THE STRUCTURE AND GRAPHITIZATION OF FINE COKE PARTICLES AND OF THERMAL CARBON BLACKS*

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Structures of cokes which were milled to particles of a few microns diameter were investigated with an electron microscope. All soft cokes studied, i.e., those formed from organics remaining fluid to about 400°C, were found to break up into lamellae (platelets) which possess a high diamagnetic anisotropy. Solid carbons produced from extruded mixes containing such finely milled cokes are highly anisotropic, their X-ray patterns showing a high degree of alignment of graphitic planes parallel to the extrusion axis. Thus, it is shown that the microcrystals in the platelets are oriented with their basal planes parallel to the plane of the lamellae. Milling of a coke while it is still raw, i.e., heated to about 600°C or lower, destroys the lamellar structure as well as the microcrystalline orientation. Hard cokes, formed by the pyrolysis of organics remaining solid throughout the heating, all break during milling into jagged, roughly equiaxed particles characteristic of amorphous substances.

Graphitization of soft coke particles results in some changes in particle outlines (development of straight edges and sharp corners) and the disappearance of the granular structure in the lamellae. However, hard coke particles and those of soft coke ground in the raw state do not change noticeably during graphitization.

Replicas of graphitized carbon-black particles (Thermax) imbedded in a resin were obtained by an especially developed technique. The replicas show that the particles have exclusively hexagonal and pentagonal faces and seem to indicate that all the particles in graphitization transform into a definite type of polyhedron. The structure extends throughout the interior of the particles as is apparent on micrographs of P-33 particles, which are small enough to transmit electrons. The faces of the polyhedra are graphitic basal planes of individual crystals which are probably hooked to their neighbors by valence bonds. Particles which have been graphitized while in contact with binder coke retain their individuality and do not coalesce with the matrix. Thus it is concluded that a carbon black particle is a closed system with respect to crystal growth, and transforms into a polyhedron probably having a surface corresponding to minimum total energy compatible with the imposed restrictions.

INTRODUCTION

Carbon and polycrystalline graphites are formed by heating organic substances in the absence of air, or in a reducing atmosphere. Regardless of whether the original material was composed of chain-like or ring-type molecules, the heating results in polymerization into solid systems consisting largely of planar condensed aromatic ring structures which are stacked to form crystallites which would be true graphitic planes were it not for the lack of the specific rotational orientation between planes. These so-called turbostratic crystallites are cross-linked to their neighbors either directly through peripheral atoms or indirectly through the intermediary of carbon atoms which exist in a disorganized phase. The disorganized phase is composed of chain molecules and carbon atoms of tetrahedral valency lodged between crystal-

21

lites. The amount of cross-linking has an important bearing upon the development of physical properties of the solid. Above the setting point, as the heat-treatment temperatures are raised, the amount of disorganized carbon decreases partially through incorporation into the crystalline phase and partly by evaporation in the form of light hydrocarbons (cracking). Strictly speaking, it is only after hydrocarbons are completely removed that cokes become *carbons*.

Carbons made from materials which do not melt but remain solid throughout coking do not graphitize as easily as those made from pitches and tars which solidify at temperatures of several hundred degrees[1]. Evidently the cross-linking responsible for stabilizing the solid form hinders the molecular motion and thus inhibits the growth of the aromatic crystallites. Such cokes are called *hard* cokes in contradistinction to those formed from fluid phase hydrocarbons and which are termed *soft* cokes, these names being suggested by very obvious differences in their mechanical properties. In this work, both types of cokes were investigated with the electron microscope in order to find differences in their structure and the results are reported below.

In passing a hydrocarbon gas or vapor through an enclosure heated to a high temperature, a sooty deposit is formed. Sooty carbons also result from the incomplete combustion of hydrocarbons. The carbon deposits from both of these processes are generally called carbon blacks. The blacks consist of very small particles which are composed mainly of turbostratic carbon crystallites. In general, the particles have a nearly-spherical shape, but there is some uncertainly about this in the case of the smallest blacks with average particle diameters of only several tens of angstroms. In large thermal blacks (formed by the first process mentioned above) Hall found indi-

cations that the surface microcrystals are preferentially oriented, their basal planes being tangent to the surfaces of the particles[2].

The details of the mechanism of carbon formation in flames and in gas phase thermal decomposition are not well understood. Parker and Wolfhard[3] suggest that the process may be a pyrolytic one wherein the fuel gas molecules are transformed into heavier hydrocarbons. Eventually the atmosphere becomes super-saturated so that droplets of heavy hydrocarbons condense out with subsequent heating resulting in the transformation into solid carbon. If so, the surface alignment of microcrystals and the spheroidal shape of the particles probably result from the surface tension acting while the particles are fluid.

The graphitization of carbon blacks is a process distinctly different from that of cokes. When carbon blacks are heat-treated the crystallites grow only to a certain limiting size which is about one-third the particle diameter. This was found by an X-ray line-width study of blacks in the size range from 50Å to 3000 Å[4]. Ragoss, Hoffman and Holst[5] investigated the carbon black "Thermax" with an electron microscope and found that when heat treated to graphitizing temperatures, the particles lose their spheroidal shape and develop polygonal outlines. Furthermore, the electrical properties of the blacks are quite anomalous and depend peculiarly upon the particle size and heat treatment. In view of these anomalies, it seemed important in order to elucidate the nature of the structure of the graphitized particles to study their morphology.

[2] C. E. Hall, J. App. Phys. **19**, 271 (1948).

[3] W. G. Parker and H. G. Wolfhard, Proc. Chem. Soc. (London) **1950**, 2038.

[4] H. T. Pinnick, J. Chem. Phys. **20**, 756 (1952).

[5] A. Ragoss, U. Hoffman and R. Holst, Kolloid-Z. **105**, 118 (1943). See also a recent paper by W. D. Schaeffer, W. R. Smith and M. H. Polley, Ind. Eng. Chem. **45**, 1721 (1953).

[1] S. Mrozowski, Phys. Rev. **85**, 609 (1952) and Errata, Phys. Rev. **86**, 1056 (1952).

II. EXPERIMENTAL

The following soft cokes were used in this study: A laboratory-prepared coke formed by heating Resin "C" (Barrett Division of Allied Chemical and Dye Corporation) in an iron vessel closed off except for a small exhaust port, a pitch coke from the Dominion Tar and Chemical Company (Canada), and the following petroleum cokes: Bradford (Kendall Oil Company), Texas (Texas Company), Cities Service, Cleves and Lima. Samples of these cokes were calcined to various temperatures in a quartz tube electrical furnace through which purified dry nitrogen was circulated. They were milled in a tumbler containing agate spheres to particles of a few microns in size.

Hard cokes were prepared by pyrolysis of a phenol-benzaldehyde polymer resin, a phenol-formaldehyde polymer (Resin No. 16248, Durez Plastic and Chemicals, Inc.), cane sugar, Cellophane, and a polyester casting resin. They were all calcined and milled as were the soft cokes.

Many carbon blacks ranging in average particle size from around 50Å to over 3000Å were studied, but only the thermal blacks P-33* and Thermax* (2000Å and 3000Å respectively) were large enough to exhibit clearly in the electron microscope polygonal outlines (after being graphitized). Of these, only Thermax was of sufficient size to be effectively studied by the replica technique used.

The powdered cokes and carbon blacks were graphitized by heating to 3000°C in a graphite tube resistance furnace. Oxidation was prevented by maintaining a flow of purified dry nitrogen through the furnace during heating. The specimens were contained in small thin-walled graphite capsules.

All electron micrographs were made with an R.C.A. electron microscope, model EMU-2B. The specimens in powder form were

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generally prepared for viewing by suspending them in distilled water containing Aerosol and Darvan as wetting and dispersing agents, the concentrations of these respectively being 1×10^{-4} g and 2×10^{-4} g per cc of the water. A Waring Blendor was used for mixing. Drops of the suspension were allowed to dry on the specimen grids covered with Formvar films. In some cases, the powders were simply dusted onto the substrates. The particles were chromium-shadowed at the angles indicated in the captions.

The morphology of carbon blacks was studied by a specially developed replica technique, the first step of which consisted of dispersing the graphitized black in a thermosetting polyester casting resin. The catalyst (benzoyl-peroxide) was added to the resin prior to the mixing-in of the black. By gradually adding the resin to the black during mixing in a mortar, good dispersion resulted. No definite proportions of black and resin were measured out, the amounts used being usually sufficient to produce a medium to a dark gray smear on the glass plate as viewed by transmission.

A convenient vessel for holding the suspension during the subsequent processing was formed by wrapping a sheet of aluminum foil over the end of a rod or test tube. After being poured into the vessel, the suspension was allowed to gel overnight, after which it was cured by heating to a temperature in the range 70–100°C. The length of time required depended upon the amount of catalyst used. An excessive amount of catalyst usually resulted in cracking of the piece. After curing, the cylindrical sample was notched at several places about a half centimeter apart, each notch circumscribing the cylinder. The sample was broken into several discs by striking sharp blows at the notches using a hammer and chisel. Each face contained protruding carbon black particles as well as pits left by those particles which remained imbedded in the comple-

mentary face. Unfortunately, it was not possible to avoid making a negative replica because Formvar evidently adheres too well to the carbon black to permit stripping. Any attempts to circumvent the additional step failed.

At this state the polyvinyl alcohol-Formvar technique described by Schwartz, Austin and Weber[6] was applied. However, the resolution obtained was insufficient to show surface details. A negative replica was made by imbedding the carbon-laden polymerized resin in polyester. Shrinkage which occurs during the curing produces compressive stresses and results in an intimate contact between the materials. The piece to be replicated was placed face up in a vessel and covered with catalyzed polyester until there was depth of a centimeter or so of resin above the surface to be replicated. After thorough curing, all excess clear resin was machined away. A notch was then cut at the interface and a screw-driver blade inserted, the twist of the screw-driver frequently being sufficient to force the two pieces apart. The surface of the negative was cleared of any loosely adhering resin fragments by spraying it with a jet of petroleum ether from a hypodermic syringe. A formvar replica of this negative was formed by flowing over the surface a drop of 0.7% solution of Formvar 15/95 "E" in ethylene dichloride. The piece was held to allow free drainage of the excess solution, which was soaked off with filter paper. It was found inadvisable to use a heat lamp to hasten drying of the Formvar as this seemed to prevent free stripping. After the Formvar was dry, the entire compound replica was immersed in water at 50–60°C for at least an hour. A drop of wetting agent (Aerosol) was added though the efficacy of this measure was not determined. After removal from the warm water and before the Formvar had the slightest

chance to dry, a 15% aqueous polyvinyl alcohol latex (hereinafter abbreviated P.V.A.) was painted onto it and allowed to dry while the sample remained under a perforated beaker. Any attempts to speed the drying resulted in failure; presumably a longer drying time results in greater adhesion between Formvar and P.V.A.

From here on, the procedure of Schwartz, Austin and Weber[6] was followed, i.e., the replica was cut into conveniently sized squares which were placed P.V.A. side down on water, thus enabling the P.V.A. to dissolve away and leave a Formvar replica floating on the water surface. The replicas were picked up on electron-microscope specimen grids and shadow-cast with chromium at the angles indicated in the captions.

A variant of the replication technique described above was applied to study the surface of a solid carbon. The carbon was made from a mix containing Thermax carbon black and Resin "C" binder in the ratio 100/40 by weight. The mix was extruded as a $\frac{1}{2}''$ diameter rod and subsequently graphitized to 3000°C. A negative polyester replica was obtained by imbedding a portion of the broken rod in polyester resin to which excess catalyst was added in quantity sufficient to cause the resin to crack and separate from the carbon surface during the curing stage. The final replica was obtained in the manner described above.

III. RESULTS AND DISCUSSION

1. Cokes

Direct view electron micrographs of particles of Texas coke and Resin "C" coke are shown in Fig. 1A and B. Both cokes were calcined to 1250°C prior to grinding. No essential differences between them are apparent. They both break up into flake-like particles or lamellae having no particular outline. There seems, however, to be a tendency for the appearance of straight edges. The short shadow lengths confirm the

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[6] C. M. Schwartz, A. E. Austin and P. M. Weber, J. App. Phys. **20**, 202 (1949).

FIG. 2. A calcined (1250°C) Texas coke particle standing on edge. The distance between the platelets is about $\frac{1}{20}\mu$. Shadow-cast with chromium at 30° from horizontal.
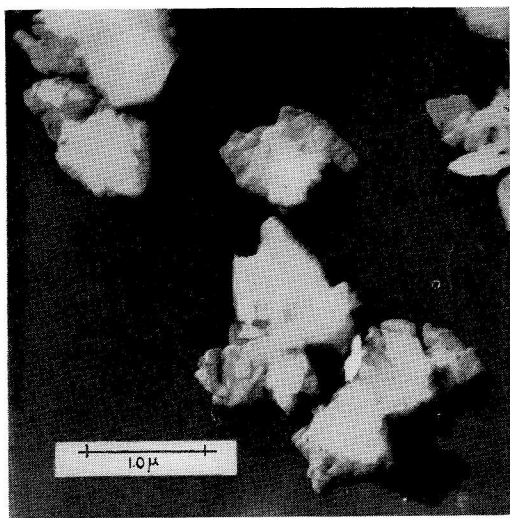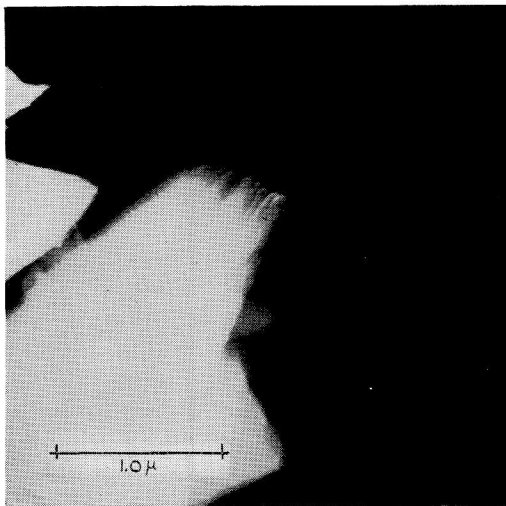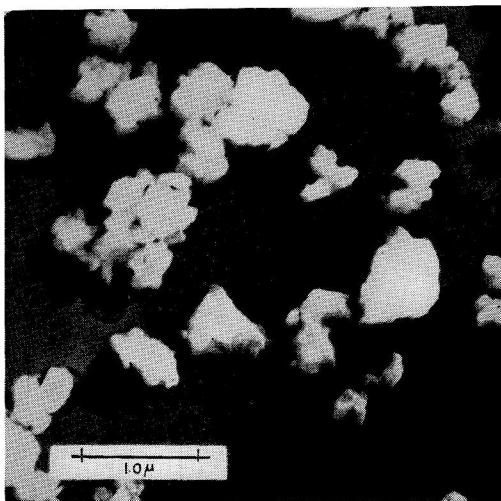

FIG. 1. Particles of calcined (1250°C) Resin "C" coke (above), and Texas coke (below). Both cokes were calcined prior to milling. Shadow-cast with chromium at 30° from horizontal.

FIG. 3. Particles of calcined (1250°C) phenol-benzaldehyde polymer coke. The coke was calcined prior to milling. Shadow-cast with chromium at 30° from horizontal.

lack of thickness in the vertical direction, which is also evident from their appreciable electron beam transmission. The step-wise change in electron transmission shows that these particles are lamellar bundles. Fig. 2 confirms this in a most direct manner inasmuch as it shows a thick particle standing on its edge and clearly reveals the stacking of the lamellae, the distance between individual platelets being about $\frac{1}{20}$ μ.

The probability of finding particles oriented in this way is greatly enhanced when they are allowed to fall onto the Formvar substrate through a magnetic field of several kilogauss. The particles become aligned so that their platelets are parallel to the field direction. All the petroleum cokes listed earlier were found to have a lamellar structure and it appears to be
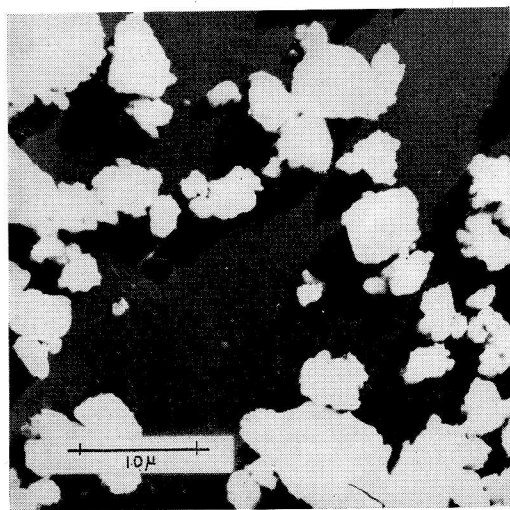
FIG. 4. Particles of Resin "C" coke which was milled after calcination to 600°C. Shadow-cast with chromium at 30° from horizontal.
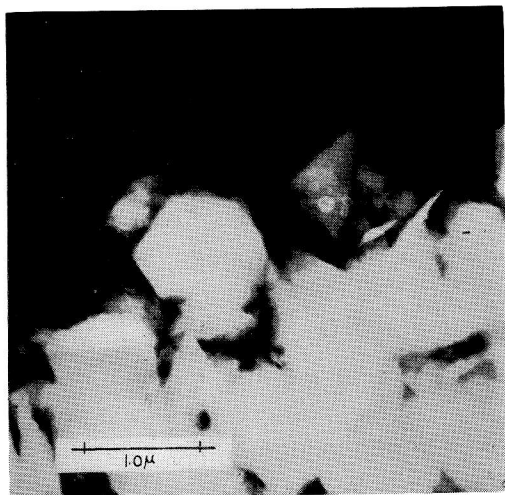

FIG. 5. Graphitized Texas coke particles made by heat-treating to 3000°C particles milled after calcination to 1250°C. Shadow-cast with chromium at 30° from horizontal.

equally well developed in all of them despite rather obvious differences in macroscopic appearance and in mechanical as well as other properties of the large pieces. These differences are due to a relatively large-scale ordering of the lamellae[7].

The micrograph of calcined phenol-benzaldehyde coke shown in Fig. 3 bears

[7] S. Mrozowski, This volume, page 31.

no evidence of lamellar structure as found in the soft cokes. The particles are roughly equiaxed as shown by their relatively long shadows and low electron transmission away from the edges. They are quite jagged and resemble fragments of broken amorphous substances.

The particles shown in Fig. 4 are those of the sample of Resin "C" coke which had been calcined only up to 600°C prior to milling and was thus in a practically raw state. The particles are equiaxed, pellet-like in shape and offer a rather striking contrast to those of the same coke shown in Fig. 1A which differs only in having been calcined to a higher temperature (1250°C).

In none of the cokes studied has it been found that graphitization produces any great changes in particle outlines. Fig. 5 and 6 illustrate this point when compared with the micrographs of calcined coke powders (Fig. 1, 3 and 4). There seems to be a tendency for development of sharp corners and straight edges in soft coke particles, as is very clearly indicated in Fig. 5, but no such changes are apparent in the cases of
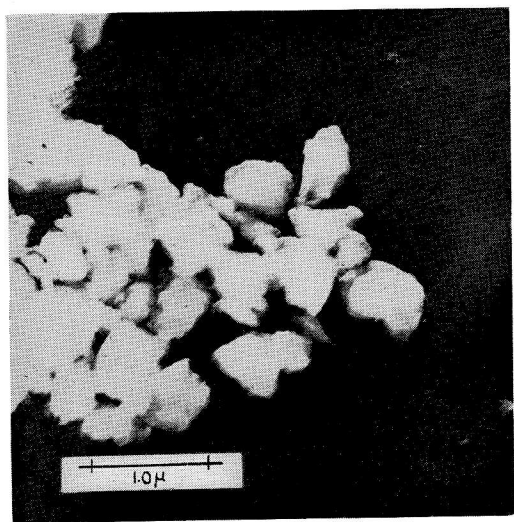

FIG. 6. Graphitized Resin "C" coke particles made by heat-treating to 3000°C a coke which was milled after heat treatment to only 600°C. Shadow-cast with chromium at 30° from the horizontal.

phenol-benzaldehyde-polymer coke (not shown) and the Resin "C" pellet-shaped particles shown in Fig. 6. Another effect of graphitization in soft cokes is the disappearance of a grainy structure in the lamellae. The individual granules are about a hundred angstroms apart in a soft coke calcined to 1250°C and may be due to statistical fluctuations in distribution of turbostratic carbon crystallites.

The mere fact that the lamellae exist suggests that they are anisotropic. The orientation of the lamellar bundles in a magnetic field indicates magnetic anisotropy, and the fact that the alignment direction coincides with the direction of the field shows that the aromatic planes are oriented parallel to the lamellar planes. The alignment in a magnetic field is a result of the very high anomalous diamagnetism of condensed aromatics.

An experiment was performed in which the finely milled Texas coke was mixed with binder pitch, the mixture containing about three parts of coke to one of binder by weight. A rod made by extruding the mix was subsequently baked and a portion of it graphitized. X-ray diffraction patterns of specimens cut out from these rods show an extremely high orientation of the microcrystals. The ratio of the intensities on the 002 diffraction ring for the directions parallel and perpendicular to the extrusion axis is about 40:1 for a graphitized rod and better than 100:1 for a baked specimen. The higher ratio is probably more representative of the degree of alignment of crystallites in the platelets, inasmuch as crystallites in the binder coke were not so highly developed and as a consequence their corresponding diffuse diffraction line interfered only slightly with the intensity evaluation. It is thus evident that the microcrystals comprising the platelets are oriented, this preferential orientation giving rise to the anisotropy observed.

The platelet-like structures found are in excellent agreement with the conclusions which Franklin[8] obtained from her exhaustive X-ray diffraction investigation of cokes. It is remarkable how well she was able, from X-ray studies alone, to discern the differences between soft and hard cokes.

The question might be asked as to when the lamellae are formed. It has been shown that the anisotropic crystallite alignment already exists in a coke which has just set (450°C)[7]. The soft coke which had been milled while in the practically raw state shows, however, no platelet structure. It therefore seems that milling destroys the preferred orientation when the coke is in a raw, somewhat plastic state.

2. Carbon Blacks

Graphitized carbon blacks when viewed directly in the electron microscope show silhouettes which are straight-sided polygons of 2; 4; 6- and 8-fold symmetry, i.e., hexagons, octagons, bevelled oblongs and bevelled squares. Such views could be projections of polyhedra having octahedral, hexagonal (D_{6h}), cubic, or tetrahedral symmetry. Replicas of graphitized "Thermax" are shown in the composite micrograph in Fig. 7. The concavity of the faces is believed to result from the high surface tension of the water with which the replicas were in contact during their preparation. Only partial views were obtained since the particles were imbedded in a resin matrix. The only types of faces which could be definitely identified were hexagonal and pentagonal. If the growth should happen to be haphazard, other types of faces should have been found. It is believed, therefore, that the growth is governed by factors which lead to the development of a definite type of polyhedron. A polyhedron is shown in Fig. 8 which has pentagonal and hexagonal faces exclusively, as well as the required projective properties. Furthermore, the net-

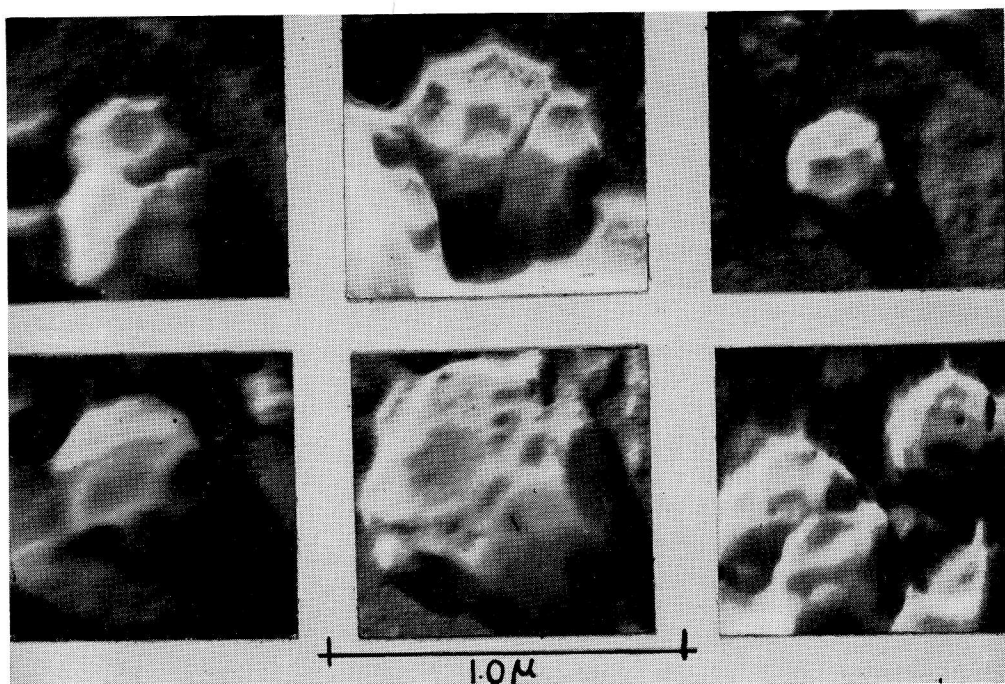[8] R. Franklin, Proc. Roy. Soc. (London) 209, 196 (1951).

FIG. 7. Several views of Formvar surface replicas of graphitized Thermax carbon black particles which were imbedded in a resin matrix. Shadow-cast with chromium at 30° from horizontal.
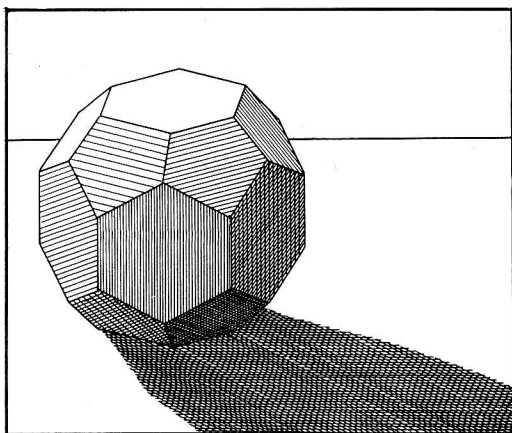

FIG. 8. A polyhedron representing the probable shape of graphitized carbon black particles.

work formed by the polygon edges satisfies the topological requirements of crystallite growth[9]. Its low symmetry seems surprising because it seems to imply the existence of a preferred direction of growth in the original particle.[10]

The micrograph in Fig. 9 represents the surface of the graphitized solid carbon rod, described in an earlier section, which was made from "Thermax" and binder pitch. The carbon black particles do not lose their individuality even after having been subjected to graphitizing temperatures while in the binder coke matrix. The explanation of this fact follows from Hall's discovery[2] that the surface microcrystals are aligned with basal planes tangent to the surface of the particle. Thus, they can only grow in the tangential direction. In addition, many of the atoms on the peripheries of these surface-microcrystallites may be connected via valence bonds to their counterparts on the adjacent crystallites. The surrounding binder coke, having random arrangement of

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[9] For a review of the topological factors governing growth processes, see the article by C. S. Smith in "Metal Interfaces—A Seminar", Am. Soc. Metals, Cleveland, Ohio (1951).

[10] It is interesting to note that similar polyhedra have been observed in biological structures. See D'Arcy W. Thompson, "On Growth and Form," 2nd Edition, Cambridge, 1942.
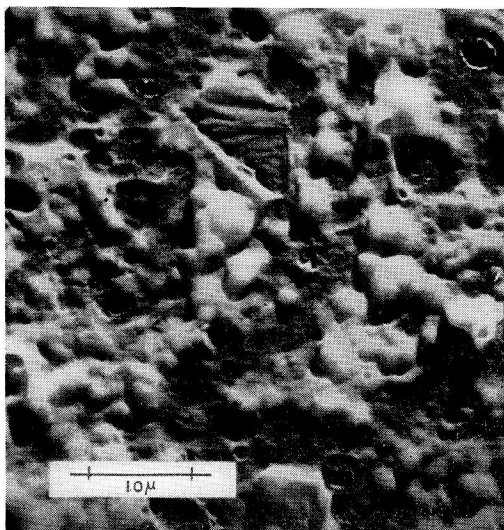
FIG. 9. Chromium shadowed Formvar replica of the surface of a broken graphitized carbon rod made of Thermax and binder pitch. Shadow angle: 45°. Triangular area in upper part may be a grain of soft coke contaminant, inasmuch as it exhibits a lamellar structure.
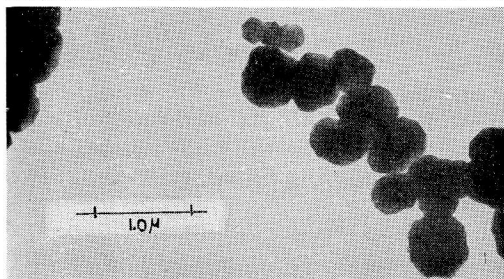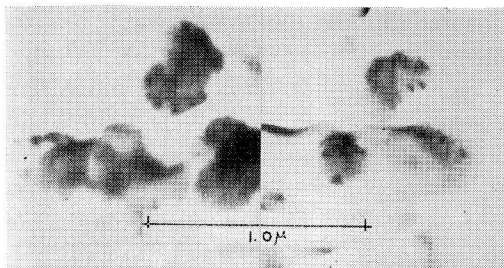

FIG. 10. Graphitized P-33 particles (above), and graphitized Thermax particles (below). Heat treatment temperature: 3000°C.

its crystallites, is unable to form many linkages with these crystallites on the carbon black surfaces which expose only their basal planes. It appears, therefore, that carbon blacks are closed systems with respect to crystalline growth.

The graphitized particles of "Thermax" and P-33 in Fig. 10 show internal structure, the differences in photographic density probably being due to Bragg scattering by the crystallites and indicating differences in orientation rather than thickness[11]. The micrographs of P-33 whose small size allows greater electron transmission clearly suggest that the particles are composed of crystals of pyramidal shape, whose bases correspond to the polyhedral faces. This internal structure shows that the orientation of microcrystals occurs throughout the particle and not merely on the surface. The basal planes of the adjacent crystallites in the polyhedral carbon blacks are probably also hooked together by valence bonds inasmuch as the particles are very rigid; no broken ones have ever been identified. The angles between adjacent planes in the polyhedron (Fig. 8) even suggest that the edge atoms are in tetrahedral valence states since for such angles there would be bond strains of no more than about 10 degrees required. There is no way, however, of avoiding lattice distortions at the edges without a change in the lattice spacing. In the P-33 particles shown in Fig. 10, narrow light areas can be seen separating the neighboring pyramidal crystallites which might be due to a decrease in Bragg scattering caused by such lattice distortions occurring near the edges of the crystallites.

If the microcrystals were oriented on a planar surface instead of a spherical one, graphitization would tend to result in formation of a single crystal as a result of the requirement that the total energy be a minimum. In the case of carbon blacks, the ultimate result of graphitization due to the restriction imposed by the original surface alignment can only be a polycrystal (polyhedral in form) having the fewest number of crystallites possible compatible with the lowest total energy. Doubtless there would be a tendency for the individual crystallites

[11] R. D. Heidenreich and L. Sturkey, J. App. Phys. **16**, 97 (1945).

to develop hexagonal outlines, but it is impossible for all of them to do so because of the impossibility of constructing a polyhedron having hexagonal faces exclusively. It seems that the polyhedron shown in Fig. 8 represents a surface of minimum total energy compatible with the imposed restriction[9].

The pellets of raw Resin "C" coke, though they externally resemble large carbon black particles, probably have a random arrangement of their microcrystals and therefore do not graphitize into polyhedra. This is of particular interest in view of the fact that such random structures correspond closely to the model of carbon black particles proposed by Biscoe and Warren[12].

IV. CONCLUSIONS

Electron micrographs of particles of calcined cokes show that all soft cokes break up in grinding into platelets and furthermore that the platelets are stacked into lamellar bundles. This structure is, therefore, basic to all soft cokes. The microcrystals in the platelets are oriented with their basal planes parallel to the lamellar planes and as a result, the lamellae exhibit strong, diamagnetic anisotropy and can be aligned mechanically to produce a highly anisotropic product. The microcrystalline orientation can be destroyed by milling the cokes while they are in the raw, somewhat plastic state. Hard cokes all break up into jagged, roughly-equiaxed particles,

characteristic of amorphous substances. Graphitization produces some minor changes in the shape of soft coke particles (development of straight edges and sharp corners) and results in the disappearance of a granular structure (the individual granules probably being clusters of microcrystallites). No changes were observed in the cases of the hard cokes, and of the disoriented soft coke pellets.

Thermal carbon blacks crystallize into polyhedra during graphitization. It seems that all replica views of such particles are consistent with the existence of a single type of polyhedron into which the spheroidal particles become transformed. The graphitized particles are polycrystals whose faces are basal planes of graphite; they are thus closed systems with respect to crystal growth and cannot grow out into the carbon matrix in which they may be imbedded. Probably this shape of the particles is dictated by the minimum energy requirement.

Since soft cokes, hard cokes, and carbon blacks are formed respectively from liquid, solid and gas phase organics, it is obvious that the phase of the starting material very decisively influences the graphitization process.

[12] J. Biscoe and B. E. Warren, J. App. Phys. 13, 364 (1942).