ELECTRODE BINDER PYROLYSIS AND BOND-COKE MICROSTRUCTURE

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The pyrolysis characteristics and coke microstructure of a large variety of electrode binders have been examined. Examination techniques included (1) thermogravimetric analysis with simultaneous differential thermal analysis, (2) optical and scanning electron microscopy, (3) proton nuclear magnetic resonance analysis, and (4) bond-coke strength measurements. Coal-tar pitches exhibited more uniformity in pyrolytic behavior than the petroleum pitches studied. Petroleum binder quality varied widely from unacceptable to essentially equal that for coal-tar pitch. While early stages of pyrolysis are basically endothermic for all binders, the later stages involve several exotherms related to the carbon polymerization process. In particular, exotherms at about 430°C and 470°C were repeatedly observed, both singly and together, which appeared to be related to binder aromaticity and degree of condensation. Quinoline-insoluble levels up to at least 20% improved bond-coke microstructure by increasing disorder with minimum coke shrinkage. However, crosslinking the binder with oxidation treatments tended to produce an undesirable amount of bond shrinkage, apparently due to early solidification of the mesophase.

Introduction

In the formation of binder-coke bonds between anode filler particles, pitch-coated compacted, calcined aggregate is subjected to a baking operation involving low heatup rates ($\leqslant 10°C/hr$, up to at least 600°C) and finishing temperatures of 1000-1200°C. During this heat treatment, the binder wets the filler and penetrates into some of the coarser pores as the temperature increases above 200°C. Near 400°C, considerable amounts of gas (from pitch distillation and decomposition) begin to be emitted and liquid binder enters the mesophase transition (1). This liquid-phase transition is from an isotropic to a relatively-anisotropic precursor of the coke produced when liquid mesophase solidifies. Structure of the binder coke depends on binder-pitch composition and how the pitch is pyrolyzed, particularly during the mesophase transition. The coke will always contain voids, pores created by gas evolution, and shrinkage cracks produced as the carbon polymer being formed contracts internally and as external bond stresses build up between filler particles. The structure of these voids depends on bond-coke texture which in turn depends on pitch characteristics and how the coking operation is carried out. Bond-coke texture can vary from highly anisotropic graphitic carbon to highly isotropic vitreous carbon, with many gradations in between. One of the more common textures encountered, particularly with coal-tar pitches, is an array of anisotropic crystallites in an isotropic matrix.

In the course of studies of various aspects of binder quality, two factors which have received considerable attention are binder pyrolysis characteristics and the resulting features of bond-coke microstructure. We have examined more than sixty binders in this manner, covering a wide range of types and quality. This paper is a presentation and interpretation of the results of this work, with conclusions regarding binder-coke quality standards.

Experimental

Thermogravimetric analysis (TGA) of binder pyrolysis was done in flowing argon using 175mg samples and with simultaneous recording of weight loss, weight loss rate (DTG), and differential thermal analysis (DTA) compared to an alumina reference sample. Samples were heated in

alumina crucibles at a rate of 1°C/min to 1000°C. At the end of a TGA run, disposition of the coke residue in the crucible was noted and the residue was crushed, impregnated with and mounted in epoxy resin in preparation for optical microscopy (OM) examination. The mounted coke residue was final-polished with 0.05 micron alumina before examination. The entire polished surface was then examined with reflected polarized light and typical microstructures photographed. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to examine selected binder quinoline-insoluble (QI) and composite samples. Separated QI specimens were mounted on 1 cm diameter metal cylinders for SEM analysis, and TEM was used to examine QI in composite binder regions which had been specially-thinned (2) for this purpose.

Nuclear magnetic resonance (NMR) analysis of pitch binders was used to determine the relative amounts of aromatic (I), α-aliphatic (II), and non-α-aliphatic (III) hydrogen atoms attached to aromatic rings. In making these measurements, deuterated-chloroform pitch solutions were used.

Compressive strength (CS) measurements were made on 1 1/2" diameter x 2" long cylindrical composite specimens. The average value of 10 samples of each composite was determined. Other composites, pitch, and coke properties were measured using standard carbon laboratory procedures.

Results and Discussion

Binder Pyrolysis

Pitch is a complex mixture of thousands of different molecular types, primarily hydrocarbons associated with much smaller numbers of other atoms (S, O, impurities et al). The coking process can be considered to involve the condensation of various aromatic and aliphatic groups, by splitting out hydrogen molecules between two carbon atoms, to produce both ordered and disordered carbon networks with the simultaneous evolution of light hydrocarbons in addition to hydrogen, carbon oxides, et al. It appears likely that pitch reactivity during the coking process, and the quantity and structure of the resulting carbon, will be greatly affected by the arrangement of hydrogen atoms on the molecular carbon skeleton. NMR techniques have been used to determine the relative amounts of three kinds of

bound hydrogen (with reference to the aromatic-aliphatic structures in pitch) which are identified in Figure 1. Type I (aromatic) and Type II (α-aliphatic) hydrogen atoms appear to contribute significantly to the formation of condensed carbon structures. Type III (non-α-aliphatic) hydrogen is sufficiently removed from the aromatic ring that it may contribute more to the volatile hydrocarbon fraction during the coking process.

Table I gives NMR hydrogen analyses of the chloroform-soluble fractions of 12 pitches (four coal-tar (CTP), seven petroleum (PP), and one modified tall-oil (MTO)) which indicate some of the variety of composition observed during this study. The coal-tar pitches are of rather uniform composition, highly aromatic with moderate Type II hydrogen content, and low on aliphatic chains and chloroform solubility. The petroleum pitches show much greater variation, are less-condensed aromatic structures with relatively high Type II hydrogen content, and show great diversity in aliphatic side chains. The tall-oil pitch has the most aliphatic character of all the pitches and does not make a good binder.

During the course of hydrocarbon pyrolysis, three principal types of reactions are known to occur (3):

1) Cracking of all non-aromatic hydrocarbons to smaller molecules (cracking and dehydrogenation, or degradation reactions).

2) Cyclization of all hydrocarbon chains to form aromatics (synthesis reactions).

3) Condensation reactions of aromatics to form polycyclic aromatic systems (also synthesis reactions).

Degradation reactions are highly endothermic processes involving rupture of carbon-carbon and carbon-hydrogen bonds. Aromatic synthesis reactions are also endothermic processes (4), but can be accompanied by polymerization and crosslinking condensation reactions which are exothermic (4, 5).

The pyrolysis of pitch binders in this study involved TGA under circumstances which produced a distillation-coking experiment with a coking value somewhat less than that by the standard Conradson technique (C.C.V.). The heating rate, 1°C/min, was made as slow as possible to simulate anode bake-rate conditions. Some examples of the diversity of binder

TABLE I

PROTON MAGNETIC RESONANCE ANALYSIS
OF VARIOUS PITCH BINDERS

Sample Identification	% CHCl₃ Insoluble	% of Hydrogen		
		Type I	Type II	Type III
C.T.P.	27.6	85	14	1
C.T.P.	28.8	82	15	3
C.T.P.	29.8	86	11	3
C.T.P.	43.5	76	15	9
P.P.	28.1	73	23	4
P.P.	0.02	55	35	10
P.P.	12.0	58	36	6
P.P.	0.3	51	39	10
P.P.	0.0	21	23	56
P.P.	32.4	58	34	8
P.P.	17.1	67	27	6
M.T.O.	7.9	17	16	67

characteristics encountered are shown in Figure 2. The most unsatisfactory binder is basic tall-oil (No. 1) pitch (S.P. (C/A) = 103°C, C.C.V. = 33%) with high-aliphatic composition. Weight loss rate (DTG) increased so rapidly, without reaching a plateau, that the TGA apparatus was fouled at 400°C. Even though volatiles loss was high, the reaction was exothermic and probably involved polymerization-crosslinking condensation reactions. Coke microstructure produced was isotropic, somewhat similar to that in Figure 24. While of significantly better quality, petroleum pitch binder (No. 2) (S.P. = 125°C, C.C.V. = 42%), made from highly-asphaltic precursors, is not a good binder and exhibited ~5% increase in carbon consumption, with dusting, when pilot-cell tested using full-size prebake anodes. The DTG curve of No. 2 (see Figure 2) shows high low-temperature volatility but does peak at a maximum weight-loss rate which is much lower than that for No. 1. However, both binders exhibited exothermic reactivity, that for No. 2 being probably due to asphaltene crosslinking reactions. Also, both binders produced coke with a highly-isotropic friable microstructure similar to that in Figure 24. The DTG curve for No. 3 petroleum pitch (S.P. = 118°C, C.C.V. = 53%) indicates a better (though still marginal) quality binder. The DTG maximum is lower and occurs at a higher temperature (slightly below 400°C) and less low-temperature volatility occurs for No. 3 than for No. 1 and No. 2 pitches. However, all three pitch-cokes expanded so much during pyrolysis as to foul the TGA apparatus at the cut-off points indicated in Figure 2. In contrast to the TGA tests of No. 1 and No. 2 binders, pyrolysis of No. 3 showed only limited exothermic character during most of the test period and the resulting pitch-coke specimen had relatively-anisotropic structure (similar to that in Figure 15) indicating mostly endothermic aromatic condensation reactions.

The remaining binders in Figure 2 are of acceptable quality for anode carbon usage. Petroleum pitch No. 4 (S.P. = 119°C, C.C.V. = 51%) made from decant oil, and coal-tar pitch (No. 5) (S.P. = 108°C, C.C.V. = 57%) have similar DTG curves with endothermic maxima at 400°C and exothermic peaks near 470°C. However, No. 4 has a higher maximum weight-loss rate and much smaller 470°C peak. These differences appear as distinguishing characteristics for many coal-tar and petroleum pitches. However, more variety in DTG pyrolysis curves was found for petroleum than for coal-tar pitches. Some examples of this variety are shown in Figure 3. No. 6 (S.P. = 108°C, C.C.V. = 54%) is a petroleum pitch with undesirable peaking of the weight-loss rate curve at

290°C suggestive of a cutback character (addition of solvent to a high-softening pitch to obtain the desired S.P.). When this pitch was distilled at 290°C-320°C until 4% distillate was removed, softening point (S.P.) increased to 135°C and the DTG curve No. 7 was obtained. The volatile constituent at 290°C is absent for No. 7, and the uneven DTG plateau which results suggests relatively-high pitch reactivity. This reactivity characteristic is even more evident after the binder was given a more severe thermal treatment by removing 14.5% distillate to increase S.P. to 157°C. The new DTG curve, No. 8, is very different from No. 6 and No. 7 and has now become a low, narrow, high-temperature plateau with an exothermic peak near 430°C instead of the original 290°C endotherm. It appears that the new exotherm may be due to crosslinking (or polymerization) reactions arising from thermal treatment of the binder during distillation.

Two other petroleum pitches in Figure 3 with somewhat different DTG pyrolysis curves are No. 9 (S.P. = 115°C, C.C.V. = 57%) and No. 10 (S.P. = 110°C, C.C.V. = 54%). No. 9 shows a rather abrupt DTG rise at 290°C, while No. 10 exhibits considerable low-temperature volatility. However, both binders have small peaks, and exotherms, at 470°C. Furfuryl alcohol polymer, No. 11, does not melt during pyrolysis but undergoes considerable exothermic crosslinking over a wide temperature range and has two broad, low DTG peaks corresponding to loss of water at low temperature and loss of CO_2, CO, CH_4, and H_2 at higher temperatures. The remaining binder pyrolysis DTG curve in Figure 3, No. 12, is for coal-tar pitch (S.P. = 117°C, C.C.V. = 57%). Typical of coal-tar pitches, the No. 12 curve has an endothermic maximum near (slightly above) 400°C, and an exothermic peak near 470°C. The same characteristic DTG curve is shown for seven other coal-tar pitches in Figure 4, together with one curve for a petroleum pitch, No. 19 (S.P. = 113°C, C.C.V. = 61%) which has received additional thermal treatment. No. 19 is more highly-condensed than most other petroleum pitches and its DTG curve, and other binder properties, tend to approach more closely those for coal-tar pitches. It has an endothermic maximum at 380°C and two exothermic maxima at 430°C and 470°C. It appears that such exotherms indicate condensation by crosslinking and/or polymerization reactions which tend to make the resulting binder-coke more isotropic (such as that in Figure 14). The degree of isotropy can vary from very great (as for highly-crosslinked No. 11, highly-aliphatic No. 1, and highly-asphaltic No. 2 binders),

to moderate (as for No. 19 and most coal-tar pitches, which are also similarly affected by high QI levels) to relatively-anisotropic (as for No. 6, No. 4, and many other low-QI petroleum pitches).

In Figure 5, DTG curves are shown to illustrate the following conditions:

1) No. 21 and No. 22 are similar coal-tar pitches with S.P. = 113°C and 98°C, showing a slightly greater low-temperature volatility of the latter, and considerably greater volatility of No. 23 (S.P. = 97°C) coal-tar pitch.

2) No. 24 (S.P. = 95°C) and No. 25 (S.P. = 100°C) are straight-run and airblown coal-tar pitches, respectively, showing reduction in low-temperature volatility of the latter.

3) No. 26 (S.P. = 108°C, QI = 14%), No. 27 (S.P. = 119°C, QI = 20%), and No. 28 (S.P. = 113°C, QI = 27%), showing increased coking value and reduced 470°C exotherms with increasing QI and decreasing beta resin.

4) No. 29 (S.P. = 103°C, C.C.V. = 55%) near-typical coal-tar pitch with 13% QI and 25% beta resin.

5) No. 30 (S.P. = 113°C, 0% QI, C.C.V. = 48%) and No. 31 (S.P. = 108°C, 3% QI, C.C.V. = 50%) petroleum pitches showing better quality of the latter (less low-temperature volatility and significant 470°C exotherm peak) with the same beta resin content.

In Figure 6, DTG curves are shown for two coal-tar (No. 32 and No. 34) and two petroleum (No. 36 and No. 38) pitches which compare pyrolysis of the whole pitch with that for vacuum (40 mm) distillation residuals (VR) to 360°C. The DTG curves for corresponding VR fractions (Nos. 33, 35, 37, and 39) clearly show the absence of low-temperature volatility as expected. Of more interest is the finding that exothermic peaks near 470°C become more prominent in the VR than in the whole pitch. These peaks are believed to be due to crosslinking reactions of beta resin with pitch oils and would be expected to become intensified in VR fractions as volatile losses increase beta resin (and QI) concentration in residuals. In fact, it has been found that

the benzene-insolubles (BI) fraction actually increased in VRs (mostly as beta resin) somewhat more than the concentration factor would indicate. This occurs due to additional thermal treatment of the pitch during vacuum distillation. The relationship of these 470°C DTG peaks to beta resin content has been clarified further by removing the BI fraction from VRs to produce residuals (VRBS) which are benzene-soluble (BS). DTG curves for VRBS fractions show little or no peaks at 470°C.

Figure 7 shows a comparison of DTG curves for the whole pitch and corresponding VR (Nos. 41 and 44) and BI (Nos. 42 and 45) fractions of two petroleum pitches (No. 40 and No. 43). While VR fractions show the expected relationship to the whole pitch, BI fractions give DTG curves with very few distinguishing features. This result appears reasonable in view of the nature of BI constituents (beta resin and QI). QI particles are already highly-condensed and do not bond well to other carbons. Beta resin is also sufficiently condensed that little melting may occur during pyrolysis. Thus, thermal decomposition occurs with less opportunity for interaction reactions and consistent with the almost featureless DTG curves observed. BI coke microstructure, such as that in Figure 24, is thus relatively isotropic and quite different from that for the corresponding whole pitch coke.

Bond-Coke Microstructure

Objective - Controlled Disordered Binder Coke. Both physical and chemical bonds are formed between filler and binder cokes in baked carbon composites. The effectiveness of the physical bonds depends on filler particle shapes and surface roughness, while chemical bonds are made through reactivity of carbon atoms at the edges of graphite crystallites in binder and filler cokes. Even with relatively smooth filler particles, such as unmilled fluid coke, it is possible to achieve good bonding and high strength composites. The fracture surface of such a composite, shown in Figure 8, indicates good physical and chemical bonds. However, if relatively-anisotropic pyrocarbon is deposited on such spherical particles and/or used as bond coke (such as occurs with some petroleum pitches), bond quality deteriorates. This occurs because 1) anisotropic carbon is weak to shear and cleavage of the basal planes, and 2) insufficient carbon edge-atom sites for chemical bonds at the binder-filler interface

with anisotropic contacting surfaces. Thus, for both filler and binder cokes, a controlled degree of crystallite disorder and more isotropic carbon appears to give better anode composite properties. For filler cokes, fluid and delayed sponge-honeycomb cokes have been found to be disordered to the degree suitable for anode carbon. Coal-tar pitch binder coke has similarly been found to be adequately disordered for good binder coke. However, with changing coal-tar pitch quality and the advent of still greater variety of petroleum pitches and other binders, bond coke can vary in many gradations from very anisotropic pyrocarbon to very isotropic vitreous carbon. However, what appears to give best overall performance (good filler protection, minimum bake shrinkage, with good strength, conductivity, and oxidation resistance) is pure, rather homogeneous, relatively fine-grained, moderately-disordered binder coke such as shown in Figure 14.

The Role of QI in Disordered Bond Coke. QI is the condensed hydrocarbon (molecular weight ~5000, C.C.V. ~95%) which exists in coal-tar and some petroleum pitches as a colloidal dispersion of submicron-to-multimicron spheres and sphere clusters (see Figure 9). The carbon structure within a baked QI sphere is onion-like with graphite layers in concentric spherical shells parallel to the surface. The layer structure can be developed further, by QI graphitization, so that it can be seen by TEM as the polyhedron shown in Figure 10 and as rosettes in a binder coke area in Figure 11. While the crystallite size is much smaller in baked carbons, crystallite orientation prevents good bond formation with surrounding carbon. QI particles have been found so loosely bonded as to be brushed from their sockets during TEM sample preparation as shown in Figure 12. It is clear then that QI structure prevents strong bonds from being formed between QI and contacting carbon. These particles affect bond structure principally by disordering the liquid mesophase during pitch pyrolysis so that when it solidifies to coke, shrinkage will be reduced and crystallites will be oriented in a random manner to produce a finer-textured stronger coke. Such a bond coke is also able to coat, bond to, and protect the filler substrate from oxidation better than more anisotropic bond coke.

It is desirable to improve interaction of the QI binder fraction so that this coke-disordering agent also helps bond the coke together. This can be done by the use of selected high-surface, chain-structured, oxidized

carbon blacks as the QI phase of the pitch. Lampblack is such a material and other still more-reactive, higher-surface blacks have recently been shown to considerably increase binder coking value by their presence (6). It has also been shown previously how lampblack addition to pitch binder increased airburn resistance of fluid coke composites by a factor of ten (7). In Figure 13, it can be further seen that lampblack substantially increases the strength of these composites, and is considerably more effective than coarser, low-surface thermal blacks whose structure is very similar to that for native binder QI.

In addition to investigating binder pyrolysis and influence of binder composition on bulk composite properties, considerable attention has been given to the associated microstructures of bond coke and binder-filler bonds. The texture of typical bond coke from a 10% QI coal-tar pitch is shown in Figure 14. The microstructure consists of islands or networks of anisotropic carbon (light areas) in an isotropic matrix (darker background). As the QI level decreases, the light areas predominate until the isotropic coke finally disappears with near-zero QI levels as shown for a petroleum pitch in Figure 15. When the QI level increases, the isotropic matrix tends to predominate as shown for coal-tar pitch with 20% QI in Figure 16. When the QI level reaches 30%, anisotropic coke diminishes to near the vanishing point as shown for 10% QI coal-tar pitch with 20% added lampblack in Figure 17.

Examination of the structure of actual binder-filler bonds in baked composites is even more helpful than separated bond coke examination because it reveals more realistically details of binder-filler interaction, such as bond coke shrinkage. Typical bonds between fluid coke and binders with 0.4% (petroleum), 10%, and 27% (coal-tar) QI are shown in Figures 18, 19, and 20. In situ bond coke shrinkage is seen to decrease as QI level increases and bond coke becomes more isotropic. The properties of baked composites with standard plant aggregate have been measured for coal-tar pitch binders with QI levels up to 27%. The results, shown in Fig. 21, indicate that properties improve up to the highest QI level. However, more binder is required for optimum pitching levels as QI increases. It is also clear that eventually the QI level will reach a point where baked properties deteriorate, particularly since QI does not appear to bond _directly_ to binder coke but improves quality _indirectly_ by increasing structural disorder. Better results might be realized if selected high-

structure reactive carbon blacks were substituted for native QI because internal QI bonding could then be achieved.

Crosslinking Reactions in Binder Coke. From the previous discussion, it would appear that suitable crosslinking reactions might be used successfully to produce controlled disorder in binder coke. A variety of possibilities exist, with binder oxidation from air-blowing experiments being often examined in the past (8). Sulfur treatments have been used for the same purpose, and can easily convert an anisotropic carbon to a highly-isotropic vitreous carbon as was done for the carbon structure in Figure 22, which contains 10% sulfur. However, with such highly-isotropic binder coke, shrinkage can become a problem as shown for the vitreous carbon bond to fluid coke in Figure 23. Bonds of this type, which can be made with thermosetting polymers such as furan resin, solidify near room temperature and shrinkage from that point can become intolerable by the time bake finishing temperatures are reached.

Another method for attempting controlled cross-linking of binder coke is the addition of suitable resins to the pitch. Results from addition of furan resins to coal-tar and petroleum pitches have not been encouraging to date. The resin does not appear very miscible with pitch and addition of as little as 10% resin causes the binder to set up in a few hours so as to preclude use in standard Soderberg operations.

In more conventional delayed coking operations, the asphaltene content of coker feed is usually kept at ~10% or less to produce suitable anode filler cokes. Asphaltenes in coker feeds are highly-dispersed colloids of 3000 to 5000 molecular weight (9), and similar in these respects to QI in pitch. However, the two materials have greatly different structures, so that asphaltenes can act as crosslinking agents while quinoline-insolubles do not. Both materials tend to have undesirably-high impurity contents.

The present study indicates that pitch already has a built-in crosslinking-polymerization agent in the BI fraction. However, more information is still needed for a full understanding of this phenomena. For example, some petroleum pitches with high beta resin content do not show the expected crosslinking tendency even though this relationship appears to exist for coal-tar pitches.

Among the factors which need to be examined are 1) compositional differences between coal-tar and petroleum pitches of beta resin and oil fractions, and 2) the degree to which QI may affect _indirectly_ the crosslinking process. When coal-tar pitch is separated into oils, beta resin, and QI fractions, it has been observed that the coking value of the whole pitch is substantially greater than that calculated from the sum of the coking values of the individual fractions on the basis of their weight fraction in the pitch. While this synergistic effect appears to be due to crosslinking of volatile oils by beta resin, there may be secondary effects due to QI which are not yet understood. It has also been found that as QI level increases, and whole-pitch coking value increases, the coking value of the quinoline-soluble (Q.S.) fraction decreases. Finally, as indicated earlier, coke made from some pitch fractions, particularly BI and beta resin coke, has very different structure from whole-pitch coke. For example, BI coke from a petroleum pitch with about 1% QI and 24% BI, shown in Figure 24, is a low-density, relatively-isotropic, friable material, in marked contrast to the related dense, anisotropic whole-pitch coke in Fig. 15.

The microstructure of coked pitch and pitch fractions examined to date indicate considerable variation in beta resin amount and composition and hence variation in crosslinking tendency. At this stage, it is conceivable that optimum balance, in composition and amount, of beta resin and QI may be the best way to obtain the desired degree of bond-coke disorder, with acceptable baked-coke shrinkage to give high quality binder-filler bonds.

Summary and Conclusions

A wide variety of anode binders have been examined with regard to pyrolysis characteristics and binder-coke microstructure. The collected data have been interpreted in an effort to develop standards of binder quality. The following conclusions have been drawn:

1) Coal-tar pitches exhibited more uniformity and higher quality than the petroleum pitches examined.

2) While the pyrolysis reactions are largely endothermic processes, significant exotherms were observed between 400°C and 500°C in the later stages of carbon polymerization.

3) These exotherms appear to be associated with cross-linking reactions of beta resins which lead to more-disordered coke microstructure.

4) There is a synergistic interaction of the three principal pitch fractions (oils, beta resin, QI), which appears to be due to beta resin crosslinking volatiles in the oils fraction, that significantly increases binder coking value.

5) Disordered binder coke is preferred for better baked carbon properties if it can be obtained without excessive shrinkage of the bond after mesophase has hardened.

6) QI disorders liquid mesophase without crosslinking and is itself not well bonded within the coke structure.

7) Selected high-surface, structured, oxidized carbon black additives are more effective than native QI or thermal blacks in producing relatively homogeneous, fine-textured, strong, disordered binder coke which interacts well with filler particles, provides increased composite airburn resistance and increases binder coking value.

8) The absence of QI, or an effective crosslinking agent, in less-condensed highly-aromatic petroleum pitches tends to work against bond quality by producing less coke per bond, of weaker structure, with more shrinkage than a medium-high QI coal-tar pitch.

9) While more pitch is required for optimum paste pitching levels, high-QI coal-tar pitch produces baked composites with equal or improved baked properties over low-QI binders. However, with sufficiently high QI levels, baked properties must deteriorate.

10) A variety of methods are available to disorder bond coke by crosslinking reactions. These include treatments with oxygen or sulfur, or other oxidizing agents, addition of asphaltenes, reactive, high-surface, structured, carbon blacks et al. However, it is necessary to optimize crosslinking to accomplish structural disorder without excessive bond-coke shrinkage. The built-in crosslinking action of beta resin in coal-tar pitch, when better understood may be the simplest expedient to achieve

high-quality binder-filler bonds.

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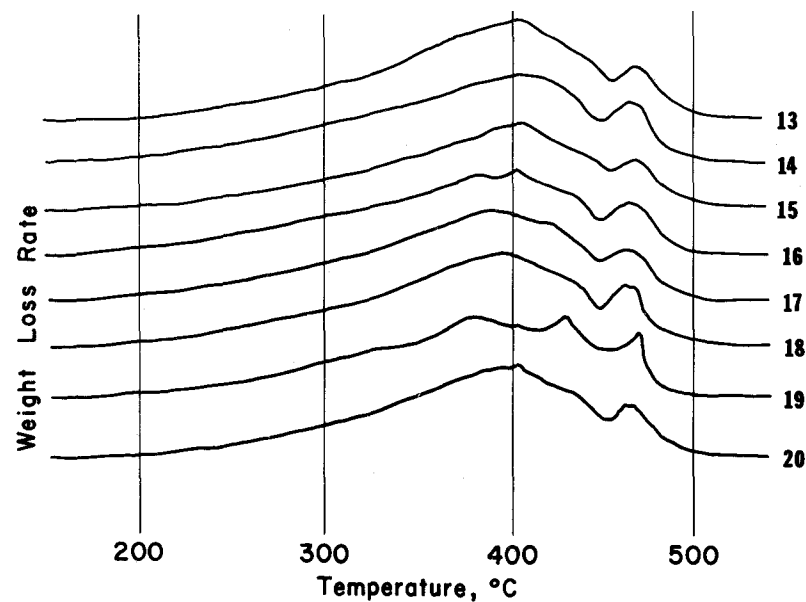
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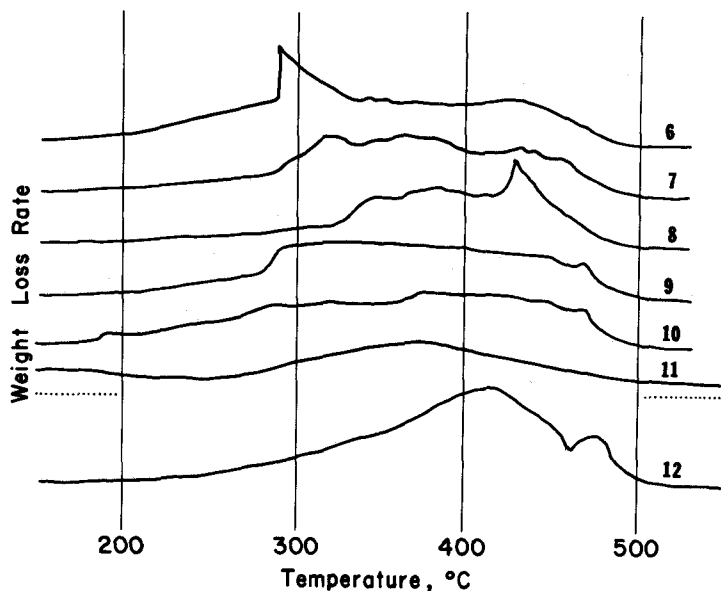
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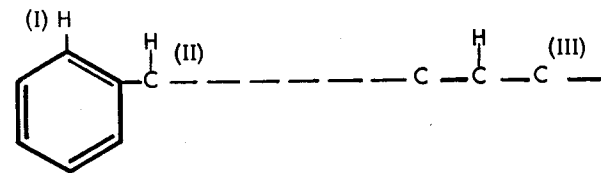
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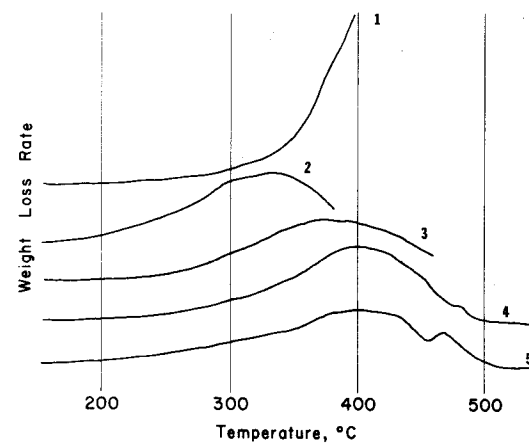
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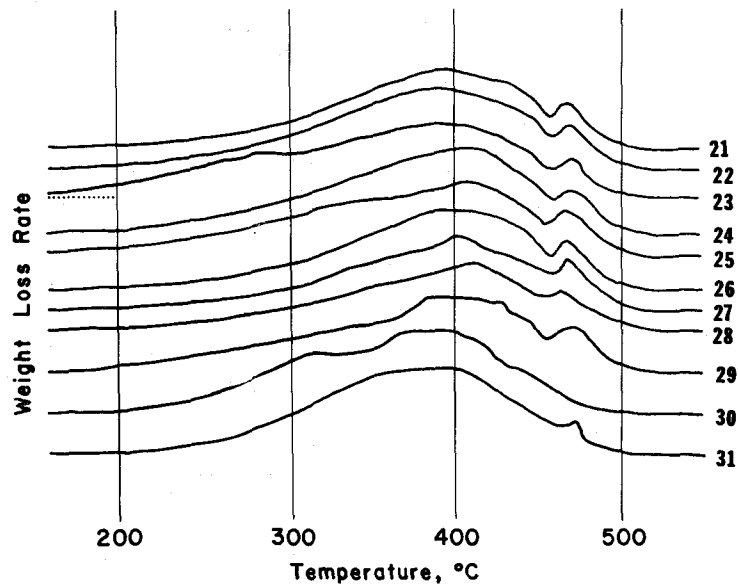
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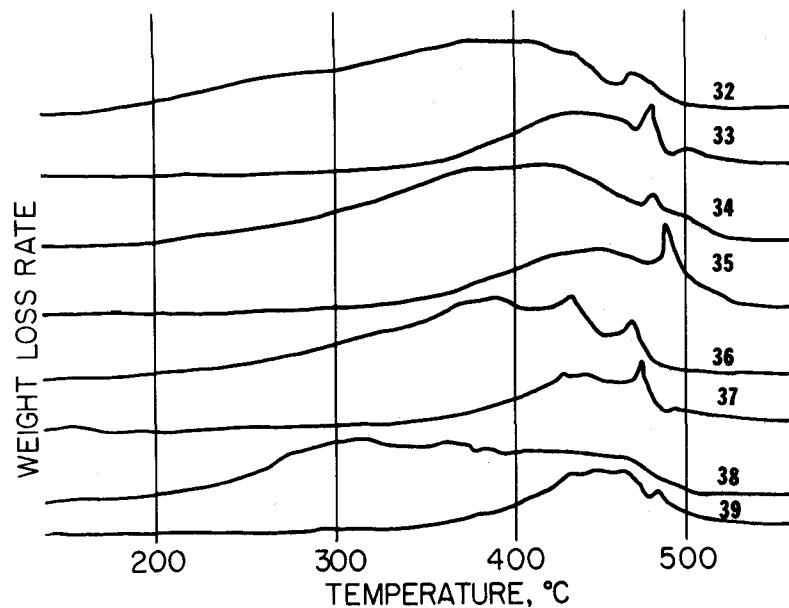
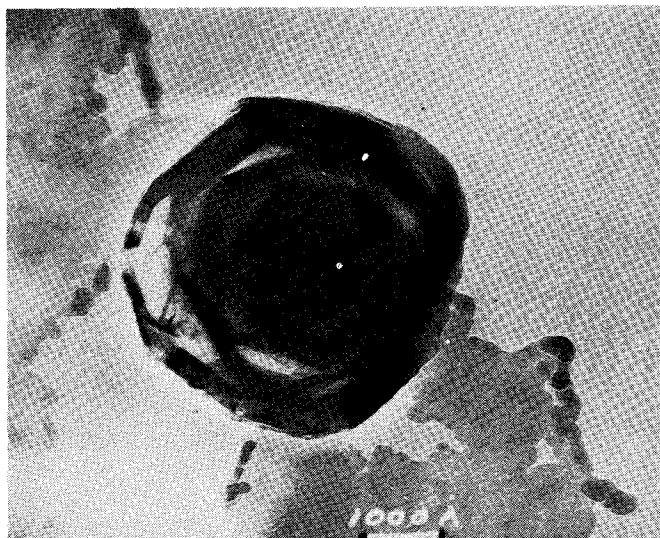6. Thermogravimetric Analysis of Binder-Coke Formation, Part V
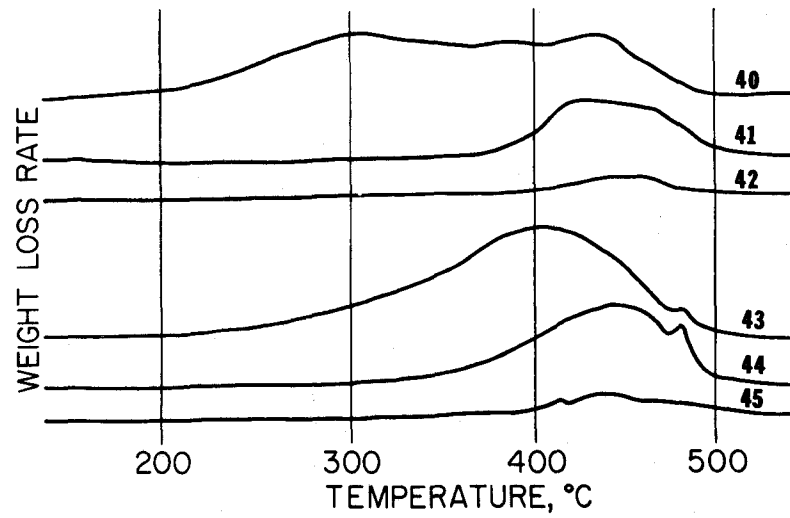
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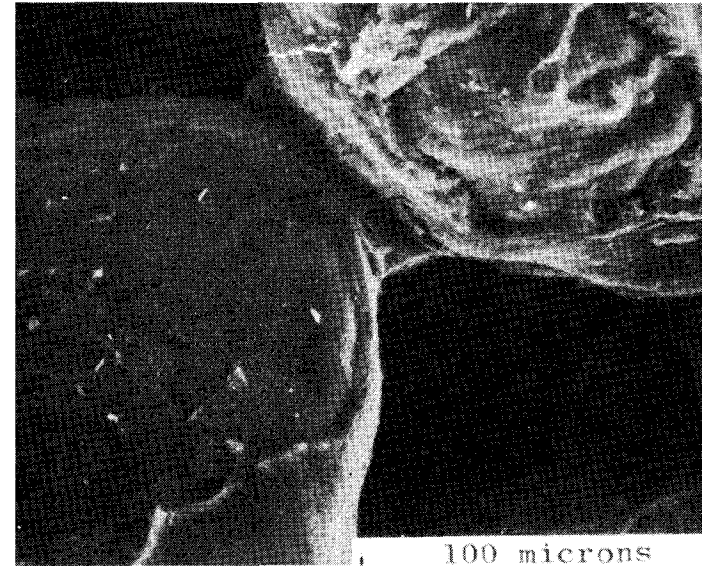
8. Fracture Surface in Baked Fluid Coke Composite with Coal-Tar Pitch Binder
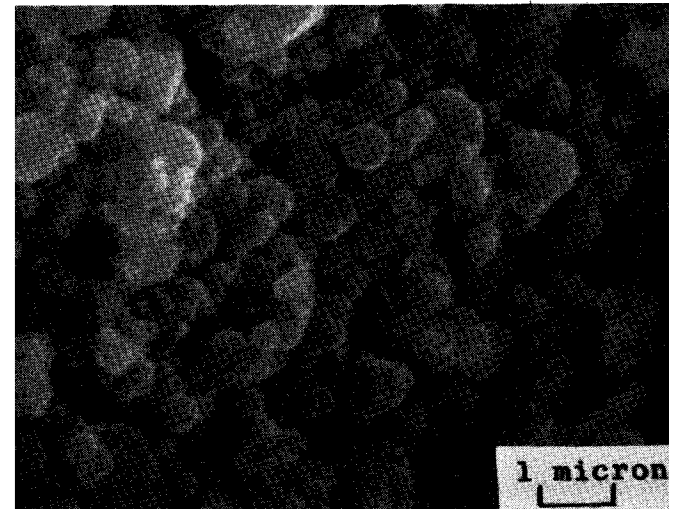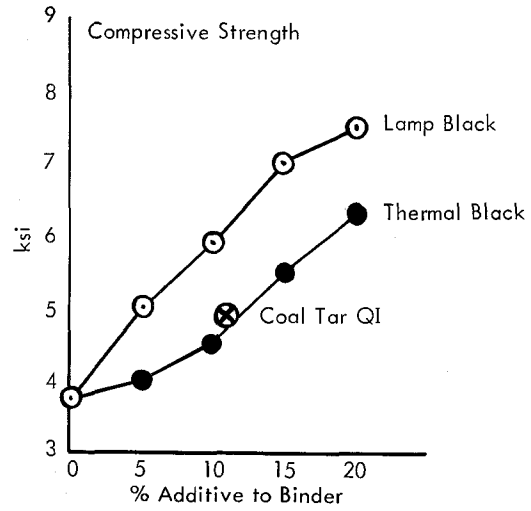

9. Quinoline-Insolubles from Coal-Tar Pitch
   (QI = 9.7%)

10. Single Quinoline-Insoluble Particle Graphitized to Show Internal Structure

11. Quinoline-Insoluble Particles in Coal-Tar Pitch Binder Coke (Graphitized to Show Microstructure)

12. Empty Cavities in Coal-Tar Pitch Binder Coke Formerly Occupied by QI Particles which Fell Out Due to Poor Bonding

13. Effect of Carbon Black Additives on Compressive
Strength of Fluid Coke Composites with Petroleum
Pitch Binder
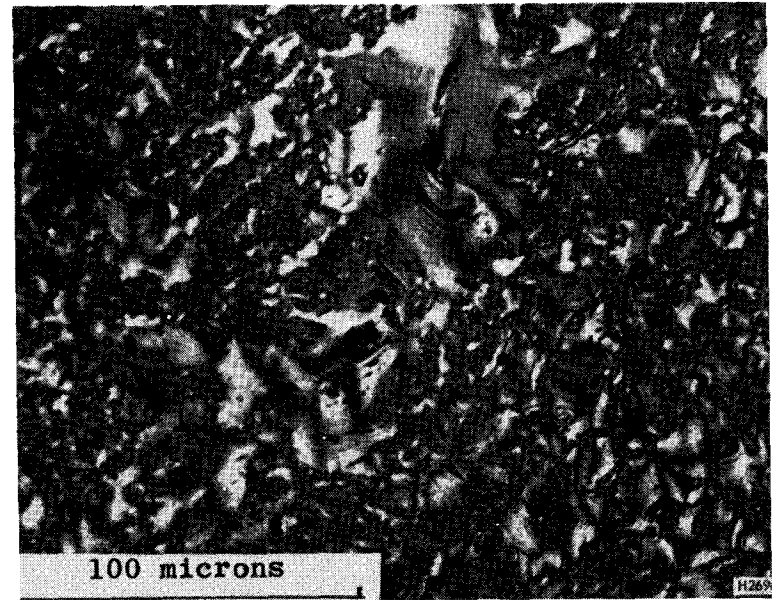
14. Microstructure of 10% QI Coal-Tar Pitch Coke
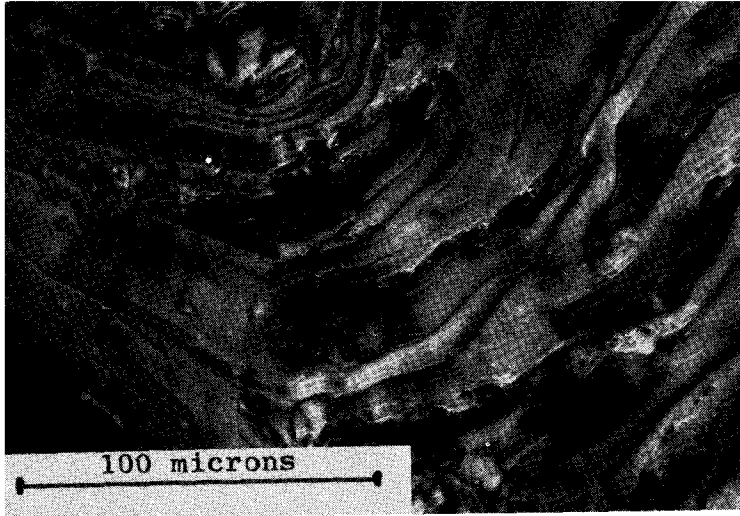
15. Petroleum Pitch Coke (0.4% QI)
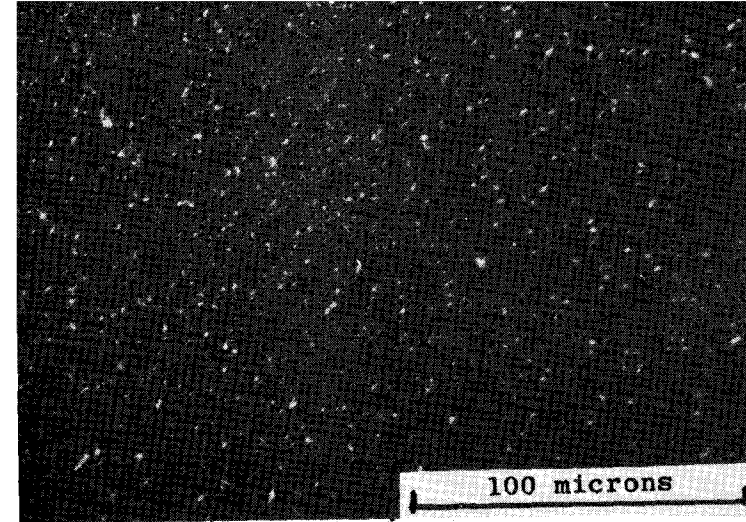
17. 10% QI Coal-Tar Pitch + 20% Lampblack Coke (30% QI)
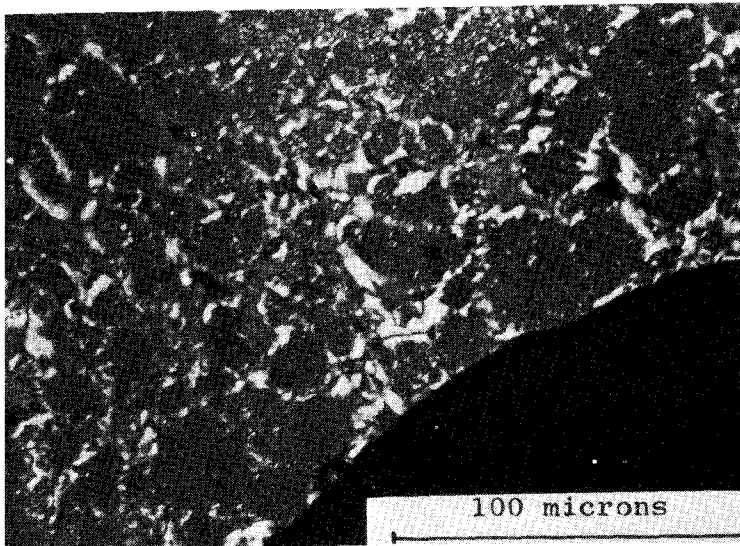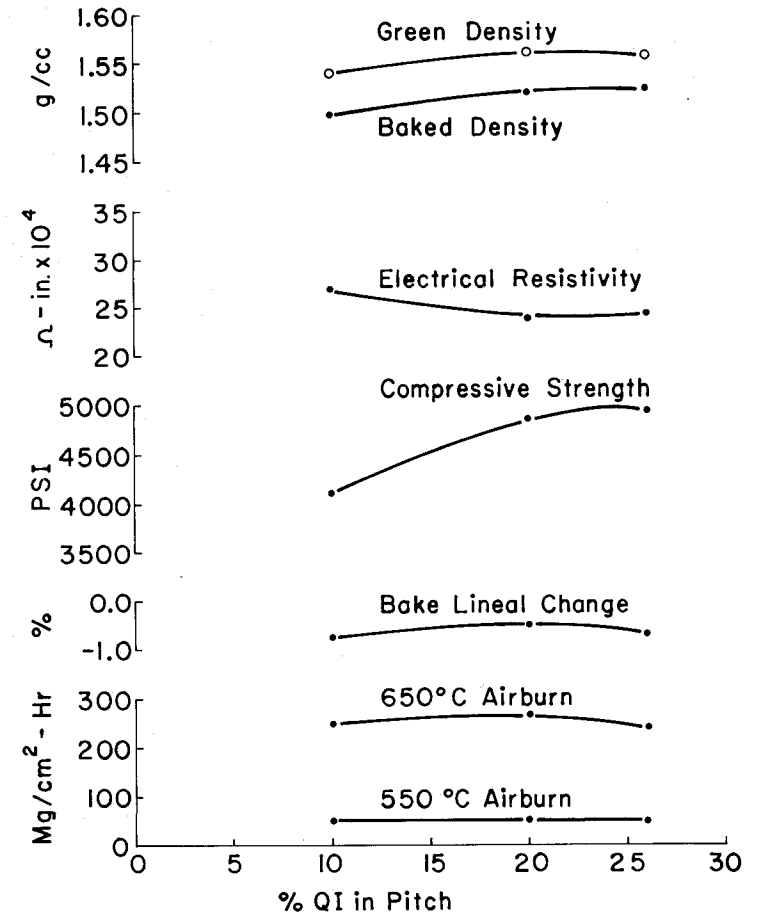

16. Coal-Tar Pitch Coke (20% QI)
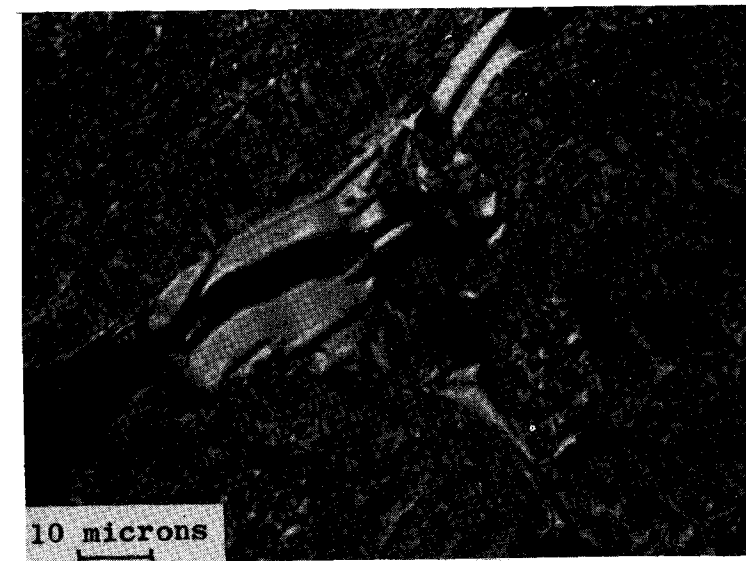
18. Bond Coke Structure in Fluid Coke-Composite with Petroleum Pitch Binder (0.4% QI)
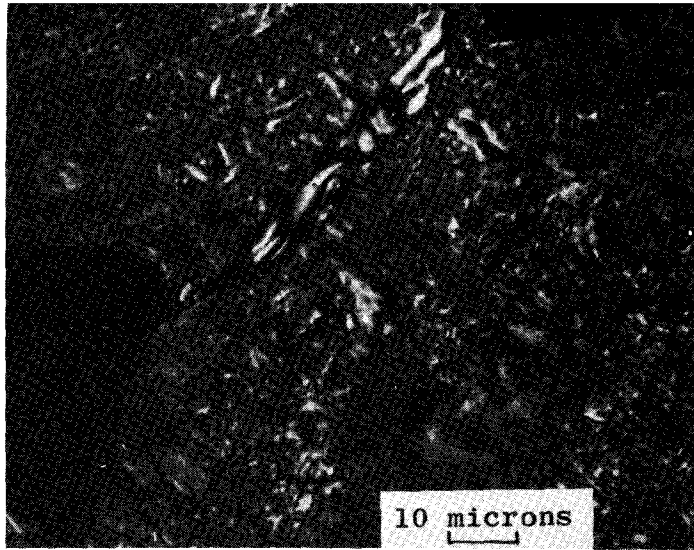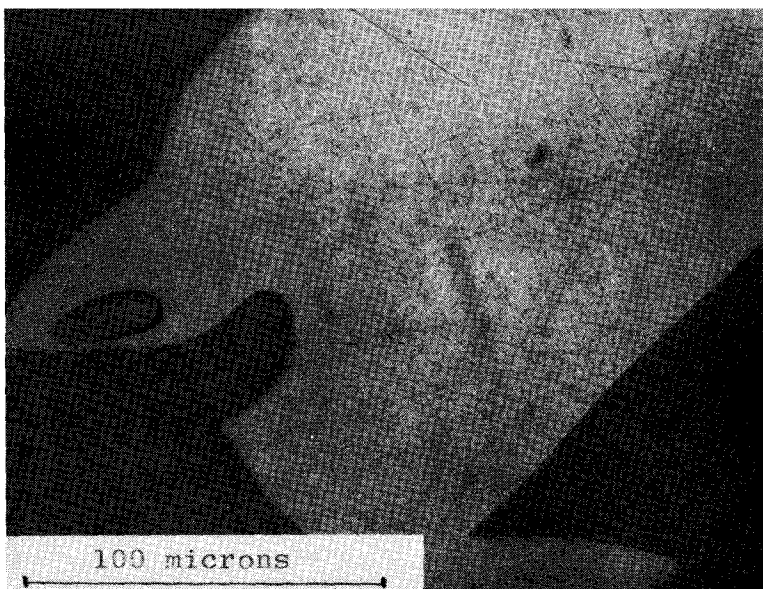
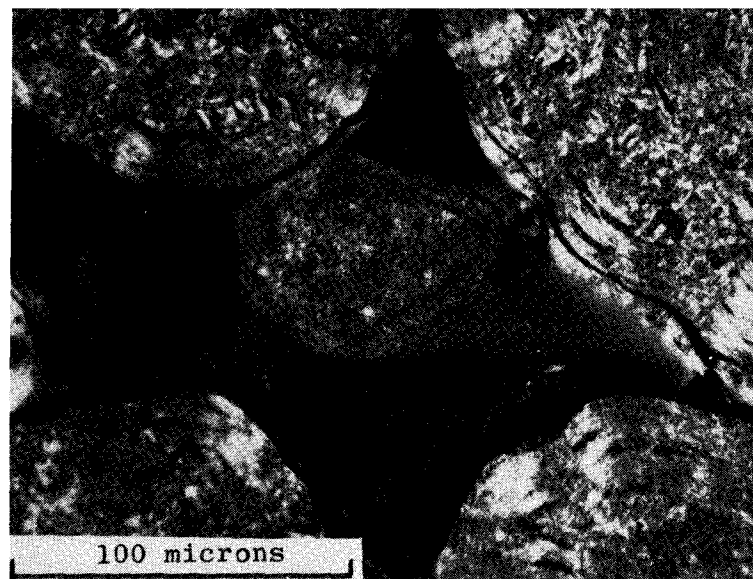19. Bond Coke Structure in Fluid Coke-Composite with Coal-Tar Pitch Binder (10% QI)
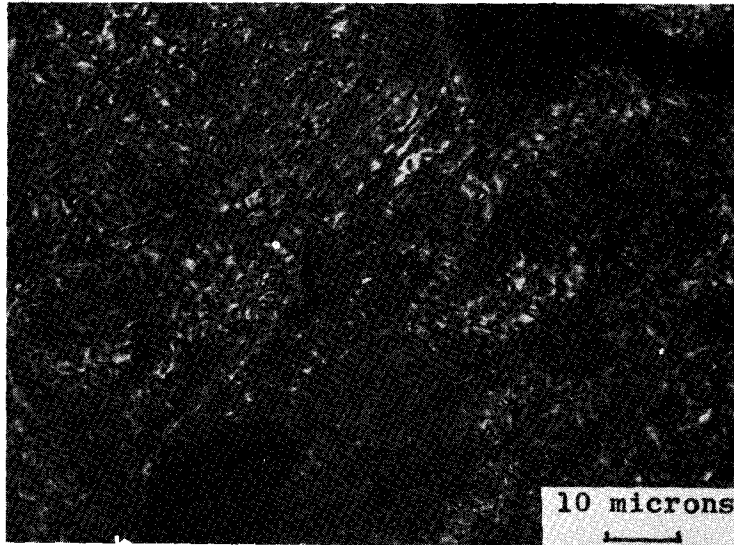
20. Bond Coke Structure in Fluid Coke-Composite with Coal-Tar Pitch Binder (27% QI)
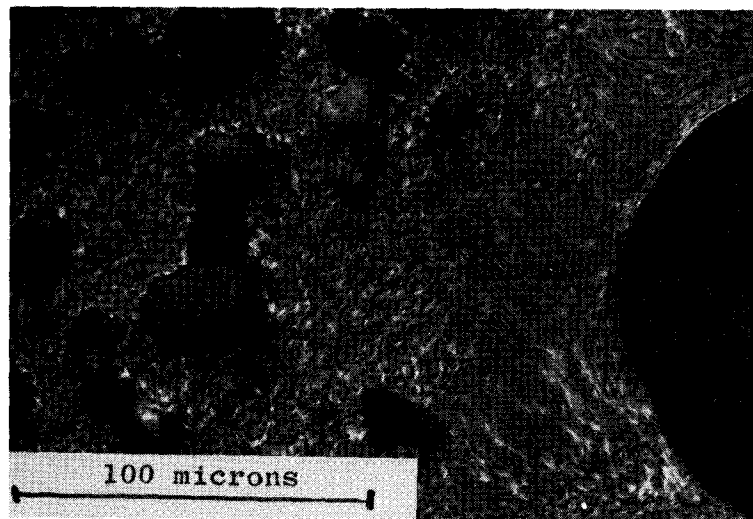

21. Variation of Composite Properties at Optimum Pitching Level with Quinoline-Insoluble Content of Coal-Tar Pitch Binder

22. Sulfur-Crosslinked Petroleum Binder Coke Containing 10% Sulfur

23. Baked Fluid-Coke Composite with Furan Resin Binder Showing Large Bond-Coke Shrinkage

24. Petroleum Pitch Benzene-Insolubles Coke