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PROPERTIES OF CARBON DERIVED
FROM PETROLEUM PITCHES

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UNION
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OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

prepared for the U.S. ATOMIC ENERGY COMMISSION
under U.S. GOVERNMENT Contract W-7405 eng 26

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Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22151
Price: Printed Copy \$4.00; Microfiche \$0.95

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Oak Ridge Y-12 Plant

P.O. Box Y, Oak Ridge, Tennessee 37830

Date Issued - June 21, 1973

Prepared for the U.S. Atomic Energy Commission
Under U.S. Government Contract W-7405-eng-26

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ABSTRACT

The effect of temperature and various additives on the properties of petroleum pitches, and carbons derived from these pitches, were studied. Pitch properties were monitored by molecular weights, softening points, and benzene insolubles; carbon properties were evaluated by crystallography, metallography, and density studies. In thermal studies, two petroleum pitches were found to be relatively stable for extended periods at 250° C. By blending various additives with samples of one of the pitches, prior to pyrolysis, a wide variety of carbon properties were obtained, thus affording avenues to control these properties by controlled modification of the precursors.

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SUMMARY

The primary goal of this study was to evaluate the properties of carbon derived from two petroleum pitches—Ashland 240 and 170 (A-240 and A-170). Included in this study were: (1) an evaluation of the thermal stability of the two petroleum pitches at 250° C; (2) a determination of the properties of carbon derived from A-240 pitch over the temperature range from 1,000 to 2,800° C, and (3) an evaluation of various additives to A-240 pitch by correlating the properties of derived carbon with the additive type and content.

The primary conclusions reached from the study were: (1) petroleum pitches A-240 and A-170 are relatively stable at 250° C for up to 28 days; (2) A-240 petroleum pitch produces carbon that densifies at approximately 1,500° C and undergoes significant three-dimensional ordering between 2,000 and 2,500° C to yield a highly crystalline carbon; (3) properties of carbon derived from A-240 petroleum pitch can be modified over a wide range by blending additives with the pitch prior to pyrolysis.

INTRODUCTION

Advent of the nuclear and space age has brought increased demands on the scientific community for specialty forms of structural materials. Much research is involved in adapting carbon for special applications in these areas.

Properties which make carbon interesting from the standpoint of structural applications are: (1) high-temperature heat resistance, (2) resistance to chemical attack, (3) constancy of properties with time, (4) its high strength-to-density ratio, and (5) a variety of forms into which carbon can conveniently be made and the variety of properties that these forms can impart in structural applications.

Properties of carbon are largely determined by the molecular structures of the precursor materials and the reaction mechanisms which the precursors undergo to become carbon. In general, the ability of a precursor to yield a graphitic structure depends upon the precursor's ability to assume the planar aromatic structure characteristic of the graphite unit cell. Thus, processes such as bond cleavage, molecular rearrangements, cyclization, aromatization, and dehydrogenation are involved in the transition of the precursor to carbon. Factors which prevent these processes from occurring in a prescribed order and at prescribed rates favor the formation of a nongraphitic carbon, and varying degrees of inhibition would result in varying graphiticity. Materials which tend to "thermoset" into highly crosslinked polymers that either do not tend to rearrange prior to pyrolysis or remain in a highly viscous state do not lead to rearrangement or reorientation due to the reduced degrees of molecular freedom. These materials do not yield graphitic carbon. However, thermoplastic materials or materials with a low degree of crosslinking allow viscosities in which molecular rearrangements and reorientations can occur, and tend to form graphitic carbons unless stable nonplanar intermediates are formed.

In addition to the degree of graphiticity of the derived carbon, several other properties must be considered before a precursor should be selected. Some of these are: (1) processability; (2) weight, volume, and strength yield on carbonization; (3) properties in the temperature range from 1,000 to 3,000° C; (4) reproducibility, and (5) economics.

This report describes an evaluation study that was made at the Oak Ridge Y-12 Plant(a) of the properties of Ashland-240 and Ashland-170 petroleum pitches (A-240 and A-170) with emphasis on the A-240 pitch. Properties were determined for the carbon derived from A-240, as well as properties of carbons derived from blends of A-240 and various additives. Several binder formulations involving A-240 and furan resins were evaluated, and their properties are listed in this report. A subsequent report in this series will emphasize the physical properties, chemistry, and reproducibility of the pitches.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Atomic Energy Commission.

PROPERTIES OF PETROLEUM-PITCH CARBONS

EXPERIMENTAL PROCEDURES

Materials

Petroleum Pitches - The A-240 and A-170 pitches were petroleum distillate fractions obtained from the Ashland Oil Company. Property differences between the two pitches reflect the greater concentration of the lower-molecular-weight compounds in the A-170.

Furan Resins and Catalyst - The furan resins and catalyst used in the binder formulations were obtained from the Quaker Oats Company. Viscosities of the furan resins varied from 50 to 40,000 centipoises (cPs) at room temperature, affording a wide range of binder properties.

Reagents - The dicyclopentadiene and pyromellitic dianhydride were reagent-grade materials obtained from usual chemical supply sources and used without further purification.

Synthetic Compounds - Furfurylideneindene and p-xylylideneindene were prepared by the room-temperature condensation of furfural⁽¹⁾ and terephthalaldehyde,⁽²⁾ respectively, with indene in the presence of an alcoholic base. Isotruxene was prepared by the reaction of indene and 1,4-naphthoquinone in the presence of tertiary amines.⁽²⁾ Structural formulas for the compounds are:

Furfurylideneindene

p-Xylylideneindene

Isotruxene

Methods

Polymer Properties - Polymer average molecular weight data were obtained with a Hewlett-Packard high-temperature vapor-pressure osmometer, Model 302, using sucrose

octacetate as the calibration standard. Pitch softening points, benzene insolubles, and carbon residues were determined according to ASTM D-36-66, ASTM D-2317, and ASTM D-189-65, respectively. Viscosities of the furan resins and binders were determined with a Brookfield Model RV viscometer. Helium densities were calculated by determining the volume of weighed samples by the displacement of helium.

Carbon Properties - Carbonization consisted of heating 30 grams of the precursors or precursor blends (prepared using a Waring blender) in a three-inch-diameter crucible to 1,000° C in an inert-gas atmosphere. This procedure was rate controlled and required approximately 60 hours. Coke yields were calculated as the percent residue after the 1,000° C carbonization step.

After carbonization, samples were fired for one hour at 2,800° C, unless specified otherwise, using a carbon induction furnace. The resulting samples were then evaluated by metallography and by X-ray diffraction.

Metallographic samples were mounted in epoxy resin and placed under vacuum to remove adherent air bubbles and to impregnate flakes. The mounted specimens were then ground successively on silicon carbide grits of Sizes 240, 320, 400, and 600. After cleaning to remove loose adherent silicon carbide, the samples were polished with Linde A (0.3 μm Al_2O_3) powder that was suspended in water on Pellon cloth on a Syntron vibrating polisher. This work was followed by a final polish on the Syntron with Gamel cloth and a water suspension of Linde B (0.05 μm Al_2O_3) powder. The samples were then cleaned in flowing water with a cotton swab and blown dry with compressed air. Photomicrographs were made using sensitive-tint illumination on a Bausch and Lomb Research 1 metallograph.

A Siemen's Crystalloflex IV recording diffractometer with copper K_α radiation was used to obtain the X-ray diffraction data. An internal standard of sodium chloride was analyzed with each sample. Interlayer spacings were calculated from the X-ray data using the methods described by Ruland.⁽³⁾ The degree of graphiticity of the carbons was also expressed in terms of a g factor defined as follows by Maire and Mering:⁽⁴⁾

$$d_{002} = g (3.355) + (1-g) 3.44.$$

STUDIES OF THE PITCHES

Properties of Pitches as Functions of the Heat-Treatment Time at 250°C

One potential application for the petroleum pitches is in the field of impregnation, which is used to increase apparent densities and decrease porosity. Impregnation pitches must be extremely fluid at the temperature of impregnation and free of suspended particles. Economical considerations prefer that the impregnation pitch have properties which allow indefinite storage of the pitch at the impregnation temperature.

Properties of A-240 and A-170 petroleum pitches were determined with respect to heating time at 250° C in efforts to determine if degradation of the pitches occurs during the duration of the study. Samples of A-240 and A-170 were heated under argon for 28 days, with sampling occurring every seven days. Data obtained are listed in Table 1 and illustrated in Figure 1.

Table 1
 PROPERTIES OF PETROLEUM PITCHES AS FUNCTIONS OF THE
 HEAT-TREATMENT TIME AT 250° C

Sample	Heating Time at 250° C (days)	Softening Point ⁽¹⁾ (° C)	Average Molecular Weight ⁽²⁾	Benzene Insolubles ⁽³⁾ (%)	Carbon Residue ⁽⁴⁾ (%)	Coke Yield ⁽⁵⁾ (%)	X-Ray Diffraction Data ⁽⁶⁾		
							d ₀₀₂ (Å)	L _c (Å)	g Factor
A-170-A	0	79.8	410	1.60	36.5	42	3.3680	450	0.837
-B	7	81.2	427	1.10	35.3	44	3.3660	600	0.860
-C	14	83.3	409	1.40	37.1	44	3.3660	500	0.860
-D	21	82.8	371	1.10	35.9	44	3.3680	450	0.837
-E	28	87.3	396	2.31	37.5	45	3.3660	350	0.860
A-240-A	0	113.8	485	3.80	48.1	53	3.3628	-	0.898
-B	7	114.5	471	5.26	49.4	54	3.3690	450	0.826
-C	14	115.2	-	5.14	48.4	55	3.3680	400	0.837
-D	21	117.2	511	8.00	48.5	55	3.3660	500	0.860
-E	28	119.0	532	10.38	48.9	56	3.3660	600	0.860

(1) Ring-and-ball method; ASTM D-36-66.

(2) Determined by vapor pressure osmometry.

(3) ASTM D-2317.

(4) Conradson, ASTM D-189-65.

(5) Carbonized to 1,000° C in an inert atmosphere.

(6) Obtained after heating for one hour at 2,800° C.

Ring-and-ball softening points of the pitches increased gradually with the heat-treatment time. This increase was probably due to the loss of volatiles. Softening points of the A-170 pitches increased at a higher rate, as expected, due to the greater concentration of lower-molecular-weight components.

Average-molecular-weight data indicated an increasing molecular weight with time for the A-240 pitch and a decrease with time for the A-170 pitch. These data are difficult to interpret because of variability in the molecular-weight determination method due to the lack of reproducibility for removing insolubles. The amount of benzene insolubles was fairly constant as the heating time increased for the A-170 samples, while increasing sharply with time for the A-240 samples. As noted previously, A-170 contains more low-molecular-weight entities than does A-240; and, thus, contains smaller amounts of benzene insolubles.

Coke yields after 1,000° C increased only slightly for the pitches as the heating time at 250° C increased, with an apparent constant coke-yield difference between the A-170 and A-240 pitches. As expected from molecular weight data, coke yields from A-170 were lower than from A-240.

Conradson carbon residues also increased only slightly as the heat-treatment time increased, with the difference in the data between A-240 and A-170 again reflecting the difference in molecular weight and volatile content.

Interlayer-spacing (d₀₀₂) and crystallite-size (L_c) values showed no significant change as the heat-treatment time increased. Microstructures typical of the carbon obtained from each of these pitches are seen in Figure 2.

Figure 1. PROPERTIES OF PITCHES AS FUNCTIONS OF THE HEAT-TREATMENT TIME AT 250° C.

In summary, there was some change in the physical properties of the pitches due to loss of volatiles; however, except for A-240 benzene insolubles, these changes were not drastic in relation to the original values and would not alter the process requirements. Little or no change was noted for coke yields and carbon properties. Thus, these petroleum pitches could be applicable for uses involving impregnation.

(a) A-170 Pitch.

I389-1 (b) A-240 Pitch.

I389-6

Figure 2. MICROSTRUCTURES THAT ARE TYPICAL OF CARBONS (AFTER 2,800° C) DERIVED FROM THERMAL STABILITY SAMPLES OF PITCHES. (250X; Sensitive Tint)

Properties of A-240-Derived Carbon as Functions of Temperature

Properties of carbons derived from A-240 were measured as functions of temperature over the range from 1,000 to 2,800° C. The 1,000° C carbon was obtained by heating the raw material on a programmed cycle to 1,000° C, with a two-hour hold time at the maximum temperature. A time of approximately 60 hours was required to complete the cycle. Successive heat treatments involved heating aliquots of the 1,000° C carbon to the respective temperature in a carbon induction furnace. All the samples, except the 2,800° C sample, were heated for 30 minutes in an argon atmosphere. A hold time of one hour was used for the 2,800° C sample. Properties of the respective carbons are listed in Table 2.

Table 2
PROPERTIES OF CARBONS DERIVED
FROM A-240 PITCH

Sample	Temperature (° C)	Helium Density (1) (gms/cc)	Carbon Data (2)		
			d ₀₀₂ (A)	L _c (A)	g Factor
A	1,000	1.92	(3)	-	-
B	1,250	2.02	(3)	-	-
C	1,500	2.15	3.4298	37	0.059
D	1,760	2.11	3.4268	69	0.077
E	2,020	2.10	3.4214	110	0.216
F	2,480	2.03	3.3770	190	0.733
G	2,800	1.82	3.3644	365	0.879

(1) Determined by helium displacement.

(2) Obtained after firing for one hour at 2,800° C.

(3) No measurable peak at the 002 plane.

Figure 3. PROPERTIES OF CARBON DERIVED FROM A-240 PITCH AS FUNCTIONS OF TEMPERATURE.

Helium densities increased to an apparent maximum as the temperature increased from 1,000 to 1,500° C, then decreased to a fairly constant value over the temperature range from 1,700 to 2,500° C (Figure 3). Between 2,500 and 2,800° C, the helium density decreased, probably indicating shrinkage and the closing of pore entrances.

Also shown in Figure 3 is the expected increase in g-factor and crystallite-size (L_c) values as the temperature increased. The crystallite growth above 2,000° C is typical of graphitizing carbons. The g-factor and L_c values for the 2,800° C carbon suggest a highly crystalline structure. This conclusion is supported by metallography (Figure 4).

In summary, densification at 1,400 to 1,600° C and the ordering of the crystal structure above 2,000° C are quite common to graphitizing carbons. The decrease in density as the temperature increased from 2,600 to 2,800° C was unexpected, but could occur due to volume shrinkage and pore closure.

I372-16

Figure 4. MICROSTRUCTURE OF CARBON (AFTER 2,800° C) DERIVED FROM A-240 PITCH. (250X; Sensitive Tint)

Properties of Carbons Derived from A-240/Pyromellitic Dianhydride Mixtures

The structure of pyromellitic dianhydride (PMDA) is such that thermal degradation results in the production of highly reactive benzyne intermediates:

This highly reactive benzyne intermediate should be useful as a crosslinking agent for controlling the degree of fluidity and/or molecular mobility of carbon precursors during polymerization and pyrolysis. In fact, Smith, et al,⁽⁵⁾ have reported that properties of carbons derived from cinnamylideneindene and isotruxene are significantly altered by the addition of PMDA to the prepolymerized blends.

Table 3
PROPERTIES OF CARBONS DERIVED
FROM A-240/PYROMELLITIC
DIANHYDRIDE MIXTURES

Sample	PMDA Content (%)	Coke Yield ⁽¹⁾ (%)	Carbon Data ⁽²⁾		
			d ₀₀₂ (Å)	L _c (Å)	g Factor
A	0	51	3.3644	365	0.879
B	2.5	50	3.3622	409	0.905
C	5.0	52	3.3690	439	0.826
D	10.0	55	3.3542	382	0.998
E	12.5	57	3.3640	352	0.884
F	15.0	59	3.3650	229	0.872
G	20.0	56	3.3748	131	0.758
H	22.5	62	(3)	-	-
I	30.0	57	(3)	-	-
J	40.0	56	(3)	-	-
K	50.0	53	(3)	-	-

(1) Obtained after firing to 1,000°C in an inert atmosphere.

(2) Obtained after firing for one hour at 2,800°C.

(3) No measurable peak at the 002 plane.

Addition of PMDA to A-240 pitch had a significant effect on the coke yields and properties of the derived carbons. Data obtained for various A-240/PMDA blends are summarized in Table 3.

As noted in Figure 5, coke yields appeared to maximize at a PMDA concentration of 30 percent, suggesting that this composition had a maximum interaction between PMDA and A-240.

Also indicated in Figure 5 is the decrease in graphitic properties that result from the presence of PMDA. G factors of the 2,800°C carbons appeared to maximize at a PMDA content of approximately 10 percent and then decrease rapidly, indicating an increasing degree of crosslinking and/or nonplanarity in the polymeric precursors. At PMDA contents higher than 20 percent, nongraphitic carbon results.

A transition in the microstructural properties of the carbons is revealed in Figure 6. Subtle changes in the microstructure occurred for samples with 2.5 and 15 percent PMDA, while more significant changes occurred as the PMDA content increased from 15 to 20 percent.

In summation, the addition of PMDA to A-240 pitch alters the properties of the carbon derived from A-240 in a reproducible and controllable manner.

Properties of Carbons Derived from A-240/Furfurylideneindene Mixtures

Furfurylideneindene (FAI), a thermosetting indene derivative which yields a noncrystalline carbon on graphitization, was blended with the A-240 in efforts to utilize the thermosetting properties of the FAI as a crosslinking agent. Data for the carbonized blends are presented in Table 4.

As indicated in Figure 7, coke yields were essentially constant for blends containing up to 60 percent FAI, with higher FAI concentrations resulting in a gradually increased coke yield.

Figure 5. PROPERTIES OF CARBON DERIVED FROM A-240/PYROMELLITIC DIANHYDRIDE MIXTURES AS FUNCTIONS OF THE PYROMELLITIC DIANHYDRIDE CONTENT.

(a) 2.5% PMDA.

H631-7

(b) 15% PMDA.

H631-10

(c) 20% PMDA.

H525-10

(d) 30% PMDA.

H525-11

Figure 6. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM A-240/PYROMELLITIC DIANHYDRIDE MIXTURES. (250X; Sensitive Tint)

As also noted in Figure 7, corresponding g factors of the 2,800° C carbons indicated an apparent maximum in carbon crystallinity for the sample containing 30 percent FAI, while higher FAI concentrations yielded gradually decreasing g factors.

Microstructures of the 2,800° C carbons, given in Figure 8, also reveal that the crystallinity decreased as the FAI content increased. Significant changes in the microstructural properties of the carbons occur for samples containing greater than 50 percent FAI. Samples containing up to 50 percent FAI yielded highly crystalline carbons. Increasing the FAI content to 60, 70, and 80 percent lead to an increasingly homogeneous and fine-grain structure, with the carbon from the 80 percent FAI/A-240 blend being extremely fine grained. Higher FAI contents yielded noncrystalline carbons.

Thus, the A-240 and FAI blends must be miscible enough prior to pyrolysis to allow the thermosetting character of the FAI to decrease to molecular reorientation of the A-240 necessary to produce carbon of high graphiticity. Since high concentrations of FAI were required to evolve a significant microstructural change, there would also be a corresponding increase in the oxygen concentration which, for certain applications, would be intolerable. For other applications, though, the FAI/A-240 system produces carbon which has reproducible and controllable properties.

Figure 7. PROPERTIES OF CARBONS DERIVED FROM A-240/FURFURYLIDENEINDENE MIXTURES AS FUNCTIONS OF THE FURFURYLIDENEINDENE CONTENT.

Table 4
PROPERTIES OF CARBONS DERIVED
FROM MIXTURES OF A-240 AND
FURFURYLIDENEINDENE

Sample	FAI Content (%)	Coke Yield ⁽¹⁾ (%)	Carbon Data ⁽²⁾		
			d ₀₀₂ (Å)	L _c (Å)	g Factor
A	0	51	3.3644	365	0.879
B	10	48	3.3582	321	0.951
C	20	51	3.3600	418	0.930
D	30	51	3.3554	370	0.984
E	40	49	3.3616	377	0.912
F	50	46	3.3644	274	0.879
G	60	51	3.3748	119	0.758
H	70	58	3.3822	95	0.672
I	80	65	3.3854	58	0.612
J	100	64	(3)	-	-

(1) Obtained after heating to 1,000° C.

(2) Obtained after heating for one hour at 2,800° C.

(3) No measurable peak at the 002 plane.

Properties of Carbons Derived from A-240/p-Xylylideneindene Mixtures

Because of the highly conjugated system of unsaturated bonding exhibited by p-xylylideneindene (XYN), the compound is highly sensitive to polymerization conditions. When heated slowly, XYN did not fuse; yet, when placed on a preheated block at or above 240° C, the compound was observed to initially fuse and subsequently polymerize. XYN yields a noncrystalline carbon upon heating to 1,000° C and subsequent firing at 2,800° C, indicating hindered molecular mobility in the stages prior to pyrolysis by the crosslinking and/or non-planar intermediate character of the XYN precursor.

Figure 8. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM BLENDS OF A-240 AND FURFURYLIDENEINDENE. (250X; Sensitive Tint)

Blends of A-240 and XYN were carbonized in efforts to utilize the potential cross-linking character of XYN to control properties of the derived carbons. Data obtained from these blends are listed in Table 5.

As indicated in Figure 9, coke-yield values increased gradually as the XYN content increased, while the graphitic properties decreased with increasing XYN content. Thus, as the XYN content increased to 50 percent, the amount of crosslinking and/or nonplanarity in the polymeric system increased.

Photomicrographs in Figure 10 show the microstructural transitions which occur as the XYN content increased. Increasing concentrations of XYN resulted in an increasingly homogeneous and fine-grain structure for the derived carbon.

Figure 9. PROPERTIES OF CARBONS DERIVED FROM A-240/p-XYLYLIDENEINDENE MIXTURES AS FUNCTIONS OF THE p-XYLYLIDENEINDENE CONTENT.

Table 5
PROPERTIES OF CARBONS DERIVED
FROM A-240/p-XYLYLIDENE-
INDENE MIXTURES

Sample	XYN Content (%)	Coke Yield(1) (%)	Carbon Data(2)		
			d ₀₀₂ (A)	L _c (A)	g Factor
A	0	51	3.3644	369	0.879
B	10	52	3.3650	287	0.872
C	20	53	3.3662	270	0.858
D	30	54	3.3696	188	0.819
E	40	56	3.3758	116	0.747
F	50	56	3.3962	81	0.509

(1) Obtained after heating to 1,000° C in an inert atmosphere.

(2) Obtained after firing for one hour at 2,800° C.

Thus, there was interaction between the XYN and A-240 in that properties of carbon derived from blends of the two materials varied significantly as the XYN content was altered. Therefore, the XYN/A-240 system provides a method of obtaining carbon in a reproducible and controllable manner.

Properties of Carbons Derived from A-240/Isotruene Mixtures

Properties of carbon derived from isotruene (ITX) correspond to those of a fine-grain, isotropic carbon with a low order of graphiticity. Thus, the physical properties of ITX must allow either a low degree of molecular mobility or the formation of nonplanar intermediates during polymerization and pyrolysis. In efforts to utilize the properties of ITX as a potential crosslinking agent, blends of A-240 and ITX were carbonized, with carbon properties listed in Table 6. As illustrated in Figure 11, coke-yield values reached an apparent maximum at an A-240 concentration of 5 to 10 percent, while g factors of the corresponding 2,800° C carbons increased steadily as the A-240 content increased.

(a) 10% XYN.

MS-71-0839-1

(b) 30% XYN.

MS-71-0839-3

(c) 40% XYN.

MS-71-0839-4

(d) 50% XYN.

MS-71-0839-10

Figure 10. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM A-240/p-XYLYLIDENEINDENE MIXTURES. (250X; Sensitive Tint)

Table 6
PROPERTIES OF CARBONS DERIVED
FROM ISOTRUXENE/A-240
MIXTURES

Sample	A-240 Content (%)	Coke Yield ⁽¹⁾ (%)	Carbon Data ⁽²⁾		
			d ₀₀₂ (Å)	L _c (Å)	g Factor
A	0	38	3.3950	91	0.523
B	5	43	3.3834	81	0.658
C	10	43	3.3812	87	0.684
D	15	40	3.3720	127	0.791

(1) Obtained after heating to 1,000° C in an inert atmosphere.

(2) Obtained after firing for one hour at 2,800° C.

Figure 11. PROPERTIES OF CARBONS DERIVED
FROM ISOTRUXENE/A-240 MIXTURES AS
FUNCTIONS OF THE A-240 CONTENT.

Due to the volatility of DCPD under normal carbonization conditions, the binary mixtures of DCPD and A-240 were autoclaved for two hours in a gas-pressure autoclave at 300° C and 300 psi (initial nitrogen pressure). At this temperature the reactive species is probably cyclopentadiene rather than the dimer.

The microstructural transition is illustrated in Figure 12. With no A-240, a fine-grained, homogeneous carbon was obtained from the ITX. However, with increasing A-240 content, the derived carbons became increasingly heterogeneous, revealing areas of high crystallinity amid areas of fine-grain structure. Thus, there appears to be a minimum interaction between the ITX and A-240 during polymerization and pyrolysis.

In summation, coke-yield values were altered only slightly by the addition of A-240 to ITX, while g factors of the 2,800° C carbons indicated an expected increase in crystallinity as the A-240 content increased. However, microstructures became more heterogeneous as the A-240 content increased.

Properties of Carbons Derived from Autoclaved A-240/Dicyclopentadiene Mixtures

The search for organic systems which contain reactive double bonds which would give rise to crosslinking characteristics that lead to thermosetting rather than thermoplastic materials involved the evaluation of dicyclopentadiene (DCPD) as a potential crosslinking additive for A-240:

Endo Form of Dicyclopentadiene

Due to the volatility of DCPD under normal carbonization conditions, the binary mixtures of DCPD and A-240 were autoclaved for two hours in a gas-pressure autoclave at 300° C and 300 psi (initial nitrogen pressure). At this temperature the reactive species is probably cyclopentadiene rather than the dimer.

(a) 0% A-240.

193-1

(b) 5% A-240.

193-2

(c) 10% A-240.

193-3

(d) 15% A-240.

193-4

Figure 12. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM A-240/ISOTRUXENE MIXTURES. (250X; Sensitive Tint)

As indicated in Figure 13, coke yields after 1,000° C for the autoclaved blends reached an apparent minimum at a DCPD content of approximately 67 percent. Microstructures of the derived carbons decreased in crystallinity from a highly crystalline carbon (Figure 14a), to a somewhat less crystalline carbon (Figure 14b), then to a homogeneous, fine-grain carbon (Figure 14c) as the DCPD content increased from 33 to 50 to 67 percent, respectively. Carbon derived from autoclaved DCPD with no A-240 content was heterogeneous, with regions of fine-grain microstructure surrounding areas of lower crystallinity (Figure 14d).

Thus, DCPD has some crosslinking effect on A-240 in that carbons of lower crystallinity were obtained as the DCPD content increased. However, concentrations of DCPD that were 50 percent and greater were necessary to invoke significant microstructural changes.

Properties of Binders Formulated with Petroleum Pitches and Furan Resins

In choosing a precursor for binder applications, the physical properties of the precursor must be considered. The precursor should: (1) be fluid at the processing temperatures, (2) wet the substrate materials, (3) not release or induce stresses in such a manner that undesirable distortion occurs in a composite product, and (4) yield carbon with mechanical properties that are compatible with the substrate material.

The properties of potential binders prepared from furan resins and petroleum pitches were determined both with and without the addition of a catalyst. Viscosities of the as-received furan resins are presented in Table 7 along with melting points for the as-received pitches.

Figure 13. COKE YIELDS (AFTER 1,000° C) OF CARBONS DERIVED FROM AUTOCLAVED A-240/DICYCLOPENTADIENE MIXTURES AS A FUNCTION OF THE DICYCLOPENTADIENE CONTENT.

Table 7
PROPERTIES OF AS-RECEIVED FURAN RESINS AND PETROLEUM PITCHES

Furan Samples	Room-Temperature Viscosity ⁽¹⁾ (cPs)	Pitch Samples	Melting Point (° C)
QX-237	39,500	QX-310	116 ⁽²⁾
QX-247	2,400	QX-312	180
QX-248	5,240	QX-313	280
QX-297	1,600		
QX-298	320		
QX-302	54		
QX-303	140		
QX-304	148		
QX-305	8,000		
QX-306	10,800		
QX-307	5,300		
QX-308	21,200		
QX-309	124		

(1) Determined with a Brookfield viscometer.

(2) Ashland Oil Company refers to this pitch as A-240. QX-312 and-313 were also obtained from the Ashland Oil Company.

(a) 33% DCPD.

H3-67C

(b) 50% DCPD.

H3-67A

(c) 67% DCPD.

H3-67B

(d) 100% DCPD.

H3-68B

Figure 14. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM AUTOCLAVED A-240/DICYCLOPENTADIENE MIXTURES. (250X; Sensitive Tint)

Two samples of each of the potential binder candidates were formulated, as specified in Table 8, after which the catalyst was added at room temperature to one of the samples. Viscosity data at 50° C for the binders without a catalyst ranged from 46 to 31,000 cPs, while binders with the catalyst were significantly more viscous at 50° C. Two of the binders exothermed to form hard, brittle solids upon the addition of a catalyst, while two others formed tacky solids.

As can be seen in Table 8, coke yields (after 1,000° C) were, as a rule, higher for binders with a catalyst than coke-yield values of binders formulated without catalysts.

Microstructures of the derived carbons after 2,800° C were quite diversified, covering the whole range of crystallinity. Addition of the catalyst decreased the crystallinity of carbons derived from QX-302, 302-1, and 302-2 binders, as seen in Figure 15.

Carbons derived from these binders formulated without a catalyst were all highly crystalline, showing no variance as the pitch/resin ratio increased. Addition of the catalyst caused a noticeable decrease in crystallinity of carbons derived from the QX-302 and 302-1 binders. Little catalytic effect was noted on carbons derived from the QX-302-2 binder. Microstructural changes in carbons from the binders formulated with a catalyst reflect the increasing pitch content in the binder, in that crystallinity increased as the pitch content increased. Microstructural changes in carbons derived from QX-303-1, 303-2, and 303-3 binders formulated with and without a catalyst (Figure 16) are a function only of the pitch/resin ratio, in that little or no microstructural changes were seen in the binder-derived carbons after the addition of a catalyst to the binder. Carbons from these binders with and without the catalyst increased in crystallinity as the pitch/resin ratio increased.

Not all of the carbons derived from these binders were homogeneous. For example, one binder (QX-303-6 without catalyst) yielded a carbon with highly crystalline areas in a noncrystalline matrix (Figure 17), indicating little solubility of the pitch phase in the binder system.

Heterogeneous catalyst effects can be seen in Figure 18. Carbon derived from the QX-303-5 binder without a catalyst was very fine grained and isotropic, while carbon derived from the binder with a catalyst contained areas of noncrystallinity in addition to areas of fine-grained microstructure. These areas indicate the immiscibility of the resin and pitch prior to pyrolysis and also the noncrystalline character of the furan resin.

Thus, binders prepared from the furan resins and the petroleum pitches offer a wide range of carbon structures while allowing considerable control over the properties.

CONCLUSIONS

The data in this report show that A-240 petroleum pitch has potential as a carbon precursor material in binders as well as filler applications. Thermal data show the material to have adequate stability for extended periods at elevated temperatures as, for example, would be necessary for impregnating applications. When evaluated on the basis of carbon properties, A-240 pitch appears to be a good candidate for applications requiring a highly crystalline,

Table 8
PROPERTIES OF BINDER FORMULATIONS

Formulation ⁽¹⁾	Resin Component	Pitch Component ⁽²⁾	Composition (wt resin/wt pitch)	Viscosity Data ⁽³⁾ (cPs)		1,000° C Coke Yield (%)	
				Without Catalyst	With Catalyst	Without Catalyst	With Catalyst
237	237	-	-	-	59,500	47	51
247	247	-	-	-	Exothermed to a Solid	31	55
248	248	-	-	-	Exothermed to a Solid	37	57
297-1	297	310	2/1	1,900	16,000	47	51
298-1	298	310	2/1	650	1,850	43	50
302	302	-	-	26	36	20	19
302-1	302	310	5/1	46	102	25	26
302-2	302	310	5.5/4.5	198	3,800	34	30
303-1	303	310	8/1	340	775	48	49
303-2	303	310	2/1	1,078	112,000	49	49
303-3	303	310	4/5	31,800	100,000	49	51
303-5	303	312	2/1	10,000	200,000	58	56
303-6	303	313	2/1	1,750	Tacky Solid	62	64
304-1	304	310	2/1	240	750	48	53
305-1	305	310	2/1	3,240	4,750	59	63
306-1	306	310	1/1	24,400	Tacky Solid	47	55
307-1	307	310	2/1	6,700	10,500	51	55
308	308	-	-	-	2,450	45	53
309-1	309	310	2/1	530	750	49	52

(1) Materials formulated by adding pitch while stirring and heating resin to approximately 60° C.

(2) QX-310 is Ashland Oil Company's A-240 pitch.

(3) Determined using a Brookfield viscometer.

(a) QX-302.

H421-6

(b) QX-302 with a Catalyst.

H3-20-6C

(c) QX-302-1.

H421-7

(d) QX-302-1 with a Catalyst.

H3-20-7CR

(e) QX-302-2.

H421-8

(f) QX-302-2 with a Catalyst.

H3-20-8C

Figure 15. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM QX-302, QX-302-1, AND QX-302-2 BINDERS FORMULATED WITH AND WITHOUT A CATALYST. (250X; Sensitive Tint)

(a) QX-303-1.

H421-9

(b) QX-303-1 with a Catalyst.

H3-20-9C

(c) QX-303-2.

H421-10

(d) QX-303-2 with a Catalyst.

H3-20-10C

(e) QX-303-3.

H421-11

(f) QX-303-2 with a Catalyst.

H3-20-11C

Figure 18. MICROSTRUCTURES OF CARBONS (AFTER 2,800°C) DERIVED FROM QX-303-1, QX-303-2, AND QX-303-3 BINDERS FORMULATED WITH AND WITHOUT A CATALYST. (250X; Sensitive Tint)

H421-13
Figure 17. MICROSTRUCTURE OF CARBON (AFTER 2,800° C) DERIVED
FROM QX-303-6 BINDER FORMULATED WITH A CATALYST. (250X;
Sensitive Tint)

anisotropic carbon. Versatility of the pitch was demonstrated by the ability to modify properties of the pitch polymer and carbon derived from the polymer by inclusion of various additives. These blends broaden the utility of the pitch-binder applications, and can be used to produce carbons that cover a wide range of crystalline properties.

(a) Without a Catalyst.

H421-12

(b) With a Catalyst.

H3-20-12C

Figure 18. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM QX-303-5 BINDER FORMULATED WITH AND WITHOUT A CATALYST. (250X; Sensitive Tint)

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ACKNOWLEDGEMENTS

The authors wish to express their thanks to Messrs Hoertz, Ball, Chapman, and Newman of the Research and Development Department of Ashland Oil and Refining Company and to Messrs Brown and Watson of the Research Division of Quaker Oats Company for the petroleum pitches and furan resins and information related to them. Thanks are also extended to the Oak Ridge Y-12 Plant Analytical Laboratory for the analytical services rendered during this program and also to the Development Division metallography group for their efforts in preparing and photographing the samples for micrographic study.

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