scale extrusion trials conducted during research studies resulted
in decreased resistivity and decreased low-temperature CTE in the
formed sections. Acenaphthylene pitch was evaluated further by substi-
tuting it for coal-tar pitch normally used in the fabrication of grade RVA[6]
by the pressure-curing process to determine if the improved properties
obtained in the extruded material could be extended to the pressure-cured

material. Ten-inch diameter plugs were pressure cured from blends
containing graphite filler material, acenaphthylene pitch and sulfur.
For comparison, plugs were also formed from blends using coal-tar
pitch and sulfur. In each case the sulfur was used to impart thermo-
setting qualities to the binder. Table 6 lists the chemical properties
of the coal-tar and acenaphthylene pitches used in this evaluation.

Table 6. Comparison of Properties of Acenaphthylene
and Coal-Tar Pitch

Property	Acenaphthylene Pitch	Coal-Tar Pitch
Melting Point, °C	180	176
Benzene Insolubles, per cent	23.90	49.40
Quinoline Insolubles, per cent	0.50	17.90
Sulfur Content, per cent	0.08	0.48
Carbon Residue Left after Heating to 800°C, per cent	73.10	69.00
Specific Gravity	1.32	1.36

Table 7 summarizes the properties of graphite which was fabri-
cated by the process and which was bonded with each of the pitches.
These data indicated that the use of acenaphthylene pitch caused a deg-
radation of all properties except resistivity. The most important factor
that influenced the resultant properties of the acenaphthylene pitch-bonded
graphite was the 6.3 per cent volumetric expansion experienced on baking
to 800°C (Table 7), which could not have occurred without cracking the
stock if the pitch-plus-sulfur system had been completely thermoset. The
indication, therefore, is that the acenaphthylene-sulfur polymerization
did not go to completion. Further investigation of the acenaphthylene
pitch as a substitute for coal-tar pitch in the pressure-curing process did
not seem warranted.

Table 7. Summary of Graphite Properties of Pressure-Cured Stock Bonded with Coal-Tar or Acenaphthylene Pitches

Property	Pressure-Cured Stock Bonded with Coal-Tar Pitch		Pressure-Cured Stock Bonded with Acenaphthylene Pitch	
	No. of Samples Tested	Average Property	No. of Samples Tested	Average Property
Pitch Level, pph	—	26	—	26
Bulk Density, g/cc	40	1.82	48	1.72
Flexural Strength*, lbs/in^2				
w.g.	20	3530	24	2875
a.g.	20	2560	24	2156
Resistivity, 10^{-4} ohm-cm				
w.g.	20	11.3	24	9.4
a.g.	20	15.5	24	13.0
Young's Modulus, 10^6 lbs/in^2				
w.g.	20	1.67	24	1.31
a.g.	20	1.01	24	0.84
Room-Temperature CTE, 10^{-6}/°C				
w.g.	4	1.28	4	1.68
a.g.	4	2.34	3	2.62
Per Cent Expansion on Baking to 800°C	—	0	—	6.3
Per Cent Shrinkage on Graphitizing to 2800°C	—	3.8	—	4.2

* $^1/_2$-inch by $^1/_2$-inch cross section; third-point loading employed

4. BINDER SYSTEMS BASED ON PITCH AND/OR THERMOSETTING RESIN

4.1. Thermosetting Resin, Prepolymerized Furfuryl Alcohol

The Armour Research Foundation had reported[5] that furfuryl alcohol (prepolymerized by activated alumina condensation with a removal of 16 per cent water of reaction) and para-toluenesulfonic acid catalyst formed a thermosetting binder system when heated to approximately 100°C. It was reported that thermosetting took place with the formation of only minor amounts of gases and baking the thermoset resin to 800°C resulted in a 57 per cent carbon-residue yield. A quantity of this high-viscosity, prepolymerized furfuryl alcohol resin was submitted by Armour Research for development trials.

The most appealing features of this binder system, as applied to the pressure-curing process, were the low temperatures needed to thermoset the binder, the relative ease of forming thermoset sections (little gas to contend with in the thermosetting operation), and the elimination of sulfur. In the first attempts to use the Armour resin, difficulties were encountered in mixing the high-viscosity resin with the graphite or coke filler materials. Use of a liquid-feed, twin-shell blender resulted in mixes containing a large number of mix balls, as is shown in Figure 6, a photograph of a plug formed from these mixes.
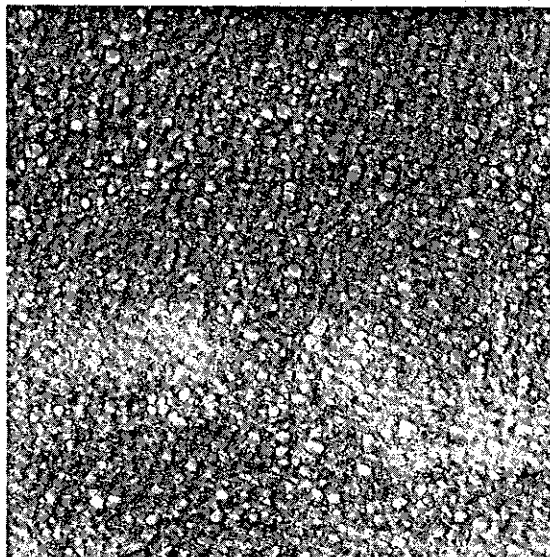
Figure 6. Photograph of 5-Inch Diameter Plug Showing Mix Balls Formed Using Armour Resin

Mulling and pressure mixing were then employed in an attempt to minimize the formation of these mix balls. Mulling is accomplished by squeezing the binder into the filler with the use of steel rollers. Pressure mixing is accomplished by applying a mechanical force on the top of a mix in a conventional bread mixer. Figure 7 is a schematic diagram of the pressure mixing technique employed. These two approaches resulted in the formation of smaller mix balls which yielded a mottled appearance to the structure in the formed article. A mulled mix was forced through 10- and 20-mesh screens in an attempt to reduce this effect. The structure of material formed from the screened mixes appeared to be a uniform distribution of much smaller sized mix balls.
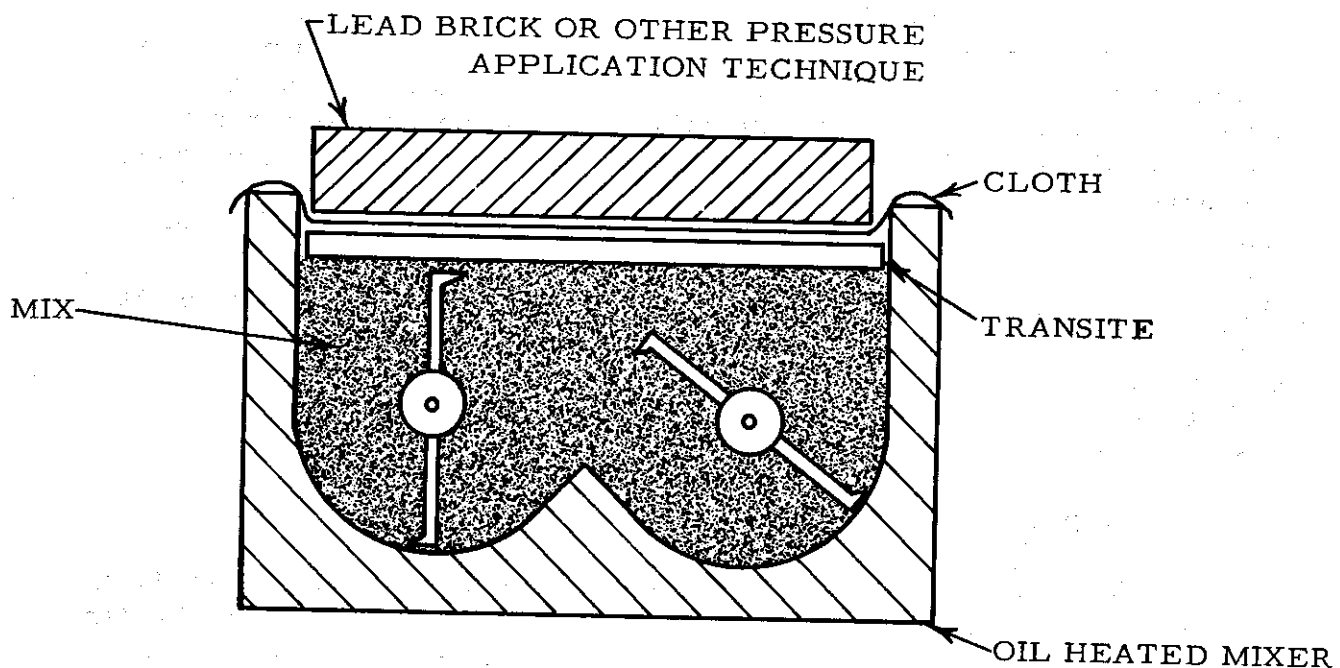
Figure 7. Schematic Diagram of Pressure-
Mixing Apparatus

A series of carbon plugs, 5 inches in diameter by 5 inches in length, were formed from mixes prepared using the previously discussed mixing techniques. A 50-ton capacity press with externally heated graphite punches and mold were used in the forming trials. Pressure curing was accomplished by heating mixes to approximately 150°C under a mechanical pressure of 1000 lbs/in^2, holding at these conditions for 30 minutes, and ejecting the thermoset plug.

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All of the graphites formed with the Armour resin, which are listed in Table 8, were baked to 800°C after curing, impregnated, rebaked to 800°C and graphitized to 2800°C. Table 8 summarizes the room-temperature physical property data for this graphite as a function of inert filler material, mixing method, mix ball size, mixing time, binder level and catalyst level. Properties of graphite using standard pitch-sulfur binder are also included. The material formed from graphite-base mixes cracked extensively on baking to 800°C and the use of graphite filler material was discontinued early in the evaluation of the Armour resin. Optimum binder level for the Armour resin system was determined to be 26 parts of binder per 100 parts of filler material, by weight, for coke-base mixes. Processing of stock at binder levels of 28 to 30 parts per 100 was difficult with most of this stock containing cracks.

The data in Table 8 show that screening of mulled mixes resulted in higher flexural strengths than obtained with the other mixing procedures with the 20-mesh material yielding the highest strengths. However, the strengths of all the graphites containing the thermosetting resin were lower than the strengths of the graphites containing the standard pitch-sulfur binder. The low strengths experienced with the Armour resin were believed to be a result of the inability to uniformly disperse the resin into filler material and the high shrinkage and weight loss which occurred when the cured article was heated to 800°C (approximately 60 per cent volumetric shrinkage and 8 per cent weight loss). The Armour resin therefore presents no obvious advantages over the pitch-sulfur system.

4.2. Pitch Plus Thermosetting Resins

A group of binder systems consisting of pitch and thermosetting resins was investigated as possible substitutes for the pitch-sulfur binder. Combinations of furfural and furfuryl alcohol were evaluated and in each case a catalyst was required to obtain a thermosetting resin system. The catalysts used were diethylsulfate, hydrochloric acid, oxalic acid, bakelite, and trichloroethylene. The potential advantages of these systems were the low temperatures required for thermosetting, the elimination of sulfur, and the high binder-coke yield of the pitch-resin system upon heating to 800°C. Increased binder coke would improve the physical properties of the formed articles.

To evaluate these pitch-resin binder systems, the resin plus catalyst was added to a blend of graphite filler material and milled coal-tar pitch. The resulting carbon mix was formed into 4-inch diameter plugs and cured to 325°C under a mechanical pressure of 1000 lbs/in². Results of the pressure-curing trials, given in Table 9 indicated that,

Table 8. Room-Temperature Properties of Armour Resin-Base Graphite* Versus Pitch-Sulfur-Base Graphite*

Piece No.	Binder System	Binder Level, pph	Catalyst Level, per cent of F.A.	Inert Filler Material	Mixing Technique	Mixing Time, min.	Mix Ball Size, Tyler Mesh	Bulk Density, g/cc	Flexural** Strength, lbs/in² W.G.	A.G.	Electrical** Resistivity, 10⁻⁴ohm-cm W.G.	A.G.	Young's** Modulus, 10⁻⁶lbs/in² W.G.	A.G.
1	Prepolymerized Furfuryl Alcohol	24	4	Graphite Flour	Pressure Mixed	5	Random	Piece extensively cracked						
2	"	24	4	"	"	5	Random	Piece extensively cracked						
3	"	24	4	"	"	5	Random	Piece extensively cracked						
4	"	24	4	"	"	5	Random	Piece extensively cracked						
5	"	20	4	Coke Flour	"	5	Random	1.59	1490	1150	12.5	15.6	1.02	0.67
6	"	22	4	"	"	5	Random	1.62	1690	980	11.7	14.3	1.11	0.84
7	"	24	4	"	"	5	Random	1.67	1700	1650	11.3	13.6	1.27	0.98
8	"	24	4	"	Mulled	5	Random	1.57	1590	1120	10.2	15.4	0.93	0.53
9	"	26	4	"	"	5	Random	1.59	1450	1130	9.0	14.2	1.05	0.55
10	"	28	4	"	"	5	Random	1.60	1990	1230	10.6	15.9	1.43	0.60
11	"	30	4	"	"	5	Random	1.61	1730	-	9.8	-	1.04	-
12	"	24	3	"	"	20	Random	1.67	1760	1590	9.3	13.9	1.49	0.67
13	"	24	3	"	"	15	10 Mesh	1.61	2040	1460	10.0	14.8	1.08	0.58
14	"	26	3	"	"	15	10 Mesh	1.64	2240	-	9.8	-	1.11	-
15	"	28	3	"	"	15	10 Mesh	Piece extensively cracked						
16	"	24	3	"	"	15	20 Mesh	1.62	2240	1710	9.8	14.0	1.08	0.67
17	"	26	3	"	"	15	20 Mesh	1.66	2250	1570	9.3	13.9	1.17	0.64
18	"	28	3	"	"	15	20 Mesh	Piece extensively cracked						
19	"	30	3	"	"	15	20 Mesh	Piece extensively cracked						
Pitch-Sulfur (10" dia. x 10" length)		26	-	Graphite Flour and Particles	-	-	-	1.82	3530	2560	11.3	16.5	1.70	1.00

*Impregnated prior to graphitizing. **n = 7 or less depending on condition plug. Flexural strength samples ½", ½" cross sections. Third-Point Loading.

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with one exception, none of the binder combinations tested presented a truly thermosetting system. Although the resins seemed to be thermoset at low temperatures, the pitch was not affected and caused the plugs to be relatively soft. The all-resinous binder, consisting of furfural, furfuryl alcohol and bakelite, produced a plug which was apparently completely thermoset but which was badly cracked after pressure curing.

Table 9. Curing Results of Pitch-Plus-Thermosetting Resin Systems *

Piece No.	Pitch Level, pph	Furfural Level, pph	Furfuryl Alcohol Level, pph	Catalyst Type	Catalyst Level, per cent of Resin (unless stated otherwise)	General Curing Results, Attempted Heating Under Pressure to Approximately 325°C
1	18	1.00	1.00	Bakelite	100	Piece soft after curing
2	0	5.50	5.50	Bakelite	100	Piece hard but extensively cracked
3	11	2.75	2.75	Bakelite	100	Piece soft after curing
4	24	4.00	0.00	5 per cent HCl Solution	120	Mix blow**
5	24	4.00	0.00	Oxalic Acid dissolved in CH₃OH	75	Piece soft after curing
6	24***	0.40	3.60	Diethylsulfate	10	Mix blow**
7	24***	0.40	3.60	Diethylsulfate	10	Piece soft after curing
8	24***	0.40	3.60	Diethylsulfate	10	Piece soft after curing
9	24***	4.00	0.00	Trichloroethylene	10	Piece slightly soft after curing
10	24***	4.00	0.00	Trichloroethylene	10	Piece slightly soft after curing
11	24***	2.00	2.00	Trichloroethylene	10	Piece slightly soft after curing
12	24***	0.40	3.60	Trichloroethylene	10	Piece soft after curing
13	24***	4.00	0.00	Trichloroethylene	10	Piece slightly soft after curing
14	24***	4.00	0.00	HCl	10 drops	Mix blow**
15	24***	4.00	0.00	Trichloroethylene	10	Piece slightly soft after curing
16	24	4.00	0.00	Trichloroethylene	10	Mix blow**
17	24	4.00	0.00	Trichloroethylene	10	Mix blow**
18	24	0.00	0.00	Trichloroethylene	6 pph	Mix blow**

* All inert filler material used in these trials was graphite flour and particles.

** Mix blow - condition where gas pressure becomes great enough to blow mix out of the mold through the ram clearances - denotes inability to process.

*** Binder level believed to be closer to 18-20 pph. Run numbers 16 and 17 employed fresh blends and mix blowing resulted

The pitch-furfural-trichloroethylene binder system was investigated further because this system produced mixes which were relatively easy to process with a greater degree of thermosetting. Room-temperature properties of cured, baked and graphitized plugs formed with varying amounts of pitch, furfural and trichloroethylene are shown in Table 10. Data from material formed by pressure curing with the pitch-sulfur binder system are included for comparison. None of the material tested was impregnated prior to graphitizing which resulted in lower strengths and density in each case. One of the cured plugs containing pitch-furfural-trichloroethylene binder retained its shape while being baked to 800°C without support, which indicates that this binder system was thermoset upon curing. The results show that plugs made from mix with a total binder level (pitch plus furfural) exceeding 25 parts per 100 were extremely difficult to cure. In addition, it was found that exudation of furfural

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Table 10. Physical Properties of Pitch-Furfural-Trichloroethylene-Base Graphite Material (4 Inches in Diameter by 4 Inches in Length)

Piece No.	175°C mp Pitch Level, pph	Furfural Level, pph	Trichloroethylene Level, per cent of Furfural	General Curing Results	Bulk Density After Curing, g/cc	Bulk Density After Baking to 800°C, g/cc	Volumetric Shrinkage After Baking, per cent	Bulk Density After Graphitizing, g/cc	Volumetric Shrinkage After Graphitizing, per cent	Flexural Strength*, lbs/in² With Grain	Across Grain	Electrical Resistivity*, 10^{-4} ohm-cm With Grain	Across Grain	Condition in Graphite State
16	24	4	10	Mix blow**	-	-	-	-	-	-	-	-	-	
17	24	4	10	Mix blow**	-	-	-	-	-	-	-	-	-	
19	22	4	10	Soft and cracked	-	-	-	-	-	-	-	-	-	
20	20	4	10	Slightly soft – OK	1.79	1.79	4.5	1.75	-0.2	1250	420	13.7	27.8	Piece flaw free
21	18	4	10	Slightly soft – OK	1.80	1.78	0.8	1.75	-0.2	1390	440	14.1	27.0	Piece flaw free
22	18	4	10	Soft and cracked	-	-	-	-	-	-	-	-	-	
23	18	2	10	Soft and cracked	-	-	-	-	-	-	-	-	-	
24	18	6	10	Soft- OK	1.79	1.78	1.1	1.75	0.2	1420	1030	14.1	17.8	Piece flaw free
25	16	6	10	Soft- OK	1.75	1.73	0.6	1.72	0.0	1090	480	16.1	25.9	Piece flaw free
26	16	8	10	Soft- OK	1.76	1.75	0.8	1.72	-0.5	1060	740	15.8	19.8	Piece flaw free
27	14	8	10	Soft and cracked	-	-	-	-	-	-	-	-	-	
28	12	12	10	Soft and cracked	-	-	-	-	-	-	-	-	-	
29	18	4	15	Slightly soft – OK	1.82	1.79	0.5	1.76	-0.2	1580	1630	16.2	15.4	Piece flaw free
30	18	4	20	Slightly soft – OK	1.78	1.72	-0.9	1.69	-0.5	-	-	-	-	Piece extensively cracked
31	18	4	25	Slightly soft – OK	1.77	1.69	-2.1	1.65	-0.6	-	-	-	-	Piece extensively cracked
32	18	4	100***	Slightly soft – OK	1.84	1.81	1.1	1.78	-0.3	1770	1360	15.4	17.4	Piece flaw free
33	18	4	100***	Slightly soft – OK	1.84	1.80	0.9	1.77	0.3	1720	-	15.0	-	Piece slightly cracked
Pitch-Sulfur-Base Graphite (4" dia. by 5" length)								1.75	-	2050	1740	13.2	16.7	Piece flaw free

* Each entry is an average of 4 determinations – Strength samples were $1/2$" by $1/2$" cross sections with center-point loading employed.

** Mix blow - condition where gas pressure becomes great enough to blow mix out of the mold through the ram clearances; denotes inability to pressure cure.

*** Trichloroethylene driven off by heating mix to 65°C

occurred at furfural levels greater than 6 parts per 100, and that the amounts of trichloroethylene above 15 per cent of the furfural resulted in high volumetric expansions on baking to 800°C.

The special technique of adding large amounts of trichloroethylene in the mixing step, mixing for 5 minutes and driving off the trichloroethylene to the 10- to 15-per cent level by heating the mix to 65°C produced the best properties (see Trial Nos. 32 and 33 in Table 10). Better properties resulted from a more uniform distribution of the pitch throughout the filler material because the pitch had been dissolved in the greater quantity of trichloroethylene.

Unusual volumetric expansion was experienced upon graphitizing the baked plugs to 2800°C and was believed to be a result of the low binder-coke content of the pitch-furfural-trichloroethylene material as compared to an all-pitch system. This low binder-carbon content would account for the lower strengths and higher electrical resistivities experienced with this material. Investigation of the pitch-furfural-trichloroethylene binder system was discontinued because no improvement, and perhaps some degradation, of graphite properties was evidenced.

5. SYNTHETIC BINDER SYSTEM BASED ON ACENAPHTHYLENE

5.1. Research Studies

5.1.1. Introduction

The many variables in carbon and graphite processing could be more easily understood and controlled through the use of a carbon binder for comparative studies which is reproducible and is not dependent on the vagaries of presently available supplies. A thorough study of the properties of a synthetic pitch binder prepared in the laboratory should help in the understanding of other binders and their effects on carbon processing.

Pitch-like products have been formed from acenaphthylene at various pyrolytic stages which indicated the possibility of producing a synthetic laboratory binder from this model hydrocarbon. These products are complex mixtures of aromatic hydrocarbons and radicals formed during the thermal degradation and condensation of the acenaphthylene. If the thermal transformation is performed in a reflux system whereby all material is retained, the volatile derivative, acenaphthene, formed in about 50-per cent yield, can be incorporated into the pitch mixture. Acenaphthene has no thermal reactivity under atmospheric conditions but its physical properties convey a plasticizing effect on the active product. The physical properties of acenaphthene are listed in Table 11.

Table 11. Physical Properties of Acenaphthene

Melting Point	95.0 °C
Boiling Point, 760 mm	278 °C
Specific Gravity, 25°C	1.195 g/cc
Coking Value, 450°C	0.0 per cent

The studies of acenaphthylene reported herein include: (a) producing synthetic pitches having different physical characteristics; (b) consistently reproducing a pitch of similar characteristics; (c) determining the chemical and physical properties and thermal behavior of the pitches; and (d) making carbon rods bonded with these pitches.

5.1.2. Experimental Procedure

Acenaphthylene (98- to 100-per cent purity) as obtained from Terra Chemicals Company was used in these investigations. All heat

treatments were conducted in a reflux system so that 100 per cent conversion to the initial pitch was attained. The physical properties of the pitch were modified by subsequent distillation of various amounts of the volatile hydrocarbon product acenaphthene.

A schematic diagram of the apparatus used for the preparation of acenaphthylene pitch is shown in Figure 8. A typical run consisted of 500 grams of acenaphthylene in a 2-liter resin flask which was placed in a heating mantle and fitted with a ground glass 4-neck cover. Thermocouples were inserted between the bottom of the flask and the mantle and directly to the mantle itself to closely monitor the temperatures. The resin flask cover was fitted with an air condenser, a 150-mm immersion thermometer which extended well below the surface of the acenaphthylene and a 100-mm immersion thermometer which measured the vapor temperatures of the system. A gas flowmeter inlet tube was attached to the fourth neck of the resin cover for reactions performed under nitrogen atmospheres. In those cases nitrogen was used to purge the apparatus and was introduced continually at the rate of 5 cc per minute throughout the run. This neck was fitted with a ground glass stopper for experiments performed in air.
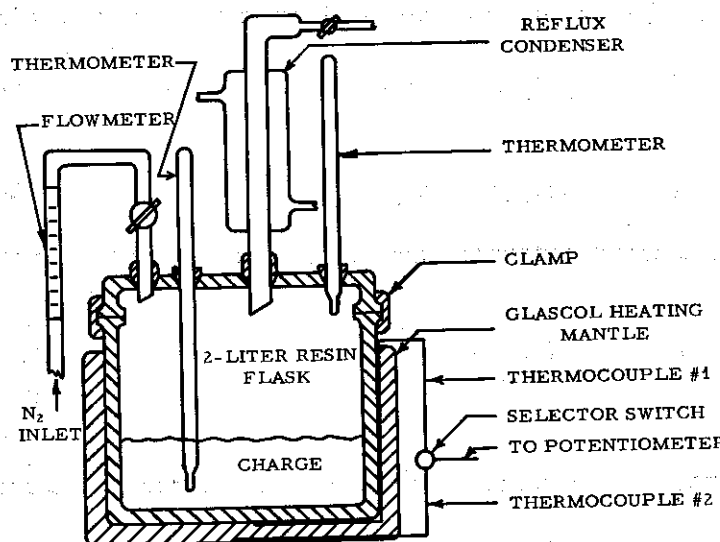

Figure 8. Laboratory Apparatus for Synthesis of Acenaphthylene Pitch

The power setting to the mantle was generally maintained at 80 volts. After heating was begun, the thermocouple and thermometer readings were continually monitored. The acenaphthylene completely melted in about 20 minutes and after about 50 minutes the molten acenaph-

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thylene began to polymerize, with a rapid rise in the temperature. The rapid exothermic polymerization was accompanied by some volatilization of acenaphthene.

Internal temperatures slowly abated after formation of a dark-red polymer. About 2 hours after initiation of the run the mantle temperature was approximately 390°C, the polymer began to soften and was converted to a black liquid-pitch product. The liquid pitch was maintained at a reflux temperature of 280°C by the formed acenaphthene and reflux times were varied from 1 to 72 hours.

After the desired reflux time, the condenser was replaced with a distillation head fitted with a thermometer and distillate receiver and the assembly was heated with an infrared lamp. In about 45 minutes, distillation of the acenaphthene commenced after which the pitch temperature constantly increased. The distillation rate was approximately 4 cc per minute. The softening point of the pitch was controlled by the amount of distillation; i.e., the softening point increased with the removal of an increased amount of distillate. Termination of the distillation was indicated by the liquid-pitch temperature and a temperature of 340°C corresponded to a 110°C-softening-point pitch product. Upon the termination of distillation the apparatus was immediately disassembled and the flask allowed to cool.

5.1.3. Results

The properties and characteristics of synthetic pitches prepared from acenaphthylene under varying reaction conditions are presented in this section. Each preparation is designated by a run number and is listed in chronological order. Several of these preparations were made to ascertain the effects of altering reaction conditions on pitch properties. Others were made to demonstrate the reproducibility of a particular binder preparation. Trials for which run numbers are omitted either have not been evaluated or were performed in a different apparatus. All measurements were made employing standard laboratory techniques.

5.1.3.1. Chemical Analysis of Acenaphthylene Pitches

Elementary analysis data for all the acenaphthylene pitches prepared in the research experiments are given in Table 12. For comparative purposes, the analysis of a coal-tar pitch is included. Reaction conditions of the trials are also given including the reaction atmosphere and the total reflux time prior to distillation of the acenaphthene. The difference between the yield figure for each run shown in Table 12 and 100 per cent is essentially the quantity of acenaphthene distilled although in all experiments small

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material losses were encountered. Utilization of a pure hydrocarbon starting material excluded other elemental contaminants such as sulfur or nitrogen from the acenaphthylene pitches.

Table 12.   Elementary Analysis of Acenaphthylene Pitches*

Run No.	Atmosphere	Reflux Time, hrs.	Yield, per cent	C, per cent	H, per cent	O, per cent	Ash, per cent	Atomic Ratio, C/H
Acenaphthylene (98 to 100 per cent)	-	-	-	94.11	5.34	0.13	0.01	1.47
1	N₂	27	64.1	94.63	4.52	0.26	0.02	1.74
2	N₂	1	51.0	95.23	4.14	0.16	0.04	1.92
3	N₂	22	54.1	95.14	4.26	0.16	0.01	1.86
4	N₂	71	60.5	94.77	4.42	-	0.03	1.78
5	Air	41	72.8	95.21	4.81	0.33	0.01	1.65
6	Air	30	69.0	94.43	4.65	0.34	0.07	1.69
7	Air	30	71.0	94.50	4.72	-	0.01	1.67
8	Air	30	65.8	94.54	4.56	-	0.03	1.73
9	Air	30	61.4	94.86	4.51	0.19	0.03	1.75
10	Air	30	64.5	94.39	4.65	0.32	0.01	1.69
11	Air	30	63.4	94.85	4.62	0.19	0.01	1.71
13	Air	30	56.4	95.17	4.39	0.15	0.02	1.81
16, 18, 19**	Air	30	64.4	94.46	4.65	-	0.19	1.69
Coal-Tar Pitch 100°C mp	(N₂ = 1.10 per cent, S = 0.53 per cent)			92.57	4.32	1.03	0.11	1.79

* Prepared from 98- to 100-per cent pure acenaphthylene.

** Composite of three identical trials.

The elementary analyses of the pitches produced under varying conditions of refluxing time and atmosphere showed a surprisingly narrow range of variability. The carbon content ranged between 94.4 per cent and 95.2 per cent by weight and the hydrogen content between 4.1 per cent and 4.8 per cent by weight. Oxygen and ash contents were very low and the variation was within the experimental error. The atomic C/H ratios of 1.7 to 1.9 indicated highly aromatic species.

The carbon-hydrogen analysis of a comparable 110°C-melting-point coal-tar pitch compared very favorably with those of the acenaphthylene pitches. The principal chemical difference was in the oxygen, nitrogen, and sulfur content. Acenaphthylene pitches contained no nitrogen or sulfur and very little oxygen.

Infrared and ultraviolet absorption spectra for a typical acenaphthylene pitch are shown in Figure 9. The infrared absorption spectrum consisted almost exclusively of carbon-hydrogen and carbon-carbon bands in aromatic species. The low intensity aliphatic carbon-hydrogen band at 3.45 microns was largely caused by the hydrogenated product acenaphthene. Chromatographic separations have been performed on several of these pitch products with qualitatively identical results. The major quantitative difference was found to be the amount of acenaphthene remaining in the product after distillation. The ultraviolet spectrum

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showed more specificity than the spectrum of a coal-tar pitch, indicating the acenaphthylene pitch mixture was less complex (i. e., contained fewer compounds).
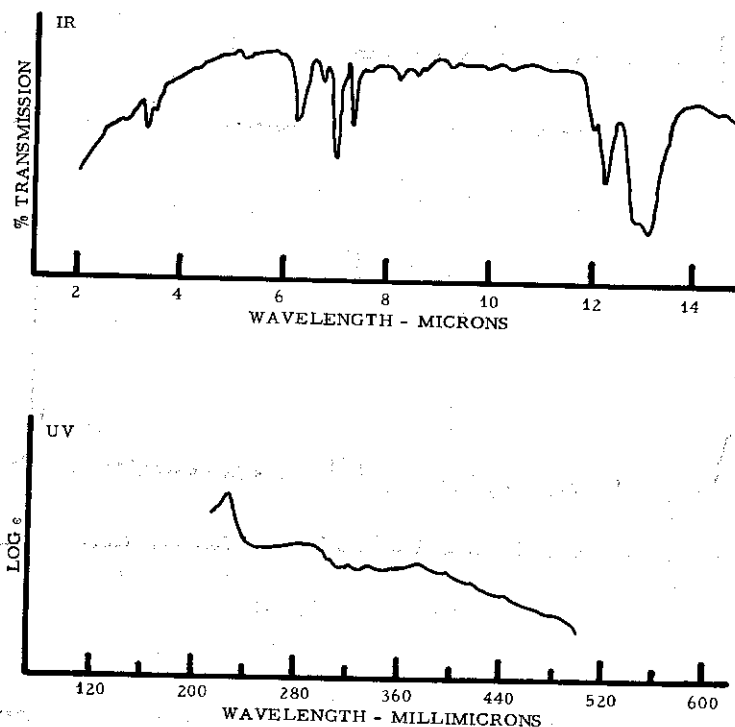
Figure 9. Infrared and Ultraviolet Absorption Spectra for a Typical Acenaphthylene Pitch

Figure 10 shows the nuclear magnetic resonance spectra for acenaphthylene and a representative acenaphthylene pitch. The almost complete aromaticity of the acenaphthylene pitch was verified by the nuclear magnetic resonance spectrum. In this spectrum the principal features were the aromatic proton resonances between 7.0 and 7.5 ppm and the aliphatic protons α to the aromatic rings at 3.34 ppm due to the acenaphthene. Vinyl olefinic proton peaks appear to be present at 6.85 and 6.00 ppm, although the high noise level interfered with their positive identification.

Elementary analysis and spectroscopic analysis of acenaphthylene pitches are of little value for control purposes as they are relatively insensitive to changes that produce large variations in physical properties.

ACENAPHTHYLENE

ACENAPHTHYLENE
PITCH

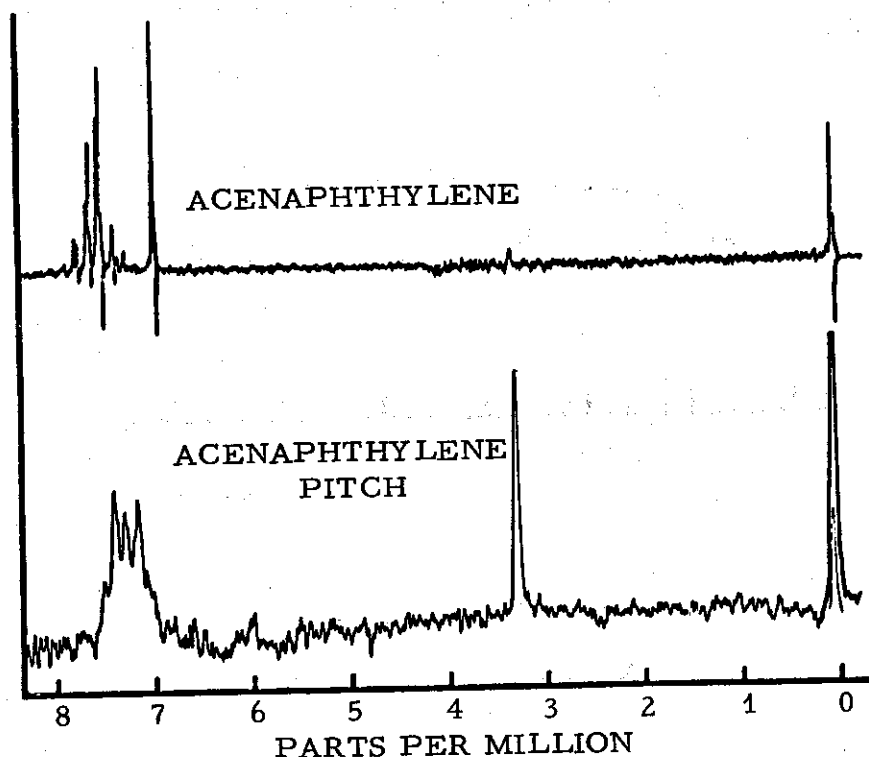8 7 6 5 4 3 2 1 0

PARTS PER MILLION

Figure 10.   Nuclear Magnetic Resonance Spectra for Acenaphthylene
and a Representative Acenaphthylene Pitch

5.1.3.2.   Physical Properties and Coking Behavior

Physical properties and coking values of the above acenaphthy-
lene pitches are compiled in Table 13.

The physical property of acenaphthylene pitch most amenable to
control was the softening point.   By the simple expedient of adjusting the
amount of acenaphthene distilled from the pitch product, the softening
point was varied from a low of about 50°C in the case where no acenaph-
thene was removed to a high of about 250°C when most of the acenaphthene
was removed.   The softening point (usually called melting point) of a pitch
is actually only another point on the viscosity-temperature curve since
pitch is structurally a liquid above room temperature.   A comparison of
the viscosity-temperature curves for a 117°C-mp acenaphthylene pitch
and a 112°C-mp, 30-medium coal-tar pitch given in Figure 11 indicated
that the two types of pitches have essentially identical viscosity charac-
teristics.

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Table 13. Physical Properties and Coking
Behavior of Acenaphthylene Pitch

| Run No.	Melting Point, °C	S. G. 25°C	Mol. Wt. in Benzene	B.I., per cent	Q.I., per cent	β* Resin	C.V. Wt., per cent
Acenaphthene	95.0	1.195	154	0.00	0.00	-	0.00
Acenaphthylene	92.5	1.185	152	0.00	0.00	-	42.00
1	134.0	1.288	450	9.88	0.13	9.75	65.69
2	251.5	1.330	420	18.94	18.91	0.03	81.23
3	173.8	1.315	495	17.95	0.59	17.36	77.51
4	146.3	1.297	420	10.91	1.64	9.27	71.22
5	94.5	1.268	460	5.80	0.13	5.67	57.75
6	107.4	1.271	395	4.45	0.36	4.09	59.98
7	103.5	1.268	385	5.10	0.15	4.95	58.87
8	123.3	1.282	425	7.93	0.20	7.73	63.18
9	134.0	1.291	450	9.45	0.20	9.25	67.42
10	117.5	1.284	435	6.28	0.26	6.02	62.43
11	117.5	1.292	450	5.90	0.28	5.62	62.89
13	162.0	1.300	-	10.85	0.82	10.03	70.12
16, 18, 19	121.5	1.282	-	9.51	0.31	9.20	60.35
Coal-Tar Pitch (P-121)	110.3	1.320	-	34.44	13.50	20.94	61.66

* β Resin = B.I. - Q.I.
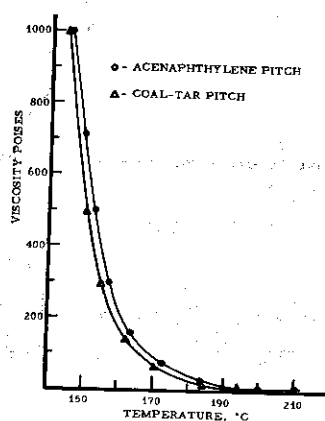
Figure 11. Comparison of Viscosity-Temperature Curves for a 117°C-mp Acenaphthylene Pitch and a 112°C-mp Coal-Tar Pitch

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Linear relationships have been found between the cube-in-air melting point of the acenaphthylene pitch, the yield of pitch, and the coking value of the pitch. These relationships are illustrated in Figure 12. However, as the yield of pitch approached 50 per cent, the softening point deviated significantly from this relationship. The coking value of the pitch was inversely proportional to the yield of pitch obtained from acenaphthylene under the experimental conditions described and was found to be constant at about 44 to 45 per cent, independent of the pitch intermediate, when calculated back to the starting acenaphthylene. The coking values of acenaphthylene pitch compared favorably with coal-tar pitch of similar softening point.
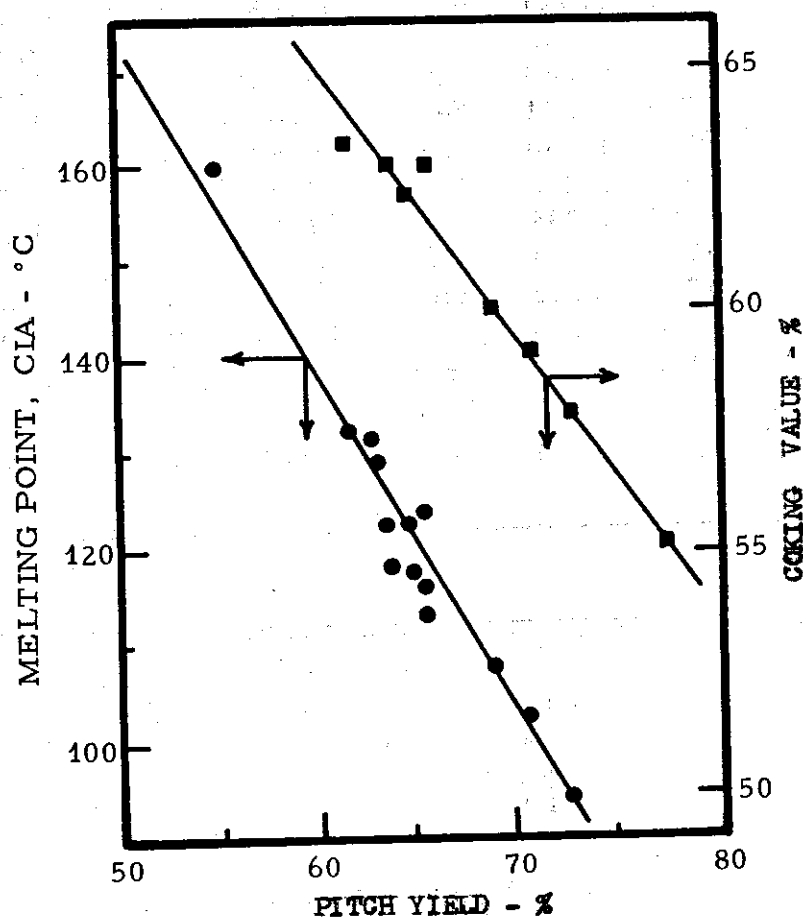

Figure 12. Relationship of Melting Point, Pitch Yield and Coking Value of Acenaphthylene Pitch

The specific gravity of a binder or impregnant pitch is an important consideration since it determines initially the number of carbon atoms that can be deposited in a given volume. The acenaphthylene pitches prepared in this study had specific gravities (at 25°C) ranging from 1.268 to

1. 330 depending on their softening points. An interesting comparison of the specific gravities of 110°C-mp coal-tar pitch and a 106°C-mp acenaphthylene pitch as a function of the temperature at which the specific gravity was measured is shown in Figure 13. The acenaphthylene pitch curve has an inflection point around 70°C, similar to the "glass temperature" or "second-order transition temperature" of amorphous polymers. Coal-tar pitches do not exhibit this behavior above room temperature. It is seen that the slopes of the curves for the two pitches are essentially identical at temperatures above the inflection point. From these results, the volumetric coefficients of thermal expansion can be calculated. The CTE of both the 30-medium pitch and the acenaphthylene pitch above the "glass temperature" is slightly over $4 \times 10^{-4}/$ °C. The CTE of the acenaphthylene pitch below the "glass temperature" is about $2 \times 10^{-4}/$°C.
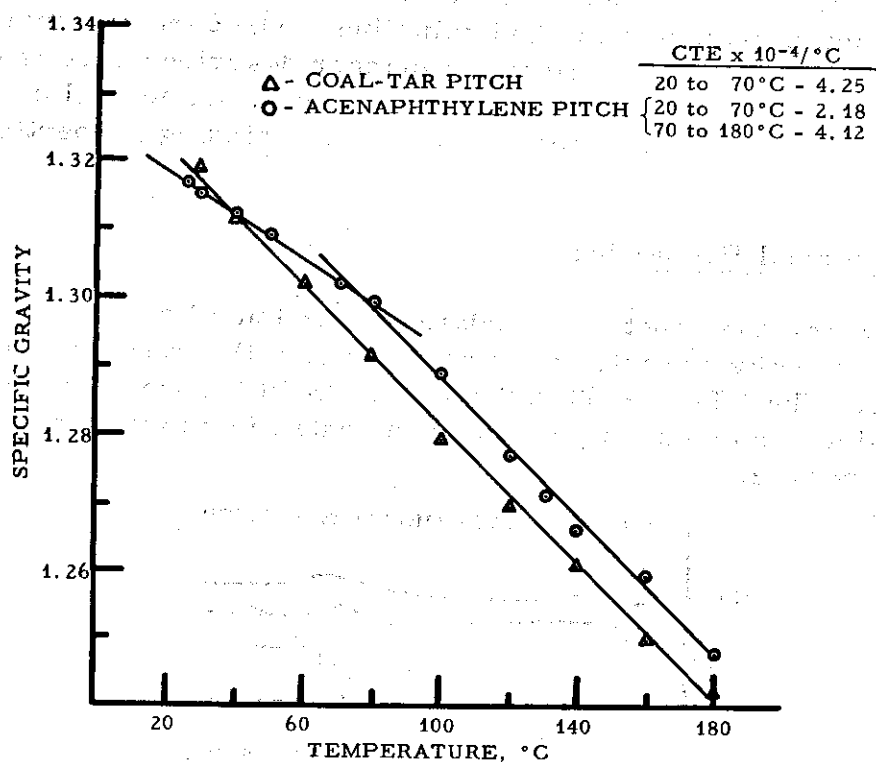
Figure 13. Comparison of Specific Gravities of a 110°C-mp Coal-Tar Pitch and a 106°C-mp Acenaphthylene Pitch as a Function of Temperature

An interesting experimental problem arises from the specific gravity versus temperature determinations. These measurements were made by determining the buoyancy of the pitch in a silicone oil in which it appeared to be completely insoluble. The usual specific gravity measurement at room temperature is made with a helium pycnometer in

which the volume of helium displaced by the sample is determined. In the case of the coal-tar pitches, the two methods agreed to the third place after the decimal point. In the case of seven measurements on acenaphthylene pitch, the helium pyconometer results were always lower by 0.01 to 0.02 units. The reasons for this discrepancy have not been determined.

A major difference between acenaphthylene pitch and coal-tar binder pitch is their solubility in solvents such as benzene and quinoline. Acenaphthylene pitch resembles 15-vacuum impregnating pitch in this respect and because of the low insolubles content should be useful for impregnation of carbon. In general, the acenaphthylene pitches have Q.I. values below 0.5 per cent. In the one case where the Q.I. was equal to the B.I. (Run No. 2 in Table 13) the pitch still contained a fairly large proportion of polymer of high enough molecular weight to resist solvation in both benzene and quinoline. The β-resin content of acenaphthylene pitches produced in the manner described here is of little significance since the Q.I. fractions are so small. In normal coal-tar terminology this fraction has been related to the binding properties of the pitch.

5.1.3.3. Thermal Properties

Perhaps the most appropriate evaluation of the thermal behavior of acenaphthylene pitch is to compare it with a normal coal-tar pitch binder. The DTA and TGA thermograms in Figure 14 compare the results obtained on two such pitches when heated in an argon atmosphere at 10°C per minute.
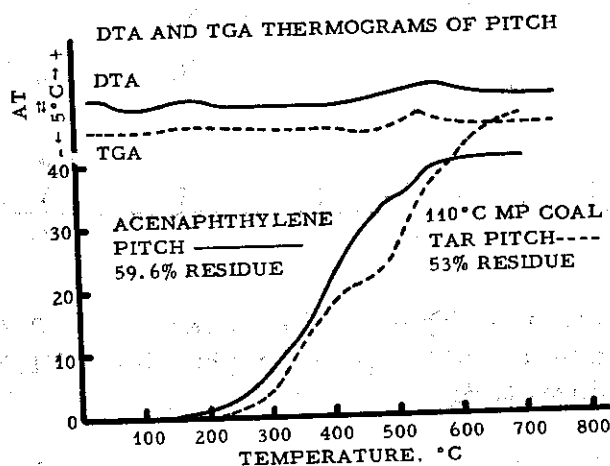

Figure 14. Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) Thermograms Comparing Acenaphthylene to Coal-Tar Pitch

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DTA thermograms show temperature regions where heat is either absorbed or evolved by the sample as a result of chemical or physical transformations. In the case of pure compounds, these transformations occur abruptly at well-defined temperatures and the endothermic or exothermic departure of the curve from the baseline is usually pronounced. In the case of complex mixtures such as pitch, numerous changes may be occurring simultaneously, some in opposite thermal directions, and the net effect is an attenuated curve with no sharp distinguishing peaks.

The DTA thermograms were nonspecific for both acenaphthylene pitches and coal-tar pitches with respect to the thermal interactions. The endothermic volatilization that occurred continuously above 200°C was almost completely masked either by simultaneous exothermic reactivity or by favorable changes in heat-transfer properties of the samples. In any case, both the acenaphthylene pitch and coal-tar pitch reacted in the same manner.

TGA thermograms show the change in weight of the sample as the environmental temperature is raised at a constant rate. The acenaphthylene pitch began to lose weight at about 150°C or 50°C below the threshold temperature of the coal-tar pitch. Up to about 400°C, the rates at which the two pitches lost weight were similar. Between 400° and 500°C the acenaphthylene pitch continued to lose weight at approximately the same rate but the coal-tar pitch rate was reduced markedly. Above 500°C the weight-loss rate of acenaphthylene pitch slowed and essentially leveled off between 600°C and 700°C while the coal-tar pitch lost weight at a very rapid rate between 500°C and 600°C. Above 650°C the weight loss curve began to level off for the coal-tar pitch. At 700°C, the acenaphthylene pitch residue was 59.6 per cent and the coal-tar pitch residue was 53 per cent. It should be pointed out that the cumulative weight loss at any given temperature for either pitch was dependent on the heating rate employed.

In the consideration of pitch as a binder material, it is sometimes argued that the quinoline insoluble fraction contributes nothing to the bonding properties of the pitch. This fraction is similar to carbon black, insoluble and nonvolatile. The primary reason for determining Q.I. is that it gives information regarding the thermal history of the coal tars from which a pitch is produced. If one corrects the weight-loss curve of the coal-tar pitch for the Q.I. content of 13.5 per cent, the weight losses then are related to the liquid content or binder fractions only. On this basis, the acenaphthylene pitch compared favorably at all temperatures with coal-tar pitch.

5.1.3.4. Binder Properties

Several of the acenaphthylene pitches prepared during this investigation were used to produce carbon rods for the purpose of determining their applicability as binders. Two groups of extruded rods were formed, one with a low-CTE coke (RM-2728) and one with a high-CTE coke (RM-2787) To determine if the low-CTE pitch coke formed from acenaphthylene would have an appreciable effect on the CTE of the rods. In all cases the acenaphthylene pitch was handled in the same manner as the normal coal-tar pitch with no problems either in mixing or extrusion. The only special precaution taken with the acenaphthylene pitch was to heat it in a covered container to prevent loss of the very volatile acenaphthene plasticizer. Extruded rods were also processed from mixes containing standard coal-tar pitches and these were used as a basis for comparison of acenaphthylene pitches. The mix composition and extrusion conditions are given in Table 14.

Table 14. Mix Compositions and Forming Conditions Used in Extruding Rods with Acenaphthylene and Coal-Tar Pitch Binders

Pitch	Coke Designation	Mix Composition Wt. per cent				Extrusion Conditions	
		Coke	Fe_2O_3	Pitch	Oil	Temp., °C	Gauge Press., lbs/in^2
100°C-mp Coal-Tar Pitch	RM-2787	100	2	35	4	110	280 to 400
Filtered 100°C-mp Coal-Tar Pitch	RM-2787	100	2	35	4	110	220 to 300
117°C-mp Acenaphthylene	RM-2787	100	2	36	4	115	600 to 950
100°C-mp Coal-Tar Pitch	RM-2728	100	2	34	4	110	320 to 360
117°C-mp Acenaphthylene	RM-2728	100	2	35	4	115	800 to 950

The green rods, $3/4$-inch diameter, were cut to 6-inch lengths, baked to 1000°C, measured for bulk density, and graphitized to 3000°C.

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The physical properties of the rods after each processing step are summarized in Table 15. Each value is the average of four measurements.

Table 15. Physical Properties of Carbon Rods Bonded
with Acenaphthylene or Coal-Tar Pitches

Sample Description Pitch-Coke	Bulk Densities, g/cc			Graphite Properties		
	Green	1000°C Baked	Graph.	Specific Resistance, 10^{-4} ohm-cm	CTE, 10^{-6}/°C	Flexural Strength, lbs/in^2
30-Med., RM-2787	1.68	1.52	1.52	8.88	1.23	-
Filtered 30-Med., RM-2787	1.67	1.49	1.49	8.09	1.13	-
Acenaphthylene, RM-2787	1.66	1.53	1.54	6.78	1.03	-
30-Med., RM-2728	1.67	1.52	1.54	8.45	0.53	1834
Acenaphthylene RM-2728	1.65	1.51	1.51	7.27	0.45	2043

The results of these experiments indicated that the acenaphthylene pitches produced carbon and graphite of comparable quality to that made with a coal-tar pitch binder.

5.2. Scale-Up Studies of Acenaphthylene Pitch

Development studies of acenaphthylene pitch required approximately 60 pounds of pitch with a melting point of about 175°C. Two hundred pounds of 90-per cent purity acenaphthylene were purchased from Terra Chemical Company. The impurity was acenaphthene which also is a by-product obtained during the manufacture of pitch from the acenaphthylene. Simple distillations were carried out in the laboratory pitch still pictured in Figure 15 and shown schematically in the flow diagram of Figure 16.

A reflux time of $26\frac{1}{2}$ hours at a temperature of 300°C was maintained during the first distillation. A violent exotherm was noted at approximately 170°C charge temperature (polymerization point) which then proceeded rapidly to 300°C. The rapid expansion caused by the exothermic reaction carried polymer and the impurity acenaphthene

into the recycle lines outside the reaction zone. It was postulated that the 10 per cent impurity (acenaphthene) was the contributing factor, since its boiling point (270°C) was rapidly exceeded and it therefore flash distilled carrying polymer with it. At the end of the reflux period, a condenser pipe was attached to the still and the temperature brought to 350°C with the acenaphthene distilled out. The temperature was reduced to 250°C and the pitch product was discharged. The melting point of the pitch produced during the first run was 186°C. Two more distillations, under similar conditions, yielded pitches with melting points of 145°C and 152°C, due to the greater acenaphthene content. These latter two pitches were combined and distilled further to give a 177°C-melting-point pitch which was then added to the 186°C pitch.

Physical property data of the above pitches are listed in Table 16 and compare favorably with the results obtained during the research studies.
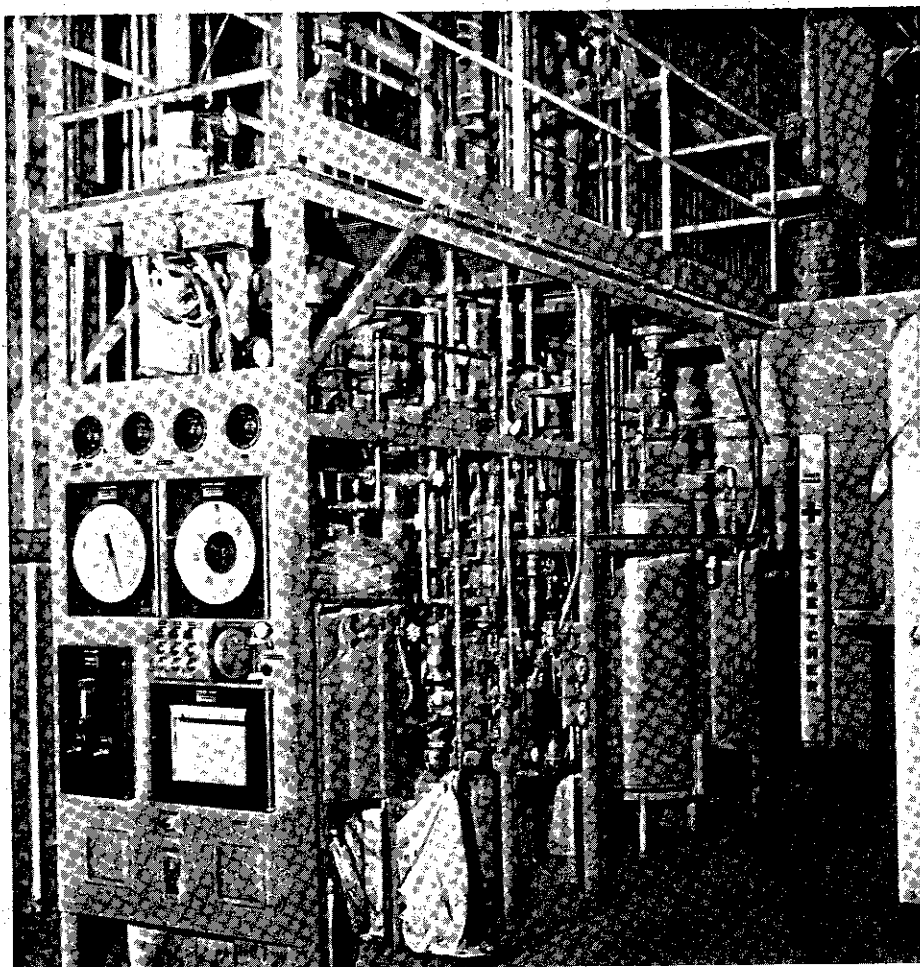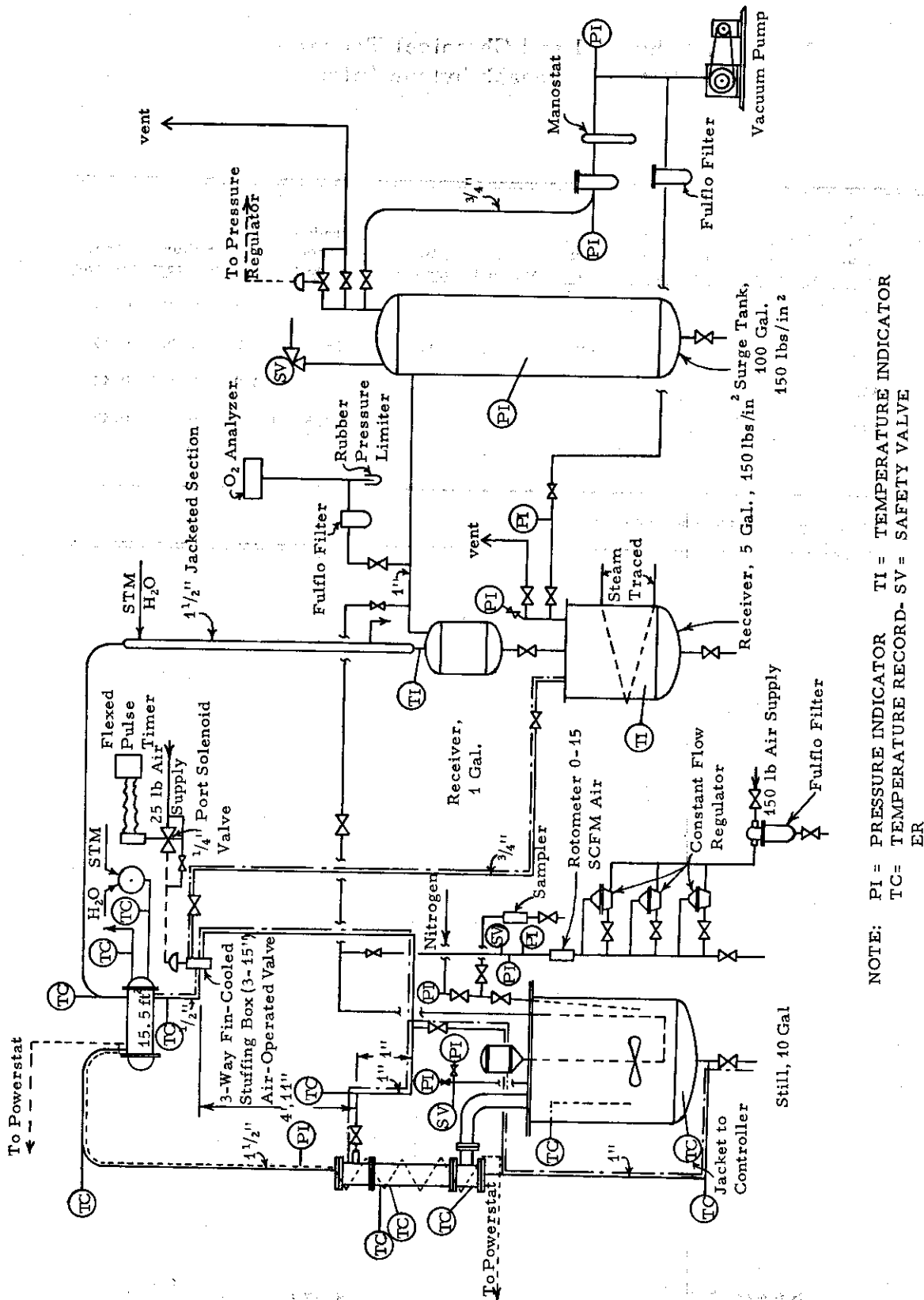

Figure 15. Laboratory Tar Distillation Unit

Figure 16. Flow Diagram, Laboratory Tar Distillation Unit

NOTE: PI = PRESSURE INDICATOR   TI = TEMPERATURE INDICATOR
TC= TEMPERATURE RECORD- SV= SAFETY VALVE
ER

------- = ELECTRIC HEATING

———— = STEAM HEATING

Table 16. Physical and Chemical Property Data of Acenaphthylene Pitch

Run No.	Reflux Time, hrs.	Distillation Temp. °C	Pitch Yield, per cent	Corrected* Pitch Yield, per cent	Melting Point, °C	Q.I., per cent	B.I., per cent	Conradson Carbon, per cent	S.G., g/cc	Sulfur, per cent	Ash, per cent
1	$26\frac{1}{2}$	352	44.9	49.9	186	0.12	27.3	75.0	1.312	0.09	0.13
2	$28\frac{1}{2}$	348	51.6	57.3	145	0.12	17.7	65.5	1.300	0.06	0.19
3	-	352	50.4	56.0	152	0.29	16.5	66.8	1.359	0.07	0.12
6	-	338	46.2	51.3	177	0.42	24.4	72.5	1.310	0.06	0.17

* Corrected for 10 per cent acenaphthene impurity.

6. LIST OF REFERENCES

(1)   Bushong, R. M. and A. A. Kellar, Union Carbide and Carbon
       Corporation, U. S. Patent No. 2,761,848, "Process of Making
       Shaped Carbon Articles."

(2)   Jones, M. T., National Carbon Company Research Laboratory
       Report ERC 336, "ST Process for Making High-Density Graph-
       ite and Carbon."

(3)   Shea, F. L. and L. H. Juel, Great Lakes Carbon Corporation,
       U. S. Patent No. 2,500,208, "High Coking Binder Compositions
       and Products Thereof."

(4)   WADD TR 61-72, Volume XI and Supplement, "Characterization
       of Binders Used in the Fabrication of Graphite Bodies," E. de
       Ruiter, A. Halleux, V. Sandor and H. Tschamler, National
       Carbon Company.

(5)   WADD TR 61-72, Volume XV, "Alumina-Condensed Furfuryl
       Alcohol Resins," C. W. Boquist, E. R. Nielsen, H. J. O'Neil
       and R. E. Putcher, Armour Research Foundation.

(6)   WADD TR 61-72, Volume XII, "Development of an Improved
       Large-Diameter, Fine-Grain Graphite for Aerospace Applica-
       tions," C. W. Waters and E. L. Piper, National Carbon
       Company.