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Carbonization and liquid-crystal (mesophase) development. Part 4. Carbonization of coal-tar pitches and coals of increasing rank

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Coal-tar pitches, from coals of different rank and with various quinoline-insoluble contents, were carbonized under pressure (67 to 200 MN m^{-2}) to maximum temperatures of 923 K. The resultant cokes were examined by optical and scanning electron microscopy in terms of size and shape of anisotropic structures within the coke. Natural quinoline-insolubles and carbon blacks both destroyed growth of the mesophase and development of anisotropy. Graphite particles (<10 μm) promoted growth and coalescence of the mesophase. Fourteen coals, of carbon content 77 to 91 wt %, VM 41 to 26%, were similarly carbonized under pressure. In the lower-rank coals no microscopically resolvable anisotropic mesophase was produced, but at a carbon content of 85% anisotropic units 1–2 μm in diameter were detected, increasing in size at a carbon content of 90% to 5 μm diameter. Results are discussed in terms of the origins of anisotropic mosaics observed in cokes, their variation in size with coal rank, and their significance in the carbonization of coal.

It is now understood that anisotropic structures in semi-cokes result from growth and coalescence of anisotropic liquid crystals (mesophase) in the plastic stage of carbonization[1,2]. Usually, the liquid crystals are spherical in shape, growing with increasing heat-treatment temperature (HTT), eventually coalescing, and losing their identity in the resultant anisotropic domains. Carbonization under pressure is relevant in this context. Marsh et al[3,4] observed that the effect of pressure upon the carbonization of anthracene and acenaphthylene was to restrain the coalescence, and hence the loss of identity, of this spherical mesophase. The spheres could be isolated as such, their morphology and size being readily assessed by scanning electron microscopy (for example see Figure 1).

The purpose of the present study was to explore further this finding, incorporating industrial coal-tar pitches and coals. This facility of isolation, examination and measurement of the liquid-crystal units affords a convenient, rapid and sensitive experimental approach. This approach is one which has relevance to properties of pitches in terms of commercial utilization in electrode production (steel and aluminium industries) and to coal utilization in terms of mechanisms of formation of metallurgical coke where ability to form anisotropic carbon is important. This latter consideration is discussed further by Marsh[2]. The immediate objectives were an examination of the pressurized carboniza-tion of pitch and coal looking for isolation of liquid-crystal units, and the experimental elucidation of the factors that influenced their size and morphology, in support of an earlier discussion of the mechanism of coal carbonization[2].

EXPERIMENTAL

Carbonizations were effected under pressures ranging from 67 to 200 MN m^{-2}, the samples being encapsulated in gold tubing to prevent loss of volatiles and ingress of compression fluid, as previously described[3,5]. Rates of heating were 1·6 K s^{-1}, as distinct from 0·08 K s^{-1} previously used, with a soaking period at the heat-treatment temperature (HTT) usually of 1·8 ks. P. W. Whang (personal communication) confirmed that the size of the isolated spheres (described as being botryoidal) formed in the carbonization of anthracene and phenanthrene was independent of heating rates in the range 0·08–1·6 K s^{-1}. Carbonized samples were examined in a 'Stereoscan' scanning electron microscope (Cambridge Instrument Co.), and polished surfaces of carbon by polarized light in a Vickers M41 research microscope with photographic facilities.

Seven characterized American coal-tar pitches[6,7] were selected for study. Chemical analyses are in Table 1; miscellaneous properties including softening point and percentage quinoline-insoluble (Q.I.) are in Table 2; relevant electrical resistivities of graphites from pitches are in Table 3. These pitches, blends of these pitches and additions of naphthalene, Graphon and SP1 Fines were carbonized.

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‡ This study was undertaken by H. Marsh, initially at Pennsylvania State University, USA, during the summer of 1971, and subsequently completed at the University of Newcastle upon Tyne, England

Table 1   Chemical analyses of American pitches

Pitch	Amount (%)						Atomic ratio C/H
	C	H	N	S	Other	Ash	C/H
BD-PSU-5	81·7	7·3	1·2	0·8	6·5	2·6	0·94
BD-PSU-9	93·2	4·5	1·0	0·3	0·9	0·1	1·76
BD-PSU-14	93·0	4·2	1·1	0·4	1·1	0·3	1·86
BD-PSU-17	92·8	4·7	1·1	0·4	1·0	0·1	1·68
SN-56-274	93·0	4·5	0·9	0·4	1·2	0·2	1·74
SN-22-761	93·3	4·2	0·8	0·8	0·9	0·1	1·86
SN-22-763	93·4	4·2	0·7	0·5	1·0	0·1	1·85

Table 2   Miscellaneous properties of American pitches

Pitch	Coking value (%)	Density at 298 K (g cm^{-3})	Softening Point (K)	Insoluble in:		Aromatic hydrogen (% of total H)
				Quinoline (%)	Benzene (%)	
BD-PSU-5	24·8	1·174	376	8·6	18·9	16
BD-PSU-9	36·2	1·300	363	9·9	20·2	85
BD-PSU-14	42·3	1·328	370	18·1	28·6	82
BD-PSU-17	32·3	1·286	359	5·1	16·3	86
SN-56-274	39·2	1·305	373	7·8	32·0	83
SN-22-761	44·5	1·328	369	14·9	32·1	81
SN-22-763	43·8	1·333	371	16·5	36·4	76

Table 3   Electrical resistivities at 2500 psi (1·67 MN m^{-2}) and 298 K for cokes (1273 K) and graphitized carbons (2933 K) from American pitches

Pitch	Electrical resistivity (Ω cm)*	
	Coke	Graphitized carbon
BD-PSU-5	0·049	0·0050
BD-PSU-9	0·039	0·0037
BD-PSU-14	0·040	0·0038
BD-PSU-17	0·034	0·0020
SN-56-274	0·032	0·0029 (2923 K)
SN-22-761	0·050	0·0049 (2843 K)
SN-22-763	0·038	0·0081 (2843 K)

*   1 ohm cm = 10^{-2} Ω m

Table 4   Details of British pitches
   All pitches based on Orgreave lean tar
Pitch A. Lean pitch distilled from Orgreave lean tar
Pitch B. From distillation of lean tar containing added natural Q.I.
Pitch C. Lean pitch to which is added natural Q.I. Silverson mixed
Pitch D. From distillation of lean tar containing low-temperature Q.I.
Pitch E. Lean pitch to which is added low-temperature Q.I. Silverson mixed
Pitch F. From distillation of lean tar containing Philblack GPF
Pitch G. Lean pitch to which is added Philblack GPF Silverson mixed

Pitch	Softening point (K)	Q.I. (%)	Coking value (%)
A	376·5	4·2	56·6
B	373·2	11·6	59·1
C	369·8	12·3	58·3
D	377·1	12·3	58·2
E	387·1	9·6	59·8
F	375·5	11·8	57·7
G	375·2	13·6	58·9

Orgreave lean pitch:	aromatic hydrogen = 80% of total H	
	carbon	93·15%
	hydrogen	4·6%
	nitrogen	1·35%
	sulphur	0·8%
	C/H	1·64

Graphon is the carbon black, Spheron 6, heated to 3000 K, particle size of 10 nm, with surfaces, essentially, of graphitic basal planes.   A transmission electron micrograph is reproduced (*Figure 2*).   SPI Fines consist of graphite flakes, 5 to 10 μm diameter, made from spectroscopic graphite by Carbon Products Division, Union Carbide (*Figure 3*).

A series of British coal-tar pitches was examined (by co-operation with Dr D. McNeil, Director of Research, Coal Tar Research Association, England).   They were based upon Orgreave lean tar.   To this tar were added inert materials (natural and low-temperature Q.I.), and from the mixture pitches were distilled.   In addition, the same inert
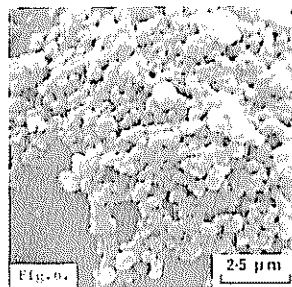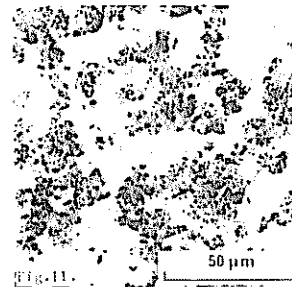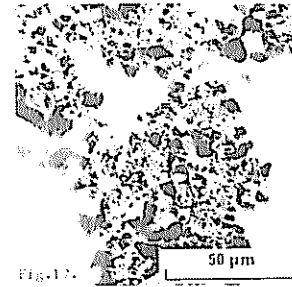
Figure 1 Mesophase spheres (botryoidal) from acenaphthylene 823 K, 260 MN m^{-2}. Scanning electron microscopy (SEM). CR4-102

Figure 2 Graphon particles. Transmission electron microscopy (TEM)

Figure 3 SP1 Fines, spectroscopic graphite flakes. (SEM). CR4-500

Figure 4 Natural Q.I. from Orgreave lean tar. (SEM). CR4-520

Figure 5 Natural Q.I. from Orgreave lean tar. TEM

Figure 6 Thermal Q.I. from Orgreave lean tar. (SEM). CR4-519

Figure 7 Thermal Q.I. from Orgreave lean tar. TEM

Figure 8 Carbon black—Philblack GPF. TEM

Figure 9 Pitch BD-PSU-5 873 K, 130 MN m^{-2}. (Optical). P22

Figure 10 Pitch SN-56-274 873 K, 130 MN m^{-2}. (Optical). P26

Figure 11 Pitch 1:1 SN-56-274, BD-PSU-5 823 K, 130 MN m^{-2}. (Optical). P43

Figure 12 Pitch 1:1 SN-56-274, naphthalene 873 K, 130 MN m^{-2}. (Optical). P48

materials were added to an Orgreave lean pitch prepared from the tar. Details are in *Table 4*. The natural Q.I. is thought to originate from vapour-phase cracking of aromatic hydrocarbon vapour at 1300 to 1600 K. It is an agglomerated isotropic material with particles 50 and 500 nm in diameter (*Figures 4* and *5*). The low-temperature (thermal) Q.I. is produced by maintaining the centrifuged tar at 673—693 K. It also is agglomerated to 20 μm in diameter, with individual particles 50–300 nm in diameter. The particles are spherical, anisotropic, and resemble small mesophase spheres, which indeed they probably are (*Figures 6* and *7*). A carbon black, Philblack GPF (*Figure 8*, diameter 50 nm) was also added. The inerts were added to the tar, which was then distilled to a pitch; the inerts when

added directly to the pitch were dispersed using a laboratory high-speed shearing dispersor (Silverson). The relative quantities of aromatic and aliphatic protons in all the pitches were measured using a Brucker HGX6 90 MHz proton n.m.r. spectrometer with solutions of the pitches in carbon tetrachloride.

A series of twelve American coals (by co-operation with Professor William Spackman, Pennsylvania State University) were similarly examined. Relevant properties are in *Tables 5—7*. Carbon and VM range from 77·3%/45·7% (PSOC 26) to 90·5%/22·9% (PSOC 133). Two British coals were examined, i.e. a Welsh anthracite (Cynheidre) and a prime coking coal (Craghead Busty: carbon 89·1%; hydrogen 5·8%; VM 26·7%; ash 4·6%).

Table 5 Proximate analyses of American coals

Coal sample		Type	(% dry basis)			(% daf)	
			Ash	VM	Fixed C	VM	Fixed C
PSOC	26	HVC	10·8	40·7	48·5	45·7	54·3
	68	HVB	5·2	39·6	55·3	41·7	58·3
	124	HVA	9·4	48·8	41·8	53·9	46·1
	123	HVA	17·4	32·6	49·7	39·6	60·4
	4	HVA	2·1	37·5	60·4	38·0	62·0
	12	HVA	2·7	38·6	58·8	39·4	60·6
	13	HVA	1·3	33·8	64·9	34·1	65·9
	2	HVA	3·9	36·2	60·0	37·6	62·4
	136	MV	2·4	24·2	73·4	24·8	75·3
	135	MV	5·0	23·6	71·4	24·9	75·2
	132	MV	3·4	22·0	74·5	22·8	77·2
	133	MV	6·1	21·5	72·4	22·9	77·1

Table 6 Elementary analyses of American coals

Coal sample		(% daf)					
		C	H	N	Cl	S	O
PSOC	26	77·3	5·6	1·1	—	7·46	8·5
	68	81·3	5·7	1·5	0·02	0·89	10·5
	124	83·6	7·0	1·4	0·06	1·10	6·9
	123	83·4	5·7	1·1	0·07	0·83	8·8
	4	83·8	5·8	1·6	0·15	0·90	7·8
	12	85·2	5·7	1·4	—	0·60	7·2
	13	85·0	5·4	1·3	—	0·35	7·9
	2	85·0	5·6	1·5	0·18	0·64	7·1
	136	88·1	4·6	1·7	0·02	0·59	4·9
	135	88·4	4·9	0·3	0·06	0·64	5·7
	132	90·4	4·0	1·1	0·01	0·71	3·8
	133	90·5	4·4	1·1	0·01	0·62	3·4

Table 7 Petrographic analyses of American coals

Coal sample		Source	Maceral Composition (%)					
			V	P—V	S—F	F	M	E
PSOC	26	Carrier Hills, Ill.	88.5	—	1·4	1·8	3·5	—
	68	Horse Canyon, Utah	81·9	—	1·9	1·6	13·4	1·3
	124	Bickmore, W. Va.	18·1	—	1·7	6·4	35·4	35·6
	123	Bickmore, W. Va.	28·6	—	7·1	7·4	34·4	21·0
	4	Deane, Ky.	67·3	16·8	0·3	2·4	8·6	4·5
	12	Benham, Ky.	59·9	6·6	7·3	1·9	18·5	5·8
	13	Benham, Ky.	37·1	39·8	3·4	4·1	12·3	3·3
	2	Deane, Ky.	26·5	4·3	3·9	2·1	36·5	26·6
	136	Hueyton, Ala.	63·2	9·0	8·9	9·9	8·9	0·1
	135	Hueyton, Ala.	83·1	2·0	2·7	5·0	7·2	—
	132	Garry, W. Va.	69·7	1·6	6·5	8·0	14·2	—
	133	Garry, W. Va.	78·8	3·9	3·3	3·9	8·4	—

V	=	vitrinites	F	=	fusinites
P—V	=	pseudo-vitrinites	M	=	micrinites
S—F	=	semi-fusinites	E	=	exinites

RESULTS

Descriptions of carbonized samples are listed comprehensively in *Tables 8–11*. Optical micrographs are reproduced in *Figures 9–14* and scanning electron micrographs in *jures 15–36*.

DISCUSSION

From the optical and scanning microscopic observations it is possible to summarize the findings in the following sections.

It is found that pressurized carbonization of pitches and coals does restrain coalescence of the mesophase liquid crystals, permitting direct electron-microscopic examination; the results are comparable to those of pressurized carbonizations of anthracene[3]. Variations in size and shape of the liquid crystals form the basis of discussion.

Pitch

Among the American pitches, well-defined spheres (i.e. anisotropic liquid-crystal structures) were formed from BD-PSU-9 (P23, *Figure 16*), BD-PSU-17 (P25, *Figure 18*) and SN-56-274 (P26, *Figures 10* and *19*), i.e. from those

Table 8 Description of carbonized American pitches

Sample No.	Pitch carbonized	HTT (K)	Pressure (MN m^{-2})	Description
P21	BD-PSU-5	823	130	Anisotropic cylinders (1 μm) attached to isotropic core (5 μm)
P22	BD-PSU-5	873	130	Anisotropic cylinders (1 μm) attached to isotropic core (5 μm), *Figures 9* and *15*
P23	BD-PSU-9	873	130	Uniform anisotropic spheres (10 μm), *Figure 16*
P24	BD-PSU-14	873	130	Sintered anisotropic spheres (7 μm), *Figure 17*
P25	BD-PSU-17	873	130	Fused anisotropic spheres (15 μm), *Figure 18*
P26	SN-56-274	873	130	Uniform anisotropic spheres (10 μm), *Figures 10* and *19*
P27	SN-22-761	823	130	Uniform anisotropic spheres (10 μm), *Figures 10* and *19*
P28	SN-22-761	873	130	Fused anisotropic spheres (8 μm), *Figure 20*
P29	SN-22-763	873	130	Sintered anisotropic spheres (8 μm), *Figure 21*
P30	SN-56-274	823	33	Coalesced anisotropic mosaic
P31	SN-56-274	798 (9 ks)	67	Sintered anisotropic spheres (9 μm)
⁻32	SN-56-274	823 (0·3 ks)	67	Anisotropic spheres in isotropic matrix
⅃3	SN-56-274	823	67	Coalesced anisotropic spheres (25 μm)
P34	SN-56-274	823 (9 ks)	67	Fused anisotropic spheres (10 μm)
P35	SN-56-274	873	67	Coalesced anisotropic spheres (40 μm)
P36	SN-56-274	733 (9 ks)	130	Anisotropic spheres in isotropic matrix
P37	SN-56-274	733 (18 ks)	130	Anisotropic spheres in isotropic matrix
P38	SN-56-274	748 (3·6 ks)	130	Anisotropic spheres in isotropic matrix
P39	SN-56-274	798	130	Fused anisotropic spheres (5 μm)
P40	SN-56-274	798 (9 ks)	130	Anisotropic spheres (15 μm)
P41	SN-56-274	823	130	Anisotropic spheres (8 μm)
P42	SN-56-274	923	130	Sintered anisotropic spheres (9 μm)

Table 9 Description of carbonized American pitch blends

Sample No.	Blend carbonized	HTT (K)	Pressure (MN m^{-2})	Description
P43	1:1 SN-56-274/BD-PSU-5	823	130	Sintered anisotropic spheres (7 μm) with internal mosaics (2 μm); cf. P8, P41. *Figures 11* and *22*
P44	1:1 SN-22-761/BD-PSU-5	823	130	Sintered anisotropic spheres (7 μm) with internal mosaics (2 μm); cf. P8, P27
P45	1:1 SN-56-274/naphthalene	823	130	Anisotropic spheres within isotropic matrix; cf.P41
P46	1:1 SN-56-274/naphthalene	823 (3·6 ks)	130	Anisotropic spheres within isotropic matrix; cf. P41
P47	1:1 SN-56-274/naphthalene	823 (7·2 ks)	130	Fused anisotropic spheres with internal mosaics (2–5 μm)
P48	1:1 SN-56-274/naphthalene	873	130	Coalesced anisotropic spheres with internal mosaics (2–5 μm); cf. P26. *Figures 12* and *23*
⅃9	SN-56-274/10% Graphon	823	130	Isotropic material and fused anisotropic spheres (1–5 μm); cf. P41
P50	SN-56-274/0·5% SP1 Fines	823	130	Anisotropic mosaics and residual spheres (1–7 μm); cf. P41. *Figure 24*

Table 10 Description of carbonized Orgreave pitch compositions

Sample No.	Blend carbonized	HTT (K)	Pressure (MN m^{-2})	Description
P51	Lean pitch	848	130	Fused anisotropic botryoidal spheres (15 μm), *Figure 25*
P52	Lean pitch	873	130	Coalesced anisotropic mosaics
P53	Lean tar + natural Q.I. distilled	848	130	Fused anisotropic botryoidal spheres (9 μm); Q.I. on periphery of spheres, *Figure 26*
P54	Lean pitch + natural Q.I. Silverson mixed	848	130	Fused anisotropic botryoidal spheres (7 μm); Q.I. on periphery of spheres, *Figure 27*
P55	Lean tar + low-temperature Q.I. distilled	848	130	Coalesced anisotropic mosaics (50 μm), *Figure 28*
P56	Lean pitch + low-temperature Q.I. Silverson mixed	848	130	Coalescing anisotropic spheres (12 μm), *Figure 29*
P57	Lean tar + Philblack GPF distilled	848	130	Fused anisotropic botryoidal spheres (2 μm); Philblack on periphery of spheres, *Figure 30*
P58	Lean pitch + Philblack GPF Silverson mixed	848	130	Fused anisotropic botryoidal spheres (5 μm); Philblack on periphery of spheres

Table 11 Description of carbonized coals

Sample No.	Coal carbonized	HTT (K)	Pressure (MN m^{-2})	Description
P59	PSOC 68	873	200	No resolvable structures, isotropic
P60	PSOC 26	873	200	Traces of anisotropic material (1 μm)
P61	PSOC 124	873	200	No resolvable structures, isotropic
P62	PSOC 123	873	200	Anisotropic units (0·5 μm), in isotropic matrix, *Figure 31*
P63	PSOC 4	873	200	Anisotropic units (0·5 μm)
P64	PSOC 12	873	200	Anisotropic units (0·5 μm), *Figures 13* and *32*
P65	PSOC 13	873	200	Fused, anisotropic spheres (1 μm), *Figure 33*
P66	PSOC 2	873	200	Fused, anisotropic spheres (2 μm), *Figures 14* and *34*
P67	PSOC 136	873	200	Anisotropic mosaics (15 μm), spheres (5 μm)
P68	PSOC 135	873	200	Anisotropic mosaics (15 μm), spheres (10 μm)
P69	Craghead Busty	873	130	Anisotropic mosaics (15 μm), spheres (10 μm), *Figure 35*
P70	PSOC 132	873	200	Anisotropic mosaics (15 μm), spheres (10 μm), *Figure 36*
P71	PSOC 133	873	200	Large anisotropic mosaics (75 μm)
P72	Welsh anthracite	873	130	Completely anisotropic without domains. No fusion had occurred

pitches lowest in Q.I. and richest in aromatic hydrogen. Those with increased Q.I. contents (up to 18·1%) at almost constant content of aromatic hydrogen (76—82%) resulted in diminished sphere size and sintering and fusing of the spheres (P24, *Figure 17*; P28, *Figure 20*; P29, *Figure 21*). Sintered spheres are distinct but joined at contacts; fused spheres are considerably mis-shapen at contacts; coalesced spheres have almost lost all morphology but their anisotropy is distinct under optical microscopy. The sintered material between the spheres in samples P24, P28, P29 is isotropic and rich in Q.I.; this material apparently prevented the growth processes leading to anisotropic material between the spheres. During carbonization of such pitches, the Q.I. does not remain evenly distributed throughout the resultant semi-coke but accumulates at peripheries of the liquid-crystal spheres and in pockets between the spheres. This results in some structural heterogeneity, affecting physical properties such as electrical conductivity. It is relevant to note that the graphite from BD-PSU-17,

the pitch of lowest Q.I. and highest aromaticity, has the lowest electrical resistivity (*Table 3*).

The low-rank pitch BD-PSU-5, C/H atomic ratio of 0·94 and 16% aromatic hydrogen, forms anisotropic units only 1 μm in diameter attached to a central core of isotropic material (P22, *Figures 9* and *15*). Not all of the constituent molecules of this pitch can form liquid-crystal structures and it is relevant to note this separation into a 'bi-phase' system.

Pitch SN-56-274 was selected for additional experiments. Although BD-PSU-17 (P25, *Figure 18*) formed larger spheres, they were more sintered than the quite botryoidal spheres of SN-56-274 (P26, *Figure 19*). In an initial survey with this latter pitch to optimize conditions of sphere formation (P30—P42), it was noted for SN-56-274 that pressures of 67 MN m^{-2} and below did not produce botryoidal spheres (as previously observed[2]). At 130 MN m^{-2} pressure, optimum conditions were 798 K, 9 ks soak time (P40), and 823 K and 873 K, soak time of 1·8 ks (P41 and P26).
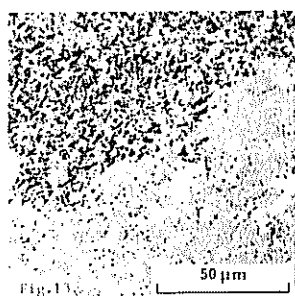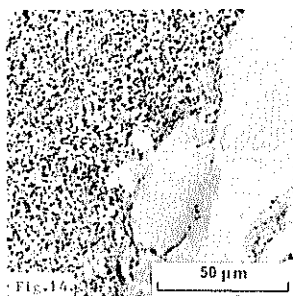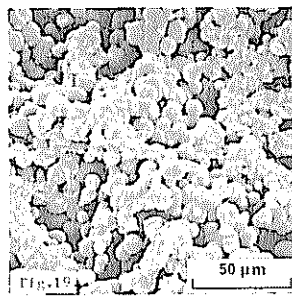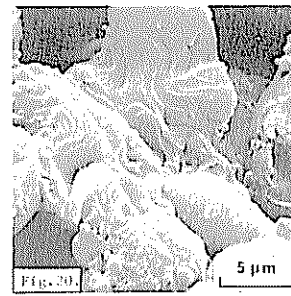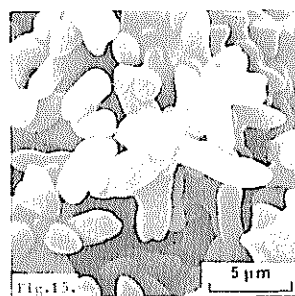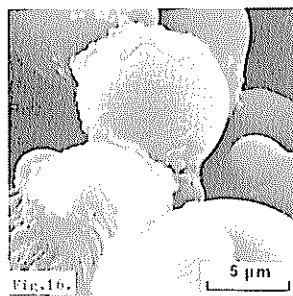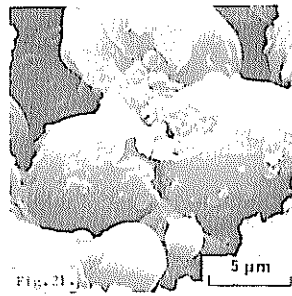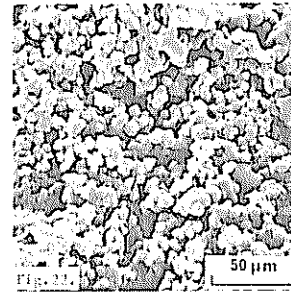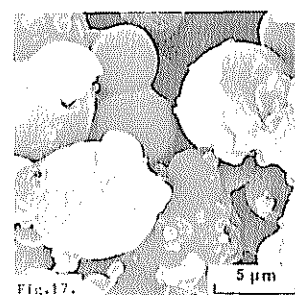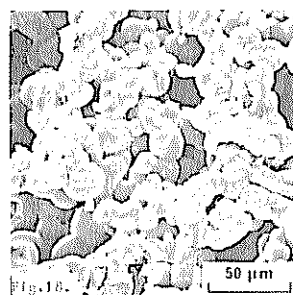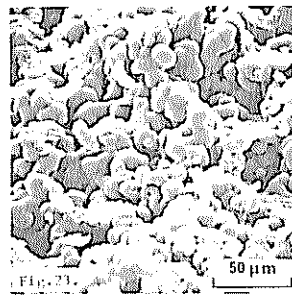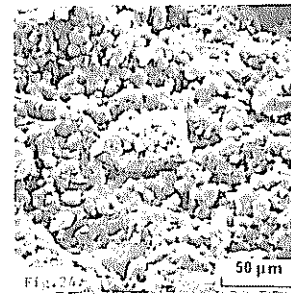
Figure 13   Coal PSOC 12 873 K, 130 MN m^{-2}. (Optical). P64

Figure 14   Coal PSOC 2 873 K, 130 MN m^{-2}. (Optical). P66

Figure 15   Pitch BD-PSU-5   873 K, 130 MN m^{-2}. P22. (SEM).
CR4-368

Figure 16   Pitch BD-PSU-9   873 K, 130 MN m^{-2}. P23. (SEM).
CR4-461

Figure 17   Pitch BD-PSU-14 873 K, 130 MN m^{-2}. P24. (SEM).
CR4-466

Figure 18   Pitch BD-PSU-17 873 K, 130 MN m^{-2}. P25. (SEM).
CR4-471

Stereoscan micrographs

Figure 19   Pitch SN-56-274 873 K, 130 MN m^{-2}. P26. CR4-419

Figure 20   Pitch SN-22-761 873 K, 130 MN m^{-2}. P28. CR4-370

Figure 21   Pitch SN-22-763 873 K, 130 MN m^{-2}. P29. CR4-476

Figure 22   Pitch 1:1 SN-56-274, BD-PSU-5   823 K, 130 MN m^{-2}.
P43. CR4-438

*Figure 23*   Pitch 1:1 SN-56-274, naphthalene 873 K, 130 MN m^{-2}.
P48. CR4-465

Figure 24   Pitch SN-56-274, 0·5% SP1 Fines 873 K, 130 MN m^{-2}.
P50. CR4-360

In co-carbonizations, at 823 K, of SN-56-274 with the low-rank pitch BD-PSU-5, all isotropic carbon disappeared, but although the sphere size remained unchanged at about 7 μm, there were internal mosaics (2 μm) within the spheres (P43, *Figures 11* and *22*). Sample P44 behaved similarly. Evidently, in the blends of pitch, the compounds which formed the isotropic carbon can be accommodated within the liquid-crystal structures and, although the structural, perfection is affected, the removal of isotropic carbon is total.

SN-56-274 was co-carbonized with naphthalene which singly forms anisotropic botryoidal spheres (7 μm) at 873 K, but is uncarbonized at 823 K [5]. SN-56-274 forms an anisotropic carbon at 798 K (P39) and hence must be chemically more reactive than the naphthalene. Samples P45–P48

(*Table 9*) show that the anisotropic liquid crystals from the pitch molecules can grow in the isotropic molten naphthalene but are reduced in size (2–5 μm, 823 K, P47). There is evidently diffusional restriction upon growth processes. At 873 K there are formed coalesced structures of small anisotropic mosaics (2–5 μm, P48, *Figures 12* and *23*). The size of the liquid-crystal units in a carbonizing system is therefore a function of the relative chemical reactivities of the constituent molecules. This situation is somewhat different from P41 where the more aliphatic constituents of the low-rank pitch form a carbon, albeit isotropic, at 823 K.

The addition of 10% of Graphon to SN-56-274, raising the Q.I. content to 18%, that of a pitch BD-PSU-14 with comparable analyses, had a more drastic effect upon liquid-crystal growth than the 18% of Q.I. in BD-PSU-14.
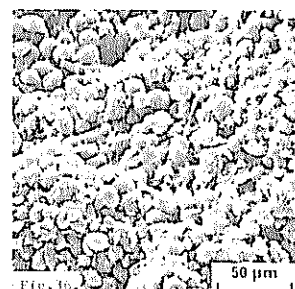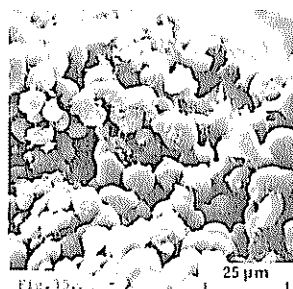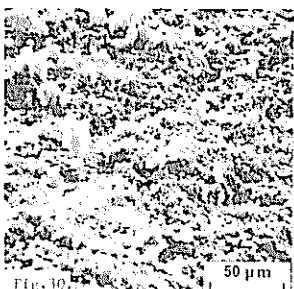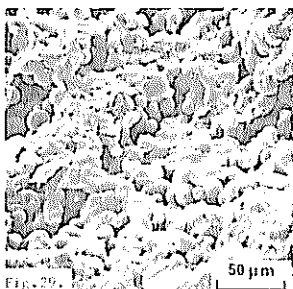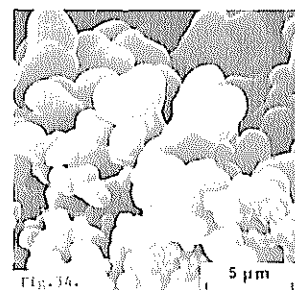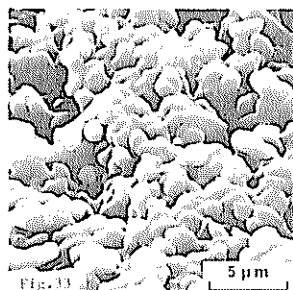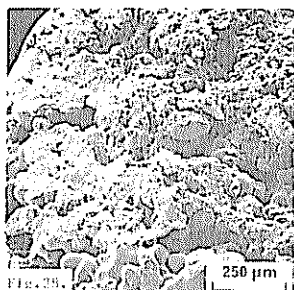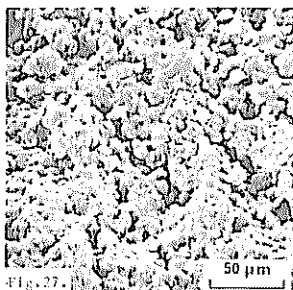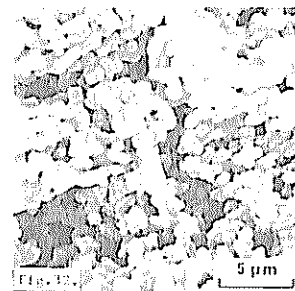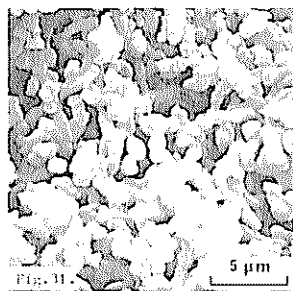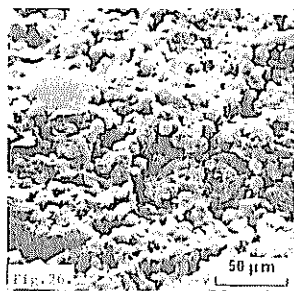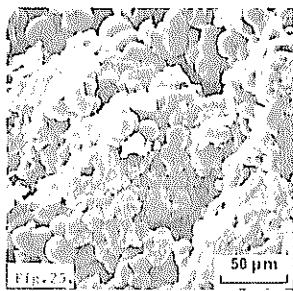
Stereoscan micrographs

Figure 25 Orgreave lean pitch 848 K, 130 MN m^{-2}. P51. CR4-549

Figure 26 Orgreave lean tar, 11·6% Natural Q.I. 848 K, 130 MN m^{-2}. P53. CR4-537

Figure 27 Orgreave lean pitch, 12·3% Natural Q.I. 848 K, 130 MN m^{-2}. P54. CR4-539

Figure 28 Orgreave lean tar, 12·3% low-temperature Q.I. 848 K, 130 MN m^{-2}. P55. CR4-545

Figure 29 Orgreave lean pitch, 9·6% low-temperature Q.I. 848 K, 130 MN m^{-2}. P56. CR4-547

Figure 30 Orgreave lean tar, 11·8% Philblack GPF 848 K, 130 MN m^{-2}. P57. CR4-541

Stereoscan micrographs

Figure 31 Coal PSOC 123 873 K, 200 MN m^{-2}. P62. CR4-363

Figure 32 Coal PSOC 12 873 K, 200 MN m^{-2}. P64. CR4-472

Figure 33 Coal PSOC 13 873 K, 200 MN m^{-2}. P65. CR4-446

Figure 34 Coal PSOC 2 873 K, 200 MN m^{-2}. P66. CR4-422

Figure 35 Coal Craghead Busty 301 873 K, 0·08 K s^{-1}, 130 MN m^{-2}. P69. CR4-570

Figure 36 Coal PSOC 132 873 K, 200 MN m^{-2}. P70. CR4-261

The average sphere size was reduced to 3 µm and the size-range widened to 1—5 µm with isotropic material between the spheres. The smaller Graphon particle, 10 nm, apparently is more effective than the natural Q.I., 300 nm diameter, in reducing the size of the liquid crystals.

The addition of only 0·5% of the graphitic SP1 Fines to SN-56-274, P50, *Figure 24*, prevented the separation and isolation of the liquid-crystal spheres, the mechanism being that the liquid crystals flowed over the surfaces of the graphite and subsequently coalesced thereon.

Carbonizing the Orgreave lean pitch (*Table 4*) established optimum conditions for mesophase sphere formation, 15 µm, of 848 K. Addition of natural Q.I., 12%, to both the tar and the pitch resulted in smaller spheres, 7—9 µm,

with the Q.I. accumulated on peripheries of the spheres preventing further coalescence (P53, P54, *Figures 26* and *27*). Addition of low-temperature Q.I., 12%, to the tar promoted coalescence of liquid crystals to mosaics 50 µm in size (P55, *Figure 28*). It was not possible, using optical microscopy, to differentiate the added Q.I. within the semicoke. Additions to the pitch promoted some coalescence of spheres without seriously affecting size as in P56 (cf. *Figures 25* and *29*). Evidently, additions of low-temperature Q.I. produce no deterioration in liquid-crystal growth processes — there may in fact be some amelioration. Additions, 12%, of Philblack GPF reduced appreciably the size of liquid-crystal units, the carbon black accumulating on the peripheries of the spheres and preventing further coalescence. As discussed above, the small size of the carbon black (50 nm) with its considerable structure (*Figure 8*) — in the sense of the carbon black industry — compared with the 500 nm size of the natural Q.I., may be a contributory factor.

Coal

The coals which were carbonized under pressure, *Tables 5–7*, and *11*, are tabulated in an order which approximates to increasing rank. The objective is to demonstrate by scanning electron microscopy the progressive development size of separated mesophase units, to measure their size, and to monitor any coalescence with increase in rank. The progression observed (*Table 11*) shows a clear development of growth in size of mesophase units with rank, *Figures 13, 14, 31–36*. It is emphasized that the morphology seen in the 'Stereoscan' microscope is anisotropic when viewed by polarized light. *Table 11* establishes that in the lower-rank coals, e.g. PSOC 68, PSOC 26, the ability to form any type of liquid-crystal unit does not exist. Anisotropic units 0·5 μm in diameter are detected in the medium-rank coals, but it is with coal PSOC 136, 88% C, 24·8% VM, that the ability is realized to form the liquid crystals such as are produced from pitch and pure organic compounds. Samples P67 to P70 are produced from coking coals suitable for metallurgical coke production. The sphere size, 10 μm, is the size found on carbonization of a lean pitch and naphthalene. Coal PSOC 133, corresponding more to a type 204 coal (NCB classification) does not form mesophase spheres. Optical examination shows a large content of non-fused material in this coke. This property, associated with increased aromaticity of the diminished fusible content in this coal, promotes coalescence of liquid-crystal material (cf. P50, *Figure 24*). The Welsh anthracite did not fuse; the anisotropy reflects the original properties of the coal.

These coals were carbonized in a closed system with no release of volatiles. Hence, the entire coal substance is carbonized. That part of the coal substance which would be lost as volatiles at atmospheric pressure forms, when carbonized under pressure, anisotropic carbon with properties that reflect the rank of the coal. Carbonizations under pressure yield higher percentages of anisotropic material in the coke with some increase in the size of the anisotropic units. These factors do however increase the overall sensitivity of this technique in quantifying liquid-crystal growth processes in terms of the carbonizing properties of coal.

CONCLUSIONS FOR METALLURGICAL COKE PRODUCTION

The conclusions from this study can be interpreted, in terms of an understanding of the development of anisotropic material in cokes from coals and coal blends, to promote further understanding of the carbonization process of coal.

(1) The relative smallness in size of liquid-crystal units in the lower-rank coals could be a consequence of heterogeneity of molecular properties in the plastic phase; liquid crystals can grow from an isotropic melt but the size is limited if an isotropic carbon is formed at an early stage of carbonization. If the isotropic plastic phase contains different molecular systems all capable of forming liquid crystals, but at temperatures differing by about 40 K, then the growth processes are again severely restricted.

(2) The size and structure of inert inclusions within the coal substance is important. Materials of colloidal dimensions, about 10 to 50 nm diameter, clearly disrupt liquid-crystal growth processes by adhering to the surfaces of the growing liquid crystal. But larger surfaces can promote coalescence of liquid crystals into larger anisotropic units which influence significantly the physical properties of cokes.

(3) Liquid crystals can accommodate within their structure material which would otherwise be isotropic, i.e. there is enforced anisotropy. This is relevant to blending of coals of rank above and below that of prime coking coals, suggesting a mechanism to maintain anisotropy which is important in the production of metallurgical cokes.

(4) The coking coals represent an optimum in facility and extent of liquid-crystal formation with a suitable balance (fortuitous) in the proportions of inert and fusible material.

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