346. *A Study of Bituminous Coal by* (a) *Exhaustive Solvent Extraction and* (b) X-Ray *Diffraction.*

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A semimicro-method for the exhaustive solvent extraction of coal with pyridine and chloroform is described. This method has been used in a detailed study of the effect of carbonisation and oxidation on the yield of α (pyridine-insoluble), β (pyridine-soluble, chloroform-insoluble), and γ (pyridine- and chloroform-soluble) fractions. The three fractions from the unoxidised and oxidised coal and the chars and cokes obtained from them at various temperatures have been examined by X-ray powder photography, and the results obtained provide further evidence in support of the views already advanced concerning the importance of the proportion of oxygen in determining the crystallographic behaviour of a carbonaceous substance on carbonisation. Although the caking properties of the original coal were completely destroyed by the oxidation, the γ extract from the oxidised coal still caked strongly on carbonisation.

PREVIOUS investigations (" The Ultra-Fine Structure of Coals and Cokes ", B.C.U.R.A., London, 1944, 176—231; *J. Inst. Fuel*, 1945, War Time Bulletin, 117) have led us to the view that bituminous coal consists essentially of two related, but crystallographically distinct substances, *viz.*, (a) bitumen and (b) residual coal. The bitumen is that part of the coal which can be extracted by organic solvents : a greater or a lesser part of the bitumen, according to the rank of coal, consists of thermally stable, polynuclear, aromatic molecules which only lose their individuality and become converted into " carbon " at temperatures in the 400—550° range. It is this part of the bitumen which confers on a coal its coking properties. The remainder of the bitumen consists of waxy, resinic, and naphthenic substances, some of which may be converted into coking bitumens during carbonisation (*Nature*, 1947, **159**, 536). Much less is known of the molecular structure of the residual coal: it contains a higher proportion of oxygen and a lower proportion of hydrogen and is thermally less stable than the coking bitumens, and its crystallographic behaviour on carbonisation indicates that it has a disordered crystal structure which is either actually or potentially cross-linked. It is probably related structurally to the humic acids and the humins.

Pyridine is known to have a high solvent and peptising action on bituminous coal. According to Wheeler and his co-workers (see Bakes, D.S.I.R. Fuel Research Tech. Paper No. 37, 1933, for references and review of work on solvent extraction of bituminous coal), the insoluble residue (α-fraction) of the pyridine extraction of a bituminous coal consists of undispersed ulmins together with resistant plant remains : the pyridine-soluble, chloroform-insoluble, β-fraction consists of dispersed ulmins, and the pyridine-soluble, chloroform-soluble γ-fraction consists of saturated and unsaturated hydrocarbons together with resinous materials.

The objectives of the present investigations were (*a*) to determine how far it is possible to correlate the results of the exhaustive pyridine extraction of a coking coal and of cokes prepared from it, with the results of X-ray investigations already reported, and (*b*) to investigate the change in the X-ray crystallographic properties which the α-, β-, and γ-fractions undergo when the caking properties of the original coal are destroyed by oxidation. In spite of the high solvent and peptising action of dry pyridine on bituminous coal, exhaustive extraction on the macro-scale is a lengthy and tedious operation : the following semimicro-procedure was therefore adopted.

A sample of the coal (about 0·02 g.), freshly crushed to pass a 240 B.S. sieve, was placed in a centrifuge tube (30 ml.) of known weight, and dried in a stream of dry, oxygen-free nitrogen at 120°. The centrifuge tube and contents, contained in a stoppered weighing tube, were weighed. Technical pyridine was dried over potassium hydroxide and redistilled, the fraction of b. p. 120—130° being collected and redistilled as required, immediately before use. The dry pyridine (3 ml.) was added to the coal in the centrifuge tube and then heated for 10 mins. under


Fig. 1.

Fig. 2.
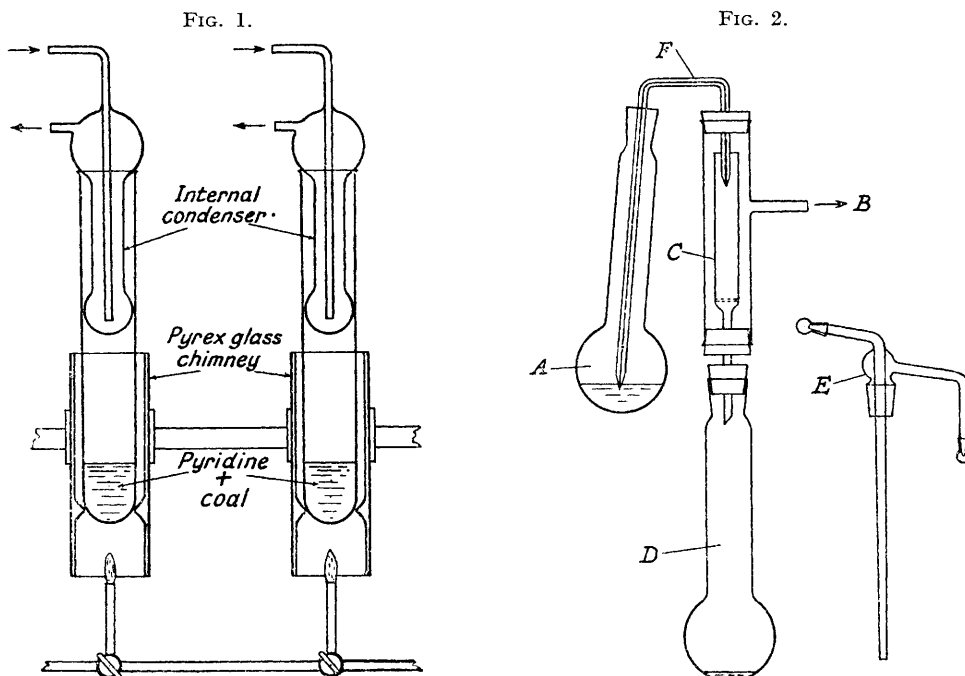
a reflux condenser which was formed by inserting a water-cooled tube in the top part of the centrifuge tube (see Fig. 1) : ingress of air was minimised by the formation of a liquid pyridine seal between the condenser wall and the centrifuge tube. A battery of such tubes was erected in order to permit several semimicro-extractions to be carried out simultaneously. After about 10 mins.' extraction the tube and contents were centrifuged, the supernatant liquid was removed by means of a suction tube, a second 3 ml. of pyridine added, and the refluxing and separation repeated. These operations were continued until the supernatant pyridine, after centrifuging, was colourless : some 3—20 extractions were necessary according to the character of the sample under investigation. The extracts were combined and the pyridine removed by distillation in a stream of carbon dioxide at low pressure (5—10 cm. Hg), followed by steam-distillation for 20 mins. : residual water was then removed in a current of dry carbon dioxide at low pressure, and the product finally dried in a current of dry nitrogen at atmospheric pressure. The distillation was carried out without transference of the solution or residue from the tared distillation flask, and the final weighing gave the percentage of pyridine-soluble matter (β + γ-fraction) in the coal.

Redistilled chloroform was purified further by passage through a column of activated alumina (14—25 B.S. sieve size, freshly heated to 150°, and cooled in a stream of dry air) 2 cm. in diameter and 25 cm. long ; 10 ml. of this chloroform left no perceptible residue on evaporation.

The $\beta + \gamma$-fraction in flask A (Fig. 2) was extracted by warming it with 2 ml. of pure chloroform which refluxed from the cold neck of the flask. The resulting liquid was drawn by suction (at B) into a sintered-glass micro-filter C. The residue in A was extracted with successive amounts of chloroform until a colourless extract was obtained : usually three extractions sufficed. The apparatus was then evacuated through B, with F closed ; air was then allowed to enter and thus forced the chloroform solution from C into the second small distilling flask D, which was provided with a detachable distillation head E. This procedure was repeated if necessary until filtration was complete. The insoluble residue on the filter was well washed with pure chloroform which was introduced as described above. Flask B was attached to the distillation head, E, and the chloroform removed from the combined filtrate and washings by distillation in a stream of carbon dioxide at reduced pressure and a temperature not exceeding

FIG. 3.
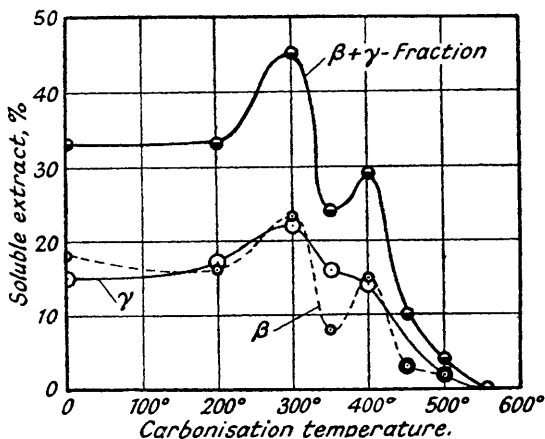
Solvent extraction of Durham coal C.383 before and after preheating.

FIG. 4.
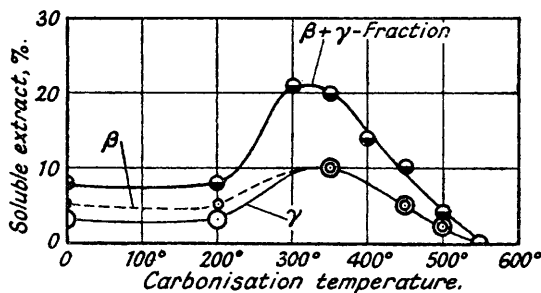
Solvent extraction of S. Wales coal C.906 before and after preheating.

100°. The last traces of chloroform were removed from the residue by heating it in a stream of carbon dioxide at low pressure (2—5 cm. Hg) for a further 15 mins. after the chloroform had ceased to distil. When the flask was cool, pure dry nitrogen was passed through it for 20 mins. and it was then stoppered and weighed. The method is probably capable of improvement : the results obtained for the proportion of γ-fraction were probably reproducible to $\pm$ 1%.

Solvent Analysis of a Durham and a South Wales Coking Coal.—It has already been shown (Blayden, Gibson, and Riley, *loc. cit.*) that if a bituminous coal is subjected to a step-wise carbonisation, the half-peak widths of the inner intense halo in the X-ray powder photographs of the products show systematic variations with carbonisation temperature. The c dimension (*i.e.*, the height) of the average, hypothetical, cylindrical, graphite-like crystallite, calculated from the half-peak width, and plotted against carbonisation temperature, passes through a more or less pronounced maximum in the neighbourhood of 550° (see Fig. 6) (experimentally, a progressive sharpening of the inner halo, up to 550° followed by a broadening). Evidence has

been put forward which suggests that this phenomenon is due to some type of unidimensional crystallisation of the mobile thermally stable bitumen molecules. It is important to determine whether or not this unidimensional crystallisation involves merely the ordering of bitumen molecules (cf. experiments on the " annealing " and carbonisation of disordered dibenzanthrone crystals already reported, *loc. cit.*), or whether it involves the progressive conversion of bitumen molecules into rigid " carbon " as the temperature is increased up to 550°.

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TABLE I.

Analyses of Durham and South Wales coals.

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	Ash, %.	Moisture, %.	Volatile matter less mois- ture, %.	Volatile matter, % (a.f.d.).	B.S. swelling no.	C, % (a.f.d.).	H, % (a.f.d.).
Durham coal C.383	2·9	0·9	26·6	27·6	0	88·5	4·8
,, ,, ,, (oxidised)	—	—	—	—	9	84·4	4·29
S. Wales coal C.906	2·6	1·0	18·5	19·2	82	90·4	4·6

Samples of the two coals and their semi-cokes (prepared from C.383 by carbonising in nitrogen at 2° per min. and soaking at the final temperature for 10 mins., and from C.906 by carbonising at 5° per min. and soaking for 10 mins.) were subjected to the semimicro-solvent extraction described above. Perhaps the most significant feature of the results obtained (see Fig. 3 and 4)

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FIG. 5.

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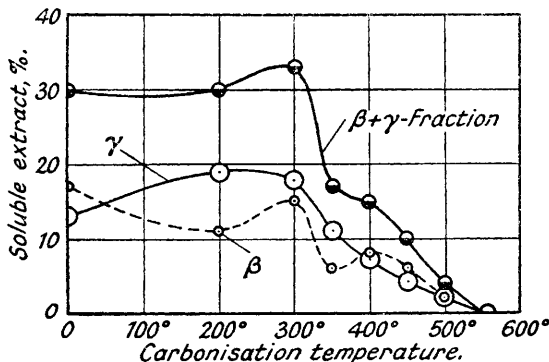
Solvent extraction of the oxidised Durham coal C.383 before and after preheating.

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is that the soluble bitumens have completely disappeared at a temperature near 550°—either through volatilisation or by decomposition into insoluble " carbon ". The decrease in the proportion of β + γ-fraction as the temperature increases from 300° to 550° suggests that the change is progressive, the less stable bitumens being converted into " carbon " at the lower temperatures. The temperature of complete disappearance of the β + γ-fraction is coincident with the temperature of the maximum on the *c* dimension carbonisation temperature curve (see Fig. 6) : this result provides further evidence in support of the interpretation of the X-ray diffraction phenomenon already put forward. The pronounced increase in the proportion of β + γ-fraction brought about by preheating in the temperature range 200—300° is interesting. Berry (results quoted by Cockram and Wheeler, *J*, 1927, 713) has also found that preheating various coals to 200°, 250°, and 350° causes a progressive increase in the proportion extracted by either chloroform or benzene. This phenomenon, which apparently affects the β- and the γ-fraction to a similar extent, may be due to the cracking of complex aggregates or possibly to the desorption of the bitumen molecules from the α-carbon. The large difference in the proportion of soluble matter in the two coals, which have similar swelling properties, is interesting and is probably wholly or partially due to the higher rank of the S. Wales coal.

Fig. 5 shows the results of solvent extraction experiments on the Durham Coal C.383 after it had been heated in air at 120° for 60 hours, its caking and swelling power thereby being completely destroyed. This pretreatment, which brings about a fundamental change in the character of the coal, causes surprisingly little change in the general behaviour of the coal to pyridine and chloroform. The original coal, C.383, contained about 15% of γ-fraction, whereas the oxidised coal, which on carbonisation gave a non-coherent powder, still contained about 13% of

γ-fraction. Fig. 6 shows the profound effect of oxidation on the X-ray crystallographic behaviour : whereas the original coal gave a pronounced peak at 500° in its *c* dimension curve, the oxidised coal gave a *c* dimension which decreased with increase of the carbonisation temperature up to 600°. The *a* dimensions (diameter of the hypothetical cylindrical crystallite) of the oxidised coal and of the products obtained by heating it in nitrogen at 5° per min. up to various temperatures, showed little difference from the results obtained with the unoxidised coal.

The above observations suggested that interesting results would be obtained by separating both the fresh and the oxidised coal into α-, β-, and γ-fractions on a macro-scale, and comparing the crystallographic behaviour of the corresponding fractions on carbonisation.

The coal was ground in a ball-mill for 24 hrs. and the air-dry product (20 g., 1·5% moisture) was heated with redistilled pyridine (200 ml.) in a 500-ml. round-bottom flask provided with an internal reflux condenser. A non-oxidising atmosphere was maintained by passing a current of

Fig. 6.
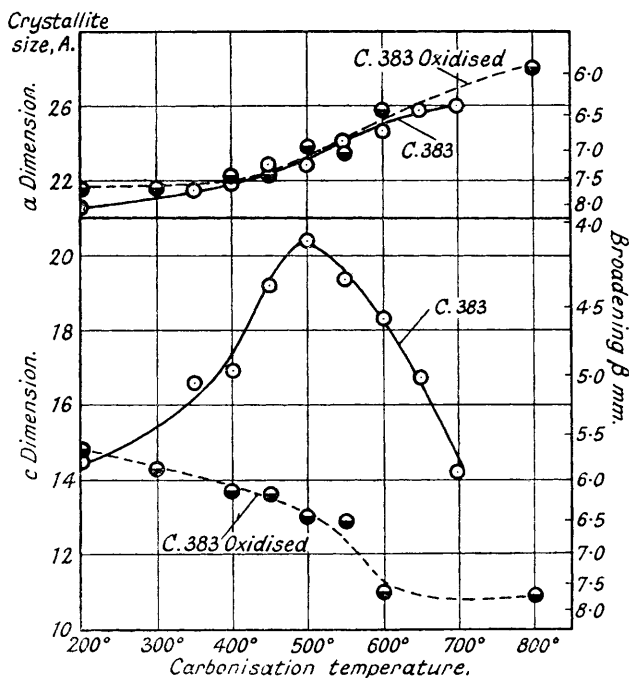
town gas through the flask by way of a tube sealed in the neck of the flask. After being heated for 12—24 hrs. the contents of the flask were allowed to cool and to stand until the finely divided coal had settled : the supernatant liquid was syphoned off and filtered through a No. 4 sintered-glass filter. The residue on the filter was returned to the flask. Fresh pyridine (200 ml.) was added and the extraction repeated : this treatment was continued until the final extract was nearly colourless. Six extractions were carried out simultaneouly and occupied some 8—10 weeks. The combined extract was concentrated by distilling off the pyridine at 100° in a current of dry carbon dioxide at reduced pressure : the pyridine was finally eliminated as completely as possible by further low-pressure evaporation in carbon dioxide followed by steam-distillation for about 2 hrs. The product (β + γ-fraction) was dried at 100° in dry carbon dioxide and then weighed.

Pure chloroform (25 ml.) was added to the β + γ-fraction and the mixture refluxed on the water-bath. The resulting solution was removed by suction through a sintered-glass filter and collected in a second distilling flask, the solid remaining on the filter being returned to the original flask. The treatment was repeated until the final extract was colourless. The chloroform-soluble γ-fraction was isolated by evaporating the chloroform from the combined extracts, in a stream of dry carbon dioxide at 100°. Typical yields from 120 g. of air-dry coal were : (β + γ)-fraction, 16·9 g. (14%); γ-fraction 5·2 g. (4·3%). These are much less than
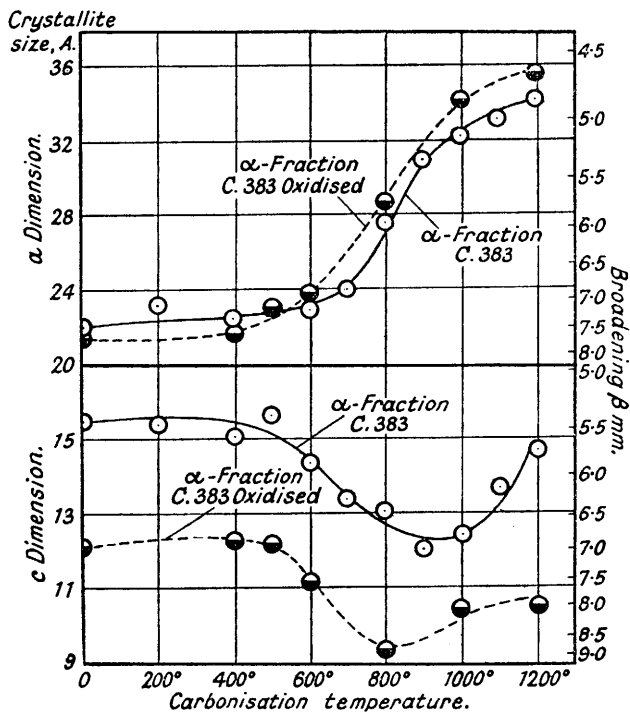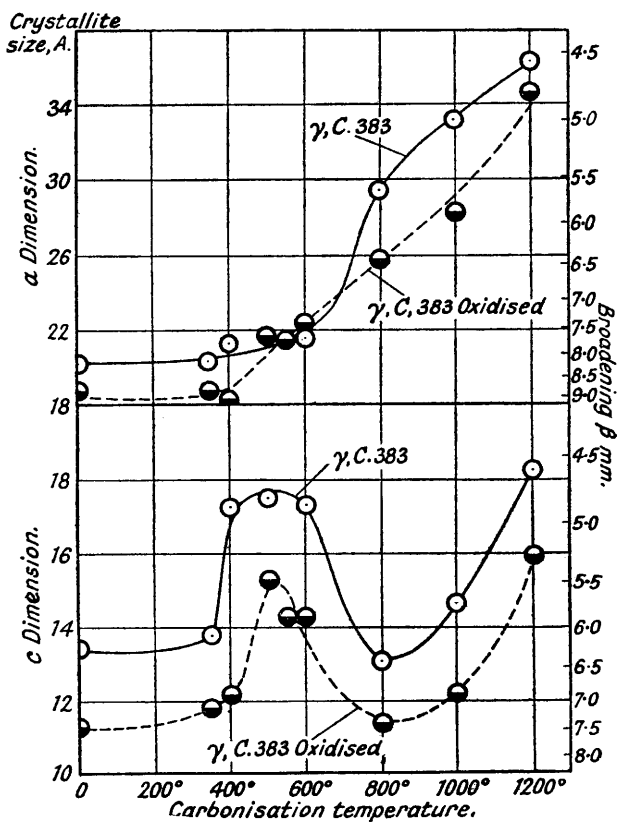
Fig. 7.

Fig. 8.

those obtained on the semimicro-scale, probably because of the more complete extraction and smaller losses when using the semimicro-method : it is possible that errors due to the presence of pyridine complexes in the extracts may be greater on the semimicro-scale.

Samples (0·8 g.) of the various fractions were carbonised in a silica boat in an atmosphere of nitrogen at a rate of 5° per min., the final temperature being maintained for 10 mins. The coke yields, which could not be determined accurately, were about 30% from the γ-fraction of the oxidised coal and about 45% from the γ-fraction of the unoxidised coal. X-Ray powder photographs of the original γ-extracts and the cokes prepared from them were made by the method already described, and crystallite dimension determinations carried out. The results obtained are given in Figs. 7, 8, and 9. The most interesting feature of these results is that the

FIG. 9.
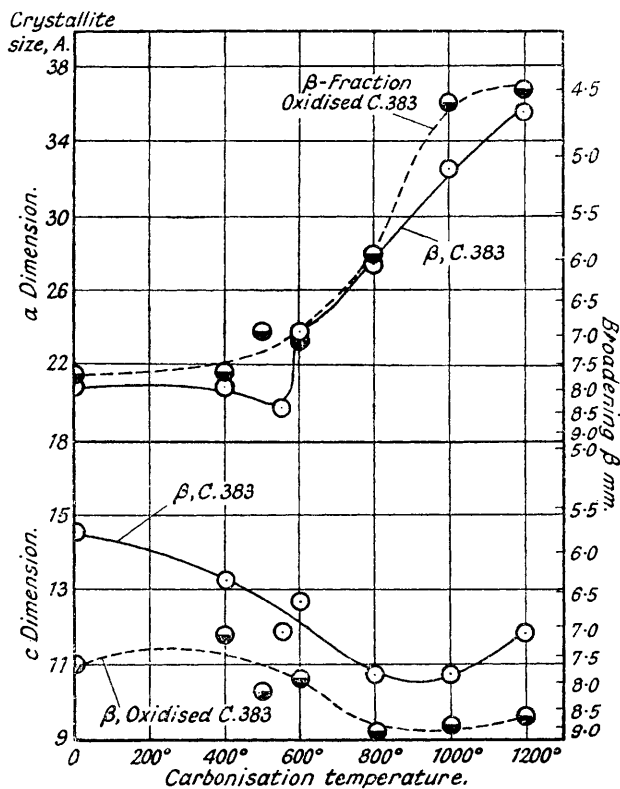
γ-fraction of the oxidised coal shows a sharp maximum at 500° in its c-dimension curve, in spite of the fact that the original oxidised coal shows no caking properties whatsoever. This result, however, in no way invalidates our view that a maximum in the c-dimension curve at 500—600° is in some way connected with the phenomenon of caking, for the γ-extract itself, on carbonisation, shows strong caking properties. This result is in accord with the observations of Barash (*Fuel*, 1927, **6**, 532; *J. Soc. Chem. Ind.*, 1929, **48**, 174T, 265T).

The a-dimension curves of the various fractions indicate that the oxidation of the coal has had little effect upon the crystallographic behaviour of the fractions on carbonisation, with respect to the a dimension. Oxidation, however, brings about important changes in all the fractions, with respect to the c dimension. Each of the c-dimension curves is depressed some 2—3 A. along its entire length. Experimentally this is a pronounced broadening of the inner 002 diffraction band. The ultimate analyses of the three fractions, unoxidised and oxidised, are shown in Table II.

These results indicate that each fraction had taken up a similar proportion of oxygen. Such systems are, of course, highly complicated and any definite explanation of this crystallographic phenomenon would require further investigation. It is, however, significant that the addition of oxygen to each of the three fractions brings about a decrease in the crystallographic order in

TABLE II.

Composition, % ash-free dry.

	Unoxidised.			Oxidised.		
	C.	H.	Diff.	C.	H.	Diff.
α-Fraction	85·7	4·3	10·0	82·0	3·5	14·5
β-Fraction	84·4	4·8	10·8	80·8	4·8	14·4
γ-Fraction	87·5	6·3	6·2	82·3	7·0	10·7

the cokes and chars prepared from these fractions. This result is in keeping with numerous observations previously reported, concerning the importance of the proportion of oxygen in a carbonaceous substance on its crystallographic behaviour on carbonisation and on the character of the resulting carbon.

The destruction of the caking properties of the original coal by oxidation and the retention of pronounced caking properties in the γ-fraction suggest that the mutual interaction of the fractions and their relative proportions are important factors in determining caking properties.