BINDER FOR THE IDEAL ANODE CARBON

by

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Abstract

Experiments with many different kinds of binder filler combinations for anode paste formulation have shown that the ideal binder, which can be made from either bituminous coal or petroleum, should produce a rather isotropic coke to best achieve the most desirable properties of anode carbon. The normal production process for coal-tar pitch results in such a binder, where the binder coke is disorganized by primary quinoline-insolubles formed in the vapor space above the coal in the coking ovens. However, for both coal-tar and petroleum pitches, the process can be improved by either changing the thermal treatment variables, or addition of selected artificial quinoline-insolubles.

Introduction

The requirements for good anode carbon are (1):

1) low oxidant-accessible surface with less than 15% porosity due to pores larger than one micron,
2) high, uniform oxidation resistance of all filler and binder cokes to air (O_2) and CO_2, and,
3) impurities present to a miximum of a few tenths of one percent carbon ash content, excluding bath salt (<1-2%), and minimum sulfur content.

Related to the above requirements, Table I indicates the ranges for important anode carbon property values.

Table I

Preferred Anode Carbon Property Value Ranges (2, 3, 4, 5)

Baked Density	1.40 – 1.65 g/cc
Electrical Resistivity	0.0050 – 0.0075 ohm-cm
Compressive Strength	350 – 500 kg/cm^2
Bending Strength	60 – 80 kg/cm^2
Young's Modulus	800 – 1000 X Bending Strength
Coefficient of Thermal Expansion	3.5 – 5.0 X 10^{-6}/°C
Thermal Conductivity	3.5 – 5.5 W/m °C
Thermal Stress Resistance	BS X TC/YM X CTE $\geq$ 1.50
Total Porosity	<30%
Nitrogen Permeability	5 – 15 centidarcy units
BET Surface Area	1 – 2 m^2/g
Airburn at 550°C	$\leq$20 (excellent) to $\geq$80 (poor) mg/cm^2/hr
CO_2 Oxidation at 970°C	$\leq$10 (excellent) to $\geq$50 (poor) mg/cm^2/hr
Laboratory Electrolytic Test (no airburn)	110 – 115% (prebake), 120 – 125% (Soderberg)

A. Tomsett and J. Johnson (Eds.), *Essential Readings in Light Metals*

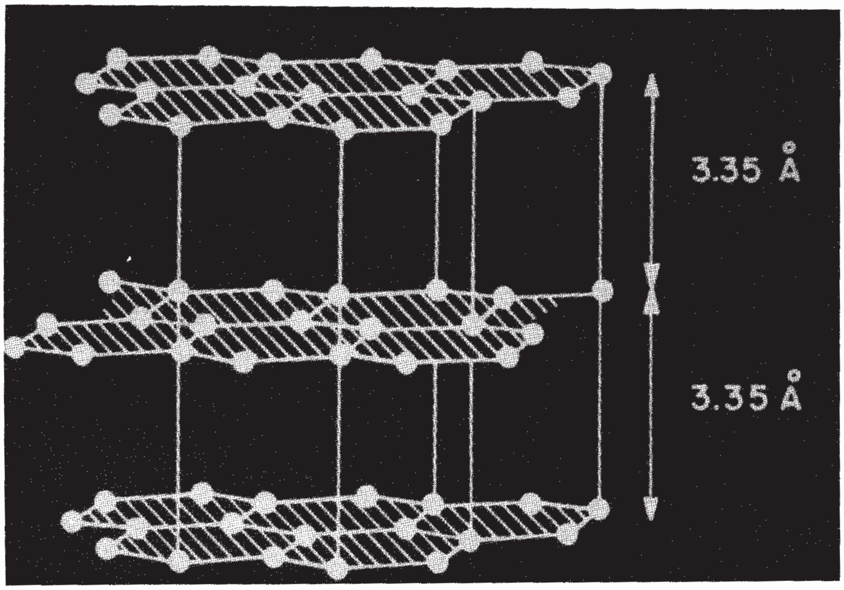

Figure 1
Graphite Crystal Structure

From the above requirements and specifications, it can be determined that the ideal anode carbon should be a composite consisting of a relatively-anisotropic (ordered) filler with low impurity content and low coefficient of thermal expansion, and a relatively-isotropic binder coke also with low impurity content. When properly formulated, such a composite would have the desired characteristics of high, uniform oxidation resistance and high thermal shock resistance (6). This composite would have a high density (1.55 – 1.60 g/cc), high strength and thermal/electrical conductivity, and a low coefficent of thermal expansion. While such a composite would give excellent anode performance at any smelter, practical considerations about economics and the quality of available raw materials would determine how closely one could approach the production of the ideal anode carbon. While such carbon consists of 80-90% filler coke, it is important that this filler be held in place by strong, conductive bonds of the remaining 10-20% of binder coke. This paper will be devoted to examination of the role of the binder coke in producing the ideal anode carbon.

Mechanism of Bond-Coke Formation

Anode filler particles are held in place by both physical and chemical bonds derived from the binder pitch. Physical bonding can occur because of the irregular, angular shapes of filler particles, and because of binder penetration into the pores present in these particles (7). Chemical bonds can be formed between the edges of graphite crystallites, of which coke filler particles are composed, and the pitch binder during pyrolysis. The mechanism for the bond formation process can be best understood by examination of the details of the chemistry and physics of carbon related to this phenomenon (8). The primary building blocks of all anode carbon are graphite crystallites, with the hexagonal structure shown in Figure 1. This structure consists of weakly-bound layers of carbon atoms arranged in hexagonal networks. Graphite crystallites are very anisotropic, having large differences in property values perpendicular and parallel to the carbon atom layers. Some of these differences are shown in Table II (9). For anode carbon, the physical and chemical properties of both filler and binder cokes depend on how the graphite crystallites are ordered. Examples of ordered and disordered crystallite structures are shown in the diagrams in Figure 2 (10) and for ordered and disordered filler coke structures in Figures 3 and 4, respectively. The degree of order for binder coke structure depends on the extent to which crosslinking reactions occur during binder pyrolysis. The most common crosslinking agent present in binder pitches is primary QI. The role of primary QI in disordering binder coke structure has been investigated extensively (8). If pitch is heated to temperatures near 400°C, spherical liquid-crystal struc-

Table II
Graphite Crystal Property Values

Property	Units	Property Value
Density	g/cc	2.267
Interlayer Spacing	Å	3.354
Electrical Resistivity	ohm - cm	
Parallel		4×10^{-5}
Perpendicular		0.01 to 1.0
Thermal Conductivity	watts/cm – °K	
Parallel		2 to 5
Perpendicular		0.4 to 0.8
Thermal Expansion	$°C^{-1}$ (20-100°C)	
Parallel		-1.5×10^{-6}
Perpendicular		27×10^{-6}
Reaction with Air (900°C)		
Parallel		2.2×10^{3}
Perpendicular		1.6×10^{-9}
Reaction with CO_2 (1100°C)		
Parallel		25
Perpendicular		0

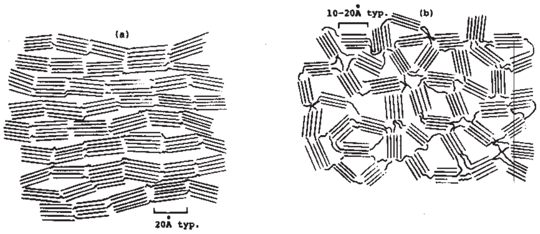

Figure 2
Diagrams Of Ordered and Disordered Crystallite Structures

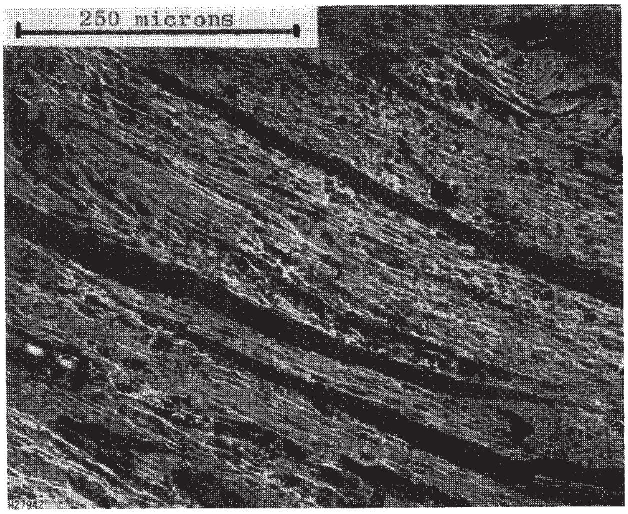

Figure 3
Ordered Filler Coke Structure

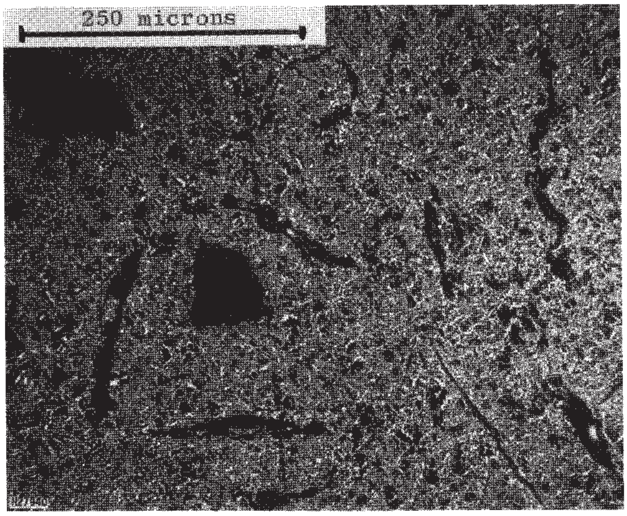

Figure 4
Disordered Filler Coke Structure

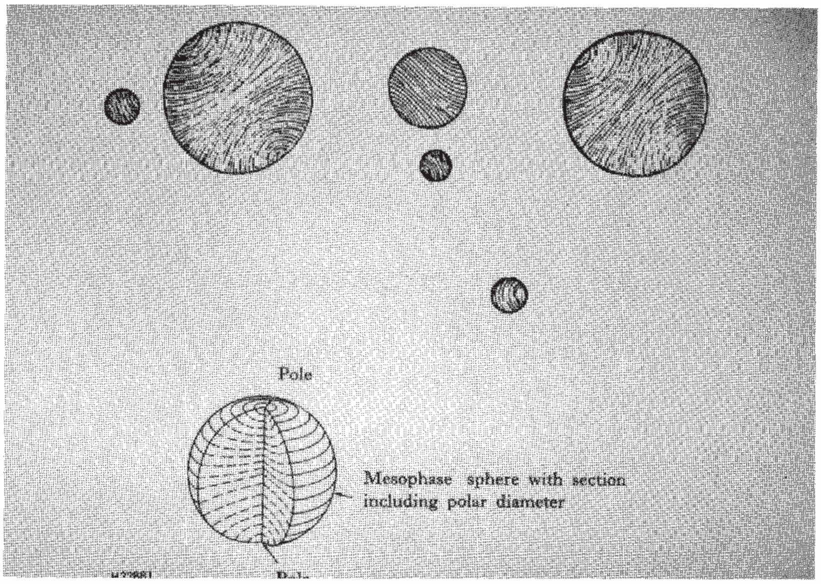

Figure 5
Structure of Pitch Mesophase Spheres at 400°– 500°C

tures, 10 to 50 microns in diameter, called "mesophase", will appear in the isotropic liquid (11). The mesophase spheres have the layered structure shown in Figure 5, where the layers are precursors of graphite layer planes which develop as pyrolysis continues. In the absence of crosslinking agents, the mesophase spheres will coalesce as shown in Figure 6. When coalesced mesophase contacts a graphite crystal, or coke particle, the mesophase layers will align parallel with the layers of the graphite and no bonding is possible at such contacts. However, at the edges of the graphite crystal, mesophase layers will align to extend these edges by chemical bonds as pyrolysis continues. These contacts of mesophse with natural graphite flakes are

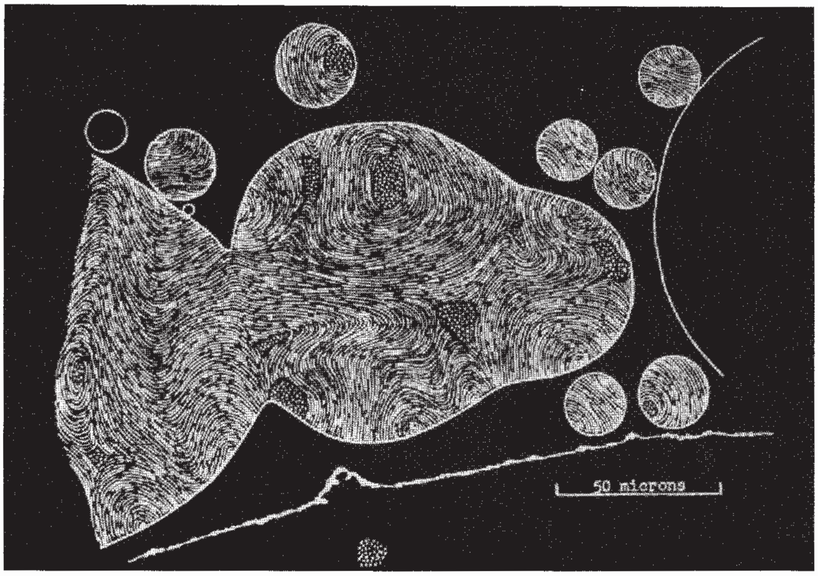

Figure 6
Coalescence of Mesophase Spheres Between Coke Particles

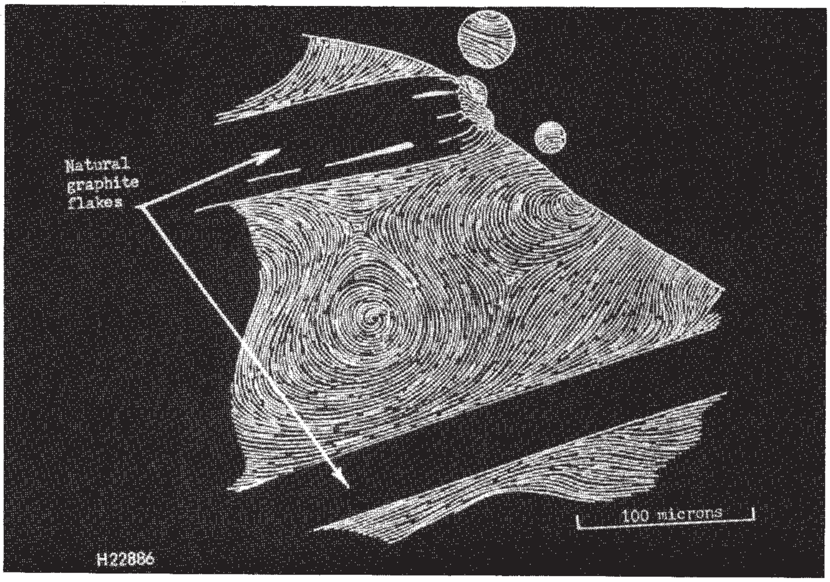

Figure 7
Alignment of Mesophase Layers With Graphite Surfaces

shown in Figure 7. As pyrolysis continues to 800°C, liquid mesophase solidifies, and shrinkage cracks develop primarily by separation of the graphite layer planes at stress points as shown in Figure 8. In the absence of crosslinking reactions to disorder the developing graphite crystallites, such structures will be weak to shear stresses and crystal cleavage which are characteristic of graphite crystal structure.

Bond Formation In Various Carbon Composites

An investigation has been made of the bonds formed between coke particles of different structure in order to understand how to produce better bonds in anode carbon composites. Bond quality depends on the shape, size, and structure of the filler particles and on binder composition. For filler particles, angular profiles permit the particles to lock in place during paste compaction, and are more easily gripped physically by binder coke. Smaller particles require more binder to coat their greater surface area, per unit weight, and are more securely held in well-mixed paste. Filler particle structure is important in two respects, (1) the amount of accessible porosity which is penetrated by binder, and (2) the relative amounts of exposed surface as crystallite graphite (a) layer planes and (b) edges. Finally, the amount and structure of binder coke will depend on the molecular composition and, in particular, the presence of crosslinking agents.

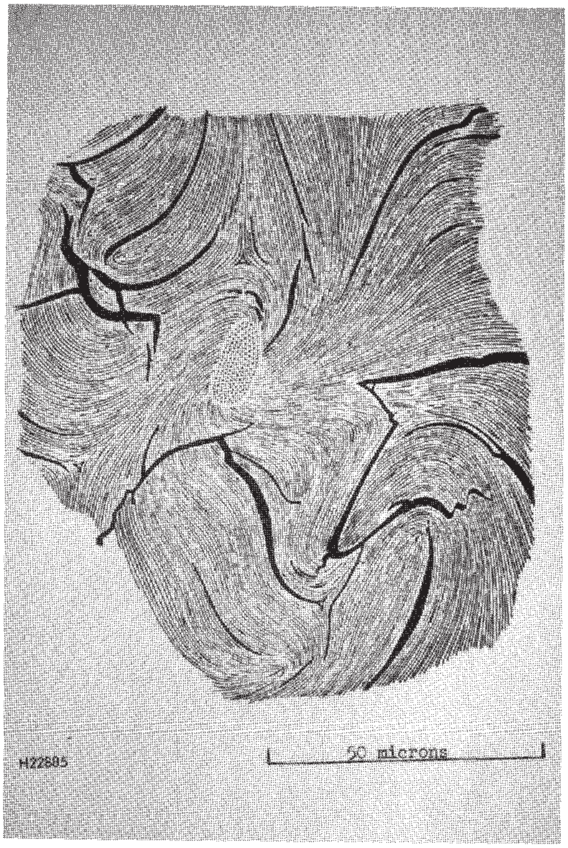

Figure 8
Shrinkage Cracks in Mesophase – Derived Coke at 800°C

Figure 9
Microstructure of Baked, Well-Mixed, Compacted Anode Paste

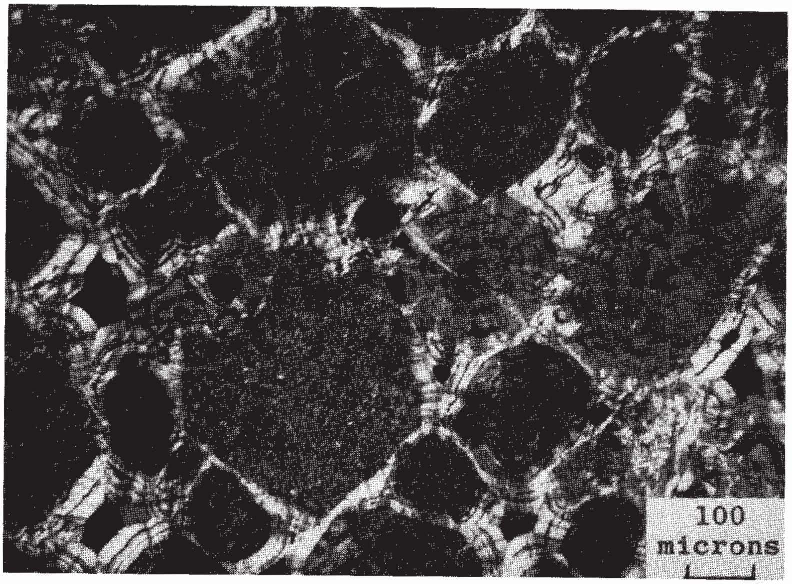

Figure 10
Anisotropic Pyrolytic Carbon-Bonded Composite

Figures 9 and 10 show the microstructures of two very different carbon composites. Figure 9 is the microstructure of a baked, well-mixed, compacted anode paste with strength and oxidation resistance satisfactory for use as anode carbon. The binder is coal-tar pitch. Figure 10 is a composite of anode filler coke bound with 22% pyrocarbon from thermal decomposition of hydrocarbons. This second composite has highly ordered binder coke where the highly oxidation – resistant graphite layer planes protect the oxidation – sensitive filler so well that the composite exceeds anode carbon specifications for oxidation resistance. At the same time, even though the amount of pyrocarbon binder is about twice the amount of pitch-coke binder for the composite in Figure 9, the composite in Figure 10 has a compressive strength of only about 700 psi, far below the strength range for acceptable anode carbon. The reason for this deficiency is the well-known weakness of graphite crystallites to shear stresses and cleavage of the basal planes.

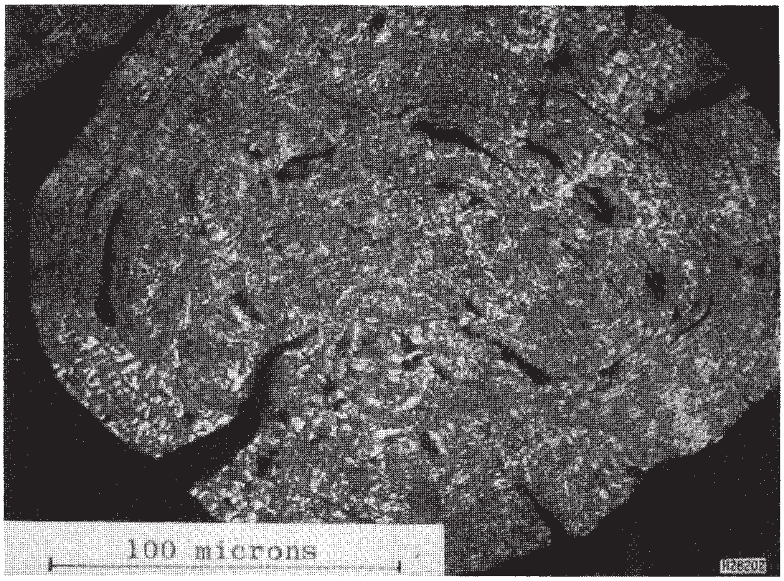

Figure 11
Onion-Like Microstructure of a Fluid Coke Particle

Figure 11 shows the cross-sectional microstructure of a fluid coke particle, one well-known anode filler coke. Such coke has an onion-like structure because of the nature of the fluid bed process used to produce it. When used as anode filler, bond formation is more difficult because of the spherical particle shape. However, by using milled particles as fines, and with binder penetration into pores, statisfactory bonds can be obtained. Figure 12 shows a fracture surface of a baked fluid coke composite with coal-tar pitch binder. The binder has coated the particle with enough bonding to the top surface so that part of this surface was removed during fracture. While satisfactory bonding can be achieved with ordinary fluid coke and coal-tar pitch with ~ 10% primary QI, this is not true for pyrocarbon-coated fluid coke with the microstructure shown in Figure 13.

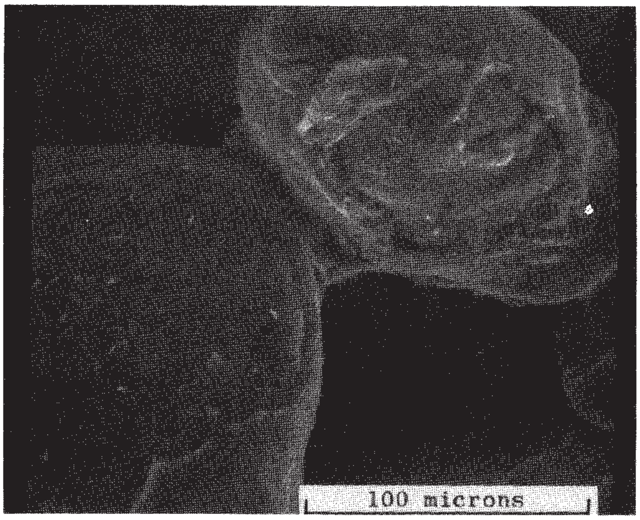

Figure 12
Fracture Surface in a Baked Fluid Coke Composite with Coal-Tar Pitch Binder

Here, the spherical particles have a surface consisting entirely of graphite crystal planes. This surface cannot form chemical bonds with the pitch binder. Hence, there is no physical or chemical bonding to these particles, and baked composite strength is that of the binder-coke matrix, which is reduced to a compressive strength of a few hundred psi as pitch primary QI is reduced to zero.

In this investigation, it has become very clear that primary QI plays an important role affecting the degree of graphite crystallite order in the binder coke between filler particles. A more disordered binder coke produces a stronger binder coke matrix with more opportunity for chemical bonding to filler particles in addition to physical bonds. In addition to strength considerations, disordered binder coke has less open porosity and thus also protects the underlying filler from air and CO_2 oxidation better than a more ordered anisotropic coke (5, 8).

Significance of Primary QI to Binder Quality

The primary QI in binder pitches has been found (8) to function as an agent to confuse mesophase sphere coalescence and thereby produce disordered binder coke which tends to increase composite strength and oxidation resistance (5). While ordinary primary QI functions quite well in this role, it has been found that selected carbon blacks work even better. In particular, lampblack with a surface area of 20 – 40 m^2/g has been found (12) to be even more effective in producing disordered binder coke. While other high-surface blacks with surface areas greater than 100 m^2/g were also examined, the most useful range was found to be ~ 20 – 70 m^2/g. Higher surface blacks were more difficult to disperse in the binder. Ordinary primary QI has a surface area of ~ 5 – 10 m^2/g, and is produced in escaping tar vapor in the space above the coal in the coke ovens. Comparison of the structures of ordinary QI and lampblack is shown in Figure 14. Both structures are formed by the well-known mechanism for carbon black formation (13, 14). The structures of typical single

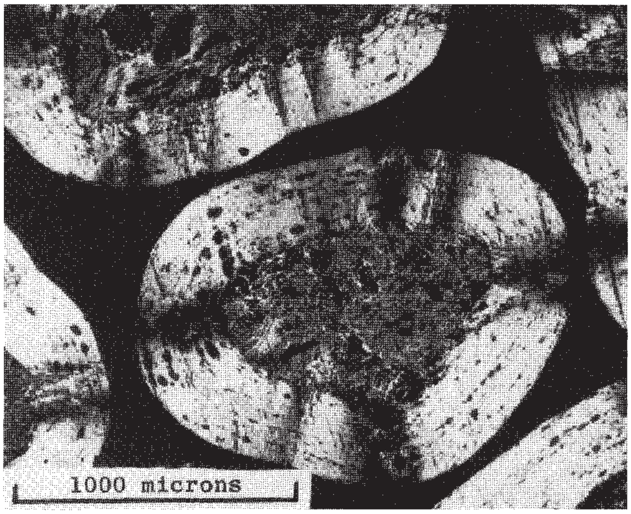

Figure 13
Microstructure of Pyrocarbon-Coated Fluid Coke

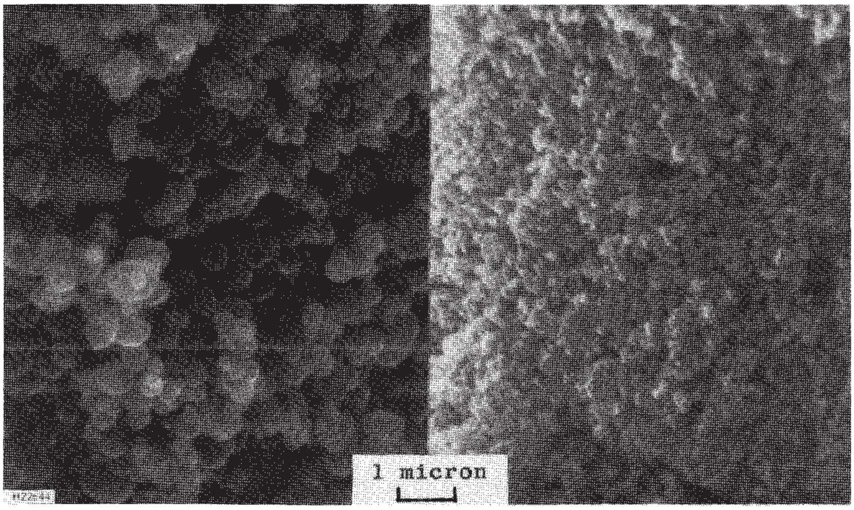

Figure 14
Comparison of Primary QI With Lampblack

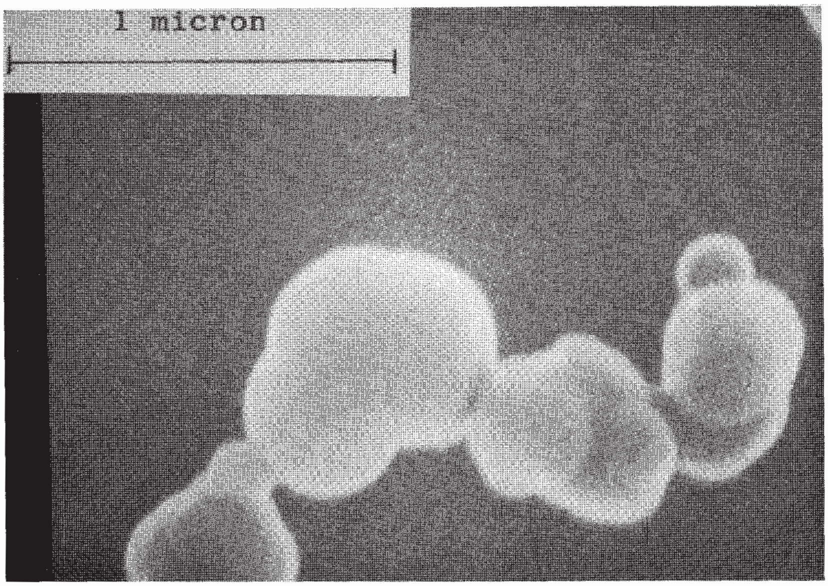

Figure 15
Microstructure of a Typical Primary QI Particle

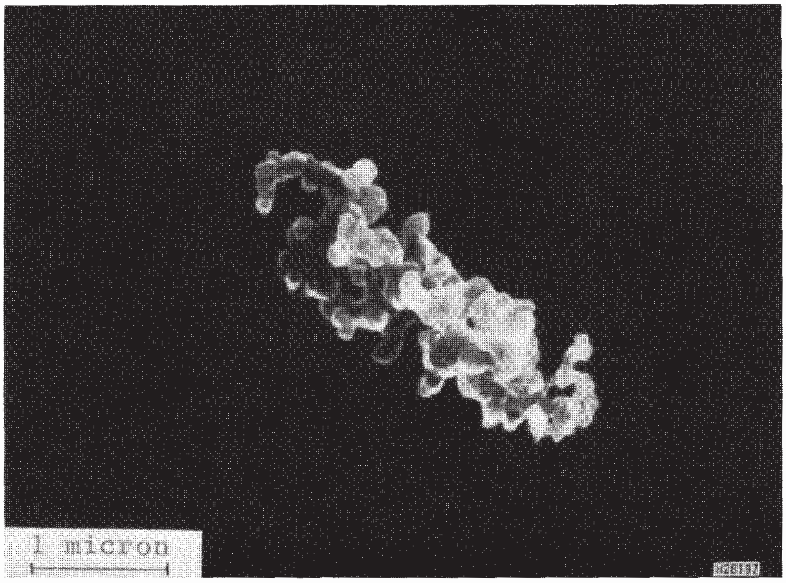

Figure 16
Microstructure of a Typical Lampblack Particle

particles of primary QI and lampblack are shown in Figures 15 and 16, respectively. During formation, a series of submicron spheres are created in the gas phase which subsequently aggregate into chain structures. Sphere size and chain length vary with residence time and temperature of the vapor phase. Binder coke structure has been examined as a function of the amount and type of QI present. With no QI present, baked coalesced mesophase coke has the structure shown in Figure 17. For a

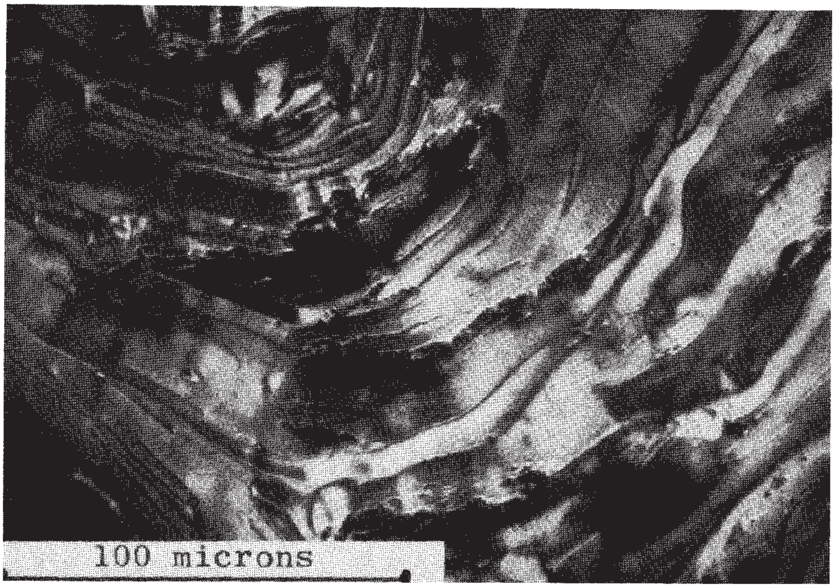

Figure 17
Structure of Baked Mesophase Coke Containing No QI

typical coal-tar pitch with 10% primary QI, the corresponding baked pitch coke has the structure shown in Figure 18. The light areas of anisotropic, ordered, coke have been substantially reduced from that in Figure 17. The dark areas of isotropic, disordered, coke occupy a considerable part of the figure, and the uneven distribution of the two areas indicate a corresponding uneven distribution of primary QI in the original pitch. When this pitch is reconstituted by replacing the original 10% primary QI with 10% lampblack, the corresponding baked pitch coke has the structure shown in Figure 19. Here, the light anisotropic coke

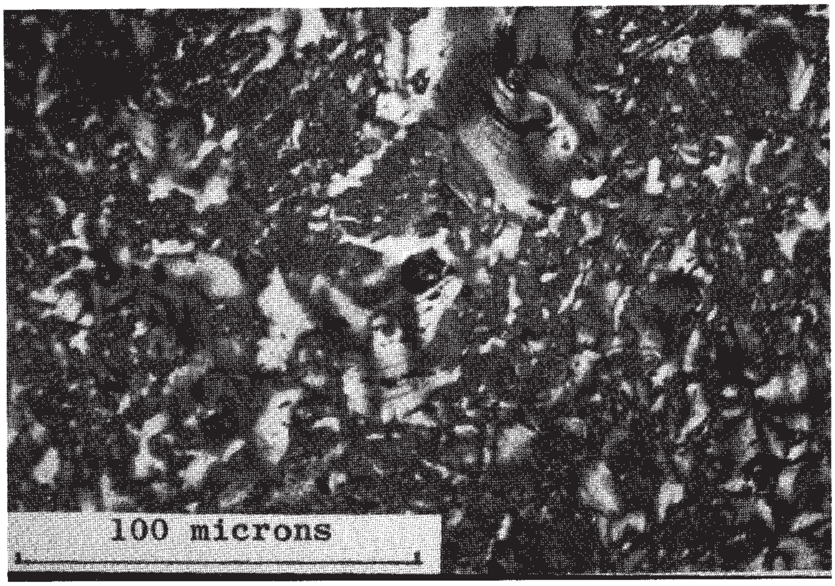

Figure 18
Structure of Baked Coke for Coal-Tar Pitch Containing 10% QI

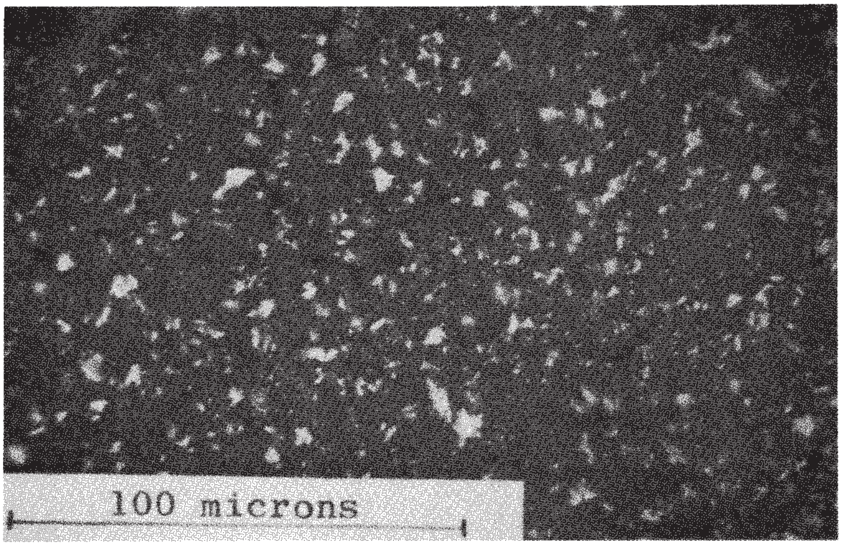

Figure 19
Structure of Reconstituted Coal-Tar Pitch Coke with
10% Lampblack Substituted for Original QI

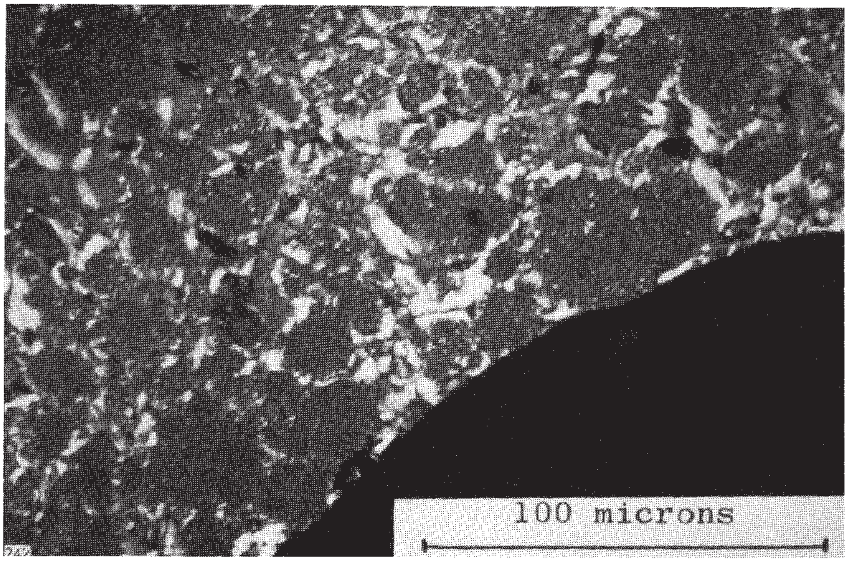

Figure 20
Structure of Baked Coke for Coal-Tar Pitch Containing 20% QI

areas are the minority constitutent, but are distributed rather evenly in the majority areas of isotropic coke. This indicates the lampblack has been rather evenly dispersed in the original pitch. The contrast continues between original primary QI and lampblack in affecting pitch-coke disorder when comparing the baked cokes from coal-tar pitch containing 20% primary QI in Figure 20 with that from mesophase containing 20% lampblack in Figure 21. Finally, when 20% lampblack is added to coal-tar pitch containing 10% original primary QI, the resulting baked pitch coke exhibits the extremely isotropic structure shown in

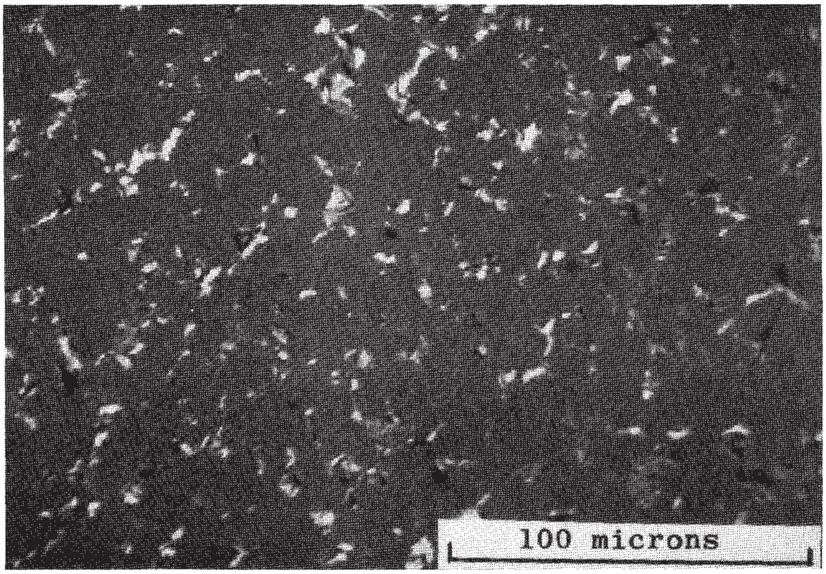

Figure 21
Structure of Baked Mesophase Coke Containing 20% Lampblack

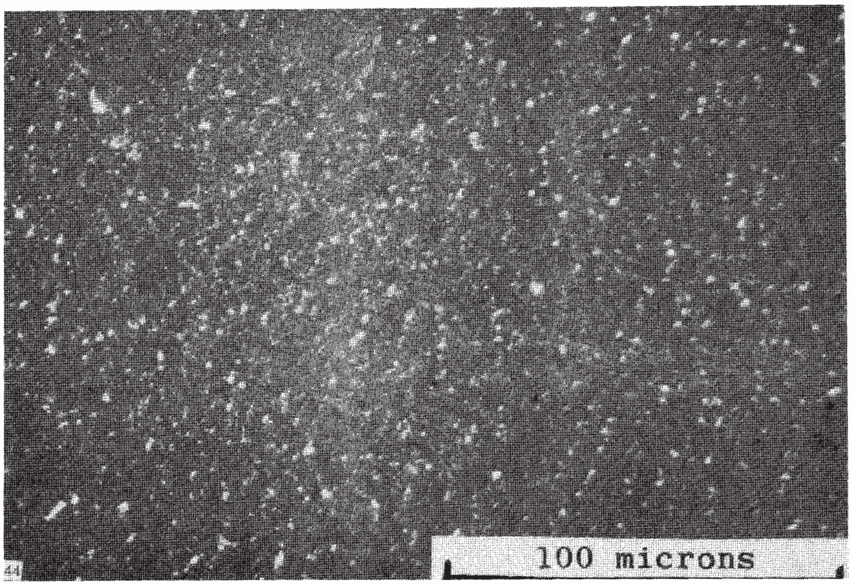

Figure 22
Structure of Baked Coke for Coal-Tar Pitch
Containing 10% QI and 20% Lampblack

Figure 22. It is thus clear that lampblack is completely compatible with pitch whether used in substitution for or in addition to original primary QI. We believe the presence of QI in binder pitches, whether original or artificial, can contribute significantly to bond-coke quality in (1) increasing bond strength significantly, and in (2) protecting the underlying filler from both airburn and CO_2 oxidation. The most contrasting form of these two bond types are shown in the microstructures of baked carbon composites in Figures 23 and 24 for petroleum pitch with no primary QI and for coal-tar pitch with 27% original QI. It has been reported (18) that the original QI in coal-tar pitches also contains significant levels of impurities in some tars, associated with coke oven operation. For such situations, low-ash lampblack might be substituted to maintain pitch QI level and improve binder quality.

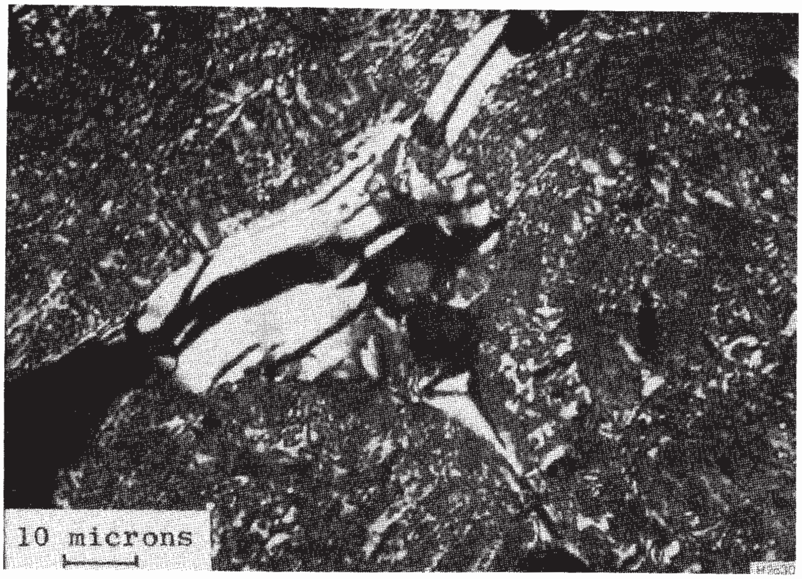

Figure 23
Microstructure of Pitch-Coke Bond from
Petroleum Pitch Containing No Primary QI

While the QI content in coal-tar pitches comes as a natural advantage of the method of production, this has generally not been true for petroleum pitches which have not received severe thermal treatment. However, PACCAL pitch (19), derived from deep thermal cracking of petroleum, did contain ~ 10% primary QI and appears to have been well received by the aluminum industry. Also, coal-tar pitch with primary QI as high as 25% has been used quite satisfactorily in an aluminum smelter.

Practical Considerations For Bond-Coke Improvement

The above results indicate that coal-tar pitch binder, with ordinary primary QI, has an important advantage in producing disordered bond coke not found in most petroleum pitches. To test this conclusion further, a few experiments have been carried out using full-size prebake anodes in normal reduction cell operation. The results (17) appear to indicate that the experimental anodes give

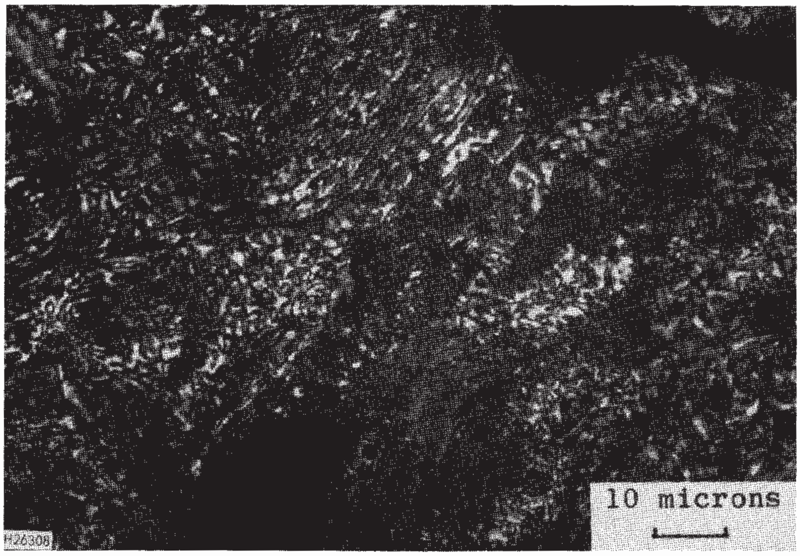

Figure 24
Microstructure of Pitch-Coke Bond from
Coal-Tar Pitch Containing 27% Primary QI

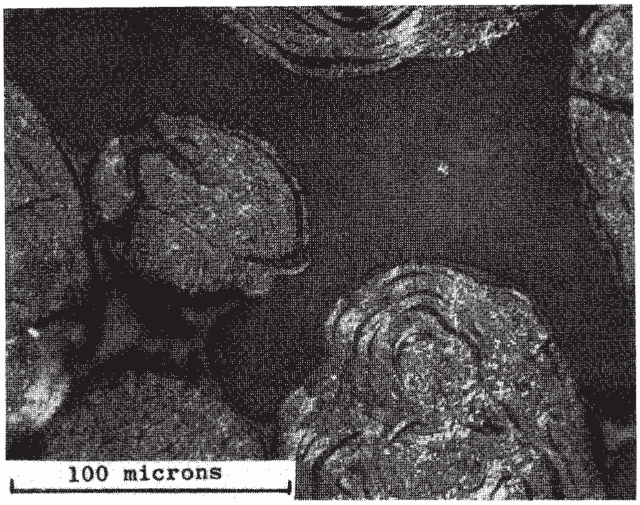

Figure 25
Poor Wetting of Filler by Pitch Binder at 160°C

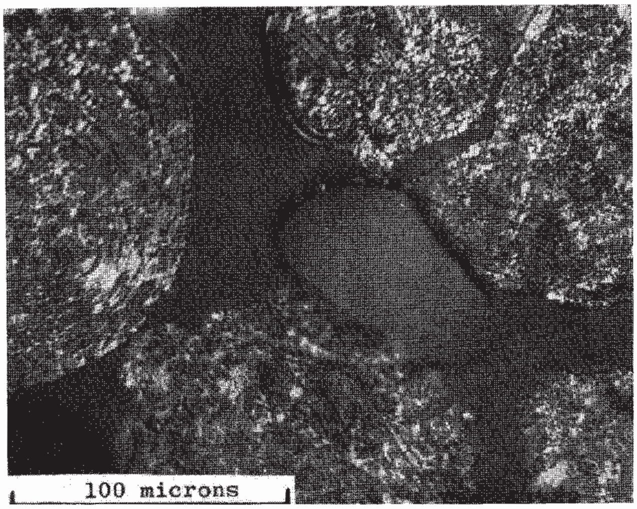

Figure 26
Good Wetting of Filler by Pitch Binder

better performance than the reference anodes, but the test needs to be expanded to involve enough anodes to give statistically significant results.

One other important factor in obtaining the highest quality bonds with QI-disordered coke is to achieve good wetting of the filler particles by the pitch binder (15, 16), with binder penetration into all existing porosity with diameters down to 5-10 microns (7). This condition may well not be achieved during the paste mixing operation. An example of poor wetting of the filler is shown in Figure 25, involving coal tar pitch binder at 160°C. While binder viscosity is low enough (a few thousand cp) to give well-mixed paste within an hour, wetting indicates a high contact angle and little pore penetration. This condition is not unusual at this temperature, and it is known (15) that complete wetting (low contact angle) with maximum pore penetration, such as that shown in Figure 26, does not occur below 180°C. However, as long as good paste mixing has been achieved, wetting and pore penetration will occur during the bake operation, and high-quality pitch-coke bonds will be produced.

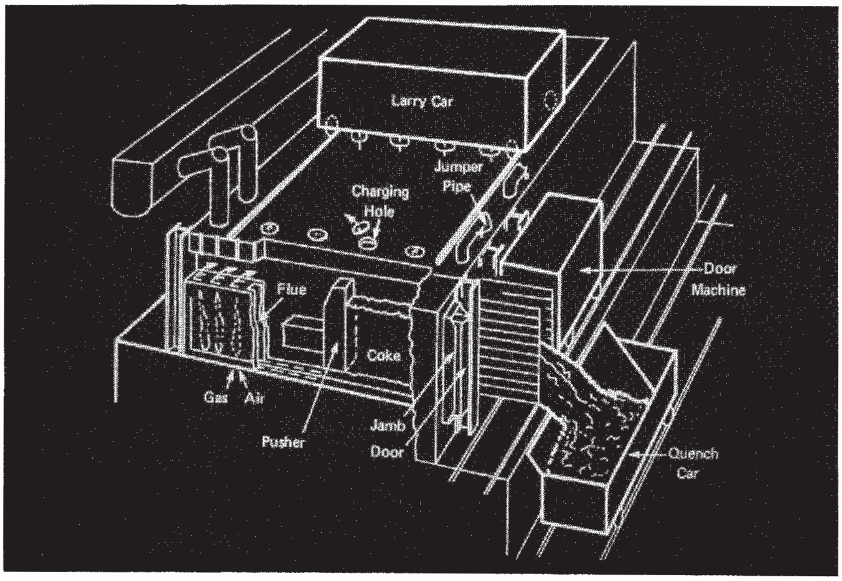

Figure 27
Diagram of Coal Coke Oven Structure

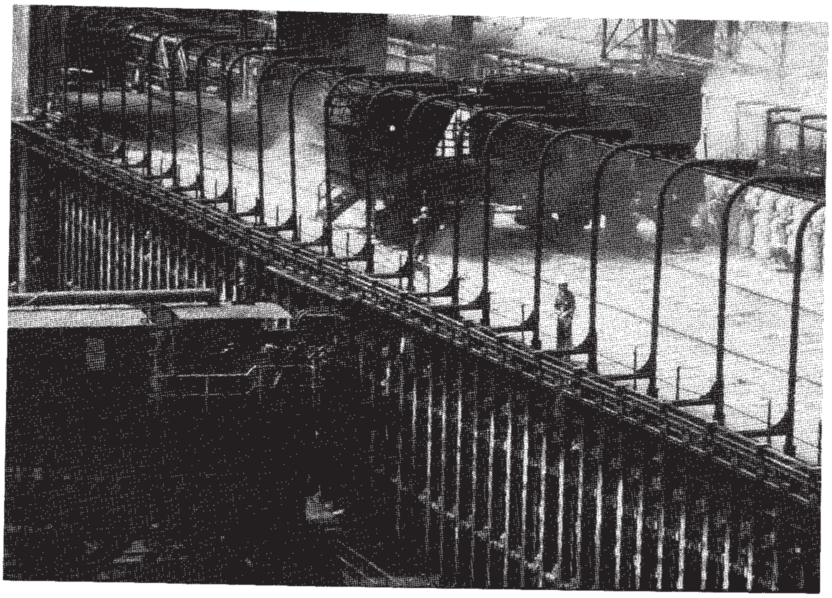

Figure 28
Photograph of Coal Coke Oven Operations

In order to apply the results of this investigation to produce the highest quality disordered binder coke, it is necessary to add lampblack-type QI to appropriate coal tars and petroleum fractions, or to generate the lampblack QI directly in these materials by changing the thermal treatment involved in binder production. Since coal-tar pitch already contains natural QI developed during coal coke oven operation, it appears easier to modify this operation to improve binder quality, than the corresponding action to improve petroleum-based binder. The required change in coke oven operation can be best appreciated by reference to the drawing of the coke oven structure in Figure 27, and the corresponding photograph of such a structure in Figure 28. In summary, coal is loaded into slot ovens which, to make furnace coke, operate at 1100-1200°C for 10- 20 hours, during which time gases, including coal-tar vapor, are emitted from the coal charge and removed from the top of the oven. Primary QI is produced in the tar vapor in the space above the coal and later becomes suspended in the condensed tar which is subsequently converted to pitch binder by distillation to remove about half of the most volatile species. The data in Table III show the variation of gas composition from a 4-meter oven over a coking cycle of 14 hours. The coal charge is 13.4 tons (dry). Oven width is 16 inches and length is 47 feet. The oven is loaded with coal to a height of 13 ft., which subsequently shrinks to 12 feet, 8 inches. Oven roof line is at 14 feet, 2 inches. From this information, and the data in Table III, it can be determined that tar vapor residence time in the oven at 1100-1200°C is 10-20 seconds to produce QI with the structure shown in Figure 15. To produce the more desirable structure of lampblack-type QI shown in Figure 16, it is necessary, according to the mechanism for carbon black formation (13, 14) to reduce coke oven vapor space by a factor of ten to reduce tar vapor residence time to 1-2 seconds. It is also necessary to increase the temperature of the vapor space by 200-300°C to 1400°C. This might be possible by careful, controlled addition of air to the top of the oven. Thus, it is necessary to evaluate the practical benefits realized by pitch binder coke disordered with lampblack QI in producing higher quality anode carbon against the cost of either adding lampblack to the binder, as artificial QI, or else changing coke oven operating conditions to produce such lampblack-QI directly in the coal tar coming from the oven.

Table III
Variation of Coke Oven Gas Analyses During Coking Period

Hours after Charging	Percent by Volume of Moisture-Free Gas						Gas Produced (Cu ft/hr)
	CO_2(+H_2S, etc)	Hydrocarbons Other Than CH_4	CO	CH_4	H_2	N_2	
1	1.6	4.6	4.9	34.8	52.0	2.1	11,900
2	1.7	4.4	4.6	33.6	53.4	2.3	10,600
3	1.8	4.0	4.5	32.4	54.8	2.5	13,800
4	1.9	3.6	4.9	31.0	56.0	2.6	13,000
5	2.0	3.2	4.9	30.0	57.2	2.7	13,000
6	2.1	2.6	5.3	28.8	58.4	2.8	13,600
7	2.2	2.2	5.5	27.6	59.5	3.0	14,000
8	2.1	1.8	6.0	26.4	60.6	3.1	13,600
9	1.9	1.4	6.7	25.0	61.8	3.2	13,200
10	1.4	1.0	6.2	22.0	66.0	3.4	14,800
11	0.8	0.4	7.0	16.2	72.0	3.6	9,100
12	0.4	–	6.5	11.0	78.0	4.1	–
13	0.3	–	4.6	5.6	84.0	5.5	–

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