# Carbonization of Pitch in Porosity

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Abstract. In the production of carbon artefacts where a binder pitch is carbonized with grist coke particles it is inevitable that the pitch will enter the porosity and surface roughness of grist coke. The effect of porosity on structure of binder coke is investigated by co-carbonizing pitches with wood charcoal containing pores of 2 μm to ~150 μm dia. Coke formed in porosity ~40 μm dia. can have a structure similar to that of mesophase carbon fibres. Porosity can cause segregation of primary QI in coal-tar pitch and can reduce the size of optical texture of binder coke. These effects can increase strength within artefacts.

## Introduction

Carbon artefacts. These consist of particles of grist coke held together by bridges of binder coke (usually a coal-tar pitch coke). The binder pitches are generally highly aromatic and contain spheres <1 μm in diameter, known as primary QI (1). Calcined grist coke and coal-tar pitch are mixed at temperatures above the softening point of the binder pitch, moulded or extruded, and the green artefact baked at 850-1200°C to carbonize the binder pitch.

In artefacts, bonding at interfaces between the binder-coke bridges and grist coke particles must be strong and is probably mechanical rather than chemical. During mixing, binder pitch penetrates into surface porosity of the grist coke such that on baking the grist coke and binder coke are interlocked. The van der Waal's dispersion forces contribute to bonding.

Optical texture. Carbon artefacts thus consist of grist coke and binder coke which are both anisotropic carbons. Polarized light microscopy of polished surfaces is a powerful tool for distinguishing graphitizable (anisotropic) from non-graphitizable (isotropic) carbon (2). The long-range molecular order in anisotropic carbons can be quantified in terms of optical texture. The larger the average size of areas in which parallel molecules are aligned in the same direction (isochromatic units) the larger is the optical texture.

Mesophase. Grist coke and binder coke are both produced via the mesophase (3). Heating a pitch results in an increase in average molecular size and aromaticity. Eventually, at about 1000 amu, stacking of molecules surface to surface becomes energetically favourable. Anisotropic growth units of discotic nematic liquid crystals grow within the fluid pitch. These anisotropic units (mesophase spheres) grow at the expense of the isotropic pitch and eventually contact each other. Mesophase spheres consisting of relatively reactive molecules have a higher viscosity due to cross-linkage between molecules and will not coalesce. The resultant coke will have a small optical texture. Mesophase spheres consisting of less reactive molecules coalesce on contact and molecular re-ordering takes place. Eventually a solid semicoke is formed.

The grist coke used to make carbon artefacts is produced by this mechanism as a bulk batch process in the industrial delayed coker. The formation of binder coke from binder pitch in the artefact differs significantly however from delayed coking in that the carbonization of binder pitch does not occur "in bulk". Binder pitch is carbonized during baking in the porosity between grist coke particles and in the surface roughness of grist coke. The dimensions are in metres for the delayed coker and in μm ($10^{-6}$m) for artefacts. It is certain that this restriction in volume affects the structure of resultant binder coke. It is known that mesophase has a tendency to stack parallel to surfaces. This effect can dominate during carbonization within small volumes. It is considered that pitch enters pores in grist coke >~5 μm diameter. Also the dynamic motion of mesophase is reduced in small volumes compared with the "in bulk" material (tonnage quantities).

Objectives. There is a need for a specific study of carbonization in porosity. The aim of this paper is to determine the effect that porosity has on the structure of pitch coke resulting from pitch carbonized within porosity.

Experimental. The model macroporosity of wood charcoal, prepared by heating Alderwood to 900°C under nitrogen, contains pores of sizes, approximately 2-150 μm dia. and 10 to 1000 μm depth.

Fourteen pitches were co-carbonized with charcoal cut into blocks approximately 3 $mm^3$. Nine coal-tar pitches were used, containing 8-25 wt% of primary QI. Five petroleum pitches were used, containing 0.1-3 wt% of primary QI.

0.5 g of charcoal and 3 g of pitch were heated in an autoclave to 500°C, 0.2 MPa pressure, then heated in a horizontal tube furnace under nitrogen to 900°C, 0.5 h soak. The charcoal was polished and examined using polarized light microscopy to reveal optical textures.

Results. The coke material formed in the pores of the charcoal exhibited two phenomena. Firstly, pores contain pitch coke with a characteristic orientation (obtained from the colour analysis of the optical texture) indicating that the constituent lamellae of the pitch coke were aligned parallel to the walls of the charcoal pore in a circumferential or onion-like structure, in transverse cross-section, Figure 1. Such orientation can be seen for both coal-tar and petroleum pitch coke in pores of diameters >~40 μm. No primary QI is seen within these structures.


Figure 1. Position A. 20 μm
Pore containing pitch coke with circumferential structure.

Secondly, it is considered that segregation or enrichment of primary QI occurred in the co-carbonizations of coal-tar pitch and charcoal (not with petroleum pitch), within the pores or at the edges of the pores, Figure 2. This seems to be analogous to what is referred to as industrial primary QI filter-cake. When viewed in the optical microscope

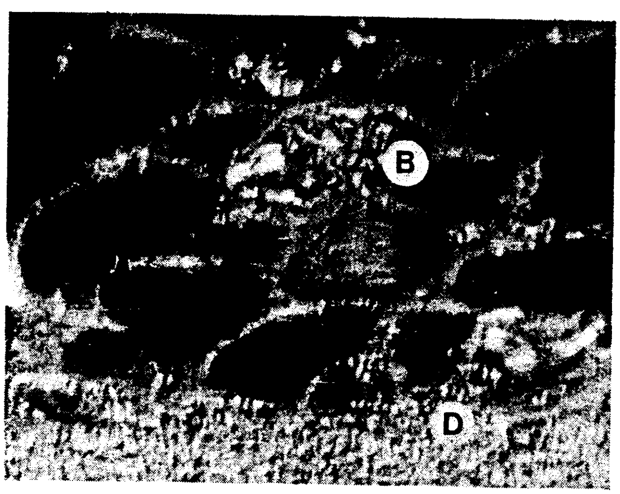


Figure 2. Position B. 20 μm
Pore containing QI and pitch coke.
Position D.
QI filter-cake.

it is seen that all pores in the available size range can contain this co-carbonization mixture of primary QI and pitch to give binder coke of mosaic (<10 μm) optical texture or isotropic coke. There appears to have been enrichment by QI at the charcoal surface and in the porosity.

Discussion. In charcoal pores below a certain size (~40 μm diameter) coke with lamellae parallel to the pore walls are formed. A similar effect was found by Atkinson (4) who carbonized petroleum and coal-tar pitches and a coal-extract on a hot-stage attached to a polarized light microscope in the presence of flat metal transmission electron microscopy (TEM) grids. The grids acted as a support for coalesced mesophase and imposed initial alignment of lamellae parallel to the grid walls. In the 240 and 120 μm grids the dynamic motion of the mesophase removed this alignment. In the 60 and 45 μm grids the alignment was maintained into the resultant carbon.

Of some relevance to this study is the realisation that the structure of the coke in charcoal porosity is similar to that of mesophase carbon fibres with a circumferential arrangement of lamellae (5). The binder coke in porosity will have the onion type cross-sectional structure, as well as the length (depth) of porosity in which it has flowed. Carbon fibres have a high strength and are used as reinforcing agents in applications requiring stiffness. This study suggests that when a binder pitch is co-carbonized with a grist coke containing porosity <50 μm diameter then the pitch will enter this porosity and resultant mesophase will align itself relative to the walls. Accordingly in carbon artefacts a mechanism exists whereby a natural reinforcement is created of binder-coke fibres within the grist coke particles. With regard to the second observation, segregation of primary QI at pore entrances to form a "filter-cake" has been observed by Tillmanns (6). Co-carbonization of pitch with this filter-cake produces a strong (tough) coke of mosaics or of isotropic carbon (7). Thus the binder coke at the entrances to pores or in surface roughness can be stronger than the bulk of the binder-coke bridge at the position of the interface. Strength increases with decreasing size of optical texture (8).

Conclusions. The structure of coke resulting from pitch carbonized in porosity differs from coke resulting from pitch carbonized in bulk. Carbonization of pitch in pores of diameter <~40 μm gives coke a circumferential carbon-fibre like structure. This may act as a natural reinforcement for carbon artefacts. Porosity can segregate primary QI such that a "filter-cake" is produced. This may result in a stronger layer of coke at the filler coke/grist coke interface.

## References

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