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# Variations in Carbon Body Properties with Coal Tar Pitch Binder Properties*†

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Carbon bodies were molded from one calcined delayed petroleum coke and twelve medium melting point coal tar pitches having significant variations in their properties. The fabricated bodies and the coke, separately, were heat treated at six temperatures between 1150 and 3000°C. The following physical properties were determined on the bodies and the petroleum coke filler: apparent and air densities, BET surface areas, and crystallographic parameters. Other properties measured on the bodies were: reactivity to $CO_2$, electrical resistivity, coefficient of thermal expansion, and flexural strength. For all bodies heated to the same final temperature, only minor differences in properties were usually observed. This leads to two possible conclusions. One, the coal tar pitches produced binder carbons of similar properties at particular heat treatment temperatures. Two, because of the minor amount of residual pitch carbon in the bodies (ca. 15%), differences in properties of binder carbons were not sufficient to produce important differences in body properties. Major changes in physical properties of the bodies were observed in going from baking to graphitizing temperatures. Such changes paralleled closely changes in properties of the filler carbon.

## Introduction

Carbon bodies are generally a composite of a filler and binder. Classes of fillers most commonly used are calcined petroleum coke, carbon black, and anthracite. As expected, the particular class of filler employed has a marked effect on the properties of carbon bodies[1~3]. Indeed, within a class it has been shown that petroleum cokes, which are the most frequently used fillers, possess wide variations in structure which in themselves markedly affect important properties of the final carbon bodies[1].

By far, the most important class of binders used in the fabrication of carbon bodies is coal tar pitch, the heavy residue derived from the distillation of coal tar which in turn is derived from by-product coke ovens. Like petroleum cokes, coal tar pitches have widely varying properties depending upon the source of coal used, the operating conditions of the coke oven, and the particular distillation and processing conditions to which the tar is exposed. Walker and co-workers[4,5] have previously studied the character of a large number of pitches and the properties of the coke and graphitized carbons derived therefrom. In this investigation, carbon bodies were molded from a single calcined delayed petroleum coke and twelve of the coal tar pitches previously studied. Important properties of the carbon bodies have been evaluated and compared, in order to determine possible relations between variability of pitch

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1) P. L. Walker, Jr., F. Rusinko, Jr., J. F. Rakszawski, and L. M. Liggett, Proceedings of the Third Carbon Conference, Pergamon Press, 1959, pp. 643-658.

2) I. Geller and P. L. Walker, Jr., Proceedings of the Fifth Carbon Conference, Pergamon Press, Vol. II, 1963, pp. 471-482.

3) F. Rusinko, R.W. Marek, W. E. Parker, and J. E. Wynn, Proceedings of the Fifteenth Annual Power Sources Conference, PSC Publications Committee, 1961, pp. 9-12.

4) P. L. Walker, Jr., C. R. Kinney, and D. O. Baumbach, J. phys. chim., 58, 86 (1961).

5) P. L. Walker, Jr. and D. O. Baumbach, Proceedings of the Fifth Carbon Conference, Pergamon Press, Vol. II, 1963, pp. 175-185.

properties and body properties.

## Experimental

A. *Preparation of Baked and Graphitized Carbons*

1. *Grinding procedure for petroleum coke and coal tar pitches*—The petroleum coke used in this program was a so-called delayed petroleum coke which originated from a refinery active in supplying coke for the commercial production of graphite. Following calcining in a vertical retort, it was reduced to −4 mesh in a jaw crusher. The coke was further reduced in size using a micropulverizer and then separated into coarse and fine fractions. The coal tar pitches were reduced to −8 mesh in a jaw crusher.

2. *Body fabrication*—In formulating the coke-pitch mixture, 875 g. of pitch (25.2% by weight) were added to 2600 g. of coke, which had its coarse and fine fractions in a one to one ratio. Before adding the pitch, the coke was heated to 140°C. in a one-gallon capacity sigma blade mixer. Following the slow addition of the cold pitch and mixing at ca. 130°C. for 30 min., the mixture was dumped, cooled, and crushed to −20 mesh.

The pulverized mixture was divided into 130 and 85 g. portions for the molding into bars 7/8×1×5—3/4 in. and 1/2×1×5−3/4 in. The sapmles were molded at 100°C., with pressures of 1080 and then 3315 psi. being applied for 10 sec. and 60 sec., respectively.

3. *Baking and graphitizing procedure*—For baking, the molded samples were loaded into a silicon carbide sagger and covered with a mixture of 16×40 mesh petroleum coke and green sand in a one to one volume ratio. The furnace was raised at a rate of 4°C./hr. to 428°C., at 8°C./hr. between 428-860°C., and at 19.3°C./hr. to 1159°C. The furnace was held at 1150°C. for 3 hr., followed by cooling to room temperature.

Graphitization of the baked specimens was performed in a graphite tube furnace in a $N_2$ atmosphere. Graphite boxes containing 10-15 baked bodies were rapidly pushed into the hot zone of the furnace. After thermal equilibrium had been obtained, heat treatments at 2000 and 2250°C. for 6 hr., at 2500 and 2750°C. for 3 hr., and at 3000°C. for 1 hr. were carried out. The soak periods were selected to achieve a "steady state" with respect to the electrical resistivity and crystallographic parameters[6].

B. *Apparatus and Procedures Used to Define the Properties of the Pitches, Cokes, and Graphitized Carbons*

1. *Chemical analyses and miscellaneous properties of coal tar pitches*—These analyses were made according to standard specification tests[7].

2. *X-ray diffraction apparatus*—A General Electric x-ray diffraction XRD-5 unit, emitting Cu radiation at 40 kv and 15 ma., was employed to determine the crystallite height, interplanar spacing, and intensity of the (002) peak for the coke and carbon bodies. A 1° x-ray beam slit, 0.2° detector slit, medium resolution Soller slits, and a Ni filter were used with the instrument.

The carbon to be analyzed was ground to 200×325 mesh. Two methods of sample preparation were used for the measurements. For the interlayer spacing and crystallite height measurements, 35 mg. of sample were dispersed in a collodion-amyl acetate solution over 3/8 in.$^2$ of a glass slide. Approximately 18% by weight of −200 mesh NaCl was admixed with the carbon as an internal standard[8]. For measurements of peak intensity, a cell having a volume of 0.97 cc. was filled with 0.8 g. of carbon.

3. *Air, helium and mercury densities*—The Beckman Air Comparison Pycnometer Model 930 was used to measure air densities on both carbon bodies and 40×60 mesh material. Helium densities were determined using a constant pressure He displacement apparatus previously described[1]. Mercury densities were determined on the coarse coke filler by Hg displacement under atmospheric pressure.

4. *Reaction rate apparatus*—The apparatus employed for studying the rate of gasification of carbon with $CO_2$ at 1 atm. pressure was previously described[4]. A 0.2 g. sample of 40×60 mesh material was gasified in a particle reactor. The carbon bodies were ground and reacted in the above size in order to minimize diffusion control[9]. The reaction rate was taken in the 10-20% burn-off region, where the rate expressed as weight of carbon reacting per unit time was essentially linear.

5. *Gas adsorption apparatus*—Adsorption isotherms were measured for $N_2$ at 78°K. using a standard apparatus[10]. Calculations of surface areas were made using the BET equation[10].

6. *Miscellaneous tests*—Measurements of the electrical resistivity, coefficient of thermal expansion (CTE), and transverse breaking strength were made using apparatus and techniques previously described[4]. Electrical resistivities and breaking strengths were me-

6) F.V. Fair and F.M. Collins, Proceedings of the Fifth Carbon Conference, Pergamon Press, Vol. I, 1962, pp. 503-508.

7) "Methods of Testing Coal-Tar Products", The Barrett Division, Allied Chemical Corp., 1950.

8) P.L. Walker, Jr., H.A. McKinstry, and J.V. Pustinger, Ind. Eng. Chem., 46, 1651 (1954).

9) P.L. Walker, Jr., F. Rusinko, Jr., and L.G. Austin, Advances in Catalysis, Academic Press, Vol. 11, 1959, pp. 133-221.

10) P.H. Emmett, A.S.T.M. Tech. Publ. 51, 95 (1941).

asured at room temperature. Values of CTE were determined between 100 and 600°C.

C. *Description of the Filler and Binders*

1. *Petroleum coke*—A partial analysis of the calcined coke was: ash, 0.6%; and S, 1.5%. The coarse coke fraction was 95% +70 mesh; the fine fraction was 97% −70 mesh and 50% −200 mesh. In the following tables the coarse coke and fine coke fractions are designated as PCC and PCF. The coke blend used as filler is designated as PCB.

2. *Pitches*—Pertinent data for the pitches were presented in previous publications[4,5]. The same identification numbers are used as in previous studies.

## Results and Discussion

A. *Effect of Heat Treatment Temperature on Physical Properties of Carbon Bodies*

1. *Pitch coking values in carbon bodies*—The coking values of the binders ranged from 48.0% for pitch 5 to 57.9% for pitch 14. The values are lower than those usually reported since the baking was done at 1150°C. instead of at the lower temperatures frequently used in commercial practice. The lignite pitch has, in addition to a low Q. I., a very low C–H ratio, these bodies, the values deviate little between bodies heat treated at given temperatures. The major exception is the body formed from the lignite pitch. This which results in its having the lowest coking value.

2. *Apparent densities*—**Table I** summarizes the effect of heat treatment temperature on the apparent densities of the representative carbon bodies. The densities were determined from the body weight and dimensions. **Table II** summarizes the volume change of representative samples in going from the green to particular heat treatment temperatures. The green densities are in line with values normally found[1]; the baked densities are lower than those normally reported[1], because of a higher baking temperature. Major decreases in apparent densities and increases in sample volume resulted in going from the baked to the graphitized bodies. While this is contrary to much of the work reported in the literature, it can be explained by the experimental procedures chosen for this study. Since the objective in this research was to compare the effects of pitch properties on the properties of bodies heat treated to various temperatures, consistency within these experiments was considered to be of prime importance. However, consistency with commercial graphite processing was not sought. Thus, a selection of heating rates during graphitization was made on the basis of experimental considerations rather than to promote high values of apparent density and volume contraction.

The validity of this approach is confirmed by the observation that in spite of the effects of heat treating rates on the apparent densities and volume changes of

**Table I** Apparent Density Data for Selected Carbon Bodies and Filler

| Sample | Apparent Density, gm./cc | | | | | | |
|---|---|---|---|---|---|---|---|
| | Green | Baked | Graphitized, °C. | | | | |
| | | | 2000 | 2250 | 2500 | 2750 | 3000 |
| 2 | 1.68 | 1.48 | 1.36 | 1.33 | 1.28 | 1.27 | 1.26 |
| 4 | 1.70 | 1.48 | 1.37 | 1.33 | 1.29 | 1.26 | 1.26 |
| 5 | 1.64 | 1.33 | 1.17 | 1.09 | 1.10 | 1.13 | 1.17 |
| 9 | 1.67 | 1.43 | 1.35 | 1.28 | 1.25 | 1.24 | 1.23 |
| 16 | 1.69 | 1.46 | 1.32 | 1.29 | 1.24 | 1.23 | 1.27 |
| PCC | — | 1.36 | 1.68 | 1.50 | — | 1.52 | 1.52 |

**Table II** Change in Volume of Selected Bodies in Going from Green to Graphitized Samples

| Sample | Volume Change, % | | | | | |
|---|---|---|---|---|---|---|
| | Baked | Graphitized, °C. | | | | |
| | | 2000 | 2250 | 2500 | 2750 | 3000 |
| 2 | +0.0 | +5.4 | + 8.8 | + 9.4 | +12 | +13 |
| 4 | +2.7 | +6.5 | + 9.9 | +12 | +13 | +14 |
| 5 | +8.0 | +9.3 | +19 | +15 | +12 | +11 |
| 9 | +3.5 | +4.5 | + 8.2 | +12 | +12 | +14 |
| 16 | +1.7 | +7.5 | +10 | +13 | +16 | +11 |

**Table III** Surface Areas for Carbon Bodies and Filler

| Sample | Surface Area, $m.^2/g.$ | | | | | |
|---|---|---|---|---|---|---|
| | Baked | Graphitized, °C. | | | | |
| | | 2000 | 2250 | 2500 | 2750 | 3000 |
| 2 | 4.8 | 0.51 | 0.52 | 0.52 | 0.60 | 0.50 |
| 4 | 3.4 | 0.56 | 0.47 | 0.61 | 0.71 | 0.65 |
| 5 | 37.3 | 0.77 | 0.53 | 0.50 | 0.58 | 0.61 |
| 6 | 3.3 | 0.50 | 0.90 | 0.56 | 0.69 | 0.78 |
| 9 | 1.1 | 0.43 | 0.44 | — | 0.87 | 0.95 |
| 11 | 1.3 | 0.50 | 0.56 | 0.59 | 0.79 | 0.79 |
| 12 | 0.77 | 0.61 | 0.49 | 0.54 | 0.67 | 0.63 |
| 13 | 6.3 | 0.45 | — | 0.54 | 0.57 | 0.50 |
| 16 | 1.1 | 0.49 | — | 0.57 | 0.62 | 0.59 |
| 18 | 2.8 | 0.45 | — | 0.53 | 0.63 | 0.65 |
| 19 | 0.78 | 0.48 | — | 0.50 | 0.66 | 0.63 |
| PCC | 0.55 | 0.32 | 0.55 | 0.53 | 0.46 | 0.31 |
| PCF | 4.2 | 1.3 | 0.97 | 0.89 | 1.4 | 0.82 |
| PCB | 2.4 | 0.82 | 0.76 | 0.71 | 0.93 | 0.56 |

suggests that changes in the apparent density of the coke with heat treatment temperature is the major cause of these results. From **Table I**, apparent density data on the coke, as measured by Hg displacement, strongly support this conclusion. Sharp decreases in apparent density of the bodies, particularly in going from the baking temperature to 2250°C., are accompanied by a substantial decrease in the apparent density of the coke.

3. *Surface areas*—**Table III** presents the surface areas of the carbon bodies and the coke. Measurements were made on the bodies ground to 40×60 mesh and the coarse and fine coke fractions. Considering the coke first, it is seen that the fine fraction has a substantially larger specific surface area than does the coarse fraction at each heat treatment temperature. This difference in area cannot be attributed primarily to a difference in external, geometric area. Rather, as discussed by Bond and Spencer[11], it appears to be attributed to the progressive exposure of previously closed micropores, as a result of cracks being produced within the particles upon grinding. Upon heat treating the calcined coke to 2000°C., there is a marked decrease in surface area, apparently in line with the elimination of most of the previously existing microporosity. The areas then go through minima and maxima with further increases in heat treatment temperature, in line with the counterbalancing effects of further micropore elimination and removal of metallic impurities, which exposes and/or creates additional porosity.

An understanding of the surface areas of carbon bodies is complex because of the separate contributions of the filler and binder areas and the unknown extent to which the binder carbon blocks the filler area to the adsorbate. Two limiting cases appear possible. One, the binder carbon may cover the filler particles completely and contain no open porosity; in this case, the body will have a surface area closely approaching the geometric area of the filler - that is, $<0.01$ m.$^2$/g. Two, the binder carbon may contain open porosity and not block any of the filler area; in this case, the body area is the sum of the contributions from the filler (as previously measured) and the binder carbon. The results in **Table III** show that the first limiting case is not operative for any of the bodies. The results further show that the second limiting case is clearly not operative for many of the samples. For example, baked body 9 has a specific surface area of 1.1 m.$^2$/g. From the baking yield of the binder in this body, it is calculated that the specific area of the body would have a minimum value of ca. 2.0 m.$^2$/g. under the conditions that the binder blocked none of the filler surface area and that the binder carbon area was negligible. In those cases where the specific surface area of the body is higher than that of the filler, it is not possible to decide whether some filler area has been blocked.

The results in **Table III** show that there is a wide variation in the specific surface area of binder carbons in baked bodies. Body 5, containing the lignite binder is an extreme case. Assuming negligible blockage of the filler carbon, the specific area of the lignite carbon is estimated to have a minimum value of ca. 250 m.$^2$/g. The binder carbon in baked body 13 has a minimum area of 25 m.$^2$/g. Upon heat treatment to 2000°C. and higher, the surface areas of these bodies decrease sharply to values comparable with those of the filler. The result is that the surface areas of all the carbon bodies heat treated between 2000 and 3000°C. are low ($<1.0$ m.$^2$/g.) and not markedly different.

4. *Air and helium densities*—**Table IV** presents density data for representative carbon bodies (1/2×1×2 in.) and the filler. Most of the densities were determined by air displacement, but it was deemed desirable to run He density checks on selected samples. For the baked bodies of low surface area, the agreement between air and He densities was good. On the other hand, for baked bodies of higher surface areas (because of high specific area in the binder carbon), the air densities were significantly higher than the He densities. This suggests that at room temperature some physical adsorption of air is occurring in the fine micropores present in the bodies with higher areas. Because the areas of the graphitized bodies were low (the amount of fine micropore area low) it was considered suitable to measure their densities by air displacement.

**Table IV** Air Densities of Selected Carbon Bodies and Filler

| Sample | Air Density, gm./cc | | | | | |
|---|---|---|---|---|---|---|
| | Baked | Graphitized, °C. | | | | |
| | | 2000 | 2250 | 2500 | 2750 | 3000 |
| 2 | 2.04* | 1.86 | 1.84 | 1.80 | 1.76 | 1.75 |
| 4 | 2.03 | 1.88 | 1.82 | 1.79 | 1.75 | 1.79 |
| 5 | 2.13* | 1.91 | 1.87 | 1.85 | 1.84 | 1.83 |
| 9 | 2.03 | 1.86 | 1.84 | 1.78 | 1.76 | 1.75 |
| 16 | 2.03 | 1.87 | 1.85 | 1.79 | 1.76 | 1.87 |
| PCC | 2.08 | 1.76 | 1.60 | 1.74 | 1.70 | 1.74 |
| PCF | 2.11 | 2.07 | 2.08 | 2.08 | 2.08 | 2.10 |
| PCB | 2.10 | 1.92 | 1.84 | 1.91 | 1.89 | 1.92 |

* He densities

The densities of the bodies decrease sharply in going from the baked samples to those heat treated to 2000°C. Further, smaller decreases in density occur in going

11) R.L. Bond, D.H.T. Spencer, and P.A.H. Tee, "The Structure and Reactivity of Pile Graphite," U.S.-U.K. Gas Coolant Compatibility Conference, Oak Ridge, Tenn., Feb., 1960.

from 2000 to 2750°C. In going from 2750 to 3000°C., the direction of the density change is random. The air densities of the bodies heat treated to 2500°C. are much lower than the He densities for bodies previously studied[1]. At the same time, there is little spread in the air densities for all these carbon bodies heat treated to 2500°C. Again, the low density of the filler appears to be primarily responsible for the low density of the bodies. That is, it is seen in **Table IV** that the filler decreased sharply in air density in going from its calcination temperature to 2000°C., paralleling the large decrease in body density. The fact that the air density of the fine filler heat treated to 2000°C. and above is markedly higher than that of the coarse filler is consistent with the low air density of the coarse filler. That is, as discussed previously for the surface area results, grinding appears to be exposing previously closed micropores. The large difference in air density for the two graphitized filler fractions is in contrast to the small difference for the two calcined fractions. It is clear that the substantial volume closed to air is developed as a result of heat treatment at temperatures somewhere between ca. 1250 and 2000°C.

It is noticed that in every case the air densities of the bodies are less than those of the filler for heat treatment temperatures between 2500-3000°C. This could be a result of the binder carbon blocking pores in the filler and/or the binder carbon having a lower air density than the filler. Both possibilities are consistent with the known presence of extensive closed bubble structure in the binder carbon, as previously discussed[12].

**Table V** Crystallographic Parameters for Selected Carbon Bodies and Filler

| Sample | Heat Treatment Temp, °C. | Interlayer Spacing, A. (15°C.) | $L_c$, A. | (002) Intensity |
|---|---|---|---|---|
| PC | calcined | 3.51 | 34 | 17.0 |
| 2 | baked | 3.51 | 32 | 15.2 |
| 4 | baked | 3.51 | 30 | 15.7 |
| 9 | baked | 3.51 | 32 | 15.8 |
| PC | 2000 | 3.42 | 226 | 57.3 |
| 2 | 2000 | 3.41 | 259 | 63.8 |
| 4 | 2000 | 3.42 | 237 | — |
| 9 | 2000 | 3.42 | 255 | — |
| PC | 2250 | 3.373 | 597 | 86.9 |
| 2 | 2250 | 3.384 | 410 | 77.6 |
| 4 | 2250 | 3.379 | 437 | — |
| 9 | 2250 | 3.386 | 347 | — |
| PC | 2500 | 3.366 | 852 | 92.9 |
| 2 | 2500 | 3.365 | 627 | 79.5 |
| 4 | 2500 | 3.369 | 598 | — |
| 9 | 2500 | 3.361 | 524 | — |
| PC | 2750 | 3.360 | 962 | 96.2 |
| 2 | 2750 | 3.360 | 727 | 92.5 |
| 4 | 2750 | 3.360 | 652 | — |
| 9 | 2750 | 3.362 | 716 | — |
| PC | 3000 | 3.357 | 1015 | 104.6 |
| 2 | 3000 | 3.355 | 700 | 94.1 |
| 4 | 3000 | 3.357 | 668 | — |
| 9 | 3000 | 3.360 | 743 | — |

5. *Crystallographic parameters*—**Table V** presents data on the interlayer spacing, average crystallite height, and relative intensity of the (002) diffraction peak for the coke filler and selected bodies heat treated at various temperatures up to 3000°C. In spite of the appreciable expansion of the coke filler upon heat treatment to graphitization temperatures, interlayer spacing data indicate that the filler was highly graphitizable. Following heat treatment to 3000°C., the crystallites in the filler had a three-dimensional orientation (graphite structure) of ca. 90%, as indicated by the Franklin relationship[13]. In the bodies, since the filler comprises ca. 85% of the weight, the angular location of the maximum in the diffraction peak (from which the interlayer spacing is calculated) will be determined primarily by the filler. Therefore, unless the binder were to have a significant depressing effect on the graphitizability of the filler, interlayer spacings calculated for the bodies should be quite comparable to those of the filler alone at particular heat treatment temperatures. Such is seen to be the case.

Akamatu and Kuroda have shown from electron diffraction studies on petroleum cokes that carbon crystallites are aligned with their c-axes nearly parallel to each other and perpendicular to the surface of the long side of the angular particles[14]. The scatter in the c-axis direction progressively decreases with increases with increasing heat treatment temperature[14]. The monotonic increase in $L_{(002)}$ for the coke filler in going from the calcined state to 3000°C. is, in fact, a result of this increasing crystallite alignment. On duplicate runs, the average deviation in intensities for all samples in **Table V** was ±2.1%. Therefore, differences in intensities between the filler and the bodies at particular heat treatment temperatures are significant. With the exception of heat treatment at 2000°C., $I_{(002)}$ of the filler is greater than that of the body. This suggests that at comparable heat treatment temperaturs crystallite alignment in the binder carbon is less than that in the filler carbon. As discussed by Noda and Inagaki[15] this is not necessarily a result of the inherent nature of the carbon produced from the pitches but rather can be a result of the restriction to crystallite

12) P. L. Walker, Jr. and Emile Raats, J. Phys. Chem., **60**, 364 (1956).
13) R. E. Franklin, Acta Cryst., **4**, 253 (1951).
14) H. Akamatsu and H. Kuroda, Proceedings of the Fourth Carbon Conference, Pergamon Press, 1960, pp. 355-369.
15) T. Noda and M. Inagaki, Proceedings of the Fifth Carbon Conference, Vol. I, 1962, pp. 559-566.

growth and alignment imposed by the limited thickness of binder surrounding each filler particle. Indeed, the results following heat treatment to 2000°C. suggest that binder coke 2 would inherently undergo more crystallite alignment than the filler at all temperatures if the limitation of binder thickness was not present.

As expected from the interlayer spacing data, the filler and the bodies undergo substantial increases in average crystallite height with increasing heat treatment temperature. The fact that the calculated crystallite heights for the filler and the bodies are different could be a result of real differences in the crystallite heights of the filler and binder or differences in crystallite alignment and/or interlayer spacings of these carbons, which would produce (002) diffraction peaks of varying widths.

The intensity of the (002) x-ray diffraction peak was measured for all the baked and graphitized (3000°C.) bodies. For the baked bodies, negligible differences in intensities existed, with the possible exception of body 5, containing the lignite binder coke. The intensity of the coke filler was significantly higher than the intensities of the baked bodies, probably because the filler was subjected to a higher heat treatment temperature during calcination than were the bodies during baking. Significant differences in $I_{(002)}$ for some of the graphitized bodies existed. Further, the $I_{(002)}$ of the graphitized filler was significantly higher than the intensities of all the graphitized bodies. The probable interpretation of this has been discussed previously. It does suggest that differences in crystallite alignment and/or crystallite size for binder carbons heat treated to different temperatures can exist.

### B. *Effect of Heat Treatment Temperature on Important Properties of Carbon Bodies*

1. *Reactivity to carbon dioxide*—The reactivity results are presented in **Table VI**. For the bodies where reactivity data are available for each heat treatment temperature, it is seen that the reactivities in all cases undergo a sharp decrease with increasing heat treatment temperature up to 2500°C. Heat treatment to temperatures above 2500°C. produces relatively minor and random further changes in reactivity. For each heat treatment temperature, there are relatively small differences in the reactivities of the different bodies. For example, at a reaction temperature of 1100°C., the maximum variation in reactivity is less than 40% in all cases (if for the baked bodies, body 5 containing the lignite binder is excluded). Previous studies on the reactivity of carbons produced from the pitches used in this work showed that their reactivities increased in going from the coke to the graphitized material[4]. The fact that this result is in marked contrast to the effect of heat treatment temperature found in the present research suggests that the binder carbon is not of prime importance in determining body reactivity. Other evidence supporting this conclusion will be forthcoming shortly.

Results are also presented for the reactivities of selected pitch cokes, ground to the same particular size as the bodies. The detailed method of preparation of the pitch coke has been previously described[4]. The reactivities of the pitch coke in all cases are markedly less than the reactivities of the corresponding baked bodies. Further, the pitch cokes 2 and 5 have the highest reactivities but yield baked bodies of the lowest reactivities. These results either lend additional support to the conclusion that the binder coke is not of prime importance in determining body reactivity or suggest that the physical state of the bulk pitch coke is different than the pitch coke in a baked body. Actually it is thought that both these possibilities contribute to the difference in reactivity, as will be seen.

Also presented in **Table VI** are results for the reactivity of the *coarse* coke filler fraction, as a function of heat treatment temperature. Unfortunately the reactivity of the fine coke filler fraction could not be determined, since it offered too much resistance to the flow of $CO_2$ up through the reactor bed. For all heat treatment temperatures except 2250°C., the reactivity of the coarse coke is less than the reactivities of the bodies at comparable heat treatment temperatures. Since the reactivities of the coarse filler coke and pitch cokes, taken separately, are in all cases less than the reactivities of the baked bodies made from the filler and corresponding pitch, it might be concluded that binder-filler interaction in a body produces a synergistic effect on body reactivity. However, before this conclusion could be made it was necessary to show that filler size did not affect reactivity. Bodies were, therefore, molded from the coarse and from the fine petroleum coke fractions and pitch 22805. The same weights of filler to binder were used in making both bodies. Coke from pitch 22805 was thoroughly studied previously;[4] its reactivity is quite comparable to some of the less reactive pitch cokes examined in this program.

It is seen from **Table VI** that the reactivity of the baked body is strongly affected by filler particle size. Further, the body composed of the coarse filler has a reactivity at 1100°C. only slightly higher than the coarse coke fraction. The average reactivity for the two bodies, 0.018 g./hr., is quite comparable with the reactivities of the regular baked bodies. Such an averaging would appear reasonable since all of the regular bodies studied contained equal weights of coarse and fine coke filler. It is concluded, then, that the interaction of coke filler and binder does not have a marked synergistic effect on body reactivity but that the filler particle size can have a major effect on body

Table VI Reactivity of Carbon Bodies and Filler to Carbon Dioxide

| Sample | Rates in g./hr. Following Heat Treatment at Temperatures Indicated, °C. | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1100* | Baked | 2000 | 2250 | 2500 | 2750 | 3000 |
| Reaction Temperature, 1000°C. | | | | | | | |
| 2 | 0.023 | 0.052 | 0.016 | 0.012 | 0.0064 | 0.0051 | 0.0056 |
| 4 | 0.0076 | 0.062 | 0.025 | 0.010 | 0.0057 | 0.0052 | 0.0063 |
| 5 | 0.018 | 0.030 | 0.027 | 0.015 | 0.0058 | 0.0053 | 0.0050 |
| 6 | 0.010 | 0.071 | 0.027 | 0.011 | 0.0065 | 0.0054 | 0.0051 |
| 9 | 0.0046 | 0.075 | 0.020 | 0.013 | 0.0065 | 0.0051 | 0.0054 |
| 11 | 0.0036 | 0.080 | 0.019 | 0.011 | 0.0059 | 0.0045 | 0.0050 |
| 12 | 0.0037 | 0.076 | 0.023 | 0.0086 | 0.0071 | 0.0046 | 0.0061 |
| PCC | — | 0.019 | 0.0068 | 0.018 | 0.0053 | 0.0037 | 0.0038 |
| Reaction Temperature, 1100°C. | | | | | | | |
| 2 | 0.057 | 0.16 | 0.12 | 0.073 | 0.037 | 0.035 | 0.039 |
| 4 | 0.015 | 0.17 | 0.15 | 0.064 | 0.035 | 0.042 | 0.046 |
| 5 | 0.060 | 0.11 | 0.16 | 0.081 | 0.043 | 0.040 | 0.033 |
| 6 | 0.051 | 0.22 | 0.15 | 0.067 | 0.038 | 0.041 | 0.038 |
| 9 | 0.013 | 0.19 | 0.14 | 0.077 | 0.037 | 0.034 | 0.039 |
| 11 | 0.010 | 0.21 | 0.13 | 0.073 | 0.036 | 0.038 | 0.033 |
| 12 | 0.012 | 0.21 | 0.16 | 0.087 | 0.040 | 0.039 | 0.039 |
| 13 | — | 0.18 | — | — | — | — | 0.036 |
| 14 | — | 0.19 | — | — | — | — | 0.041 |
| 16 | — | 0.21 | — | — | — | — | 0.034 |
| 18 | — | 0.16 | — | — | — | — | 0.037 |
| 19 | — | 0.17 | — | — | — | — | 0.037 |
| 22805** | — | 0.084 | — | — | — | — | — |
| 22805*** | — | 0.27 | — | — | — | — | — |
| PCC | — | 0.067 | 0.030 | 0.087 | 0.036 | 0.028 | 0.027 |

* Reactivity of pitch coke.
** Body containing coarse filler and pitch 22805.
*** Body containing fine filler and pitch 22805.

reactivity*. At least two possible causes appear reasonable for the filler particle-size effect on reactivity of of bodies. One, as has been shown, the fine filler has a larger surface area than the coarse filler. It is suggested that this is a result of more cracks (more macropores to connect micropores) in the fine filler. Hence, if the extent of particle reaction is, in part, diffusion controlled, the availability of more cracks (through which the reacting gas can travel from the exterior to the interior of the particles) will result in an increase in reactivity. Second, it is known that during the baking of carbon bodies, the calcined filler expands but the binder loses volatiles and contracts. This results in cracking of the binder[16]. The probability of a crack traveling completely through the binder layer surrounding a particle is an inverse function of the binder thickness. Since the binder layer thickness is thought to increase with an increase in filler particle size[17], the binder surrounding the fine filler would be expected to have a higher permeability to the reacting gas.

* The reader should be remined that previously it was shown that the use of petroleum coke fillers of different origin and properties, but of the same particle size, consist, also results in carbon bodies of widely different reactivities.

16) O. Bowitz, O. C. Bockman, J. Jahr, and O. Sandberg, Proceedings of the Industrial Carbon and Graphite Conference (London) 1958, pp. 373-377.
17) S. Mrozowski, Proceedings of the Second Carbon Conference, U. of Buffalo, 1956, pp. 195-216.

**Table VII** Electrical Resistivity, Coefficient of Thermal Expansion, and Flexural Strength of Selected Graphitized Bodies

| Samle | Heat Treatment Temp., °C. | Elect. Resist. ohm-cm. $\times 10^4$ | | CTE $\times 10^3$/°C. | | Flexural Strength psi. |
|---|---|---|---|---|---|---|
| | | ∥ | ⊥* | ∥ | ⊥* | |
| 2 | 2000 | 52 | 65 | 3.2 | 4.0 | 984 |
| | 2250 | 35 | 65 | 3.3 | 3.8 | 1080 |
| | 2500 | 17 | 22 | 2.8 | 3.7 | 988 |
| | 2750 | 14 | 17 | 2.5 | 3.4 | 1082 |
| | 3000 | 13 | 16 | 2.6 | 3.4 | 958 |
| 4 | 2000 | 48 | 61 | 3.3 | 4.3 | 1304 |
| | 2250 | 26 | 32 | 2.8 | 3.7 | 1483 |
| | 2500 | 17 | 23 | 2.5 | 3.8 | 1302 |
| | 2750 | 14 | 20 | 2.7 | 3.5 | 1173 |
| | 3000 | 14 | 20 | 2.4 | 3.3 | 1322 |
| 5 | 2000 | 71 | 87 | 3.2 | 4.0 | 696 |
| | 2250 | 45 | 59 | 2.9 | 3.5 | 667 |
| | 2500 | 29 | 38 | 2.7 | 3.6 | 602 |
| | 2750 | 28 | 31 | 2.6 | 3.2 | 643 |
| | 3000 | 23 | 29 | 2.5 | 3.1 | 572 |
| 9 | 2000 | 50 | 66 | 3.2 | 4.2 | 1405 |
| | 2250 | 28 | 49 | 3.0 | 3.9 | 1205 |
| | 2500 | 17 | 23 | 2.7 | 3.4 | 1144 |
| | 2750 | 14 | 20 | 2.5 | 3.1 | 1206 |
| | 3000 | 14 | 19 | 2.5 | 3.3 | — |
| 16 | 2000 | 50 | 72 | 3.3 | 4.0 | 1162 |
| | 2250 | 27 | 49 | 2.6 | 3.6 | 1262 |
| | 2500 | 17 | 25 | 2.7 | 3.4 | 1196 |
| | 2750 | 13 | 19 | 2.4 | 3.4 | 1188 |
| | 3000 | 15 | 18 | 2.5 | 3.2 | — |

* With respect to grain direction

Again, if the reactivity is being partially controlled by diffusion, an enhancement in reactivity will result.

2. *Electrical resistivity*—The electrical resistivity data for representative graphitized bodies are included in **Table VII**. Substantial decreases in resistivity occur as a result of increasing heat treatment temperature between 2000 and 2500°C. Further increases in heat treatment temperatures result in additional resistivity decreases which are moderately small for most bodies. For particular heat treatment temperatures, the resistivities of the bodies are very similar, body 5 from the lignite pitch belong the major exception. It is concluded that wide variations in the properties of coal tar pitch binders which are selected for body fabrication result, in themselves, in relatively minor differences in electrical resistivities of the bodies. For comparable heat treatment temperatures, the electrical resistivities of these bodies are somewhat higher than those usually found[17], presumably because of the lower apparent density of the bodies.

3. *Coefficient of thermal expansion*—Table VII also includes CTE results. In most cases the CTE, both parallel and perpendicular to the molding direction, decreases between 20 and 30% with an increase in the graphitization temperature from 2000 to 3000°C. Generally, the decrease is greater in going from 2000 to 2500°C. than from 2500 to 3000°C. At particular heat treatment temperatures, the CTE are very similar. This is consistent with the conclusion of Okada[18] that the filler particules play the main role in the thermal expansion of carbon bodies.

4. *Flexural Strength*—The flexural strengths of the carbon bodies, measured perpendicular to the direction of applied molding pressure, are presented in **Table VII**. The flexural strengths of all the bodies are considerably lower than is usually found[19], obviously because of the unusually low apparent densities of the bodies. Since the standard deviation in flexural strength values is at least ±7%[20], and may be even greater[19], negligible differences in strength for most of the bodies exist. Body 5, which has markedly lower densities than the other bodies, and body 2 are exceptions. The lower strengths of bodies made from pitch 2 cannet be attributed to unusually low densities.

## Conclusions

It appears that the spread in properties among medium melting point coal tar pitches commonly used for commercial carbon body fabrication today does not produce major differences in body properties, when all other fabrication and heat treatment conditions are identical.

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18) J. Okada, Proceedings of the Fourth Carbon Conference, pp. 553-558.
19) W. P. Eatherly and E. L. Piper, "Nuclear Graphite", Academic Press, Inc., 1962, P. 45.
20) D.W. Gillmore, Ph. D. Thesis, The Pennsylvania State University, 1954.