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IMPROVED GRAPHITE SYSTEMS
FOR
ADVANCED FUEL ELEMENT FABRICATION

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IMPROVED GRAPHITE SYSTEMS
FOR
ADVANCED FUEL ELEMENT FABRICATION

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FOREWORD

The research reported herein was conducted at Great Lakes Research Corporation, Elizabethton, Tennessee for Westinghouse Electric Corporation, Astronuclear Laboratory under Subcontract Number 59-CYD-21007, "Improved Graphite Systems for Advanced Fuel Fabrication". The program was under the direction of Mr. E. G. Fatzer of WANL.

The principal investigator was Dr. M. P. Whittaker, Section Head, Graphite Section, Great Lakes Research Corporation. Major contributions to the work reported were made by Mr. L. I. Grindstaff, Mr. R. Hund, and Mr. F. C. Miller.

ABSTRACT

This program had two primary objectives. The first task was to prepare three experimental flour samples for evaluation by Westinghouse Astronuclear Corporation in fuel element fabrication and to investigate possible replacements for Thermax in the element formulation. The second task was to characterize and evaluate a second iteration of pitch/furan binders developed for WANL by the Quaker Oats Company.

In the first phase of the program, which is described in part A of this report, three 150 lb. flour samples were prepared and delivered to WANL. All three flours were prepared from dense, fine grained billets using the same basic process as employed in the fabrication of Grade 1076 flour. One sample was, in fact, a low fired (1000°C) counterpart to the 1076 material. The remaining two samples, one high fired (2700°C) and the other low fired, were formulated from an air blown coke. Small 5/8" rods fabricated using these flours in the WANL formulation had apparent densities of 1.95 g/cc and coefficients of thermal expansion ranging from 60.1 to 73.4x10⁻⁷/°C. (20-1500°C). The air blown coke from which two of the flours were prepared was characterized by exceptionally uniform, isotropic structure. The coefficient of thermal expansion of bodies prepared from the air blown material was significantly higher than obtained on artifacts produced from untreated petroleum coke employing the same type processing.

An attempt was made to find a more suitable filler than the Thermax presently being used in NERVA fuel element fabrication. Two candidate fillers were petroleum coke based materials, i.e., micronized high-fired and low-fired GLC-1076 flour. Also, three carbon blacks obtained from the Cabot Corporation were evaluated to determine the effects of high surface area materials. On the basis of A. D., CTE, and resistivity none of the Thermax replacement candidates was more suitable than Thermax itself.

In the second phase of the program, discussed in part B of this report, a total of 19 different binder formulations and 4 hardeners were investigated. The study included calculation of binder yields both in unfilled binders as well as extrusions, plastometer studies of the resoftening ranges, fractional distillation, DTA and TGA analyses, determination of x-ray diffraction parameters, and photomicrographic analysis. Physical property measurements were made on graphitized 5/8" dia. extrusions containing 85 pts. GLC-1076 flour (2700°C)/15 pts. Thermax filler.

Binder coke structures were found to vary from glassy carbon to a relatively coarse-grained isotropic coke. The physical properties of some of the binders were found to approach those determined for extrusions containing "Varcum-type" binders. Plastometer studies on cured, unfilled binders indicated that resoftening ranges exist, and it is felt that the upheating rate through the resoftening range can affect the final coke structure.

It is recommended, as a result of this investigation, that additional studies on selected binders be done to establish the relationship between coking upheating rate and ultimate binder structure. It is also recommended that the required pitch additions to the furan component be made during the formulation of the binder rather than be added to the extrusion mix. The recommended hardener for the pitch/furan binders is graphite supported QX-314.

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I. INTRODUCTION

As the performance requirements for the fuel elements for the NERVA engine increase, the graphite matrix for these elements must be improved to withstand additional thermal cycling, and be more compatible with the fuel phase and protective coating.

A. Experimental Flours

Under this contract three experimental flours were to be produced for evaluation in this application. Based upon favorable results obtained with GLC-1076 flour, the same basic process was to be employed in fabricating the three 150 lb. samples. One flour would be prepared from the same raw material as GLC-1076 except that the precursor bodies would be fired to only 1000°C rather than 2700°C. The other two samples, one high fired and the other low fired, would be prepared from air-blown coke produced in the GLRC laboratory.

Physical properties of the graphitized fuel elements are believed to be significantly influenced by the carbon black filler. In an effort to find a replacement for the Thermax presently being used, five candidates were evaluated in 5/8" dia. extrusions. Criteria for evaluation was based on the incorporation of the candidate materials in place of Thermax in standard mix formulations of GLC-1076 flour and Varcum 8251 binder.

B. Binder Evaluation

The specific objective was the characterization and evaluation of a second iteration of binder candidates developed for WANL Subcontract No. 59-NYD-14277, "Improved Graphite Systems for Advanced Fuel Element Fabrication".

From the recommendations made in the final report of this previous work, two Quaker Oats pitch/furan binders were selected on the basis of final coke structure and coke yield for modification and further characterization. QX-228 was found to produce a relatively graphitic, anisotropic binder coke while QX-237 produced a less graphitic; more isotropic structure. Both binders tended to show some indications of resoftening between 300°C and 450°C; and, therefore, could not be considered truly thermosetting. In the second iteration of binders a total of thirteen liquid binders, two powdered pitch additives, and four hardeners were evaluated. The variables which were investigated as a result of the latest modifications were type of hardener, furan resin concentration, state of pitch during addition (powdered vs. liquid), pitch softening point, process modifications toward more graphitic binder cokes and reduced ash, increased booster hardener, and type of furan resin.

The main criteria used in evaluating the various binder formulations were coke yield and final binder coke structure. The coke yields were determined both from quantities of unfilled resins catalyzed with QX-240 liquid hardener and from binder coke yields in extrusions using various hardeners furnished by Quaker Oats Company. Coke structure evaluations were made from photomicrographs and x-ray diffraction data. Coking behavior was observed from fractional distillation, DTA, TGA, and plastograph studies. In addition physical property measurements were made on 5/8" dia. extrusions, and viscosity and carbon and hydrogen measurements were made on the as received binders. Qualitative observations were made wherever applicable to the processibility of the various binders.

Also included in the binder evaluation phase of this program is a limited study on the effect of catalyst on resin-binder coke yield. Curing of furfuryl alcohol resins is accomplished by the addition of either mineral or organic acids. The curing rate depends upon temperature and the activity of the catalyst. It is conceivable that certain organic acid catalysts could be incorporated as part of the polymer structure and lead to increased binder coke yields. Presently maleic anhydride seems to be the preferred catalyst. However other catalysts could outperform maleic anhydride via increased coke yields and improvements in graphitizability of the binder resin. The catalysts evaluated in this investigation were phthalic anhydride, pyromellitic dianhydride (PMDA) and toluene sulfonic acid (p-TSA).

II. SUMMARY AND RECOMMENDATIONS

A. Experimental Flours and Thermax Replacements

1. Experimental Flours

Three one hundred and fifty pound flour samples were produced and submitted to WANL for performance testing. All three samples were fabricated by the same process used to produce GLC-1076 grade flour. The process is specifically designed to yield a uniform, isotropic product. By air-blowing a petroleum feedstock, it was possible to produce a coke which was much more uniform and isotropic than any product produced in a commercial delayed coker. By combining the uniform air-blown raw material with the 1076 type processing, flours with the optimum degree of uniformity and isotropy were produced. Graphite artifacts formulated from the three experimental flours using Varcum binder were characterized by uniformly high apparent densities (1.95 g/cc) and high CTE's ($60.1-73.4 \times 10^{-7}/^{\circ}\text{C}$). The highest CTE values were obtained with the air-blown coke. The low fired flours resulted in higher CTE's but somewhat lower flexural strengths. While the characteristics of the samples, particularly the air-blown materials, appear to be ideal for the NERVA fuel element system, the true quality can be established only by performance testing. These experimental flours can be produced on a commercial scale if they yield a superior element. The characteristics of the flours can also be modified by changing the processing and/or the raw materials if the testing indicates that this is desirable.

2. Thermax Replacements

Five candidate fillers were evaluated as possible replacements for the Thermax presently being used in the NERVA fuel element fabrication. Two of the candidates were petroleum coke based materials and the other three were commercial carbon blacks. On the basis of A. D., CTE, and resistivity none of the Thermax replacement candidates was more suitable than Thermax itself. It is not recommended that any of these materials be included in product testing.

B. Binder Evaluation and Resin-Catalyst Study

1. Binder Evaluation

All of the pitch/furan binders were found to be either glassy or isotropic in final coke structure. None could be classified as truly anisotropic. The fact that no highly graphitic binder cokes could be detected by x-ray diffraction

or that no anisotropic structures could be seen in micrographs leads to the conclusion that the slower curing and baking rates of the unfilled binders used in this investigation resulted in a more homogeneous binder structure and prevented pitch/furan separation. Plastometer, DTA, and TGA studies indicated that the pitch/furan binders do have the potential to resoften which could cause phase separation. However, the heating rates used in these tests were in excess of 3°C/min. vs. the standard baking rate of 3.3°C/hr. The tests were useful, therefore, in determining temperature ranges of maximum thermal activity which are critical with respect to establishing optimum baking conditions.

DTA results show that definite furan/pitch interactions do exist during curing. For this reason the curing of the unfilled binders were modified in this investigation in order to decrease the severity of the exothermic curing reaction and to allow the pitch/furan components to fully react. As a result, the processing conditions for the unfilled resins closely followed the extrusion processing conditions. The effects on binder structure can be noted in the x-ray diffraction results and the micrographs.

The method by which the powdered pitch was added to the liquid furan component also appears to be critical. Binder coke yields of the unfilled resins were noted to be different from the binder yields of the extrusions. Powdered pitch was added to the unfilled furan at elevated temperature (80-90°C) and mixed well prior to the addition of hardener. For extrusions, the powdered pitch was added to the flour and flour supported hardener and mixed at 45°C. The liquid furan was added and mixed well into the dry ingredients. It is felt that the 45°C mixing temperature of the extrusions prevented complete solubilization of the pitch. Better and more uniform results would be obtained if the pitch and liquid furan were mixed as in the case of the unfilled binders prior to the addition of flour.

The pitch furan binders of this series were formulated by the Quaker Oats Company to test the following specific variables and relationships:

a. QX-302 series vs. QX-228 and 229 (first iteration) to determine the effect of furan resin concentration and the state of pitch addition (powdered vs. liquid). The viscosity of QX-302 was too thin for proper extrusion although the properties were good. QX-228 and 229 were more graphitic binders and more anisotropic in structure than any of the QX-302 series. The structures of QX-302 and 302-1 were essentially glassy, while the QX-302-2 binder coke was isotropic and fine-grained. As the pitch content was

increased in the series, the resoftening range increased from virtually none for QX-302 to a range of 200°C to 480°C for QX-302-1 and 200°C to 450°C for QX-302-2. QX-302-2 appeared to have the best combination of physical properties in extrusions and, as expected, the more graphitic character was reflected in CTE, E. R., and MOR.

b. QX-303-1, 303-2, 303-3 vs. QX-237 to determine the effect of furan resin concentration and state of pitch addition. As pitch concentration is increased in the QX-303 series the structure changes from glassy to fine-grained isotropic. X-ray diffraction shows that both QX-303-2 and 303-3 are more graphitic than QX-237. QX-237 and QX-303-2 appear nearly equivalent in most respects. The binder yield in extrusions tends to increase as more powdered pitch is added. With respect to physical properties QX-237 appears slightly superior to QX-303-2, and QX-303-1 is superior to both. Plastometer studies indicated a wide resoftening range for QX-303-3. The resoftening ranges of QX-303-1 and 303-2 were narrower than that of QX-237. Curing reactions as detected by DTA indicate that QX-237 undergoes less of an exotherm than the QX-303 series. As the pitch content is increased, the curing exotherm becomes more extended.

c. QX-303-2 vs. QX-303-6 to determine the effect of pitch softening point. X-ray diffraction results show that QX-303-6 is slightly more graphitic than QX-303-2; however, the structure of QX-303-6 shows that the pitch carbon is suspended in a matrix of glassy carbon. Due to the low volatile matter content of the 280°C softening point pitch, binder carbon yield of QX-303-6 is higher than QX-303-2. As might be expected the DTA curve for QX-303-6 shows relatively little furan/pitch interaction, and plastometer results indicate only slight resoftening in the coking range. With the exception of low CTE the QX-303-6 binder has superior physical properties in extrusions. However, QX-303-6 is essentially infusible pitch particles in a furan matrix.

d. QX-304-1 vs. QX-303-2 to determine the effect of furan process modification for a more graphitic binder. Both resins exhibit essentially equivalent C/H ratios and similar binder carbon yields. The resoftening range of QX-304-1 is greater than that of QX-303-2. X-ray diffraction shows QX-303-2 to be more graphitic than QX-304-1, and this is supported by the micrographs where QX-303-2 has a fine-grained isotropic structure and QX-304-1 is essentially glassy. The physical properties of extrusions containing QX-304-1 are superior to those containing QX-303-2.

e. QX-297-1 vs. QX-304-1 to determine the effect of a furan process modification for reduced ash. Ash analyses were not made on any of the binders. At the recommended curing agent level of 4% QX-297-1 did not achieve a full cure. Although QX-297-1 exhibited a higher C/H ratio than QX-304-1, its binder carbon yield was slightly lower. QX-297-1 also was found to have an extended resoftening range, but this could be due to insufficient curing. QX-297-1 was found to be slightly less graphitic than QX-304-1 by x-ray diffraction, although micrographs show the same glassy structure for both binders. The physical properties of extrusions showed no advantage to either binder.

f. QX-298-1 vs. QX-309-1 similar process modification as in e., above. As in the case of QX-297-1, QX-298-1 did not achieve a full cure at the recommended hardener level. QX-298-1 also exhibited an extended resoftening range. X-ray diffraction results show QX-309-1 to be less graphitic, although both binders are glassy in structure. Binder coke yields are essentially equivalent for both binders. In extrusions QX-309-1 resulted in a slightly higher density but lower CTE than QX-298-1. The MOR and MOE of extrusions containing QX-309-1 were higher than for QX-298-1.

g. QX-309-1 vs. QX-304-1 to determine the effect of a furan process modification (increased booster hardener). No distinct differences could be detected. Binder carbon yields of QX-309-1 in extrusions were only slightly higher than QX-304-1. QX-309-1 did show a narrower resoftening range than QX-304-1 (420-480°C vs. 400-470°C). QX-304-1 was slightly more graphitic than QX-309-1 as determined by x-ray diffraction. In extrusions, the densities, CTE's, and resistivities were essentially equivalent. QX-309-1 exhibited a higher MOE while QX-304-1 exhibited a higher MOR, which tends to agree with the x-ray diffraction results.

h. QX-308 vs. QX-237 similar process modification as in g., above. QX-308 exhibited higher binder carbon yields in extrusions, although the C/H ratio of QX-237 was higher. The resoftening range of QX-308 was narrower than that of QX-237. X-ray diffraction showed QX-237 to be more graphitic, and this tends to be supported by the micrographs. DTA curves show that QX-237 undergoes two curing exotherms while QX-308 shows a single, continuous curing exotherm. Furan/pitch disassociation reactions also occur earlier with QX-308.

i. QX-305-1, QX-306-1, QX-307-1 vs. QX-303-2 to determine the effect of different furans. QX-306-1 was found to be somewhat incompatible with the Ashland 240 pitch and was quite difficult to solubilize. Pitch also had a definite thickening effect on the QX-306 liquid resulting in high viscosities and high binder level requirements in extrusions. QX-303-2 and QX-307-1 were found to be more graphitic than QX-306-1 and QX-305-1 by x-ray diffraction. Micrographs show QX-303-2 to

be highly isotropic, while QX-307-1 and QX-306-1 showed isolated areas of isotropic structure in a glassy phase. QX-305-1 appeared to be completely glassy in structure. With respect to binder yields QX-305-1 was found to have the highest value, followed by QX-307-1, 306-1 and 303-2. The resoftening ranges, as determined by the plastometer, were narrowest for QX-303-2 and widest for QX-305-1. With the exception of the lowest CTE, extrusions containing the QX-305-1 binder had the best physical properties. If CTE is taken into consideration, QX-307-1 appears to be the best candidate. DTA showed QX-305-1 to have the least pitch/furan interaction, which possibly accounts for its wide resoftening range. Both QX-305-1 and QX-307-1 show some superiority in physical properties and binder yield over QX-303-2; however, QX-303-2 does exhibit a desirable binder structure being being relatively graphitic and isotropic.

On the basis of x-ray diffraction studies, micrographs, coke yields, and physical properties it is apparent that certain pitch/furan binders exhibit comparable properties to the "Varcum-type" resins. The pitch/furan binders also exhibit a range of coke structures from glassy to relatively coarse-grained isotropic structure. Of the binders which appear to have the most potential it is recommended that the following binders undergo additional investigation:

- QX-237-1 - isotropic structure, a standard
- QX-303-1 - glassy structure
- QX-302-2 - isotropic structure, but with plastic range
- QX-303-2 - isotropic structure, narrow plastic range
- QX-307-1 - mixture of isotropic and glassy phases

It is further recommended that the principal area of investigation be the effect of upheat rate through the critical resoftening range since this range has a determining effect on the final structure of the binder.

It is recommended that pitch additions to the furan component be made at the time of formulation of the binder to ensure adequate solubilization of the pitch phase.

The recommended hardener for all of the pitch furan binders should be the graphite-supported QX-314.

2. Resin - Catalyst Study

A limited amount of work was done to determine the effects of various polymerization catalysts on coke yields and structures obtained from Varcum 8251.

The catalysts used exhibited widely different reactivities based on their initial exothermic reactions. Toluene sulfonic acid (p-TSA) was the most reactive. The Varcum polymerized immediately on addition of this catalyst. Maleic anhydride and pyromellitic dianhydride (PMDA) exhibited the same reactivities while phthalic anhydride was the least reactive. Coke yield was highest with p-TSA (57.7%) while the other three catalyst gave essentially the same coke yield (48-49 wt. %). No significant differences in the 2200°C carbons were detected by x-ray diffraction analyses.

III. DISCUSSION

Part A. Experimental Flours

1. Precursor Preparation

A vacuum tower bottom (VTB) from Derby's Refinery, Witchita, Kansas was selected as the coker feed for preparation of air-blown coke. Typical feedstock properties for this material are shown in Table I. Preliminary cokings of the VTB were carried out on a small scale to determine optimum conditions for air-blowing and subsequent coking. Cokes were obtained by coking without air-blowing and by air-blowing at various conditions. Within a temperature range of 350-400°C, the effects of air-blowing on coke structure appeared to be mainly dependent on air-blowing time. As air-blowing temperatures increased, blowing times by necessity were decreased due to a faster increase in viscosity of the charge at higher temperatures. The effect of air-blowing on the CTE of the cokes is shown in Figure 1. The CTE measurements were made on 5/8" diameter extruded rods fabricated from 52% minus 200 mesh coke flour and coal-tar pitch binder. The rods were graphitized to 2900°C.

Batch cokings were carried out in an experimental coker to produce approximately 500 pounds of raw air-blown coke. The feedstock was air-blown 8 hours at 350°C prior to coking. Air was introduced and dispersed at the bottom of the coking vessel at a rate of 1-1.5 CFH/Kg. of charge. About 50 pounds of coke was produced per run. Comparative data is shown below for coke obtained without air-blowing and for the air-blown coke. In Figure 2 the microstructure, as revealed by optical microscopy, of the untreated coke and air-blown coke are compared. The air-blown material is characterized by a uniform, isotropic structure. The untreated coke is less uniform with relatively large areas of isotropic and anisotropic structure.

<u>Property</u>	<u>Regular</u>	<u>Air-Blown</u>
CTEx10 ⁻⁷ /°C (RT - 1500°C)	14.6	51.8
E. R., ohm-inx10 ⁻⁵	42.0	84.0
MOR, psi.	2347	1314
X-ray data, 2700°C		
d-spacing, Å	3.366	3.374
L _c , Å	463	301
% Graphite	68.2	54.1

The air-blown coke was composited prior to processing to the required high-fired and low-fired flours.

TABLE I
TYPICAL FEEDSTOCK PROPERTIES FOR DERBY'S
VACUUM TOWER BOTTOMS

API Gravity (60°C)	18.8
Sulfur, Wt. %	0.52
Viscosity, SUS, 210°F	1000
Filtration Residue, Wt. %	0.07
Conradson Carbon, Wt. %	10.4
Raw Coke Yield, Wt. %	16.9

FIGURE 1

CTE OF AIR-BLOWN COKE FROM DERBY'S VTB
vs. AIR-BLOWING TIME

Air Blown Coke 300X

Untreated Coke 300X

FIGURE 2

2. Processing

a. Forming

The coke was micronized in a Fluid Energy Mill to ca. 1.21 microns, average particle diameter, as determined on a Fisher Sub-Sieve Sizer. The micronized coke was then formed into 6" dia. x 6" long billets.

b. Baking

The formed samples were packed in 36" ϕ stainless steel saggars employing graphite packing media. Baking to 1000°C was accomplished in electrically heated furnaces. The baking cycle covered a period of nine and one-half days including a three day cooling period. The temperature-time profile for the baking operation is illustrated in Figure 3. Flour Nos. I and III were produced from baked bodies whereas Flour II was obtained from graphitized samples.

c. Graphitization

The bodies which required additional heat treatment were graphitized to 2700°C in a Lindberg Induction Furnace under a nitrogen atmosphere. The graphitization cycle covered a period of 32 hours, of which eight hours were required for heat-up to 2700°C and 24 hours for cooling. The graphitizing cycle is illustrated in Figure 4.

d. Milling

Initially, the baked or graphitized specimens were reduced in the Hannifin hydraulic press to ca. minus 2" size so that the material could be further reduced in the Fitzpatrick Mill. This minus 2" size material was passed through the mill with no screen and four other passes were made with subsequently finer screens in the mill until the material was minus 10 mesh.

The flour samples received the final grinding to 70-80% minus 325M in a Mikro-Pulverizer with a cyclone collection system. The screen analyses for all three flours are tabulated in Table II.

3. Characterization

In addition to the screen analysis, the three flour samples produced under this contract were characterized by physical properties obtained on 5/8" diameter extruded rods. A standard extrusion rod for comparison was made from high-fired GLC-1076 flour and Thermax with Varcum 8251 as the binder and 4% maleic anhydride as activator for the Varcum. An 85/15 ratio of flour to Thermax was used in all of the 5/8" extruded rods with the Varcum binder system.

FIGURE 3
BAKING CYCLE

FIGURE 4
GRAPHITIZATION CYCLE

TABLE II
SCREEN ANALYSES OF FLOURS

<u>Flour No.</u>	<u>65M</u>	<u>100M</u>	<u>200M</u>	<u>325M</u>	<u>400M</u>
I (1000°C 1076)	99.96	99.42	91.23	71.98	63.25
II (2700°C Air Blown)	99.71	98.25	88.19	73.60	64.98
III (1000°C Air Blown)	99.63	96.35	92.95	75.00	67.01

The physical properties of the graphitized rods are tabulated in Table III. The apparent densities of the three experimental flours are equivalent (1.95 g/cc) and slightly higher than the GLC-1076 flour extrusion of 1.93 g/cc. The coefficients of thermal expansion of the bodies formulated from the three flours are higher than that of the GLC-1076 flour body, $51.0 \times 10^{-7}/^{\circ}\text{C}$, and cover a relatively wide range, 60.1 to $73.4 \times 10^{-7}/^{\circ}\text{C}$ (20-1500°C). Flour III, which was made from air blown coke and baked to only 1000°C before milling, produced a body with the highest CTE and a modulus of rupture equal to the GLC-1076 flour extrusion (ca. 4860 psi.). The rod formulated from Flour II had the highest MOR, 5620 psi. In general, the low fired flours produced bodies with higher CTE's but lower strengths than the high fired GLC-1076 flour extrusion.

4. Thermax Replacements

In an attempt to find a more suitable filler than Thermax, several candidate materials were evaluated in standard 5/8" diameter extrusions. The extrusions incorporated 85 parts GLC-1076 flour and 15 parts of the various fillers including Thermax. Varcum #8251 with 4 pph maleic anhydride was used as binder in each case. Two of the candidate fillers were petroleum coke based materials, i.e., micronized GLC-1076 and micronized, low-fired GLC-1076. Three fillers were high surface-area, commercially available carbon blacks. These materials are identified in Table IV. The three carbon blacks were obtained from Cabot Corporation. Physical property data and processing behavior for the Thermax replacement extrusions are shown in Table V. The extrusion with the highest surface area black, Carbolac 1, split severely during curing and was not further processed.

None of the rods produced with replacement materials gave graphitized A. D.'s as high as the Thermax rods. All replacements required a higher binder content to attain comparable extrusion pressures. The high surface area blacks did not increase the binder coke yield as expected. Significant reductions in CTE's were observed with the carbon black extrusions. Electrical resistivities were lower in the micronized petroleum coke rods than in the Thermax rods. Electrical resistivities in the carbon black rods were extremely high. It is concluded from these experiments that none of the Thermax replacement candidates is more suitable than Thermax itself.

TABLE III
PHYSICAL PROPERTY DATA ON 5/8" RODS CONTAINING
THERMAX, VARCUM BINDERS, AND VARIOUS FLOURS

Flour No.		I	II	III
Material	GLC-1076	1076	Air-Blown	Air-Blown
HTT, °C	2700	1000	2700	1000
Binder Level, pph	23.5	26	30	25
Extrusion Pressure, psi.	678	530	870	630
A. D., g/cc				
Cured	1.87	1.70	1.80	1.67
Baked, 1000°C	1.86	1.66	1.85	1.65
Graphite, 2700°C	1.93	1.95	1.95	1.95
Binder Coke Yield, Wt. %				
Cured-Baked	64.5	67.0	61.3	59.8
Wt. Loss, %				
Cured-Baked	7.5	7.3	9.7	8.6
Baked-Graph'd.	1.2	3.7	0.5	2.1
Cured-Graph'd.	8.6	11.0	10.2	10.9
Vol. Shrinkage, %				
Cured-Baked	7.4	5.1	12.0	7.4
Baked-Graph'd.	4.7	18.2	5.3	17.3
Cured-Graph'd.	11.7	22.4	16.6	23.4
ER, 10 ⁻⁵ ohm-in.	66.0	69.8	73.5	73.6
CTE, 10 ⁻⁷ /°C (20-1500°C)	51.0	60.1	63.4	73.4
MOR, psi.	4860	3690	5620	4760

TABLE IV
CHARACTERIZING DATA* FOR THERMAX AND VARIOUS
THERMAX REPLACEMENT CANDIDATES

<u>Material</u>	<u>Type</u>	<u>Surface Area</u> <u>m³/g</u>	<u>Part. Dia.</u> <u>mμ</u>
Thermax	Thermal	7.7	343 (1)
Micro.-1076 (2700°C)	Petrol. Coke	-	4600 (2)
Micro.-1076 (1000°C)	Petrol. Coke	-	4300 (2)
Vulcan XC-72R	Furnace	220	30 (1)
Monarch 71	Channel	380	16 (1)
Carbolac 1	Channel	950	9 (1)

*Data published by Cabot Corp. for carbon blacks.

(1) Data from electron micrographs.

(2) Data from Fisher Sub-Sieve Analyzer.

TABLE V

PHYSICAL PROPERTY DATA FOR 5/8" DIAMETER EXTRUDED RODS
(GLC-1076 FLOUR, VARCUM BINDER AND VARIOUS THERMAX REPLACEMENTS)

Filler	A	B	C	D	E	F*
	Thermax	Mic.1076 Hi-Fired	Mic.1076 Lo-Fired	Vulcan XC-72R	Monarch 71	Carbolac 1
Binder Level, pph	23.5	33.5	30.8	45	38	48
Extrusion Pressure, psi.	678	871	823	968	968	920
A. D., g/cc						
Cured	1.87	1.82	1.78	1.77	1.78	
Baked	1.86	1.84	1.78	1.77	1.76	
Graph'd.	1.93	1.89	1.87	1.86	1.80	
Binder Coke Yield, wt. %						
Cured-Baked	64.5	62.2	58.1	65.3	61.0	
Wt. Loss, %						
Cured-Baked	7.5	10.4	10.4	11.8	11.7	
Baked-Graph'd.	1.2	1.5	1.9	2.2	1.8	
Cured-Graph'd.	8.6	11.7	12.1	13.7	13.3	
Vol. Shrinkage, %						
Cured-Baked	7.4	11.3	10.1	11.9	10.6	
Baked-Graph'd.	4.7	3.9	6.8	6.7	3.9	
Cured-Graph'd.	11.7	14.8	16.2	17.8	14.0	
E.R., ohm-inx10 ⁵	66.0	53.0	52.2	119.0	96.1	
CTEx10 ⁷ /°C						
RT-1500°C	51.0	50.7	51.7	39.0	35.0	
MOR, psi.	4860	3920	4170	1530	3910	

*Rods split severely during curing.

Part B. Binder Evaluation

1. Starting Materials

A total of thirteen furan resin samples was furnished by the Quaker Oats Company. Two of the resins, QX-247 and 248, were pre-polymerized furfuryl alcohols similar to Varcum 8251 which was investigated previously. These resins differed from Varcum in that they were prepolymerized to the specified viscosity and were not cut back with a monomer solvent to achieve the desired viscosity. The remaining eleven resins were developed to be used in conjunction with petroleum pitch to provide a high yield, graphitic, thermosetting binder.

Two powdered petroleum pitches, produced by Ashland Oil, Inc., were provided in order to evaluate the effects of varying amounts of pitch and the effect of pitch softening point. Specifically, the grades of pitch used were Ashland No. 240 (115°C s.p.) and Ashland experimental grade 126-0 (280°C s.p.). The relative amounts of the resin/pitch blends, as specified by Quaker Oats Company, are given in Table I.

Four curing agents were used in this investigation. QX-240 liquid hardener was used for all binders (4 wt.-% hardener) in coking studies, x-ray diffraction and photomicrograph samples, DTA and TGA analyses, and in one set of extrusions with QX-237 binder. QX-299 hardener supported on GLC-1074 flour was used only with extrusions of QX-247 and 248 "Varcum type" resins (8 wt.-% hardener). QX-314 hardener supported on GLC-1076 flour was used in the extrusion of all binders except QX-247 and 248 (4 wt.-% hardener). QX-315 hardener, also supported on GLC-1076 flour, was used in the extrusion of the QX-302 series of binders and the QX-308 and QX-209-1 binders (8 wt.-% hardener). It was noted upon receipt of the QX-315 hardener that some separation and settling of the liquid phase had occurred; this was not observed in the other flour-supported hardeners.

2. Blending

Those resins which required the addition of powdered pitch (see Table I) were mixed in 600 gm. lots using electric stirrers. In order to achieve sufficient solubilization of the pitch in the resin it was necessary to heat the resin between 80°C and 90°C, without the curing agent, add the pitch slowly while stirring, and continue stirring for one hour after the pitch addition. Upon addition of the powdered 280°C softening point pitch to QX-303 resin (QX-303-6) solubilization was not complete, due to the high quinoline insoluble portion of the pitch (69.6%).

TABLE I
BINDER COMPOSITIONS

<u>Sample No.</u>	<u>Parts of Liquid Furan Resin</u>	<u>Parts of Powdered Petroleum Pitch</u>
Varcum 8251	1	0
QX-237	1	0
QX-247	1	0
QX-248	1	0
QX-297-1	2 QX-297	1 Ashland No. 240 Pet. Pitch
QX-298-1	2 QX-298	1 Ashland No. 240 Pet. Pitch
QX-302	1	0
QX-302-1	5 QX-302	1 Ashland No. 240 Pet. Pitch
QX-302-2	5.5 QX-302	4.5 Ashland No. 240 Pet. Pitch
QX-303-1	8 QX-303	1 " "
QX-303-2	2 QX-303	1 " "
QX-303-3	4 QX-303	5 " "
QX-303-6	2 QX-303	1 Ashland 280°C softening point pitch
QX-304-1	2 QX-304	1 Ashland No. 240 Pet. Pitch
QX-305-1	2 QX-305	1 " "
QX-306-1	1 QX-306	1 " "
QX-307-1	2 QX-307	1 " "
QX-308	1	0
QX-309-1	2 QX-309	1

However, no settling out of the pitch appeared to occur. Blending of QX-306 resin with the Ashland No. 240 pitch (QX-306-1) was not possible. The powdered pitch tended to coagulate in the resin. Using a coarser fraction of powdered pitch (60/100M) enabled blending, but upon standing at room temperature the mixture became unpourable.

Mixing procedures for the binders in extrusions were different from the blending of unfilled resins described above. For extrusions the 85 pts. high fired (2700°C) GLC-1076 flour/15 pts. Thermax filler was blended at 45°C. The required amount of powdered pitch was added to the filler and blended at 45°C for ca. 10 minutes. The required hardener was added followed by the resin and mixed at 45°C for one hour. The mix was passed once through the 5/8" dia. extrusion press, broken up, and re-mixed for an additional 45 minutes. It is felt that the mixing procedure used for extrusions does not allow for maximum solubilization of the pitch component in the resin due to the lower mixing temperature and the presence of the flour/Thermax filler. The differences in the degree of solubilization, and therefore the degree of resin/pitch interaction prior to curing, appear to affect the final binder coke yield and possibly the final structure. There was also some indication during blending without fillers that the curing agent (QX-240) preferentially reacts with undissolved pitch in the resin. This was particularly true with binders QX-298-1 where improperly mixed samples would show pitch separation as soon as hardener was added. Also, it was impossible to add powdered pitch to the resins if the hardener had been added previously.

3. Characterization

a. Viscosities

Viscosities were measured for the blended, unfilled binders at room temperature and at 45°C, the extrusion temperature. Again the differences between the mixing procedure for the unfilled binders and the binders in extrusion mixes must be emphasized. The measured viscosities may not necessarily correlate with extrusion rheology. Brookfield viscosity values are given in Table IIa. Although there was a wide range of viscosities, all of the binders were capable of being extruded with the high fired GLC-1076 flour/Thermax filler.

At the request of Quaker Oats personnel the viscosities of the first iteration of binders were checked against earlier data to give an indication of shelf-life stability. The comparisons are shown in Table IIb. Only QX-223 showed any tendency toward actual separation of phases. While the room temperature viscosities of the binders show some increase in values due to age, the 45°C viscosities indicate that no gross changes had taken place.

TABLE II

a) AS RECEIVED VISCOSITIES OF QUAKER OATS BINDERS; SECOND ITERATION

<u>Binder</u>	<u>Room Temp. Centipoises</u>	<u>45°C Centipoises</u>	<u>Binder</u>	<u>Room Temp. Centipoises</u>	<u>45°C Centipoises</u>
Varcum 8251	420	79	QX-303-1	-	89
QX-247	2,130	215	QX-303-2	-	553
QX-248	2,380	254	QX-303-3	>50,000	18,150
			QX-303-6	-	1,220
QX-237	19,500	2,580	QX-304-1	2,900	260
QX-297-1	47,500	1,900	QX-305-1	>50,000	4,750
QX-298-1	14,000	660	QX-306-1	>50,000	>50,000
QX-302	25	14.5	QX-307-1	>50,000	8,800
QX-302-1	47.5	25	QX-308	12,500	600
QX-302-2	2,685	200	QX-309-1	5,550	225

b) VISCOSITY STABILITY OF FIRST ITERATION OF QUAKER OATS BINDERS

<u>Binder</u>	<u>4/2/71 Centipoises Room Temp.</u>	<u>8/13/70 Centipoises Room Temp.</u>	<u>4/2/71 Centipoises 45°C</u>	<u>10/8/70 Centipoises 45°C</u>
Varcum 8251	490	352	76	82
QX-223*	15,625	6,600	1,375	576
QX-225	40,300	29,200	1,905	1,600
QX-228	3,375	3,350	475	530
QX-229	980	775	160	148
QX-234	82,000	53,300	4,860	5,100
QX-237	27,750	19,500	2,000	2,580

*Separation occurred during standing.

b. Carbon/Hydrogen Analyses

Determinations of the percent carbon and hydrogen and calculations of the C/H ratios were made for all of the Quaker Oats binders after they had been cured at 100°C for 24 hours. Where required the pitch additions were made as previously described for the unfilled binders. The results are presented in Table III. Although no attempt was made to determine specific types of carbon and hydrogen (such as aromatic or aliphatic species), general indications of the graphitizability of the various binders can be determined. Considering the type of binders being evaluated in this study, it can be assumed that low values of the C/H ratios and sums of the carbon and hydrogen percentages is indicative of a high furan content and, therefore, a glassy carbon type of binder. High C/H values and carbon and hydrogen summations are typical of more pitch-like, graphitizable binders. The pitch-like binders may also be expected to have a somewhat higher binder coke yield than those binders higher in furan content.

c. Binder Carbon Yields

1. Unfilled Binders

The mixing procedure for preparing unfilled binders was described in Section B.2. After mixing the binders were allowed to cool to 45°C, and 4 wt.-% of QX-240 hardener was added and stirred for 15 minutes. The binders were cured at 70°C for 24 hours after which the temperature was raised to 100°C over an eight hour period and held for 18 hours. After curing each of the binders was weighed and sealed in a steel can. The cans were packed in a sagger containing coke/sand packing and were baked to 520°C at a rate of 8.3°C/hr. to 250°C and 3.3°C/hr. to 520°C. Upon removal from the packing the samples were re-weighed to obtain a cured-to-520°C weight loss as shown in Table IV. Attempts were made to graphitize the 520°C materials, but excessive volatilization was noted in some of the binders. As a result the 520°C binder coke was re-baked to 720°C at a rate of 6°C/hr. Weight losses between 520°C and 720°C were recorded (Table IV). The samples were then placed in graphite tubes and induction graphitized in argon to 2700°C. As before, weight losses were recorded. The total binder yields from cured-to-2700°C were calculated from the incremental weight losses.

The binder coke yields calculated from the unfilled binders, shown in Table IV, do not necessarily agree with the binder yields calculated from the 5/8" dia. extrusions. The difference could be due, in part, to the different curing agents used, but the difference is most likely due to the high degree of pitch/resin mixing during preparation of the unfilled binders. The yields tend to agree most closely with those binders containing little or no pitch (QX-247, 248, 302-1, 303-1).

TABLE III
CARBON AND HYDROGEN ANALYSES OF BINDERS CURED AT
100°C WITH 4.0 WT.-% QX-240 HARDENER

<u>Binder</u>	<u>Carbon %</u>	<u>Hydrog. %</u>	<u>C/H</u>	<u>Binder</u>	<u>Carbon %</u>	<u>Hydrog. %</u>	<u>C/H</u>
Varcum 8251	72.41	5.16	1.17	QX-303-1	79.72	6.05	1.10
QX-247	72.27	5.39	1.12	QX-303-2	83.24	6.02	1.15
QX-248	71.96	5.38	1.11	QX-303-3	85.72	5.80	1.23
				QX-303-6	84.30	5.70	1.23
QX-237	83.02	5.94	1.16	QX-304-1	83.78	6.09	1.15
QX-297-1	82.81	5.76	1.20	QX-305-1	81.85	5.39	1.26
QX-298-1	84.11	5.80	1.20	QX-306-1	82.98	5.03	1.37
QX-302	82.27	5.87	1.17	QX-307-1	83.65	5.73	1.22
QX-302-1	84.09	5.50	1.27	QX-308	80.73	6.06	1.11
QX-302-2	82.85	6.08	1.14	QX-309-1	82.88	5.91	1.17

TABLE IV
WEIGHT LOSS AND BINDER COKE YIELDS OF QUAKER
OATS BINDERS, CURED WITH 4.0 WT.-% QX-240

<u>Binder</u>	<u>% Wt. Loss</u> <u>100°C-520°C</u>	<u>% Wt. Loss</u> <u>520°C-720°C</u>	<u>% Wt. Loss</u> <u>720°C-2700°C</u>	<u>% Yield</u> <u>100°C-2700°C</u>
Varcum 8251	15.0	19.4	11.6	60.5
QX-247	15.4	18.6	14.1	59.2
QX-248	15.3	18.2	14.1	59.5
QX-237	15.4	11.7	6.8	69.6
QX-297-1	16.1	11.4	6.2	69.7
QX-298-1	15.5	11.9	6.8	69.4
QX-302	16.8	9.6	7.2	69.8
QX-302-1	14.5	10.1	7.9	70.8
QX-302-2	14.6	14.5	18.9	59.2
QX-303-1	16.0	9.4	20.8	60.3
QX-303-2	14.0	7.3	9.0	72.6
QX-303-3	14.9	8.1	6.7	73.0
QX-303-6	11.6	6.1	12.6	72.5
QX-304-1	13.2	10.2	7.9	71.8
QX-305-1	12.3	8.5	7.4	74.3
QX-306-1	12.3	11.1	6.9	72.6
QX-307-1	12.7	8.1	8.6	73.3
QX-308	14.6	9.6	8.5	70.6
QX-309-1	10.5	12.7	7.7	72.1

From the weight loss data at the three temperature intervals it can be seen that the pure furan resins such as Varcum, QX-247 and QX-248 are quite similar in behavior. The pitch/furan binders all tend to show less weight loss in the 520-720°C interval than the "Varcum-type" binders. QX-302-2 (5.5 pts. resin/4.5 pts. pitch) and QX-303-1 (8 pts. resin/1 pt. pitch) both showed relatively high weight losses in the 720-2700°C interval although the relative pitch contents are quite different. From the relatively high weight losses indicated in the overall range of 100-720°C it appears that the baking operation is the most critical step in processing.

2. Extrusions

Mixing procedures for the extrusions were described in Section B.2. Various curing agents were used in the extrusions in accordance with the recommendations made by the Quaker Oats Company. A QX-299 GLC-1074 flour supported hardener was used with the Varcum 8251 and the QX-247 and 248 binder; a QX-314 GLC-1076 flour supported hardener was used with all other binders. As stated earlier, QX-240 liquid hardener and QX-315 GLC-1076 flour supported hardener were used with selected binders for comparison. Upon extrusion of the 5/8" dia. rods the samples were cut to ca. 5" lengths and cured overnight at 75°C and cured an additional 24 hours at 100°C. The extrusions containing the QX-297-1 and QX-298-1 binders with QX-314 hardener did not fully cure under the above conditions, but the samples were suitable for baking.

Baking was carried out in stainless steel saggers with a sand/carbon packing media. Two baking cycles were used in order to evaluate the effect of upheat rate through a 250°C to 550°C critical range. Half of the extrusions were baked in accordance with the following schedule:

8.3°C/hr. - 100°C to 250°C

3.3°C/hr. - 250°C to 550°C

6.2°C/hr. - 550°C to 720°C

The remaining half of the extrusions followed the same schedule except that the rate through the critical range was reduced to 1.7°C/hr. As shown by the baked binder yields in Table V, only the QX-302 binder showed any significant increase in coke yield as a result of the slower rate. The other binders appeared to be essentially insensitive to baking rate. The high baked binder yield of the extrusion containing the QX-302 binder is not realistic although the yield is definitely high. During extrusion with the QX-302 some of the binder was squeezed behind

Table V

Binder Coke Yields From 5/8" Dia. Extrusions Containing
85 pts. GLC 1076 Flour and 15 pts. Thermax

Extrusion Binder	St'd. Rate Cure to 720°C Binder Yield %	Slow Rate Cure to 720°C Binder Yield %	Slow Rate 8 Hr. to 2700°C Cure→2700°C % Binder Yield	Slow Rate 30 Hr. to 2700°C Cure→2700°C % Binder Yield
Varcum 8251+QX-299	64.5	-	-	59.3
QX-247 + QX-299	63.1	64.2	58.8	59.5
QX-248 + QX-299	63.5	62.7	56.9	59.2
QX-237 + QX-240	60.0	60.2	54.8	-
QX-237 + QX-314	64.2	66.9	58.3	-
QX-297-1 + QX-314	59.7	58.9	54.3	-
QX-298-1 + QX-314	60.7	61.3	57.3	-
QX-302 + QX-314	77.2 (1)	83.0	78.1	-
QX-302 + QX-315	74.0	76.4	70.6	-
QX-302-1 + QX-314	71.1	76.2	71.0	-
QX-302-1 + QX-315	70.1	75.2	70.1	-
QX-302-2 + QX-314	57.9 (2)	58.9	53.9	53.4
QX-302-2 + QX-315	58.5	58.3	52.4	-
QX-303-1 + QX-314	65.3	66.4	61.7	-
QX-303-2 + QX-314	57.7	59.4	54.0	-
QX-303-3 + QX-314	54.9	54.7	48.6	49.0
QX-303-6 + QX-314	75.0	75.6	70.7	70.2
QX-304-1 + QX-314	61.8	63.0	57.3	-
QX-305-1 + QX-314	71.4	74.6	68.8	-
QX-306-1 + QX-314	62.2	63.6	57.2	-
QX-307-1 + QX-314	63.9	64.6	59.5	-
QX-308 + QX-314	68.2	70.2	64.1	-
QX-308 + QX-315	60.7	61.1	54.6	-
QX-309-1 + QX-314	63.0	63.8	58.5	-
QX-309-1 + QX-315	57.6	57.9	55.2	-

(1) High value due to binder loss during extrusion

(2) Some pitch loss during bake

the ram due to its extremely low viscosity, but for purposes of calculation it was assumed that all of the binder remained in the mix. However, the high yield and baking sensitivity of QX-302 is supported by the data from the QX-302 variations, namely QX-302-1 and QX-302-2. Binder yield is shown in Table V to decrease as more pitch is added to QX-302 as well as the sensitivity to the baking rate. QX-303-6 also exhibits a high binder coke yield but no increase in yield due to reduced baking rate. The high yield is attributed to the presence of the 280°C softening point pitch which has a much lower volatile content than the standard Ashland No. 240 pitch. The two binder series, QX-302 and QX-303 (excepting QX-303-6), indicate the effects due to increasing amounts of pitch in the extrusion binder. In both cases, the binder coke yield is decreased due to pitch additions, which does not agree with the results on unfilled binders shown in Table IV. As stated before, the differences are most likely due to the differences in degree of mixing achieved in preparing the unfilled binders vs. the extrusion mixing procedure. It therefore appears that the pitch should be first mixed with the uncatalyzed resin at the highest possible temperature prior to use in extrusions. In some cases, however, the resulting viscosity of binder would make extrusion difficult and would require high binder levels as in case of QX-303-3, 306-1, and 307-1. Tables IV and V definitely indicate that higher yields are obtained if the pitch and resin are given a chance to interact.

The flour-supported hardeners QX-314 (4 wt.-%) and QX-315 (8 wt.-%) are compared in extrusions containing the QX-302 series, QX-308 and QX-309-1 in Table V. As shown, QX-314 was definitely found to produce higher binder carbon yields than QX-315. The difference was not particularly significant for the QX-302-2 binder, but this might be expected due to the high pitch loading of the binder. The liquid hardener, QX-240, was compared with the flour-supported QX-314 hardener in QX-237 binder. Again the highest binder coke yield occurred with the use of QX-314 hardener.

Graphitized (2700°C) binder yields are also included in Table V. All of the extrusions were graphitized at a rate of ca. 10°C/min. (4.5 hrs. to 2700°C) which was found to cause spalling of the samples containing the QX-247 and 248 binders. Additional samples were graphitized according to a standard 30 hour schedule together with samples containing other binders for a comparison of rate effects. The extrusions containing QX-247 and 248 did not spall in the 30 hr. cycle; and, as in the case of the baked binder yields, graphitization rate appeared to have no effect on yield.

d. Fractional Distillations

Samples of the unfilled binders were cured at a temperature of 100°C using the QX-240 hardener. The procedure was in accordance with ASTM D-50-26 except that the temperature intervals were modified slightly for uniformity. The results are shown in Table VI. The main purpose of the

TABLE VI

FRACTIONAL DISTILLATION OF UNFILLED BINDERS
WITH 4% QX-240 HARDENER

Binder	% Loss on Cur- ing 100°C	% Loss Room Temp. 200°C	% Loss 201°C 250°C	% Loss 251°C 300°C	% Loss 301°C 350°C	% Loss 351°C 400°C	Residue % of Cured Binder	% Vapor Loss	Initial Boiling Point
Varcum 8251	7.0	10.6	4.2	6.9 (296°C)	-	-	52.7	18.6	100°C
QX-247	1.8	14.0	3.6	0.8	0.5 (315°C)	-	58.1	21.2	98°C
QX-248	2.2	10.8	3.9	2.4	1.7 (327°C)	-	60.6	18.4	104°C
QX-237	7.1	2.7	5.0	6.6	2.0	1.1 (351°C)	56.3	26.3	115°C
QX-297-1*	5.1	14.6	5.8	2.2	5.4 (304°C)	-	60.7	7.2	91°C
QX-298-1*	5.3	11.5	2.6	2.8	3.7 (311°C)	-	67.7	6.4	81°C
QX-302	9.9	9.8	2.8	4.8	2.4	1.2 (361°C)	61.4	7.7	100°C
QX-302-1	8.5	6.5	4.0	1.8	3.6	3.7 (400°C)	63.4	8.5	100°C
QX-302-2	2.3	7.0	6.5	4.0	2.1 (350°C)	-	69.6	8.5	89°C
QX-303-1	6.4	6.5	3.0	5.2 (259°C)	-	-	65.8	13.1	88°C
QX-303-2	5.3	3.8	2.5	4.6	3.5	6.1 (379°C)	59.2	15.0	103°C
QX-303-3	5.1	2.7	4.6	4.4	3.1 (331°C)	-	70.1	10.0	110°C
QX-303-6	2.8	5.3	4.2	4.6	4.2 (309°C)	-	70.9	8.2	100°C
QX-304-1	5.7	3.6	5.6	3.5	10.0 (340°C)	-	59.6	12.0	110°C
QX-305-1	3.3	1.8	2.8	6.0 (289°C)	-	-	76.5	9.6	128°C
QX-306-1	2.7	2.6	4.4	4.0	0.7	8.1 (360°C)	57.5	20.1	114°C
QX-307-1	3.3	2.7	4.4	6.2	1.0	3.2 (351°C)	63.8	15.4	134°C
QX-308	10.7	1.5	4.1	3.5 (288°C)	-	-	74.6	5.6	137°C
QX-309-1	5.0	5.3	6.8	4.1	3.4 (332°C)	-	57.1	18.3	120°C

*Not fully cured at 100°C

fractional distillation studies was to determine temperature regions of maximum activity which occur during the initial coking process. The actual residue yields of this test are not intracomparable as the end points of the various distillations are arbitrarily determined by the occurrence of a sudden drop in vapor temperature of the binder. Additional losses would be expected upon further baking, particularly with those binders containing high pitch contents. It should be emphasized that the temperature intervals of Table VI are vapor temperatures; the actual binder temperature is considerably higher.

The binders were cured in the distillation flasks, and the curing losses reflect the weight of sample lost through loss of water of reaction and/or low boiling point solvents or modifiers. This data is of interest since generally those binders with the greatest curing losses would tend to cause the extrusions to be more susceptible to curing cracks. QX-302, QX-302-1, and QX-308 are quite high in curing loss.

Considering the weight losses in the room temperature to 200°C vapor temperature interval it is apparent that those binders rich in the furan component or relatively unreactive towards the pitch component tend to lose considerable weight in this region. This is shown by the binders QX-247, 248, 297-1, 298-1, 302 and Varcum. In the particular case of QX-297-1 and 298-1 it is not probable that high losses in this interval were due to insufficient hardener. Relatively high losses in other vapor temperature intervals are assumed to be due to dissociation reactions between the pitch and furan components. Vapor losses appear to lie in two distinct ranges -- binders below 10% loss and those above 13% vapor loss. The vapor losses consisted primarily of a dense, yellow smoke which began evolving at vapor temperature above 200°C and could be attributable to a breakdown of the furan polymer. The "Varcum-type" binders showed a particularly high vapor loss as a group. Also the QX-303 series of binders, with the exception of QX-303-6 containing the 280°C pitch, showed similar high vapor losses. QX-237 showed the highest vapor loss of any binder and was ca. three times higher than the value reported for the first iteration of binders. The difference could be due either to the amount of hardener used in curing (6.7% vs. 4.0%) or to a difference in upheal rate during distillation. As all binders in the second iteration used the same hardener concentration and followed the same upheal rate, it is felt that the relative vapor losses are representative. QX-306-1 was earlier found to be relatively incompatible with pitch additions, and the high vapor loss appears to reflect predominately the breakdown of furan. Pitch volatiles in all cases were readily condensed into tars and acenaphthene towards the end of the distillation run also indicating preferential destructive distillation of the furan polymer.

e. Plastometer Studies

Samples of the cured (4% QX-240 hardener), unfilled binders were tested in a Geisler Plastometer in order to determine the re-liquification or plastic range of the binders. The samples were heated at a rate of 3°C/min. to 500°C while the measuring head rotor was set at 15 gram-cm of torque. The rotation of the measuring head indicated the onset of plasticity, and the set point was indicated when the rotor stopped. As soon as the rotor stopped, the samples holder was opened to check to consistency of the binder. For those binders in Table VII where only a single temperature is shown, the binder was found to soften to a rubbery consistency.

As would be expected, none of the "Varcum-type" binders showed any tendency to become plastic. All of the furan/pitch blends, with the exception of QX-302, indicated some plastic range. Further pitch additions to QX-302 did result in a rather extended plastic range (QX-302-1 and 302-2). Since plasticity during the baking operation could conceivably cause problems of dimensional stability in extrusions, the ideal binder should exhibit little or no plasticity upon further heat treatment. Of the furan/pitch blends, the QX-303 series, QX-306-1, QX-307-1, QX-308 and QX-309-1 appear the most attractive in this respect. However QX-306-1 was found to resist mixing with the powdered pitch additions. It should be stated that, while no problems with softening in the 5/8" dia. extrusions occurred due to re-softening of the binder phase, further investigation in this area should be done.

f. X-ray Diffraction

X-ray diffraction scans were made on powdered (-200M) samples of unfilled binders which had been heated to 2700°C. Peak intensities (002), L_c crystallite sizes, d-spacings, and percent graphite were calculated from the (002) peaks. The binders were divided into two sets: a) those which were graphitized directly from a 520°C pre-bake and b) those which required an intermediate 720°C bake to prevent problems with re-softening during the early stages of graphitization. The results are presented in Table VIII.

All binders indicate low graphitizability. This is particularly true in the case of QX-237 when the results from the previous iteration are considered. In the first iteration the percent graphitizability for QX-237 at 2700°C was reported as 46.4% while the present data shows a value of 5.5%. The only differences in the treatment of the binders were the amount of hardener used and the upheat rate used to obtain the coke. Assuming both amounts of hardener were

Table VII

Plastic Ranges of Binders as Determined by the
Geisler Plastometer on Cured, Unfilled Binders

Binder	Plastic Range °C	Binder	Plastic Range °C
Varcum	None	QX-303-1	420 Rubbery
QX-247	None	QX-303-2	390 Rubbery
QX-248	None	QX-303-3	320 - 450
		QX-303-6	400 Rubbery
QX-237	385 - 480	QX-304-1	400 - 470
QX-297-1	200 - 455	QX-305-1	245 - 400
QX-298-1	200 - 450	QX-306-1	420 - 460
QX-302	None	QX-307-1	410 - 430
QX-302-1	200 - 480	QX-308	390 - 450
QX-302-2	200 - 450	QX-309-1	420 - 460

Table VIII

X-Ray Diffraction Parameters of Unfilled Binders
After 2700°C Heat Treatment
(4% QX-240 Hardener)

Binder		% Graphite	002 d-Spacing Å	X'tal Size L _c Å	Peak Intensity c/s
Varcum 8251	a)	5.0	3.451	46.8	793
QX-247	a)	0.0	3.488	29.9	643
QX-248	a)	0.0	3.482	29.9	617
QX-237	b)	5.5	3.442	70.2	1,507
QX-297-1	b)	5.0	3.450	50.7	1,287
QX-298-1	b)	5.0	3.445	45.7	1,080
QX-302	a)	0.0	3.464	38.2	717
QX-302-1	b)	5.0	3.456	46.3	1,060
QX-302-2	b)	33.0	3.393	183.0	3,800
QX-303-1	a)	5.0	3.451	59.6	1,213
QX-303-2	a)	24.0	3.406	151.0	3,050
QX-303-3	b)	33.0	3.391	174.0	3,433
QX-303-6	a)	32.5	3.398	120.0	2,600
QX-304-1	b)	5.0	3.445	59.6	1,393
QX-305-1	a)	1.0	3.474	36.6	763
QX-306-1	a)	5.0	3.459	43.7	770
QX-307-1	a)	10.0	3.426	100.0	2,167
QX-308	a)	1.0	3.488	63.9	1,387
QX-309-1	b)	5.0	3.455	45.5	953

a) Graphitized from 520°C coke

b) Graphitized from 720°C coke to prevent re-softening

sufficient to fully cure the binder, the most probable cause of the differences in values would be the heating rate. For the first iteration the binders were coked to 520°C in glass flasks at a rate of 40°C/hr., while the second series of binders were coked to 520°C and/or 720°C using the same upheal cycle as the extrusions (Section B.3.c.2.). It is felt that the slower heating rate through the critical zone (250-550°C) prevented gross separation of the pitch phase in the plastic range and kept the pitch more closely bound to the furan resulting in a more isotropic coke structure. In contrast, coking in the glass flasks to 520°C resulted in relatively strong reactions during destructive distillation of the pitch and furan phases causing a high degree of re-liquification and separation. It is felt, therefore, that additional work is required to study the effect of upheal rate during initial carbonization on the final structure of pitch/furan blends. The baking rates used in this study were both relatively slow and no differences with respect to binder yields were found to occur. However, at faster baking rates it is entirely conceivable that the binder structure could change from isotropic to anisotropic by forcing pitch phase separation.

With respect to the graphitizability of the various binders, the most graphitic, in order of decreasing graphitizability, were QX-302-2, QX-303-3, QX-303-6, and QX-303-2 when all of the x-ray parameters are considered. Those binders which may be assumed to be intermediate in graphitizability were found to be QX-307-1, QX-237, QX-304-1, QX-303-1, QX-297-1, and QX-308. The essentially amorphous or glassy binders were QX-298-1, QX-302-1, QX-309-1, Varcum, QX-306-1, QX-305-1, QX-302, QX-247, and QX-248. The x-ray data agrees well with the micrographs discussed qualitatively in the following section.

g. Metallographic Studies

Samples of cured (4% QX-240 hardener) unfilled binders were baked to 720°C and graphitized to 2700°C. The heat treated samples were crushed to -60M and mounted for the photomicrographs presented in Figures 1 through 19. All micrographs are 250X magnification under crossed nicols.

The structural features tend to support the x-ray diffraction results discussed in Section B.3.f. None of the binders were found to be truly anisotropic in structure. As anticipated, the Varcum 8251 and QX-247 and 248 are completely glassy in structure (Figures 1 through 3) and there are no features which would distinguish the three binders from each other.

In Figure 4, the QX-237 binder shows only isolated areas of fine-grained isotropic coke in an otherwise glassy matrix. This structure does not agree with earlier data and results from QX-237, but it is felt that the difference in coking up-heat rates is responsible for the structural variation.

The binders QX-297-1 and QX-298-1 appeared completely glassy. No evidence of a separate pitch coke phase could be detected (Figures 5 and 6). Fracture surfaces were also indicative of a glassy carbon structure.

The QX-302 binder series (Figures 7 through 9) illustrates the effect of increasing pitch content in the furan. In Figure 7, the QX-302 binder appears completely glassy. The addition of powdered Ashland 240 pitch to QX-302 to make QX-302-1 (5 pt. resin/1 pt. pitch) does not result in any structural changes as shown by Figure 8. However, when the resin/pitch ratio is changed to 5.5:4.5 as in the case of QX-302-2, a very fine-grained isotropic structure results (Figure 9).

The same effects are noticeable for the QX-303 binder series (Figures 1 through 13). Small additions of powdered Ashland 240 pitch to the QX-303 liquid as in the QX-303-1 (8 pts. resin/1 pt. pitch) binder in Figure 10 do not change the glassy structure. Changing the resin/pitch ratio to 2 pts. resin/1 pt. pitch results in an isotropic structure (Figure 11). The shadings within the particles tend to indicate domains of preferred orientation which go to extinction as the sample is rotated on the stage. A further increase in pitch content to 4 pts. resin/5 pts. pitch as in the QX-303-3 binder (Figure 12) maintains the isotropic structure but with increased graininess. Figure 13 represents the QX-303-6 binder which is a 2 pts. resin/1 pt. pitch blend using the Ashland 280°C softening point pitch. Inclusions of insoluble carbon particles can be seen in a glassy carbon matrix. In addition, regions of isotropic structure are present.

The QX-304-1 and QX-305-1 binders, Figure 14 and 15, respectively, are both shown to be glassy in structure. Figure 14 (QX-304-1) shows a grain which was partially chipped during polishing and illustrates the conchoidal fracture typical of glassy structures.

Figures 16 and 17 represent the binders QX-308-1 and QX-307-1. In both binders, isolated areas of isotropic are present in an otherwise glassy matrix. QX-307-1 shows more and larger regions of isotropic structure than QX-306-1. Also, the shadings which appear on the grains of QX-307-1 tended toward extinction when the stage was rotated indicating some areas of preferred orientation.

No isotropic coke structure could be detected in graphitized samples of QX-308 and QX-309-1 (Figures 18 and 19). These binders appeared to be essentially glassy carbon.

h. Physical Properties of Extrusions

1. Dimensional and Weight Changes

A compromise was made in selecting the binder level of the extrusions. An attempt was made to maintain a relatively narrow range of binder levels in order to more easily compare relative weight and dimensional changes occurring during processing. However, due to the wide range of binder viscosities optimum extrusion pressures were not always attained. A summary of cure-to-bake and cure-to-graphite dimensional changes are given in Tables IX and X, respectively.

During bake, samples either maintained or lost density. Those samples containing binders high in furan concentration tended to maintain density as a result of balanced weight losses and volumetric shrinkages, while extrusions with a high pitch phase binder tended to have higher weight losses in the 720°C baking range. Upon graphitization to 2700°C, all samples exhibited densification when compared with the baked densities due to high volume shrinkages; however, not all extrusions regained or surpassed the original cured densities. Extrusions showing the greatest densification contained the Varcum or "Varcum-type" binders. Among the extrusions containing the pitch/furan binders, density increases were most notable for QX-303-6 which contained the 280°C softening point pitch and QX-305-1. Other pitch/furan bonded extrusions also showed some degree of overall densification, namely QX-306-1, QX-307-1, and QX-308. It is felt that additional density improvements could be achieved by further optimization of the mixing and processing conditions.

2. Graphitized Physical Properties

The graphitized physical properties of the 5/8" dia. are presented in Table XI. Low temperature CTE's (0-50°C) were determined for all samples while high temperature CTE's (20-1500°C) were determined for selected samples. Based on the high and low temperature CTE's of the selected samples a relatively constant proportionality factor was found to exist between the high and low temperature values. This factor (1.3) was used to calculate values for the other samples. The accuracy is felt to be within the experimental error of the test. All of the CTE's were found to lie within a

Table IX

Dimensional Changes, Cure-to-Bake, in 5/8" Dia. Extrusions;
85 Pt. GLC 1076 Flour/15 Pt. Thermax

Binder Used	Binder Level (pph)	Extrusion Pressure (psi)	Cured (100°C) A.D.(g/cc)	Loss Cure-to- Bake(720°C) ΔWt. (%)	Cure-to- Bake(720°C) ΔVol.(%)	Baked (720°C) A.D.(g/cc)
Var. 8251+QX-299	23.5	680	1.86	7.5	-7.4	1.86
QX-247+QX-299	31.5	210	1.81	8.8	-8.2	1.79
QX-248+QX-299	30.0	425	1.81	8.5	-8.2	1.80
QX-237+QX-240	28.0	1485	1.82	8.7	-3.7	1.73
QX-237+QX-314	28.0	1270	1.80	7.5	-3.7	1.73
QX-297-1+QX-314	30.0	1270	1.80	9.4	-3.9	1.70
QX-298-1+QX-314	30.0	1695	1.79	9.0	-3.9	1.70
QX-302+QX-314	28.0	1270	1.69	5.4/3.7 ⁽¹⁾	-3.8	1.68
QX-302+QX-315	28.0	1695	1.70	5.4	-5.4	1.70
QX-302-1+QX-314	29.0	955	1.76	6.5/5.3	-5.4	1.73
QX-302-1+QX-315	30.0	530	1.75	6.9/5.7	-5.0	1.72
QX-302-2+QX-314	32.0	480	1.76	10.1	-5.3	1.66
QX-302-2+QX-315	31.0	475	1.77	9.8	-3.6	1.65
QX-303-1+QX-314	28.0	1270	1.82	7.5	-4.4	1.76
QX-303-2+QX-314	30.0	900	1.72	9.6	-6.7	1.66
QX-303-3+QX-314	30.0	1695	1.76	10.4	-6.2	1.64
QX-303-6+QX-314	41.8	3180	1.75	7.3	-7.3	1.76
QX-304-1+QX-314	30.0	530	1.75	8.6	-5.8	1.69
QX-305-1+QX-314	30.0	1695	1.73	6.2	-8.6	1.78
QX-306-1+QX-314	40.0	1270	1.60	10.6	-8.2	1.56
QX-307-1+QX-314	30.0	955	1.72	8.2	-7.1	1.70
QX-308 + QX-314	28.0	1380	1.80	6.8	-6.0	1.78
QX-308 + QX-315	28.0	1005	1.82	8.6	-3.4	1.72
QX-309-1+QX-314	30.0	530	1.78	8.4	-5.0	1.72
QX-309-1+QX-315	30.0	425	1.79	9.8	-4.5	1.69

(1) Where values differed by more than 0.5% between the standard and slow bake, both values are given std./slow.

Table X

Dimensional Changes, Cure-to-Graphite, in 5/8" Dia.
Extrusions; 85 Pt. GLC 1076 Flour/15 Pt. Thermax

Binder Used	Loss Cure-to-* Graph(2700°C) ΔWt. (%)	Cure-to-* Graph(2700°C) ΔVol. (%)
Varcum 8251 + QX-299	8.6	-11.7
QX-247 + QX-299	9.9	-15.1
QX-248 + QX-299	9.9	-13.2
QX-237 + QX-240	9.9	- 7.4
QX-237 + QX-314	9.1	- 7.1
QX-297-1 + QX-314	10.6	- 7.3
QX-298-1 + QX-314	9.9	- 8.1
QX-302 + QX-314	4.8	- 7.9
QX-302 + QX-315	6.4	-10.1
QX-302-1 + QX-314	6.5	-10.0
QX-302-1 + QX-315	6.9	-10.1
QX-302-2 + QX-314	11.2	- 8.9
QX-302-2 + QX-315	11.2	- 7.8
QX-303-1 + QX-314	8.4	- 7.8
QX-303-2 + QX-314	10.6	-10.2
QX-303-3 + QX-314	11.7	- 9.8
QX-303-6 + QX-314	8.6	-13.6
QX-304-1 + QX-314	9.8	- 9.4
QX-305-1 + QX-314	7.2	-17.4
QX-306-1 + QX-314	12.2	-14.8
QX-307-1 + QX-314	9.3	-11.0
QX-308 + QX-314	7.8	- 9.9
QX-308 + QX-315	9.9	- 7.6
QX-309-1 + QX-314	9.6	- 8.9
QX-309-1 + QX-315	10.3	- 8.7

*Samples graphitized from slow bake

Table XI

Graphitized (2700°C) of 5/8" Dia. Extrusions
of 85 Pts. GLC 1076 Flour/15 Pts. Thermax

	<u>A. D.</u> <u>(g/cc)</u>	<u>CTE</u> <u>0-50°C</u> <u>(10⁻⁷/°C)</u>	<u>CTE</u> <u>1500°C</u> <u>(10⁻⁷/°C)</u>	<u>E. R.</u> <u>(10⁻⁵ohm-in)</u>	<u>MOE</u> <u>(10⁶psi)</u>	<u>MOR</u> <u>(psi)</u>	<u>α</u> <u>(cm/sec)</u>
Varcum 8251+QX-299	1.93	39.2	(50.9)	66.0	-	4860	-
QX-247 + QX-299	1.90	43.7	54.0	74.0	1.57	3950	0.7
QX-248 + QX-299	1.91	43.6	(56.6)	71.9	1.72	3535	
QX-237 + QX-240	1.78	44.0	(57.1)	71.8	1.28	3310	
QX-237 + QX-314	1.77	44.2	56.2	70.0	1.31	3095	0.7
QX-297-1 + QX-314	1.74	44.8	55.5	73.5	1.12	2140	0.7
QX-298-1 + QX-314	1.75	43.4	(56.3)	72.9	1.24	2770	
QX-302 + QX-314	1.75	42.6	56.1	93.2	1.20	23.5	0.5
QX-302 + QX-315	1.77	41.4	(53.7)	87.1	1.30	2565	
QX-302-1 + QX-314	1.82	40.2	(52.2)	80.0	1.44	2825	
QX-302-1 + QX-315	1.80	38.7	(50.2)	77.4	1.54	3535	
QX-302-2 + QX-314	1.71	43.2	(56.1)	74.1	1.17	3005	
QX-302-2 + QX-315	1.71	44.0	(57.1)	76.1	1.16	3210	
QX-303-1 + QX-314	1.80	41.2	(53.2)	68.5	1.45	3450	
QX-303-2 + QX-314	1.72	40.9	55.6	73.4	1.02	2405	0.6
QX-303-3 + QX-314	1.68	44.7	(58.0)	78.1	1.01	2355	
QX-303-6 + QX-314	1.84	37.2	50.1	61.0	1.48	4055	0.7
QX-304-1 + QX-314	1.76	42.0	56.9	72.3	1.18	2900	0.6
QX-305-1 + QX-314	1.87	36.9	(47.9)	71.4	1.68	3860	
QX-306-1 + QX-314	1.65	38.5	(50.0)	99.6	1.66	2335	
QX-307-1 + QX-314	1.77	42.5	(55.2)	74.7	1.32	3160	
QX-308 + QX-314	1.84	38.9	50.3	74.4	1.46	2380	0.5
QX-308 + QX-315	1.77	41.4	(53.7)	72.5	1.34	2755	
QX-309-1 + QX-314	1.77	42.2	53.5	72.6	1.30	2680	0.6
QX-309-1 + QX-315	1.76	42.6	(55.3)	76.2	1.18	2105	

( ) = Calculated high temperature CTE's.

relatively narrow range, irrespective of the binder used ($36.9 - 44.8 \times 10^{-7}/^{\circ}\text{C}$; $0-50^{\circ}\text{C}$ and $47.9 - 57.1 \times 10^{-7}/^{\circ}\text{C}$; $20-1500^{\circ}\text{C}$). The highest CTE's were found to occur in extrusions containing QX-237, QX-297-1, QX-302-2, and QX-303-3 which is the case of QX-302-2 and 303-3 contain relatively high pitch contents. The lowest CTE's were found in extrusions containing the QX-303-6 and QX-305-1 binders, both of which exhibit otherwise attractive physical properties.

Electrical resistivities, as in the case of CTE's, also lie within a relatively narrow range. The QX-302 binder in extrusions resulted in the highest resistivities, which might be expected for a binder with low pitch content. However the resistivity of QX-302 is also somewhat higher than that of the glassy "Varcum-type" binders. The resistivities of the QX-302 series of binders was noted to decrease as the pitch fraction was increased. This would be expected since a more graphitic constituent is added to the binder. However, the QX-303 series shows a definite increase in resistivity as the pitch component is increased. This effect may be due to differences in solubility of the pitch in the resin or possibly to density effects. With the exception of high resistivity binders such as QX-302, QX-302-1 and QX-306-1 the values are quite close in magnitude to the "Varcum-type" resin. The high resistivity of the QX-306-1 bonded extrusion could be attributed to several factors such as low density, high binder level, or pitch/furan incompatibility. The low resistivity of the QX-303-6 extrusion is probably due to both high density and the relatively low volatile matter, graphitizable 280°C pitch component.

The modulus of elasticity (MOE) is an indication of the brittleness of the samples and would tend to be high for those extrusions containing a predominately glassy carbon binder phase. The MOE's of extrusions containing QX-305-1 and QX-306-1 approach those containing the "Varcum-type" resins although both contain petroleum pitch. The MOE of the QX-306-1 extrusion is quite high considering the density of the sample. Extrusions containing QX-302-1, QX-303-1 and QX-303-6 are moderately high in MOE, and with the exception of the QX-303-6 extrusions are also relatively low in pitch. The effect of pitch additions on MOE are dramatically demonstrated for the QX-303 series of samples; also density effects would tend to cause variations in MOE.

The strengths (MOR) of the extrusions are relatively good. A number of pitch/furan bonded extrusions have MOR values approaching those of the "Varcum-type" resins, QX-247 and 248. Most notable of pitch/furan binders is QX-303-6,

which contains the high softening point petroleum pitch. Also high in strength were extrusions containing QX-237, QX-302-2, QX-303-1, QX-305-1 and QX-307-1, where QX-303-1 contains the lowest amount of pitch.

Thermal diffusivity (α) was determined for selected samples at room temperature, by the flash technique. With the exception of the extrusion containing QX-302 the spread in values was not great. No distinction could be made between the pure furan resin (QX-247) and the pitch/furan blends by this method. The reason for the low value for the QX-302 extrusion is not known. Other physical property values show no indication of exceptionally different properties for this sample.

Based on an overall summary of the physical properties, extrusions containing QX-303-6 and QX-305-1 appear to be equivalent to the "Varcum-type" resins although the CTE's are relatively low. If higher CTE's are required as significant criteria, then the binders QX-237, QX-302-1 and QX-303-1 should also be recommended although there is some trade-off in strength. All of the densities are low with respect to the Varcum 8251 and the "Varcum-type" resins (QX-247 and 248), but, as stated earlier, it is felt that processing conditions can be further optimized - particularly in the areas of binder level and mixing techniques.

i. DTA and TGA Results

1. DTA Curves

The DTA curves showed well-defined temperature intervals of exothermic and endothermic activity. The apparatus used was the same as described in the report for the first iteration of binders. The upheate rate was maintained at 6°C/min., and the samples were heated in an argon atmosphere. For the second iteration 40% of catalyzed binder was mixed with 60% high-fired GLC-1076 flour; this flour was also used as the inert standard. Pitch additions, where required, were made in accordance with the mixing procedure for extrusions; that is, powdered pitch was mixed with the flour prior to addition of hardener and resin. The hardener was 4% QX-240 in all cases.

The resulting DTA curves can be classified into three types as follows:

Type 1 - a single exothermic curing region is followed by an endothermic region associated with the boil-off of the water of reaction. A second extended endothermic trend which builds up to a maximum plateau and then falls off is associated with destructive distillation of the polymer. This type of curve was typical for the pure furan resins such as Varcum 8251, QX-247, and QX-248.

Type 2 - an initial, double exothermic peak occurs as the resin begins curing and resin/pitch interactions take place. There is no detectable endotherm due to the boiling off of the water. The endothermic plateau is not as pronounced as in the case of the Type 1 curves, and in some cases is not present until higher temperatures are reached. An extended endothermic plateau occurs during destructive distillation as in all of the other curves. This type of curve is typical for QX-297-1, QX-298-1, QX-303-6, QX-304-1, QX-305-1, QX-308 and QX-309-1.

Type 3 - a single, relatively broad exothermic range, typical of curing and resin/pitch copolymerization occurs at the onset of the run. No endothermic plateau occurs during destructive distillation as in all of the other curves. This type of curve is typical for QX-297-1, QX-298-1, QX-303-6, QX-304-1, QX-305-1, QX-308 and QX-309-1.

With respect to the Type 2 and Type 3 curves, the Type 2 appears to indicate the greatest degree of resin/pitch interaction during initial polymerization. In the case of the QX-303-6 binder, which includes the addition of the relatively unreactive 280°C softening point pitch, the initial exothermic region is only an extended, relatively shallow plateau. A quantitative summary of the various binders according to type is presented in Tables XII, XIII, and XIV.

Although the DTA data in Table XII are similar in distribution, the endothermic peak for Varcum 8251 is significantly greater than the same peaks for QX-247 and 248. The data would tend to indicate that the Varcum resin is more reactive. However, the QX-247 and 248 have been prepolymerized to achieve the desired viscosity and therefore contain less monomer. The endothermic plateaus of the three resins appear nearly equivalent with respect to dissociation reactions.

The DTA data summarized in Table XIII, while all basically similar, indicate varying degrees of resin/pitch interaction. It may be assumed that QX-237, QX-302, QX-303, QX-306 and QX-307 are generally the same type of resin. The effect of increasing amounts of pitch additions can be seen in the QX-302 and 303 series where the overall exothermic range is extended to higher temperatures. The endothermic range of this type of binder is not as pronounced as for the "Varcum-type" resins indicating that dissociation reactions are not as thermally active.

The third type of DTA data as given in Table XIV shows a continuous exothermic curing and resin pitch interaction region without the double peak associated with the previous set of binders. The exothermic region is almost immediately followed by an extended endothermic region of dissociation reactions. For this reason it is felt that in these binders

Table XII

DTA Results of WANL Binders in GLC 1076 Flour to 550°C in Argon
Type I Curves

<u>Binder Used</u>	<u>Exothermic Peak</u>		<u>Endothermic Peak</u>		<u>Endothermic Plateau</u>	
	<u>Range</u> °C	<u>Maximum</u> °C/Amplitude	<u>Range</u> °C	<u>Maximum</u> °C/Amplitude	<u>Range</u> °C	<u>Maximum</u> °C/Amplitude
Varcum 8251 + QX-240	25-76	50/6 Units	76-128	88/12.5 Units	172-530	356 378/8.5 Unit
QX-247 + QX-240	25-88	58/7.5 Units	88-126	96/4 Units	174-518	328/6 Units 360/9 Units
QX-248 + QX-240	25-86	56/7.5 Units	86-116	96/4 Units	168-510	358 378/9 Units

*40% by weight of binder in GLC 1076 flour (high-fired)

Table XIII

DTA Results of WANL Binders in GLC 1076 Flour to 550°C in Argon
Type 2 Curves

Binder Used	1st Exothermic Peak		2nd Exothermic Peak		Endothermic Range	
	Range °C	Maximum °C/Amplitude	Range °C	Maximum °C/Amplitude	Range °C	Maximum °C/Amplitude
QX-237 + QX-240	25-118	76/5.5 Units	76-206	118/5.5 Units	372-490	386/3 Units
QX-302 + QX-240	25-124	76/7 Units	114-188	134/4.5 Units	250-516	378/2.5 Units
QX-302-1 + QX-240	25-160	69/8 Units	85-199	116/4.5 Units	236-392	264/3 Units 355/2 Units*
QX-302-2 + QX-240	25-136	70/8 Units	50-234	109/6 Units	284-430	360/3.5 Units
QX-303-1 + QX-240	25-140	78/8 Units	62-182	100/6 Units	182-500	210-380/2.5 Units
QX-303-2 + QX-240	25-145	73/7.5 Units	63-208	113/5 Units	229-486	293/2.5 Units 371/3.5 Units
QX-303-3 + QX-240	25-154	72/6.5 Units	72-290	122-154/5 Units	330-470	290/2 Units
QX-306-1 + QX-240	25-148	85/7.5 Units	58-230	112/6.5 Units	268-452	352 404/3.5 Units
QX-307-1 + QX-240	25-138	72/7.5 Units	72-166	115/5.5 Units	178-420	382/5.5 Units

*QX-302-1 Slight Exothermic range 392°C - 450°C with maximum at 424°C (2 units)

Table XIV

DTA Results of WANL Binders in GLC 1076 Flour to 550°C in Argon
Type 3 Curves

Binder Used	Exothermic Range		Endothermic Range	
	Range °C	Maximum °C/Amplitude	Range °C	Maximum °C/Amplitude
QX-297-1 + QX-240	25-186	82/8 Units	186 - 298 354 - 448	226-240/2 Units 396/2 Units
QX-298-1 + QX-240	25-215	67/8 Units	215 - 400	1 Unit
QX-303-6 + QX-240	25-250	180-150/4 Units	286 - 444	1 Unit
QX-304-1 + QX-240	25-220	74/9 Units	282 - 570	386/3 Units
QX-305-1 + QX-240	25-162	90/9 Units	176 - 504	370/7.5 Units
QX-308 + QX-240	25-161	69/8.5 Units	161 - 448	352/5 Units 379/5.5 Units
QX-309-1 + QX-240	25-148	82/8.5 Units	148 - 439	353/5 Units 380/5.5 Units

the pitch and furan do not interact in the curing stage as much as the previous set of binders. The binders QX-297-1 and 298-1 show very little endothermic activity probably due to insufficient hardener to effect a full cure. QX-303-6, although generally representative of this third type of DTA behavior shows little exothermic or endothermic activity. However, this is to be expected, since the 280°C softening point pitch is essentially an unreactive raw coke.

Based on the Varcum 8251 and the QX-247 and 248 curves, dissociation of the resin does not appear to begin before 170°C. Addition of the powdered pitch to the resin appears to generally increase the temperature at which dissociation becomes detectable to 225°C or higher. Only five of the pitch/furan binders showed a relatively early onset of dissociation as listed below:

QX-309-1	148°C
QX-308	161°C
QX-305-1	176°C
QX-307-1	178°C
QX-303-1	182°C

It is believed that the endothermic region of dissociation is the most critical range in the processing of pitch/furan binders. In this region pitch/furan bonds established during curing are being broken, allowing resoftening to take place. These reactions generally reach their maximum activity between 300°C and 400°C and are essentially complete by 500°C. It is felt that a slow upheal rate beginning at 300°C is required to prevent gross separation between the pitch and the furan. Beyond 500°C the structure is probably set, and upheal rate is not as critical.

It is also felt that the exothermic curing region is also important in determining binder structure. Curing of the "Varcum-type" resins appears to be complete by 130°C, which overlaps the softening point of the Ashland 240 pitch and allows copolymerization to occur. Between 100°C and 140°C the furan/pitch interaction appears to reach a maximum for those binders where two distinct curing peaks appear (Table XIII). Therefore, it is felt that between 100°C and 140°C copolymerization reactions are taking place which would require close control to achieve the desired cross-linking. Since the "Varcum-type" resins are capable of producing strong exotherms in this region, it is possible to cure too quickly in this interval for pitch/resin reactions to develop fully. Although the problem is not likely to occur when filler material is present, it is possible that in the curing and coking of unfilled pitch/furan binders different binder structures than would normally occur in extrusions would be present. For this reason the unfilled resins in this study were subjected to the same baking rates (90°C-720°C) as the extrusions.

2. TGA Curves

Thermogravimetric analyses were made on the binders with 4% QX240 hardener. As in the case of the DTA samples, 40% by weight of binder was mixed with 60% GLC-1076 flour. The analyses were made in order to supplement the information obtained from the DTA curves and to detect temperature regions where maximum weight loss takes place. Samples were run in air to 460°C and in argon to 650°C at a rate of 6°C/min.

Upon comparison of weight losses to 450°C in air vs. argon, it was noted that there was no significant difference in weight loss due to atmosphere. This did not agree with the findings from the first iteration binders which showed a trend of higher binder yield in air to 400°C for more "pitch-like" binders. The reason for the differences in results is not known at this time. One possible cause could be the use of lower gas flow rates in the analyses of the second iteration of binders.

All of the TGA curves were essentially the same. A high rate of weight loss was indicated in the initial curing stage to ca. 140°C-200°C. A second range of high weight loss rate was a maximum between 300°C and 420°C. For the pitch/furan binders this region occurred between 360°C and 440°C. From 520°C to the endpoint of 650°C weight losses were negligible. The TGA data, therefore, substantiated the existence of a critical temperature range between 300°C and 450°C. As a result, it is felt that additional work must be done in order to establish optimum processing parameters during both the curing and the baking steps. These areas determine the final structure of the binder coke.

4. Phenolic/Pitch Binders

Due to time limitations and the large number of binders in the Quaker Oats series, only a limited amount of work was done towards the development of a phenolic pitch binder system. Three phenolic resins were evaluated on the basis of binder yield and compatibility with Ashland No. 240 petroleum pitch. Monsanto's SC-1008 resin was selected for use in extrusions with tetrahydrofuran (THF) used as the pitch solvent. Resin pitch ratios of 2:1 and 1.6:1 were mixed with 30% by weight of the pitch of THF solvent. When attempts were made to increase the amount of pitch in the resin, problems were encountered in pitch separation. The 1.6:1 resin pitch ratio appeared to be the maximum amount of pitch which could be used in the system, and some separation was noted to occur with this ratio upon standing for 24 hours.

Flour/Thermax extrusions were made following the same procedures used with the Quaker Oats binders except that no hardener is required for the phenolic resin. The following cured data was obtained:

<u>Sample</u>	<u>Binder Level (pph)</u>	<u>Extrusion Press. (psi.)</u>	<u>Cured (100°C) A.D. (g/cc)</u>
2:1 Resin/Pitch	39	585	1.63
1.6:1 Resin/Pitch	50	850	1.61

The extrusions were baked to 720°C using both the standard and slow cycles. As in the case of the pitch/furan binders, little difference was noted in the effects of baking rate on the pitch/phenolic extrusions. Cure - to - bake data is given below:

<u>Sample</u>	<u>Baked Std.</u>	<u>A.D. Slow</u>	<u>Binder Std.</u>	<u>Yield (%) Slow</u>	<u>Volume Std.</u>	<u>Shrinkage (%) Slow</u>
2:1 Resin/Pitch	1.59	1.56	53.6	54.1	10.4	7.6
1.6:1 Resin/Pitch	1.52	1.53	63.1	65.0	6.9	7.7

Samples taken from the slow bake were graphitized to 2700°C on the 8-hour cycle. The graphitized physical properties are tabulated below:

<u>Sample</u>	<u>A.D. (g/cc)</u>	<u>Binder Yield (%)</u>	<u>E. R. (10⁻⁵ohm-in.)</u>	<u>MOR (psi.)</u>	<u>MOE (10⁶ psi.)</u>	<u>CTE (10⁻⁷/°C)</u>
2:1 Resin/Pitch	1.69	48.7	96.0	2415	1.13	41.6
1.6:1 Resin/Pitch	1.57	57.9	152.8	760	0.50	41.2

As shown the properties were generally inferior to the Varcum or pitch/furan bonded samples. Low yields and relatively low volumetric shrinkages resulted in low density samples. It is felt that the addition of THF solvent over and above the solvents in the resin (60% solids) contributed to the low densities; however, during mixing much of the THF volatilized. Upon boiling off of the THF, pitch appeared to separate from the binder and deposit on the particles resulting in two distinct binder phases which could have been detrimental to bonding. No further work was done in this area.

5. Resin-Catalyst Evaluation

A limited amount of work was done to determine the effects of various polymerization catalysts on the coke yields and structures obtained from Varcum 8251. Laboratory cokings of 1000 g. batches of Varcum with 4 pph of each catalyst used were carried out in 4 liter resin flasks. In addition, Varcum was coked without further addition of catalyst. Each coke was heated to a final temperature of 550°C over a period of 8 hours. The heating rate was slowest during the exothermic temperature ranges. Raw coke yields and the volatile matter content of each coke were determined. Finally, each coke was heat treated to 2200°C to determine relative graphitizabilities by x-ray diffraction analyses. Heat treatment to 2700°C yielded carbons which produced rather complex diffraction peaks that were unsuitable for comparative purposes. Data from these experiments are summarized in Table XV.

The catalysts used exhibited widely different reactivities based on their initial exothermic reactions.

Toluene sulfonic acid (p-TSA) was the most reactive. The Varcum polymerized immediately on addition of this catalyst. Maleic anhydride and pyromellitic dianhydride was the least reactive. Coke yield was highest with p-TSA (57.7%) while the other three catalyst gave essentially the same coke yield (48-49 wt. %). No significant differences in the 2200°C carbons were detected by x-ray diffraction analyses.

TABLE XV
DATA FOR LABORATORY COKINGS OF VARCUM #8251
WITH VARIOUS CATALYST (4 PPH)

<u>Property</u>	<u>#30</u>	<u>#51</u>	<u>#33</u>	<u>#34</u>	<u>#35</u>
Catalyst	None	Phthal. Anhyd.	p-TSA*	PMDA**	Maleic Anhyd.
1st Exotherm, °C	246	152	30	121	121
2nd Exotherm, °C	None	266	None	260	266
Coke Yl'd. (550°C) Wt. %	33.8	49.0	57.7	49.1	48.0
V. M. (550°C Coke) Wt. %	15.6	12.1	13.3	12.4	11.0
X-ray, 2200°C d-spacing Å	3.499	3.502	3.500	3.502	3.502
L _c , Å	27.9	27.5	28.9	28.6	28.5

*Para-toluene sulfonic acid.

**Pyromellitic dianhydride.

APPENDIX - PART B

FIG. 1 - Varcum 8251 2700°C 250X

FIG. 2 - QX-247 2700°C 250X

FIG. 3 - QX-248 2700°C 250X

FIG. 4 - QX-237 2700°C 250X

FIG. 5 - QX-297-1 2700°C 250X

FIG. 6 - QX-298-1 2700°C 250X

FIG. 7 - QX-302 2700°C 250X

FIG. 8 - QX-302-1 2700°C 250X

FIG. 9 - QX-302-2 2700°C 250X

FIG. 10 - QX-303-1 2700°C 250X

FIG. 11 - QX-303-2 2700°C 250X

FIG. 12 - QX-303-3 2700°C 250X

FIG. 13 - QX-303-6 2700°C 250X

FIG. 14 - QX-304-1 2700°C 250X

FIG. 15 - QX-305-1 2700°C 250X

FIG. 16 - QX-306-1 2700°C 250X

FIG. 17 - QX-307-1 2700°C 250X

FIG. 18 - QX-308 2700°C 250X

FIG. 19 - QX-309-1 2700°C 250X