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CARBONS PRODUCED FROM KNOWN ORGANIC COMPOUNDS

II--ANTHRACENE-BIPHENYL AND PHENANTHRENE-BIPHENYL SYSTEMS

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Binary mixtures (systems) of typical graphitizable and non-graphitizable hydrocarbons were carbonized and heat treated to study the graphitizability of the resulting carbons. The hydrocarbons selected were anthracene, phenanthrene and biphenyl. The first two are isomers and are highly graphitizable; biphenyl is non-graphitizable. Carbonizations were carried out in a pressure vessel containing either anthracene-biphenyl or phenanthrene-biphenyl mixtures at 73-98 atm and 550°C. The resulting chars were dried, ground, calcined at 950°C to form a coke, then heat treated at 2800°C. These carbons were studied by optical microscopy, X-ray diffraction, helium density, and electrical resistivity measurements. For the anthracene-biphenyl system, carbons of homogeneous texture were not produced, rather fractions of highly graphitic and poorly graphitic carbons were obtained. For the phenanthrene-biphenyl system, carbons which are more homogeneous on a macro-scale were produced, their graphitic character decreasing sharply as the amount of biphenyl in the original mix was increased.

INTRODUCTION

Part I of this series¹ reported that cokes derived from the carbonization of anthracene, phenanthrene and their mixtures were all highly graphitizable. This paper describes results obtained when these materials are carbonized together with the non-graphitizable compound biphenyl. Biphenyl was reported as a compound having poor graphitizability by Milliken² and Kinney.^{3,4,5}

Many aromatic compounds were studied individually in the condensed phase by Union Carbide's Carbon Products Division.⁶ These studies showed that if the molecular structure is planar (fused rings), the compound will probably graphitize; but if the original molecule is non-planar or if non-planar intermediates are

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formed, the material may be non-graphitizable. This explanation adequately describes the behavior of the three compounds used as starting materials in this study.

For convenience, Table 1 lists the significant properties of these starting materials. Note that the structural isomers anthracene and phenanthrene have fused rings and planar geometry. These are graphitizable. Biphenyl is an aromatic hydrocarbon able to undergo rotation about the inter-ring bond, making it non-planar and non-graphitizable.

EXPERIMENTAL

Preparation of the 950°C Cokes and 2800°C Carbons

(1) Starting Materials

All of the starting materials were obtained from Rütgers-werke and Teerverwertung AG, Duisburg-Meiderich, West Germany. The anthracene was of specified 99% purity and had an observed sealed capillary tube melting point of 216-217°C. The phenanthrene was specified to be sulfur-free and of 98% purity. The observed capillary tube melting point was 98-100°C. The biphenyl was of specified 98% purity and had an observed capillary tube melting point of 68.5-70.5°C. No attempt was made to further purify these materials.

(2) Pressure Vessel

The pressure vessel (American Instrument Company, Silver Spring, Maryland, Catalog No. 41-4495) was constructed of chrome-vanadium steel and measured 4-3/8 in OD x 2-9/16 in ID x 21 in inside depth, with a capacity of 1780 cc. It was bolted into an electrical heating jacket mounted on a mechanical shaking mechanism (American Instrument Company, Catalog No. 406-801DB). Nitrogen was introduced into the vessel to displace air. For further details, refer to reference 7.

(3) Temperature Control in the Pressure Vessel

A thermocouple was inserted in the heating jacket. This was connected

to a Leeds & Northrup Speedomax G recorder, equipped with a controller. The bulk temperature was monitored with a second thermocouple inserted in the vessel thermowell.

The bulk heating rate was set to increase linearly at one degree per minute from 60° to 550°C, at which point the soak period automatically started. The soak period was varied for the different samples from 7 to as long as 18 hr depending on the rate of reaction. After the reaction was largely complete (as shown by a near zero slope in the pressure-time curve), power was shut off. Biphenyl, however, never reached constant pressure, so the soak period was an arbitrary 16.3 hr in Run No. 2. The assembly was then allowed to cool to about 30°C with the aid of a small fan; this cooling generally required 12 hr. The contents of the pressure vessel could then be easily removed.

(4) Method used to Calculate Gas Generation in the Pressure Vessel

An indication of the amount of gas evolved during pyrolysis in the pressure vessel was obtained by calculating the ratio of moles of gas evolved to moles of reactant charged, n_g/n_c . The moles of gas evolved was calculated from the ideal gas law using the pressure and temperature at the end of the cooling period.

(5) Drying and Calcining

The furnace used for drying and calcining the samples was a Hoskins 1870 water tube furnace with a 2 in OD x 3 ft length of quartz tube. Prepurified grade N₂ was passed at >2 liters per min through a drying train and a deoxidizing furnace before passing into the quartz tube. Temperature measurement and control were effected with a single Inconel-sheathed thermocouple positioned in the sample zone and connected to a recorder-controller. In all cases, the heating rate was 5°C per minute, and the soak time was two hours. The soak temperature was 300°C for drying and 950°C for calcining. Cooling required about 12 hr.

Drying of samples was accomplished by pulverizing the material and loading about 140 g directly into the quartz tube, tamping it entirely within the heated

section. Calcining of 24 g samples was performed in a small Vycor boat placed inside the quartz tube.

(6) Graphitizing

The furnace used for graphitizing was a graphite-resistance type furnace manufactured by Richard D. Brew & Co., Inc., Concord, New Hampshire. It had a cylindrical sample holder 3 in diam x 6 in high, machined from graphite. About 8 g of the powdered samples could be introduced into each of six holes in the sample holder. An optical pyrometer was sighted through a prism and a quartz window into a central hole in the sample holder. It was necessary to clean carbon deposits from the quartz window before each reading. The optical pyrometer used was Leeds & Northrup No. 8632-C, having three ranges above 760°C. Corrections were applied to the readings to convert brightness temperature to true temperature. Argon was circulated through the furnace at 8 ft³ per hr and 1 atm pressure. The furnace was controlled manually. The heating and cooling rates were linear at 15.5°C/min from 800-2800°C. The soak period and soak temperature were 0.5 hr at 2800°C in all cases.

Characterization of the 950°C Cokes and 2800°C Carbons

(1) X-ray Diffraction Measurements

X-ray diffraction measurements were made on the 2800°C carbons in the laboratories of Airco Speer using a General Electric XRD-5 unit emitting Cu α radiation through a 0.7 mil Ni filter with the tube operating at 16 ma and 50 kv. From 20-65% KCl was used as an internal standard. Some samples required addition of collodion-amyl acetate to keep them suspended in the open frame holder. Materials that were graphitic were measured using the (004) diffraction peak. Materials that were still "hard carbons" were measured from the (002) peak. Measurements were made of the interlayer spacing, the crystallite height or L_c , and the relative intensity of the (002) peak.

(2) Optical Microscopic Examination

Optical microscopic photographs were made at Airco Speer by introducing a few milligrams of the 200 x 325 mesh cokes in an amber colored epoxy resin (HYSOL RE-2038, Hysol Corp., Olean, New York) with the necessary curing agent in a cylindrical mold and removing air bubbles under vacuum. When cured, a solid matrix was formed, one surface of which was ground optically flat. This surface was photographed through a "Leitz Panphot Metallograph" using 500X magnification and reflected polarized light.

(3) Helium Density Measurements

Helium densities of the 42x65 mesh cokes and 2800°C carbons were measured using the constant pressure helium densitometer constructed by W. Stacy and described in detail by Bessant.⁸

(4) Resistivity Measurements

Electrical resistivities of the cokes and graphites were measured on 2 g samples of 42x65 mesh material. Seven-thousand psi was hydraulically applied to the sample during measurement. The apparatus was described by Baumbach.¹⁰

RESULTS

Preparation of the Cokes

Table 2 shows experiment identification numbers, the charge introduced into the pressure vessel, the amount of recovered char and tar, soak time, maximum pressure, residual pressure, and temperature after cooling. The char (solid residue removed from the pressure vessel) recovery reflects some tar content and handling loss, as well as the extent of conversion to solid carbon. Tars are viscous dark liquids, most of which are produced by biphenyl, as shown in Run No. 2. The overall coke yield is calculated from the weight of solid residue remaining after the char is dried at 300°C and calcined at 950°C.

Characterization of the 950°C Cokes and 2800°C Carbons

(1) Optical Microscopic Examination

Photomicrographs of the calcined cokes are shown in Figs. 1 and 2. The particle size of the coke is 200x325 mesh (44-74 microns) and the original photographs were taken using 500X magnification. The dark areas in these photographs are the epoxy resin.

The anthracene-biphenyl system is shown in Figs. 1a-1d in order of increasing initial biphenyl concentration in the pressure vessel. Fig. 1a shows the coke resulting from pure anthracene, which has smooth, curved surfaces, many flow lines resulting from shear forces acting on a viscous mass, and the fissures resulting from gas evolution. At the opposite extreme, Fig. 1d shows the coke produced from pure biphenyl. It appears to have a smooth and flat "glassy" surface free from flow lines and fissures with a few pinholes. Fig. 1b shows the coke produced from a 25% biphenyl-75% anthracene mixture. Three distinct types of particles are visible. The particle labeled 1 resembles the anthracene coke. Particles 2 and 3 have rough surfaces. Fig. 1c depicts the coke which results from a 50% mixture. Three recognizable kinds of particles are present: the pure anthracene particle 1, the pure biphenyl particle 2, and an intermediate particle 3 resembling 2 in Fig. 1b above.

The second system examined was the phenanthrene-biphenyl system. Fig. 2a shows the coke obtained from pure phenanthrene. It is also characterized by curved surfaces, flow lines, and fissures. Fig. 2b shows the effect of adding 5% biphenyl to the phenanthrene. The particles labelled 1 resemble those of Fig. 2a which particle 2 resembles those of Fig. 2c. Particle 3 may be a biphenyl particle. Its presence is anomalous. Figs. 2c and 2d show the effect of addition of 10% and 25% biphenyl respectively. The higher concentration produces a gradation in particle appearance. Note the resemblance between particle 1 in

Fig. 2d with the particles in Fig. 2c, and particle 2 of Fig. 2d with particle 3 of Fig. 1b. At 50% biphenyl, Fig. 2e, a marked transformation to "glassy" particles results.

Both anthracene coke and phenanthrene coke have the appearance of "delayed coke." Delayed coke is petroleum coke made by the delayed coking process, and it is known to produce excellent, anisotropic graphite. The 90% phenanthrene-10% biphenyl coke (Fig. 2c) has more the appearance of "pitch coke" because it resembles the coke generally resulting from coal tar pitch, that is, a less ordered, more isotropic variety of carbon. Biphenyl coke is termed "glassy" meaning a poorly ordered, completely isotropic, hard carbon, normally incapable of producing graphite. Making use of this terminology, the microscopic results are summarized in Table 3.

(2) X-ray Diffraction Studies

The interlayer spacing is plotted versus starting composition in Fig. 3. The dashed portions indicate uncertainty. Note that at least 25% by weight biphenyl may be tolerated in the anthracene without affecting the interlayer spacing of the highly graphitized component. However, in the phenanthrene-biphenyl system, an entirely different effect is observed. As little as 5% biphenyl produces a marked increase in interlayer spacing.

Table 4 presents values tabulated as a function of starting composition for both systems. There is clearly a sharp drop in L_c with the addition of as little as 5% biphenyl to phenanthrene. This does not occur in the anthracene-biphenyl system. It should be emphasized, however, there whereas the diffraction arises from essentially the entire one phase system for the phenanthrene-biphenyl carbons, the diffraction is expected to arise primarily from the more graphitic phase for the heterogeneous anthracene-biphenyl carbons. Certainly diffraction from the glassy phase would hardly be in evidence for samples containing a significant graphitic phase.

If a powdered sample is placed on an X-ray slide, the intensity of the (002) peak is a function of the number of graphitic layer planes oriented parallel to the slide. The greater the intensity of the (002) peak, the greater the extent of crystallite alignment.¹¹ Fig. 4 depicts the relative intensity of the (002) peak as a function of initial biphenyl content for both systems. The presence of KCl no doubt affects the shape of the curves, but certain observations can be made. The relative crystallite orientation of the anthracene-biphenyl system is unaffected with increasing biphenyl concentration in the range studied (i.e., up to 50%). The portion of the curve above 50% is dashed because of insufficient data. The phenanthrene-biphenyl system shows a sharply decreasing alignment of the crystallites, as the biphenyl concentration is increased.

(3) Relationship of Gas Generation to Interlayer Spacing

Fig. 5 shows a plot of interlayer spacing of the 2800°C carbons versus the ratio n_g/n_c (residual moles of gas per mole charged) for both systems. Due to clogged lines, the datum point for 25% biphenyl-75% anthracene is not shown and that for 50% biphenyl-50% anthracene was estimated from pressure readings at 550°C which were extrapolated to 30°C. The two points at 3.366 and 3.363 Å are for the pure phenanthrene and pure anthracene, respectively. The scattered point is from Run No. 4.

(4) Helium Densities

Fig. 6 shows helium densities as a function of biphenyl content for both cokes and 2800°C carbons in the anthracene-biphenyl system. Fig. 7 shows the same information for the phenanthrene-biphenyl system. The cokes increase in density and the 2800°C carbons decrease in density as the starting concentration of biphenyl is increased for both systems.

(5) Electrical Resistivity

The electrical resistivity of the 950°C cokes and 2800°C carbons from both systems are presented in Fig. 8. An arbitrary pressure of 7000 psi was applied

to the samples. Note the large decrease in resistivity when the cokes were subjected to the 2800°C graphitization temperatures.

DISCUSSION

Formation of Coke Phases

The coke phases have been described as delayed, pitch, or glassy depending on whether they produce highly anisotropic, slightly anisotropic, or isotropic graphite. These phases may be produced by a combination of different reaction rates, solubility effects and free radical interactions during the carbonization step.

Tilicheev, using an iron pressure vessel at 450°C, reported first order rate constants for the cracking of hydrocarbons (Table 5)¹² Also shown in this table are the ratios of the rate constants with respect to biphenyl, and the half-lives calculated by $t_{1/2} = \ln 2/k_1$. From the information in Table 5 one can surmise that, in a 50% phenanthrene-biphenyl solution, both components will carbonize at about the same rate. However, in a 50% anthracene-biphenyl solution, the anthracene, being 1200 times greater in reactivity, carbonizes and precipitates out of the biphenyl. Eventually, of course, the biphenyl also chars.

The photomicrographs of the phenanthrene-biphenyl cokes (Fig. 2) are single phase, consistent with the above reasoning. The photomicrographs of the anthracene-biphenyl cokes (Fig. 1) clearly show anthracene coke particles separated from biphenyl coke particles, also in accord with the above reasoning.

Biphenyl is entirely gaseous at 550°C since its critical temperature is 528°C.¹³ This was confirmed by observing a sealed glass tube containing biphenyl at 550°C.* Observations in similar tubes, using an initial concentration at 600 g/l, clearly show that 50% anthracene-50% biphenyl and 50% phenanthrene-50% biphenyl mixtures are initially liquids, completely miscible and of low

*Thus, the char produced from biphenyl is a kind of low temperature, high pressure pyrolytic carbon.

viscosity. Apparently, a gas-in-liquid solution exists at this concentration.

It is reported that phenanthrene is more soluble in common organic solvents than is its isomer, anthracene.¹⁴ Therefore, phenanthrene above its melting point may also be a better solvent than anthracene. In accordance, phenanthrene is reported to dissolve bituminous coal at 350°C while anthracene apparently does not.¹⁵ This behavior of phenanthrene suggests that it may be a greatly superior solvent for biphenyl as well as other species produced during carbonization, compared to anthracene.

Now consider a system of equal parts anthracene and biphenyl being heated up from about 300°C at 1°C/min with agitation. Both are liquids completely soluble in each other. Free radicals form in both materials† but much faster in anthracene. At 450°C the reaction is 1200 times faster than in biphenyl. Some of the anthracene free radicals may react with the biphenyl producing an adduct such as 4-(9-anthryl)-1-phenylbenzene, which may then polymerize with other free radicals. Other anthracene radicals condense with anthracene molecules to produce a char phase which precipitates out of solution. At 550°C almost all of the anthracene has either reacted with biphenyl or condensed with itself. The biphenyl adduct will char to form a second copolymer-type phase. Finally free radicals form in the remaining biphenyl and a third phase ensues from the thermal polymerization of biphenyl.

Reasons for Greater Graphitizability in Anthracene-Biphenyl System

It is clearly shown by the X-ray diffraction and relative intensity data (Figs. 3 and 4), by the crystallite heights (Table 4), helium densities (Figs. 6 and 7), and electrical resistivities (Fig. 8) that in every case the carbons produced from the anthracene-biphenyl system are more graphitizable than those produced from the phenanthrene-biphenyl system, for a given biphenyl concentration.

†The existence of free radicals during pyrolysis in anthracene phenanthrene, and biphenyl has been frequently demonstrated.^{6,16-19}

This can be explained as follows. If the biphenyl concentration is initially low, the coke consists of pure anthracene coke and probably a small amount of anthracene-biphenyl copolymer. If biphenyl concentration is initially high, anthracene coke, anthracene-biphenyl coke, and biphenyl coke are formed (Fig. 1c). Anthracene coke is highly graphitizable, biphenyl coke is definitely not graphitizable, and the anthracene-biphenyl coke is somewhat intermediate, depending on the relative proportion of its two components. But Cornuault and coworkers have shown that when a graphitizable carbon is bound to a non-graphitizable one, an interaction can occur that enhances the graphitization of the latter.²⁰ Thus a non-linear variation in graphitizability with changing biphenyl content is observed in this system (Fig. 3).

In the phenanthrene-biphenyl system, since both molecules can form free radicals at roughly the same rate, they interact with each other. Possibly, the greater solubility of biphenyl gas in phenanthrene may be an important factor. The homogeneous copolymer that ensues is the single pitch coke phase of Figs. 2b-e. Since there is a single phase, the graphitizability is more nearly linear with changing biphenyl content (Fig. 3). This copolymer has non-planar structures built in and will always be less graphitizable for a given biphenyl concentration than will the multiple-phase cokes from the anthracene-biphenyl system.

The formation of several coke phases seems to cast off non-planar structures from the graphitizable phase and improve the graphitizability of the anthracene-biphenyl system, as opposed to the phenanthrene-biphenyl system.

Relationship of Gas Generation to Interlayer Spacing

In the polymeric char formed at 550°C, supposedly there may exist benzene rings as found in biphenyl, fused rings as found in anthracene, and cross-linking. Disordered structures are produced when biphenyl-like linkages are able to rotate and bend about the C-C inter-ring bond. Fused rings would be less likely to rotate or bend, clearly producing more coplanar structures.

Consider a collection of small molecules undergoing thermal condensation to produce the graphite lattice. Each molecule that reacts can form n bonds and release $n/2$ moles of hydrogen where $n = 1, 2, 3, \dots$. If $n = 2$, polymerization continues but rotation of the molecules is possible. If $n = 3$, rotation stops and a coplanar macromolecule is more probable. If cracking occurs, parts of the molecule are destroyed; but these are probably strained rings, side chains, and bridgeheads which could not contribute to a graphitic structure. Cracking does, however, release more free radicals (which in turn can produce further condensation) and x moles of methane, ethane, etc. Then the graphitizability of the char should increase with the number of moles of gas released n_g , where $n_g = \frac{n}{2} + x$, for every mole of reactant converted. Moles of reactant converted are related to moles of reactant charged, n_c , by the kinetic rate constant or by the equilibrium constant of the reaction. It seems plausible, therefore, that graphitizability should increase with n_g/n_c .

In Fig. 5 most of the mixtures containing biphenyl fall on a straight line relating interlayer spacing to gas generation. Pure phenanthrene and pure anthracene released more gas producing an inflection. This was perhaps caused by $n = 3$ or 4 and more extensive condensation taking place.

Union Carbide tabulated gas generation and interlayer spacings for 21 experiments,^{6†} but only six of their experiments show the above relationship (o-terphenyl, p-terphenyl, hydrogenated terphenyls, dibenzothiophene, 9-9-bifluorene, and fluorene). Six experiments are reported to have had "known gas leakage." The remaining nine points will unexplainedly fall far to the left side of the curve in Fig. 5.

CONCLUSIONS

Binary mixtures (systems) of typical graphitizable and non-graphitizable

† For 3000°C carbons, not strictly comparable with the 2800°C carbons in this work.

hydrocarbons were carbonized and heat treated to study the graphitizability of the resulting carbons. The hydrocarbons selected were anthracene, phenanthrene and biphenyl. The first two are highly graphitizable; biphenyl is non-graphitizable. Carbonizations were carried out in a pressure vessel containing either anthracene-biphenyl or phenanthrene-biphenyl mixtures at 73-98 atm and 550°C. The resulting chars were dried, ground, calcined at 950°C to form a coke, then heat treated at 2800°C. The carbons were characterized by optical microscopy, X-ray diffraction, helium density, and electrical resistivity.

These systems have shown themselves to be ideal for fundamental studies in the mechanism of graphitization. It is now possible to prepare graphite in any desired degree of graphitization from known starting materials free of catalytic impurities.

Broad decreases in graphitizability were exhibited in both systems as the biphenyl content was increased. This was demonstrated in the 2800°C carbons by increases in interlayer spacing and electrical resistivity; as well as by decreases in crystallite height, relative crystallite orientation, and helium density. Therefore, the addition of small amounts of biphenyl or similar compounds to the refinery heavy fuel oil before the thermal cracking step should produce petroleum coke of controllable isotropy for nuclear graphite. Likewise the removal of biphenyl or similar aromatic, non-planar compounds or their precursors, such as benzene, from the heavy fuel oil may improve the graphitizability of the coke.

A triple phase separation was observed in cokes from the anthracene-biphenyl system and not in the phenanthrene-biphenyl system. This was presumably brought about by the much greater reaction rate of anthracene during carbonization compared to that of biphenyl. Probably as a result of the phase separation and the Cornuault effect,²⁰ the two systems were not equally affected by equal concentrations of biphenyl. The anthracene-biphenyl system always maintained a much higher degree of graphitizability than did the phenanthrene-biphenyl system. The 2800°C carbons

from the latter system were disordered at even a 5% biphenyl concentration.

A relationship between the quantity of gas generated during carbonization and the degree of graphitization later attained exists. This suggests a quality control technique applicable to the refinery or to the coke oven. A small sample can be carbonized and the pressure developed after the reaction is complete may serve as an index of ultimate graphitizability, if the system is well-defined. This should assist the refinery in adjusting processing conditions. Similarly, coal tar pitch can be checked for graphitizability without the necessity of forming, baking, and graphitizing a test piece.

The important role of kinetics on the carbonization process and the effect on graphitizability has been indicated. This deserves further study.

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Table 1

PROPERTIES OF STARTING MATERIALS

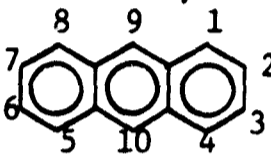
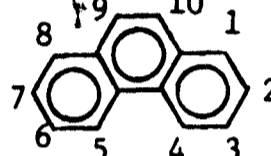
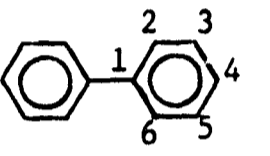
	Anthracene	Phenanthrene	Biphenyl
Structural formula and numbering scheme			
Empirical formula	$C_{14}H_{10}$	$C_{14}H_{10}$	$C_{12}H_{10}$
Molecular wt g/mol	178.2	178.2	154.2
Melting point °C	218	100	70
Normal boiling point °C	342	340	255
Origin	Coal tar contains 1.1%	Coal tar contains 4.0%	Produced from benzene at 750°C
Family	Polynuclear Aromatic Fused Ring Hydrocarbon	Structural Isomer of Anthracene	Polynuclear Aromatic Hydrocarbon
Geometry	Flat	Flat	Possible rotation about the inter-ring bond

Table 2

CHARGES, YIELDS, AND PROCESS CONDITIONS

Run No.	Charge g	Recovery		Soak Time at 550°C hr	Max. pressure at 550°C psig	Residual pressure and temperature psig °C		
		Char g	Tars g				Overall Coke Yield %	
1	200 Anthracene	166.4	0	80	7	1420	560	90
2	250 Biphenyl	133.4	63.6	41	16.3	1060	55	200
3	250 Phenanthrene	217.6	0	84	17.2	1110	52	410
4	100 Phenanthrene 100 Biphenyl	161.7	-	68	18	840	245	55
5	125 Phenanthrene 125 Biphenyl	184.2	20.5	61	18†	950	240	30
6	125 Anthracene 125 Biphenyl	144	30.9	52	18	1100	*	*
7	187.5 Anthracene 62.5 Biphenyl	160.1	14.1	58	18	*	*	*
8	187.5 Phenanthrene 62.5 Biphenyl	173.3	4.2	57	18	950	290	25
9	225 Phenanthrene 25 Biphenyl	204.6	0	68	18	975	325	41
10	237.5 Phenanthrene 12.5 Biphenyl	201.7	0	69	18	940	310	35

†Clogged line to pressure gauge

Mixed for 24 hr at 300°C before charring

Table 3
PHASE TRANSFORMATIONS IN COKES

<u>Fig. No.</u>	<u>Starting Composition</u>	<u>No. of Phases Observed</u>	<u>Description of Phases</u>
1a	Anthracene	1	Delayed
1b	25% Biphenyl-75% Anthracene	2	Delayed, Pitch
1c	50% Biphenyl-50% Anthracene	3	Delayed, Pitch, Glassy
1d	Biphenyl	1	Glassy
<hr/>			
2a	Phenanthrene	1	Delayed
2b	5% Biphenyl-95% Phenanthrene	1	Pitch*
2c	10% Biphenyl-90% Phenanthrene	1	Pitch
2d	25% Biphenyl-75% Phenanthrene	1	Pitch
2e	50% Biphenyl-50% Phenanthrene	1	Glassy
1d	Biphenyl	1	Glassy

*One glassy particle was also observed.

Table 4
CRYSTALLITE HEIGHTS OF 2800°C CARBONS

<u>Starting Composition</u>	<u>Run No.</u>	<u>L_c, A</u>	
		<u>(002)</u>	<u>(004)</u>
Anthracene	1	>1000	946
25% Biphenyl-75% Anthracene	7	>1000	841
50% Biphenyl-50% Anthracene	6	>1000	540
Phenanthrene	3	988	420
5% Biphenyl-95% Phenanthrene	10	494	252
10% Biphenyl-90% Phenanthrene	9	432	199
25% Biphenyl-75% Phenanthrene	8	216	130
50% Biphenyl-50% Phenanthrene	4	71	-
50% Biphenyl-50% Phenanthrene	5	72	-
Biphenyl	2	35	-

Table 5
TILICHEEV'S FIRST ORDER KINETIC RATE CONSTANTS FOR CRACKING
OF HYDROCARBONS AT 450°C¹²

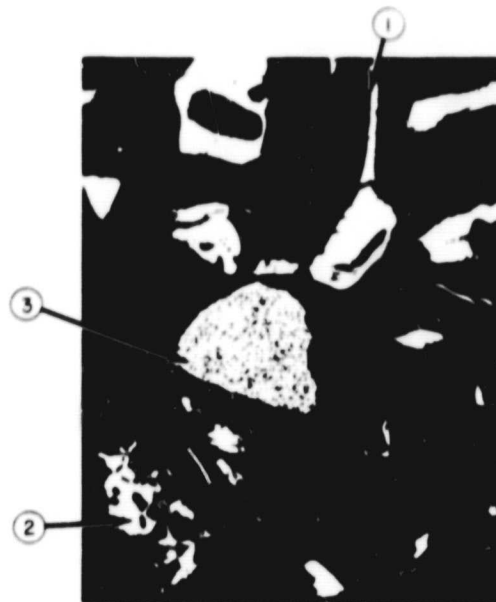
<u>Compound</u>	<u>k₁, sec⁻¹</u>	<u>Ratio</u>	<u>t_{1/2}</u>
Anthracene	3.2 x 10 ⁻⁴	1200	36 minutes
Phenanthrene	8.7 x 10 ⁻⁷	3.2	9 days
Biphenyl	2.7 x 10 ⁻⁷	1	1 month

FIGURE CAPTIONS

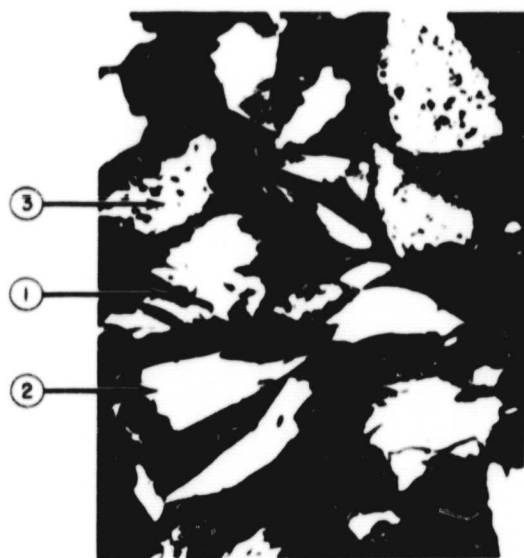
1. Photomicrographs of cokes from the anthracene-biphenyl system
2. Photomicrographs of cokes from the phenanthrene-biphenyl system
3. Variation of interlayer spacing of 2800°C carbons with starting composition of anthracene-biphenyl and phenanthrene-biphenyl systems
4. Change in relative crystallite orientation of 2800°C carbons with the starting composition of the anthracene-biphenyl and phenanthrene-biphenyl systems
5. Dependence of interlayer spacing of 2800°C carbons on gas generation during charring in anthracene-biphenyl and phenanthrene-biphenyl systems
6. Change in helium density of 950°C coke and 2800°C carbon with the starting composition of the anthracene-biphenyl system
7. Change in helium density of 950°C coke and 2800°C carbon with the starting composition of the phenanthrene-biphenyl system
8. Change in electrical resistivity of 950°C cokes and 2800°C carbons with the starting composition of the anthracene-biphenyl and phenanthrene-biphenyl systems



a. PURE ANTHRACENE



b. 75% ANTHRACENE
25% BIPHENYL



c. 50% ANTHRACENE
50% BIPHENYL



d. PURE BIPHENYL

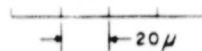
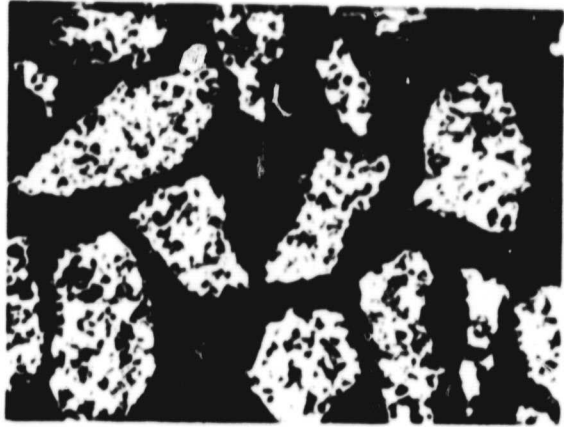
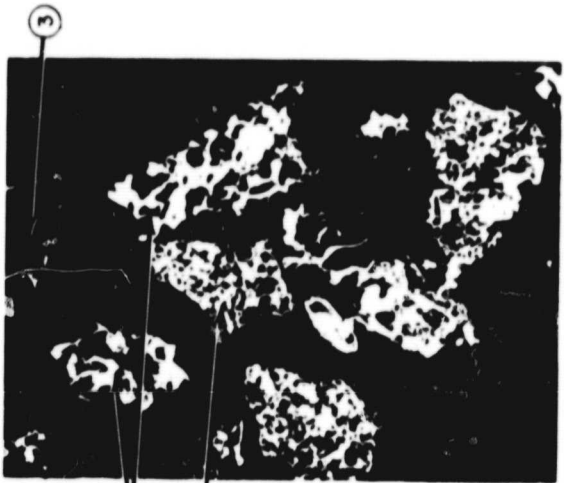


FIG. 1, PHOTOMICROGRAPHS OF COKE FROM THE ANTHRACENE - BIPHENYL SYSTEM



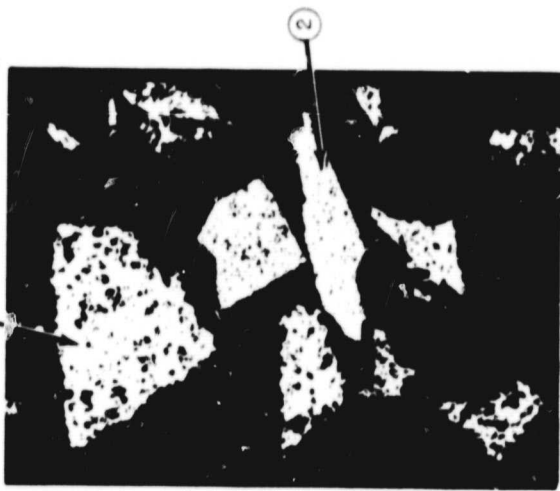
a. PURE PHENANTHRENE



b. 95% PHENANTHRENE
5% BIPHENYL



c. 90% PHENANTHRENE
10% BIPHENYL



d. 75% PHENANTHRENE
25% BIPHENYL



e. 50% PHENANTHRENE
50% BIPHENYL

FIG. 2. PHOTOMICROGRAPHS OF COKES FROM THE PHENANTHRENE - BIPHENYL SYSTEM

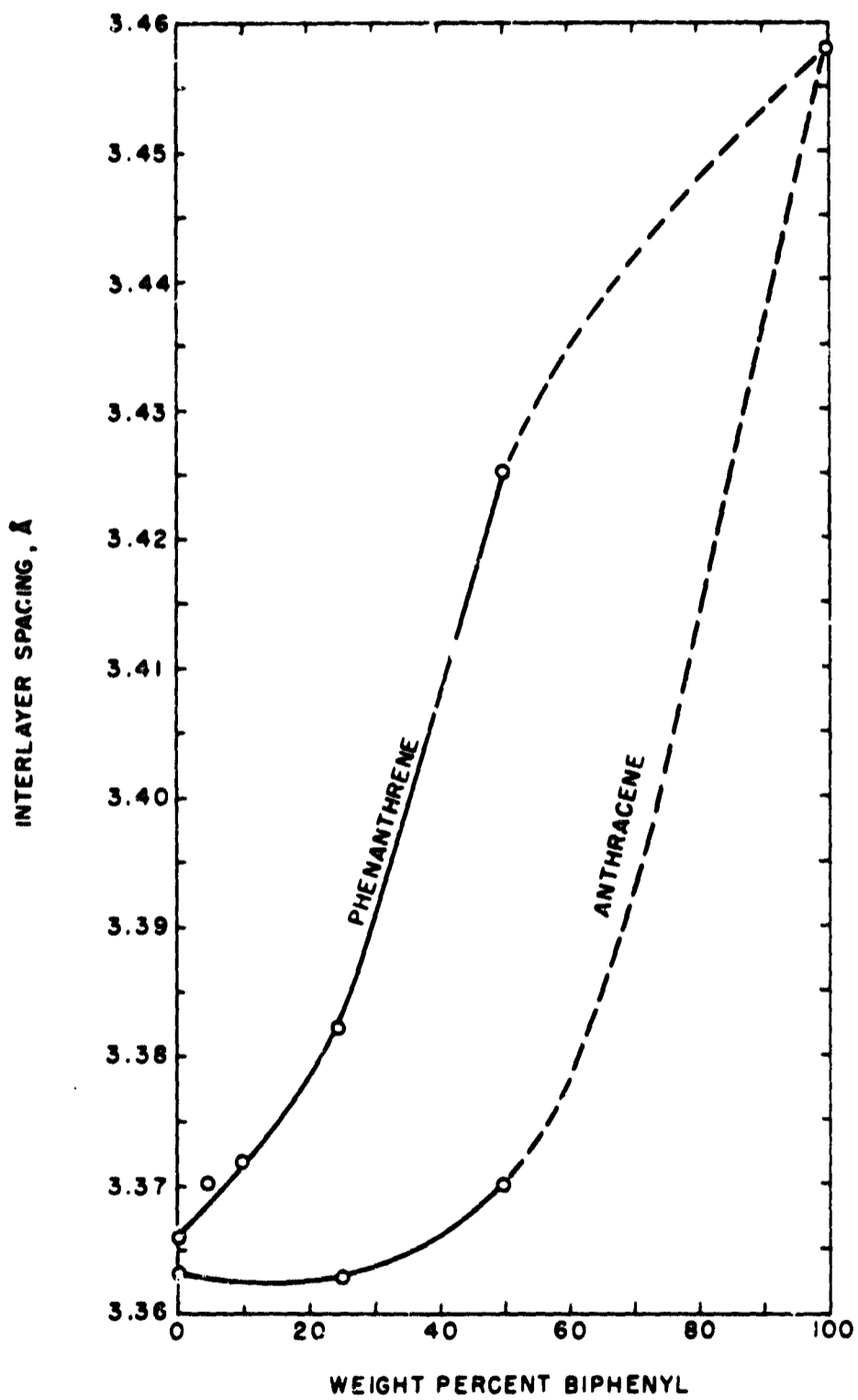


FIG. 3. VARIATION OF INTERLAYER SPACING OF 2800°C CARBONS WITH STARTING COMPOSITION OF ANTHRACENE-BIPHENYL AND PHENANTHRENE-BIPHENYL SYSTEMS

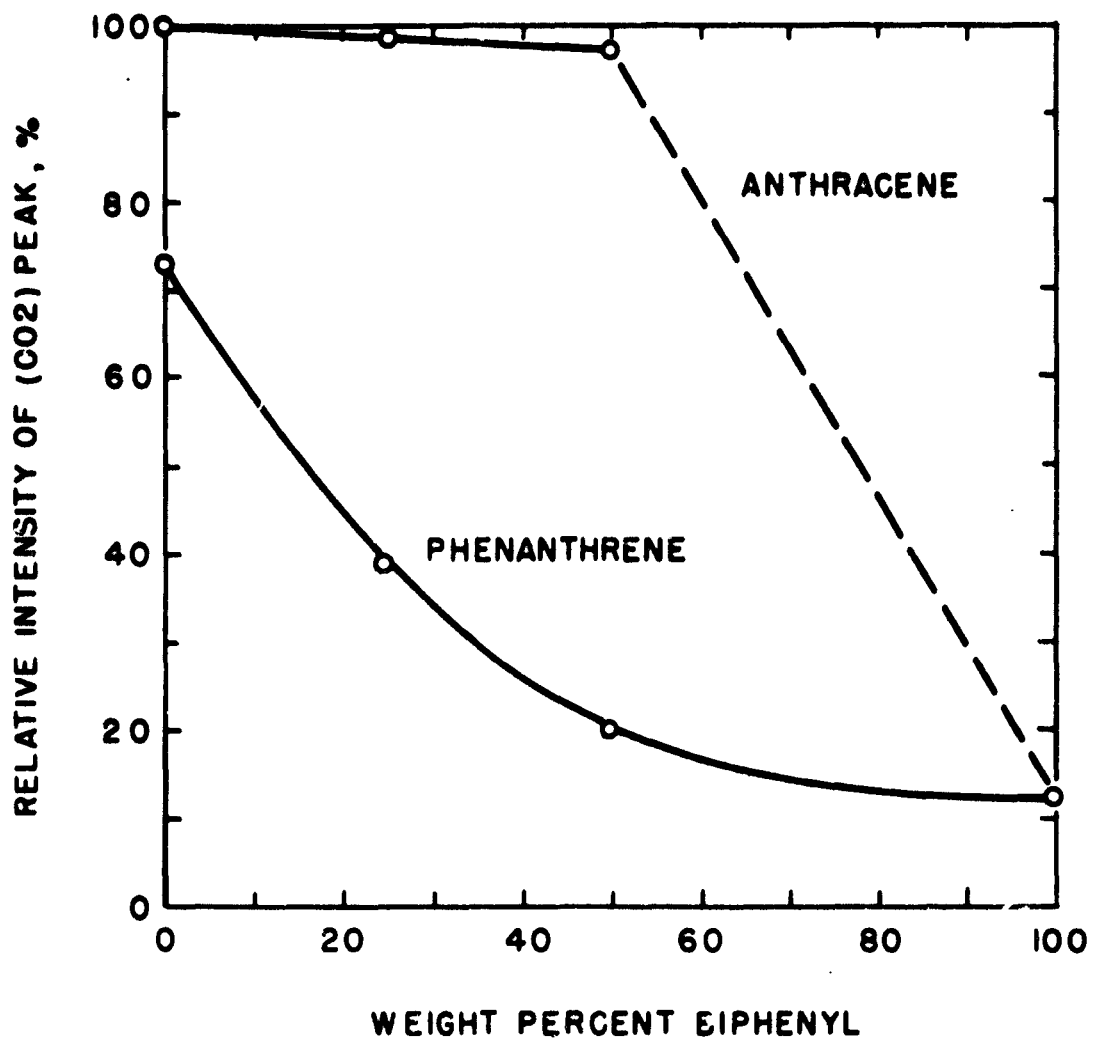


FIG. 4 . CHANGE IN RELATIVE CRYSTALLITE ORIENTATION OF 2800°C CARBONS WITH THE STARTING COMPOSITION OF THE ANTHRACENE-BIPHENYL AND PHENANTHRENE-BIPHENYL SYSTEMS

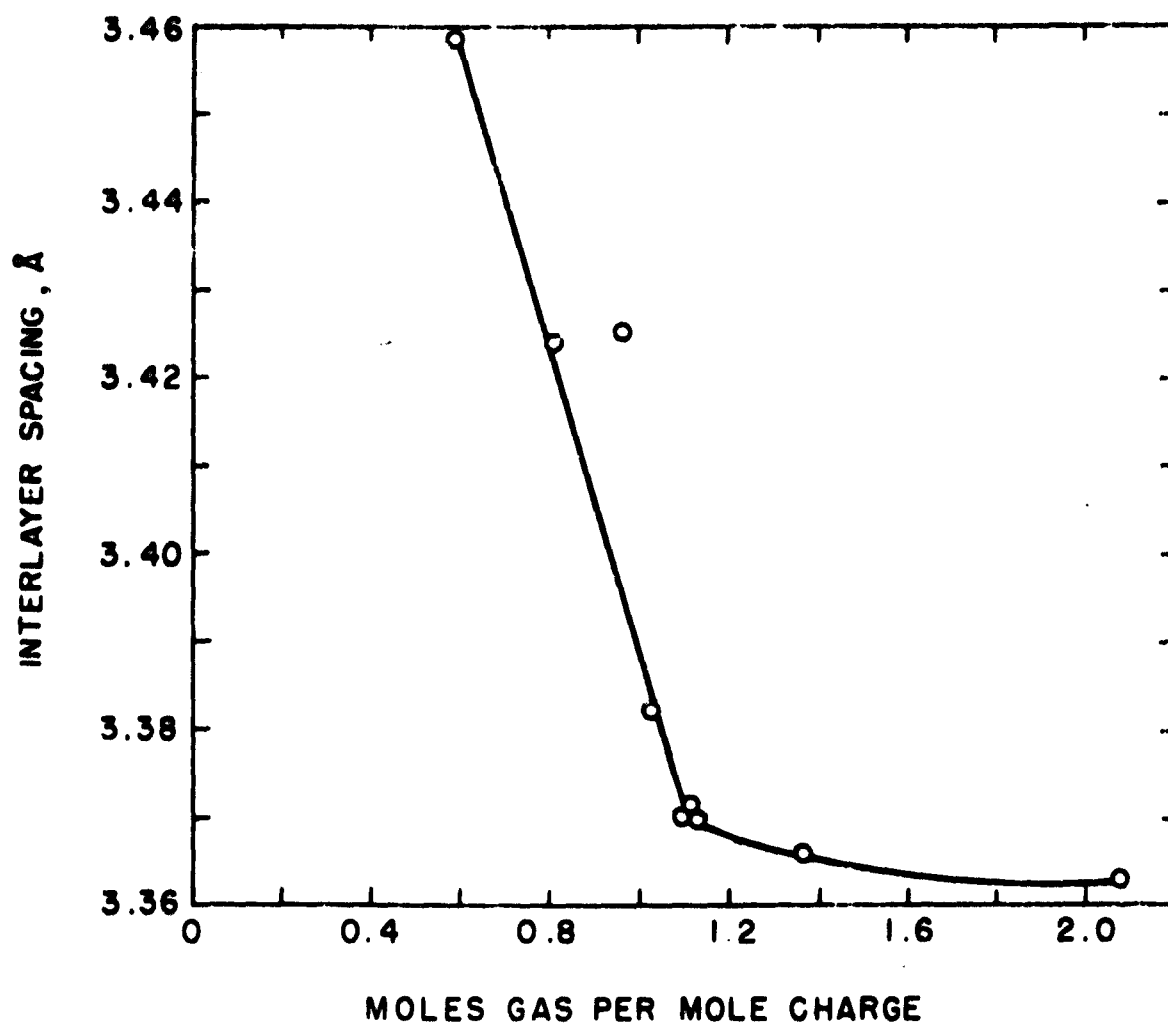


FIG. 5. DEPENDENCE OF INTERLAYER SPACING OF 2800°C CARBONS ON GAS GENERATION DURING CHARRING IN ANTHRACENE-BIPHENYL AND PHENANTHRENE-BIPHENYL SYSTEMS

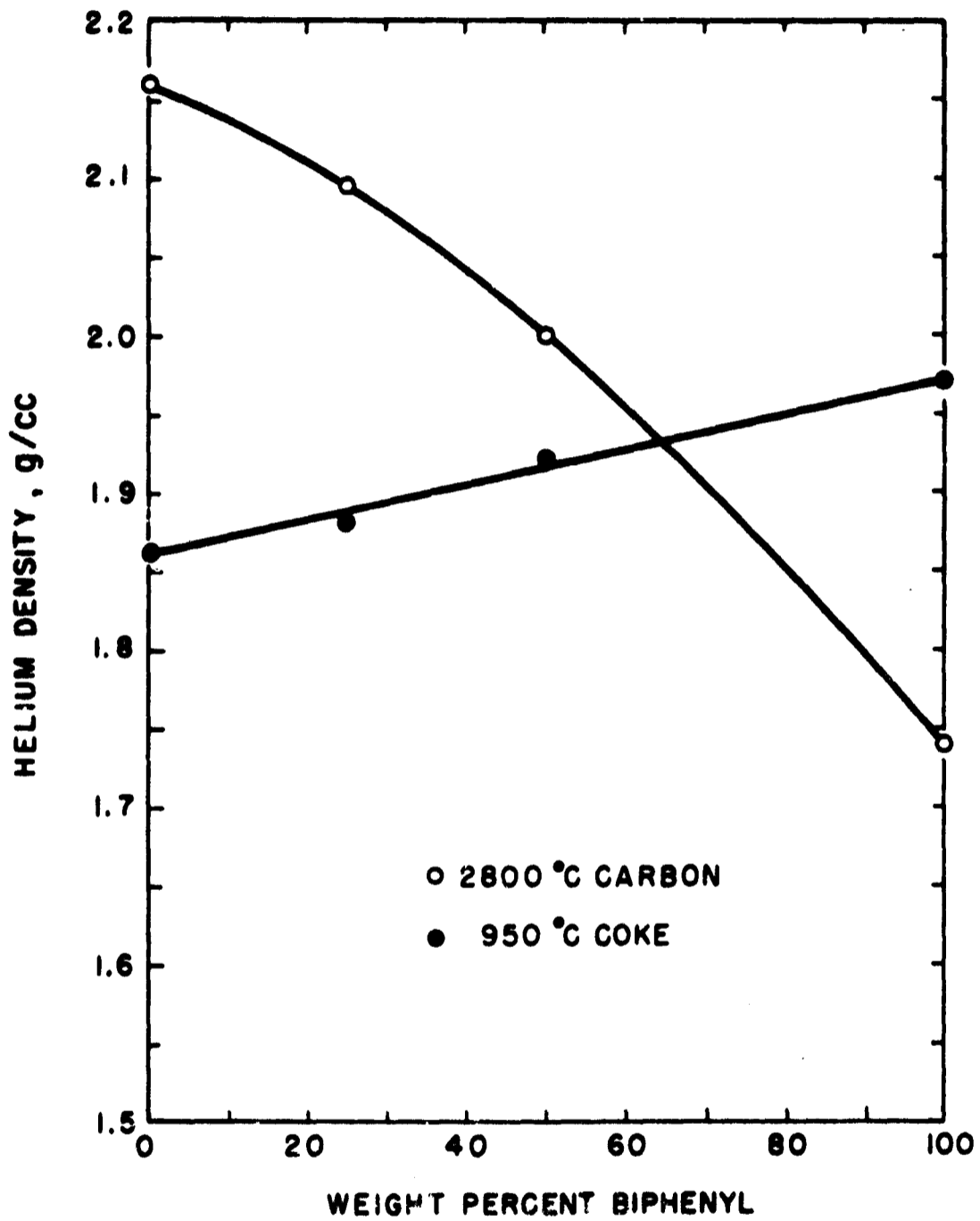


FIG. 6. CHANGE IN HELIUM DENSITY OF 950°C COKE AND 2800°C CARBON WITH THE STARTING COMPOSITION OF THE ANTHRACENE-BIPHENYL SYSTEM

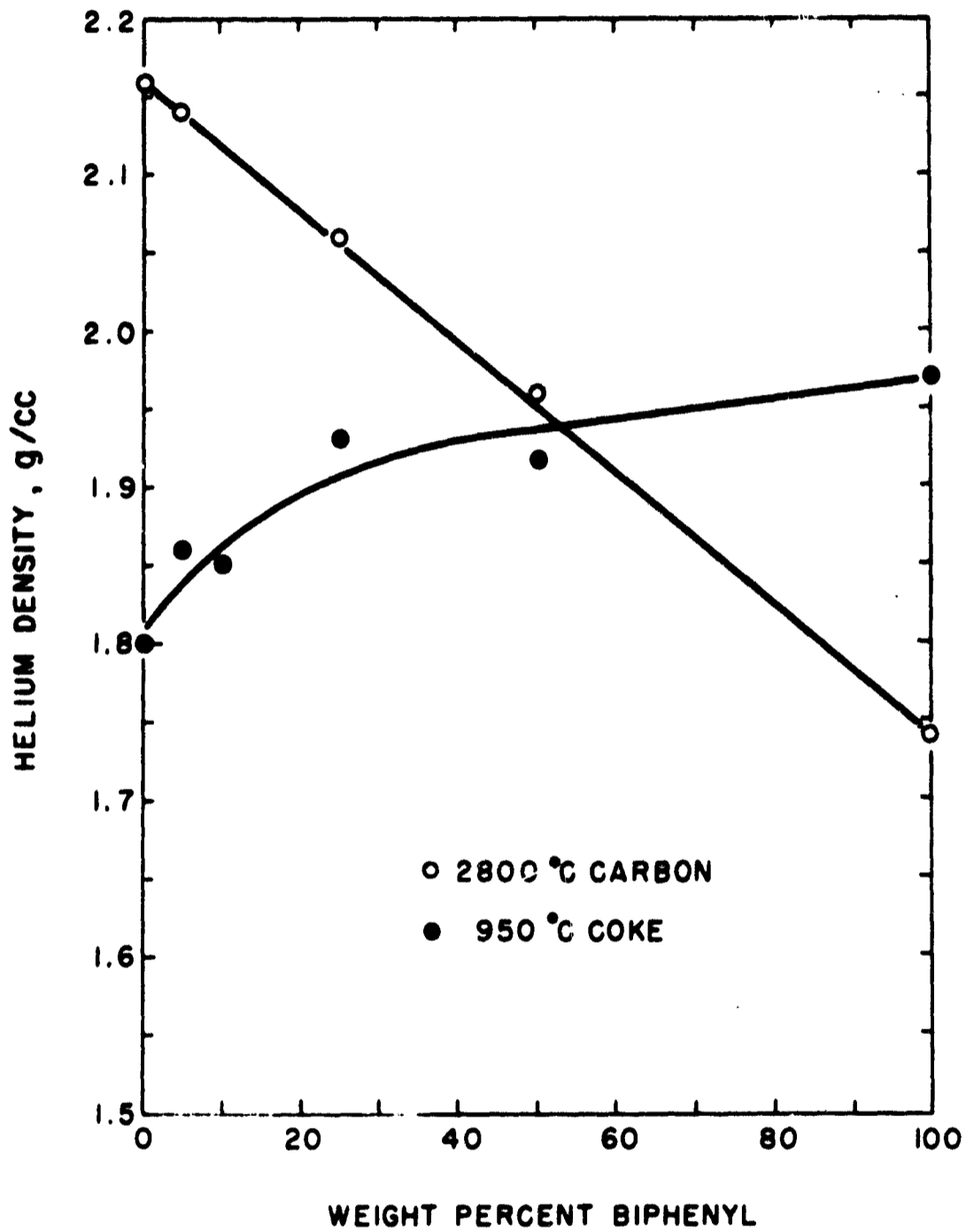


FIG. 7. CHANGE IN HELIUM DENSITY OF 950°C COKE AND 2800°C CARBON WITH THE STARTING COMPOSITION OF THE PHENANTHRENE-BIPHENYL SYSTEM

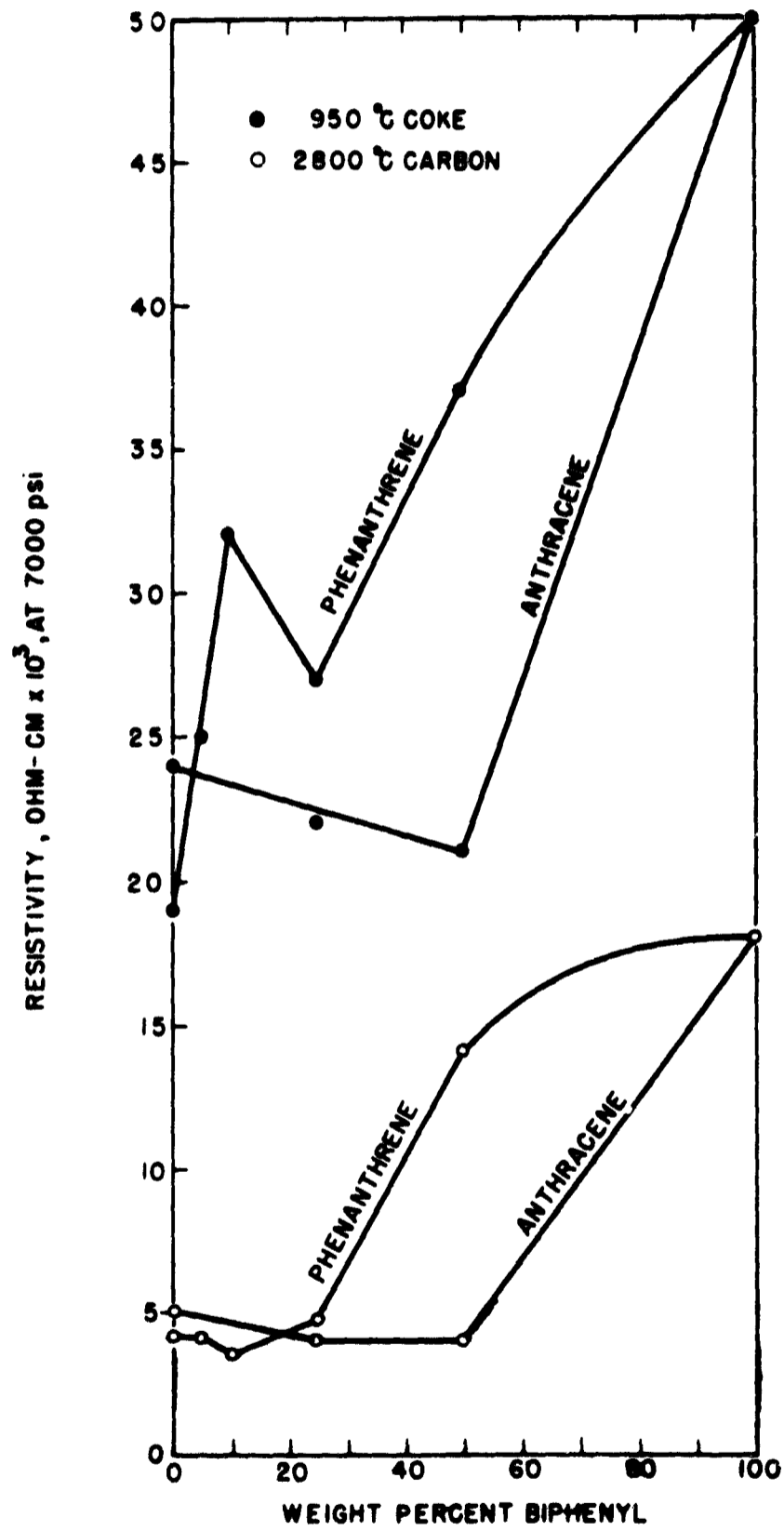


FIG 8 CHANGE IN ELECTRICAL RESISTIVITY OF 950°C COKES AND 2800°C CARBONS WITH THE STARTING COMPOSITION OF THE ANTHRACENE-BIPHENYL AND PHENANTHRENE-BIPHENYL SYSTEMS