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Use of oxidized needle-coke in the preparation of carbon artifacts

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This study examines the microstrength, optical texture and bonding of baked carbons made from oxidized filler cokes and a pitch binder. Commercial needle-cokes and coke from a coal extract, after oxidation in the range of 0 to 20 wt % loss, were mixed with a coal-tar pitch and baked to produce a series of carbon artifacts. The microstrengths of these artifacts were measured and the interfaces between coke components were examined by optical microscopy. The microstrengths of carbon artifacts containing oxidized needle-coke filler decreases with increasing extent of oxidation of the filler. However, the strength of carbon artifacts containing oxidized coal extract coke filler increases with increasing extent of oxidation of the filler. Differences in wettability of the filler particles by the pitch appear to cause these changes in microstrength. The pitch appears to be unable to penetrate into the oxidation topography of the needle-coke surface at levels of oxidation below 20 wt % but can penetrate into the larger surface features of the oxidized coal extract filler coke. Penetration of the pitch into the oxidation topography of the filler cokes produces a wetted/keyed interface and improves the bonding between the filler and binder cokes in the resultant artifact.

1. Introduction

In the manufacture of carbon artifacts [1] petroleum coke (filler) after calcination is mixed with pitch (binder) and formed, while the pitch is molten, into "green" blocks or carbon artifacts which possess the form of the finished graphite artifact [2, 3]. Subsequent baking of these carbon artifacts converts them into a low resistance product which is strong and capable of withstanding hard service. Baking accomplishes these results by a distillation-coking action on the binder. As the temperature of carbonization increases, the binder successively softens, melts, loses its lighter constituents by distillation and is converted into coke of low volatile matter content ($< 1\%$).

The bonding of the filler with binder coke obviously controls the strength of the resultant artifact. However, the nature of the bonding has not been studied extensively [4]. Lahaye *et al.* [5] report that the bonding of resins to carbons was influenced by surface oxidation. Porosity and surface roughness is known to influence bonding in carbon fibre composites [6].

Previous studies of Ragan and Marsh [7, 8] report the influence of oxidation during calcination upon the strength and surface topography of needle-cokes and a coal extract coke. This paper considers the influence of surface topography upon binding interactions in carbon artifacts made with oxidized needle-coke and coal extract coke as fillers.

This study examines the microstrength, optical texture and bonding in baked carbons resulting from the use of oxidized needle-coke in the preparation of the artifacts.

2. Experimental details

2.1. Materials used

The fillers used were: calcined Conoco needle-coke, calcined Shell needle-coke, and calcined

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TABLE I Analyses of cokes used as fillers

	Coefficient of Thermal Expansion (K^{-1})	wt % C	wt % H	wt % N	wt % Ash
Calcined Conoco needle-coke	NA	97.94	0.51	0.72	0.90
Calcined Shell needle-coke	4.0×10^{-6}	98.89	0.77	0.12	–
Calcined NCB coal extract coke No. 18*	4.6×10^{-6}	98.09	0.45	1.25	0.50

*Extracted from Annesley Coal (NCB Coal Rank 701) with non-hydrogenated solvent type D160.

NCB coal extract coke No. 18. Analyses of these cokes are in Table I.

The binder pitch used was BSC No. 2 coal tar electrode binder pitch. Analysis of this pitch is in Table II.

2.2. Filler preparation

The fillers, needle-coke and extract coke were all initially crushed $< 1180\,\mu m$ (−14 BS mesh) and then ball milled to $< 355\,\mu m$ (−44 BS mesh) such that the particle size was that of industrial fine stock used in graphite manufacture, i.e. $< 355\,\mu m$.

20 g samples of the fillers were oxidized in a Carbolite horizontal tube furnace at 913 K, at $4\,K\,min^{-1}$ in a mixture of 5% oxygen : 95% nitrogen. A range of reaction times were used, from 5 to 25 h to produce weight losses of 5 to 25 wt %.

2.3. Artifact preparation and baking

After grinding and oxidation, the fillers were mixed with BSC No. 2 coal-tar electrode binder pitch in the ratio of 65% filler : 35% binder, by weight. Mixing was carried out by melting the pitch in a Pyrex beaker on a hot plate and adding the filler gradually. After each addition of filler the mix was kneaded to ensure good contact between the filler and binder pitch. The mix was then reheated and further filler added. This operation was repeated until all the filler had been added and mixed.

TABLE II Analyses of BSC No. 2 coal-tar electrode binder pitch

Softening point (R.B.)	380 K
Quinoline insolubles	13.8 wt %
Toluene insolubles	40.1 wt %
Density	$1.324\,kg\,m^{-3}$
Carbon	91.9 wt %
Hydrogen	4.3 wt %
Nitrogen	1.2 wt %

The filler/binder mix or paste was then placed in a preheated silica boat. Hot-pressing of the paste in the boat was carried out by hand (with glove protection). Pressing continued until visible compaction of the paste was complete. The boat was then heated in a Carbolite horizontal tube furnace at 1273 K, at $4\,K\,min^{-1}$, 1 h soak in nitrogen, resulting in a fully shrunk, unbroken, baked artifact of boat-like form.

2.4. Microstrength testing

Before grinding the resultant artifacts, a piece was cut from each by hack-saw and retained for examination by optical microscopy. The remainder of each artifact was then ground to $600\,\mu m$ to 1.18 mm (14 to 25 BS mesh). 6 g of this sized carbon was separated into 3 x 2 g batches for use in the microstrength apparatus [7]. The microstrength determinations were carried out at 600 revolutions using the procedure previously described [7].

2.5. Optical microscopy

The pieces cut from the baked artifacts were mounted in polyester resin and so orientated that a surface normal to the pressing direction was presented for polishing, i.e. parallel to extrusion direction. The blocks were given the high polish necessary for examination in reflected light using a series of alumina powders. The optical texture of the polished artifact surfaces were examined and photographed in reflected plane polarized light using a Vickers M17 Photoplan microscope. Photographic exposure settings were controlled by a Vickers J.S. 37 Auto Exposure controller.

3. Results

3.1. Microstrength indices

The reduction indices R_1, R_2 and R_3 resulting from microstrength testing of carbon artifacts prepared

TABLE III Microstrength indices for carbon artifacts from calcined, and calcined oxidized, Conoco needle-coke with 35% BSC No. 2 electrode binder pitch

Needle-coke % weight loss by oxidation	Microstrength indices (wt %)		
	R_1	R_2	R_3
0% oxidized	19.6	45.6	33.9
5% oxidized I	15.7	47.1	36.6
5% oxidized II	14.9	49.7	34.6
10% oxidized	16.8	47.6	35.5
15% oxidized	12.6	48.5	38.5
20% oxidized	8.9	42.4	47.8

with calcined and calcined (oxidized) Conoco and Shell needle-coke fillers are in Tables III and IV. These show that, for both needle-cokes, increases in extent of oxidation of the filler results in decreases in strength of the resultant artifacts.

The two values for reduction indices in Table III from Conoco needle-coke at 5 wt % oxidation represents values for two separate artifacts prepared to assess variation in artifact strength resulting from chance variation in preparation techniques.

The reduction indices R_1, R_2 and R_3 resulting from microstrength testing of carbon artifacts prepared with calcined, calcined (oxidized), coal extract No. 18 fillers are in Table V and show that for the extract coke, increasing the extent of oxidation of the filler increases the strength of the resultant artifact. The maximum increase in artifact strength occurs at 10% oxidation, a 70% increase in R_1, and further oxidation of the coal extract filler produces slight decreases in strength at the 20 and 25 wt % levels of oxidation.

3.2. Optical microscopy of artifacts

Fig. 1 shows the optical texture of a carbon artifact from calcined Conoco needle-coke with 35% BSC No. 2 electrode binder pitch. Position A shows acicular flow domains from the needle-coke well bonded to coarse-grained mosaic binder pitch coke (Position B).

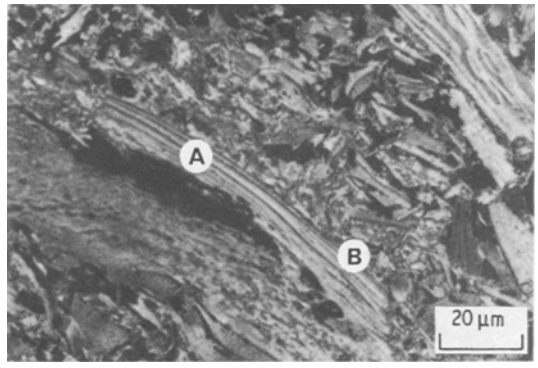

Figure 1 Optical micrograph of carbon artifact from Conoco needle-coke with 35% BSC No. 2 electrode binder pitch. HTT 1273 K, 4 K min^{-1}, under nitrogen. Position A shows acicular flow domain from the needle-coke well bonded at Position B with coarse-grained mosaic binder coke.

Fig. 2 shows the optical texture of a carbon artifact from calcined Conoco needle-coke (5% oxidized) with 35% BSC No. 2 electrode binder pitch. Position C shows acicular flow domains from the needle-coke to be poorly bonded to coarse-grained mosaic binder coke with extensive fissuring developed at the interface between the needle-coke and binder coke (Position D).

Fig. 3 shows the optical texture of a carbon artifact from calcined Conoco needle-coke (10% oxidized) with 35% BSC No. 2 electrode binder

TABLE IV Microstrength indices for carbon artifacts from calcined, and calcined oxidized, Shell needle-coke with 35% BSC No. 2 electrode binder pitch

Needle-coke % weight loss by oxidation	Microstrength indices (wt %)		
	R_1	R_2	R_3
0% oxidized	20.5	46.6	31.9
5% oxidized	11.4	45.0	42.6
10% oxidized	9.5	43.0	46.5
15% oxidized	11.0	46.6	41.4
20% oxidized	13.4	45.0	40.3

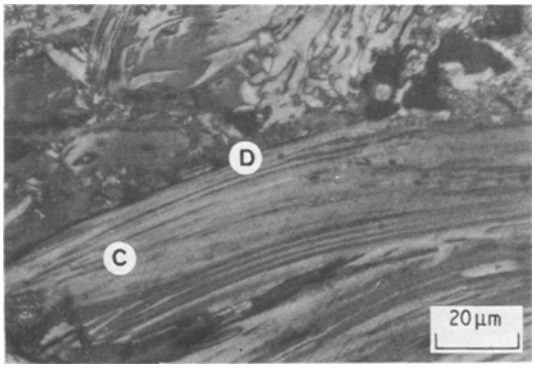

Figure 2 Optical micrograph of carbon artifact from Conoco needle-coke (5% oxidized) with 35% BSC No. 2 electrode binder pitch. HTT 1273 K, 4 K min^{-1} in nitrogen. Position C shows acicular flow domain from the needle-coke poorly bonded to coarse-grained mosaic binder coke with extensive fissuring developed at interface (Position D).

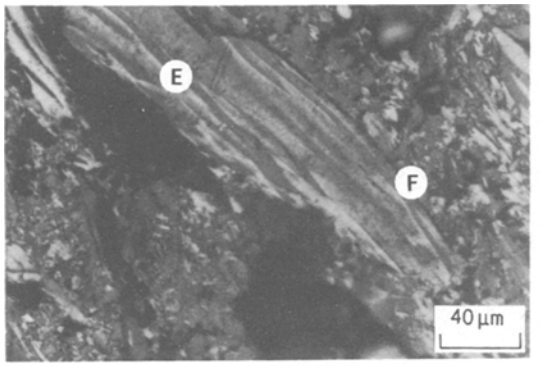

Figure 3 Optical micrograph of carbon artifact from Conoco needle-coke (10% oxidized) with 35% BSC No. 2 electrode binder pitch. HTT 1273 K, 4 K min^{-1} in nitrogen. Position E shows acicular flow domain from the needle-coke poorly bonded to coarse-grained mosaic binder coke, with extensive development of fissuring at the interface (Position F).

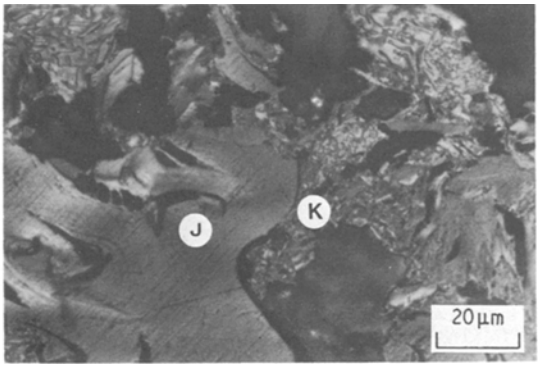

Figure 5 Optical micrograph of carbon artifacts from Shell needle-coke (5% oxidized) with 35% BSC No. 2 electrode binder pitch. HTT 1273 K, 4 K min^{-1}, in nitrogen. Position J shows domain from the needle-coke, with extensive fissuring at the interface (Position K).

pitch. Position E shows acicular flow domain poorly bonded to coarse-grained mosaic with extensive fissuring developed at the interface (Position F).

Fig. 4 shows the optical texture of a carbon artifact from calcined Conoco needle-coke (20% oxidized) with 35% BSC No. 2 electrode binder pitch. Position G shows a domain partially bonded to fine-grained mosaic with limited development of fissuring at the interface (Position H). Position I shows fine-grained mosaic binder coke filling a contraction fissure, 4 μm wide, in the domain.

Similarly, for calcined Shell needle-coke, the optical texture of a carbon artifact from Shell needle-coke with 35% BSC No. 2 electrode binder pitch shows acicular flow domain from the needle-coke to be well bonded to medium-grained mosaic binder coke.

Fig. 5 shows the optical texture of a carbon artifact from calcined Shell needle-coke (5% oxidized) with a 35% BSC No. 2 electrode binder pitch. Position J shows a domain from the needle-coke poorly bonded to coarse-grained mosaic, with extensive development of fissuring at the interface (Position K).

Similarly, for calcined Shell needle-coke the optical texture of a carbon artifact from Shell needle-coke (10% oxidized) with 35% BSC No. 2 electrode binder pitch shows acicular flow domain poorly bonded to coarse-grained mosaic with extensive development of fissuring at both interfaces.

Also, the optical texture of a carbon artifact from calcined Shell needle-coke (20% oxidized) with 35% BSC No. 2 electrode binder pitch shows acicular flow domain bonded to fine-grained mosaic with limited development of fissuring at the interface.

Fig. 6 shows the optical texture of a carbon artifact from calcined NCB coal extract coke No. 18, with 35% BSC No. 2 electrode binder pitch. Position L shows medium-grained mosaic from the extract coke poorly bonded to medium-grained mosaic binder coke with extensive fissuring at the interface (Position M).

Fig. 7 shows the optical texture of a carbon artifact from calcined NCB coal extract coke

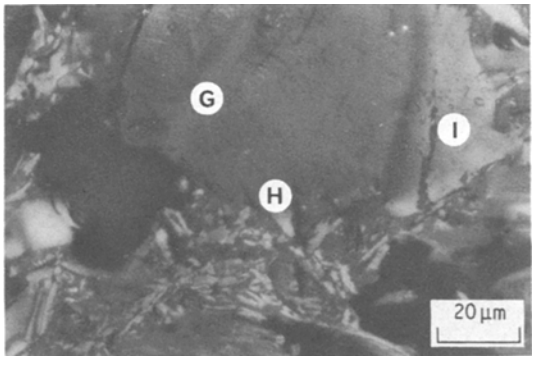

Figure 4 Optical micrograph of carbon artifact from Conoco needle-coke (20% oxidized) with 35% BSC No. 2 electrode binder pitch. HTT 1273 K, 4 K min^{-1}, in nitrogen. Position G shows domain from the needle-coke bonded with fine-grained mosaic binder coke with limited development of fissuring at the interface (Position H). Position I shows binder coke filling a contraction fissure in the domain.

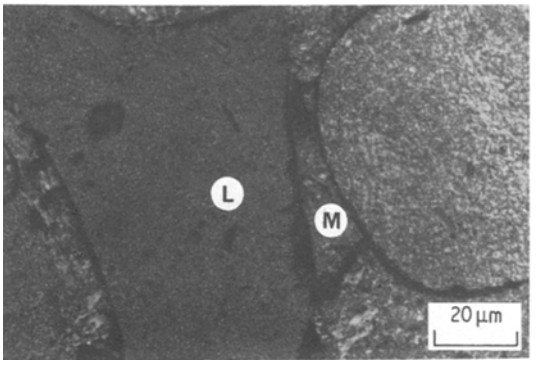

Figure 6 Optical micrograph of carbon artifact from NCB coal extract No. 18 with 35% BSC No. 2 electrode binder pitch. HTT 1273 K, 4 K min^{-1}, under nitrogen. Position L shows medium-grained mosaic from extract poorly bonded to medium-grained mosaic binder coke with extensive development of fissuring at the interface (Position M).

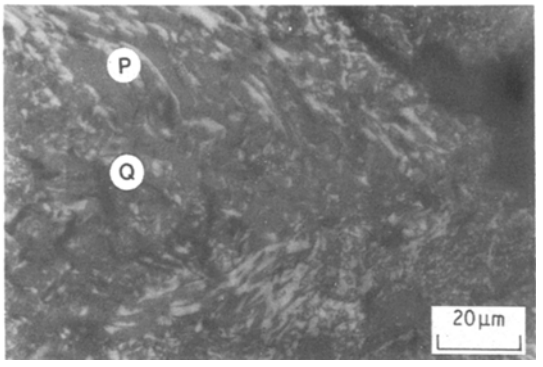

Figure 8 Optical micrograph of carbon artifact from NCB coal extract coke No. 18 (10% oxidized) with 35% BSC No. 2 electrode binder pitch. HTT 1273 K, 4 K min^{-1}, in nitrogen. Position P shows coarse flow anisotropy from the extract bonded to medium-grained mosaic binder coke with small development of interfacial fissuring (Position Q).

No. 18, (10% oxidized) 35% BSC No. 2 electrode binder pitch. Position N shows medium-grained mosaic from the extract coke partially bonded to coarse-grained mosaic binder coke with limited development of interfacial fissuring (Position O).

Fig. 8 shows the optical texture of a carbon artifact from calcined NCB coal extract coke No. 18, (10% oxidized) with 35% BSC No. 2 electrode binder pitch, Position P shows coarse-flow anisotropy from the extract coke bonded to medium-grained mosaic binder coke with a limited number of interfacial fissures (Position Q).

The optical texture of a carbon artifact from calcined NCB coal extract coke No. 18 (20% oxidized) with 35% BSC No. 2 electrode binder pitch shows coarse-grained mosaic from the extract coke well bonded to coarse-grained mosaic and small domain binder coke.

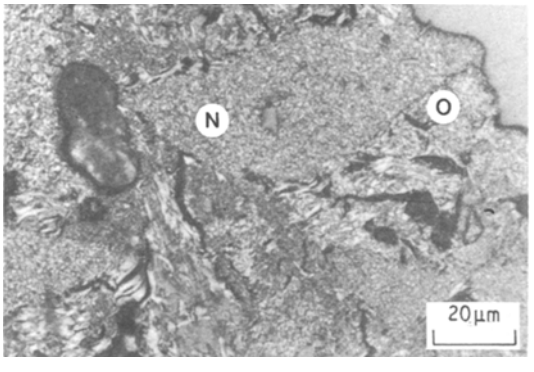

Figure 7 Optical micrograph of carbon artifact from NCB coal extract coke No. 18 (5% oxidized) with 35% BSC No. 2 electrode binder pitch, HTT 1273 K, 4 K min^{-1}, under nitrogen. Position N shows medium-grained mosaic from extract bonded to coarse-grained mosaic, binder coke with limited development of fissures at interface (Position O).

4. Discussion

Consideration of the microstrength indices in Tables III and IV for the needle-coke fillers shows that the initial strengths of the artifacts are very similar. With increasing oxidation of the needle-coke filler particles the strength of the resultant artifacts decline, the greatest change in strength occurring with 5% oxidation.

Comparison of Fig. 1 with Fig. 2 shows that bonding between the needle-cokes and binder pitch coke is markedly effected by the change from non-oxidized to oxidized surfaces of the needle-cokes. The non-oxidized needle-coke appears well bonded to binder coke, as a result of the wetting of the needle-coke by the molten binder during mixing. However, the 5% oxidized needle-coke appears poorly bonded to binder coke with large fissures developing at the interfaces between the filler and binder components.

The poor bonding between the oxidized needle-coke fillers and binder pitch coke results from a deterioration in wettability of the filler particles as a result of oxidation. Lahaye *et al.* [5] report that surface features, $< \sim 5\,\mu m$ in size, would not be penetrated by molten pitch. Fig. 4, Position I shows a contraction fissure in Conoco needle-coke of $\sim 5\,\mu m$ width containing coke after its penetration by binder pitch. Also, it has been

shown [7] that these two needle-cokes at 5 and 10% levels of oxidation, possess surface pits $<4\,\mu m$ in size, i.e. too small for penetration by the binder pitch. Hence, oxidation at these levels limits the extent of the surface of the needle-cokes wetted by the binder pitch and this results in fissured interfaces between filler and binder coke components.

The deterioration in bonding results in the decline in artifact strength shown in Tables III and IV. However, with increasing oxidation to 20% the change in strength becomes less marked. This results from the surface pits in the needle-cokes attaining sizes of 5 to $8\,\mu m$, i.e. of a size easily penetrated by molten binder pitch during mixing [7]. Fig. 4 Position H shows the resultant improvement in bonding between the filler and binder components at these extents of oxidation.

Comparison of the microstrength indices in Table III for the two artifacts prepared from calcined Conoco needle-coke (5% oxidized) show little difference. This would suggest that changes in strength shown by the artifact examined are not those resulting from chance variation in the preparation technique.

Consideration of the microstrength indices in Table V for artifacts containing coal extract coke filler show that the artifact containing non-oxidized filler is of comparable strength to those containing similar needle-coke fillers. However, upon oxidation of the extract coke filler, the strength of the artifacts increases with increasing oxidation, the greatest change occurring in response to 10% oxidation.

Comparison of Fig. 6 Position M with Fig. 8 Position Q shows that the bonding between the extract coke filler and binder pitch coke is also markedly effected by change from non-oxidized to oxidized surfaces of extract coke. The non-oxidized extract coke appears poorly bonded to binder coke. However, oxidation of the extract coke filler improves bonding with binder coke and at levels of oxidation $>10\%$ filler and binder appear well bonded.

TABLE V Microstrength indices for carbon artifacts from calcined, and calcined oxidized, NCB coal extract coke No. 18 with 35% BSC No. 2 electrode binder pitch

Coal extract % weight loss by by oxidation	Microstrength indices (wt %)		
	R_1	R_2	R_3
0% oxidized	23.8	48.5	26.8
5% oxidized	29.0	46.6	23.4
10% oxidized	40.8	41.3	16.8
15% oxidized	40.0	42.8	16.2
20% oxidized	37.8	43.6	17.6
25% oxidized	38.0	43.7	17.2

The poor bonding between the extract coke and the binder coke probably results from the high value of CTE of coal-extract coke (Table I). The high value for the coefficient of thermal expansion suggests that during cooling, shrinkage of extract coke is sufficiently large for it to "pull away" from the binder coke.

The increased bonding between the oxidized extract coke filler and binder coke probably results from penetration of the oxidized, roughened, filler surfaces by the molten binder pitch. The typical optical texture of the extract coke is coarse- to medium-grained mosaic, i.e. 10 to $1.5\,\mu m$. It has been shown that surface pitting of the extract coke resulting from oxidation was of the same order of size as the optical texture, i.e. 10 to $1.5\,\mu m$ [7]. Also, $\sim 10\%$ oxidation was required to develop these surface pits to sizes of 5 to $10\,\mu m$, i.e. the extent of oxidation where improvements in bonding and artifact strength are most evident [7].

The ability of the binder pitch to penetrate surface pits $>4\,\mu m$ diameter in filler particles was shown previously for interactions with needle-coke fillers. The improvement in bonding between the oxidized extract coke particles and binder pitch coke probably results from increased penetration of particle surfaces by molten binder pitch, during mixing, resulting in improved contact between the filler and binder coke. The increased bonding would counteract the "pulling away" behaviour exhibited by the filler during baking, due to its high CTE value, and results in the improvements in artifact strength shown in Table V.

5. Conclusions

The microstrength of carbon artifacts containing oxidized needle-coke filler decreases with increasing extent of oxidation of the filler. However, the strength of carbon artifacts containing oxidized coal extract coke filler increases with increasing extent of oxidation of the filler. Differences in wettability of the filler particles by the pitch appear to cause these changes in microstrength. The pitch appears to be unable to penetrate into the oxidation topography of the needle-coke surface, at levels of oxidation below ~ 20 wt %, but

can penetrate into the large surface features of the oxidized coal extract filler coke. Penetration of pitch into the oxidation topography of the filler cokes produces a wetted/keyed interface and improves the bonding between the filler and binder cokes in the resultant artifact.

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