

IMPROVEMENT OF THE  
COKING PROPERTIES OF COAL  
BY THE ADDITION OF OIL

Thesis presented for the Degree of  
Doctor of Philosophy

BY

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"Improvement of the Coking Properties of  
Coal by the Addition of Oil".

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Summary of Thesis presented by <sup>Joseph</sup>~~James~~ Parker Allinson, M.Sc.  
(Tech.) for the degree of Doctor of Philosophy.  
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Part I.

This serves to introduce the present research and is chiefly historical. It deals briefly with methods of assessing the coking ability of coals and also with early, modern, and contemporary investigations upon coke formation. The author's earlier work on the distillation of oil from coals is described fully since it forms both the starting point and the basis of the present research. This work showed that the power of retention of oil which is capable of "wetting" the surface of the coal, up to temperatures of 420°C., was an essential characteristic of coking coals. Part II deals with attempts to add more oil mechanically to improve the coking performance of various coals.

Part II.

The oil-coal mixtures used throughout the research were prepared by "Trenting" (i.e. mixing the finely ground coal with oil in the presence of water) the coal with oils of various types in a small churn. In the preliminary experiments a non-coking coal was employed and varying amounts of oil were added. The coal-oil mixtures were preheated to 420°C., the residue crushed and reheated to 600°C., in the Gray-King Assay apparatus.

A range of coals varying in carbon content was then treated and similarly preheated and reheated, and it was discovered that the poorly coking coals had their coking abilities improved. Two of these poorly coking coals were then studied in detail, a large number of oils differing in origin and character being added. The effect of addition of benzene was particularly studied, and it was shown that benzene added to a poorly coking coal lost its identity as such, whereas when added to a non-coking coal it was all distilled as benzene in the preheating experiments.

The influence of oil addition upon the swelling power of coals as measured in the Sheffield Laboratory Coking Test, and also upon the "weathering" properties (the loss of swelling and coking ability upon exposure to air oxidation) of various coals was also studied, and these helped to explain some of the effects of the addition of oil.

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# The Influence of Oil Addition upon the Coking Properties of Coal

## INTRODUCTION.

The coking of coal has long been of great importance to industry, and the production of strong metallurgical coke an economic necessity to any progressive nation. This has made the possession of coal suitable for coke manufacture very desirable, because only with such coals can an iron-making industry be developed. A definition of a coking coal is "One which, with modern methods of carbonisation, yields a massive coke, in which the identity of the original coal is completely lost and the product is a uniform fused cellular mass." Unfortunately, this power of coke formation is restricted to coals which have certain definite characteristics, and the percentage of coking coal of the total coal mined is usually low. The coal suitable for coke manufacture is not uniformly distributed; one coalfield may have a large proportion of its coal suitable for coke manufacture, whilst another may yield totally or partially unsuitable coal. The Durham coalfield yields coal which gives strong metallurgical cokes when heated, whereas the Derbyshire and Staffordshire coals are scarcely capable of giving a coherent residue under similar coking conditions. Other fields give coals which are part coking and part non-coking. Everywhere we find coals that appear to be on the fringe of the coking coals, coals that form cokes on heating, which are of a soft, friable nature and useless for metallurgical work. These coals should be very suitable subjects for any research dealing with improvements in the coking ability of coal, and it is this type of coal which will, for the most part, be used in the present research. In this research it is proposed to study the part played by the oil released from the coal substance during coking, and to try and improve coking ability by augmenting this oil by suitable additions. This will necessitate a primary investigation upon the distillation of the oil from coal during coking before attempts can be made to improve the coking ability of the coal by oil addition. The present research consideration will first be given to the effect of the "inherent" oil during coking, and will then deal with the addition of oil and the effects, beneficial or otherwise, upon the cokes produced.

## ASSESSING THE COKING ABILITIES OF COALS.

Since the coking ability of coal is to be an important factor in the present thesis, it is of interest that the various methods of assessing the values of coking coals should be recorded.

One of the roughest tests employed is the determination of the "volatile matter" present in the coal. It has long been known that there exists a rough relationship between "volatile matter" and coking ability. South Wales coals have a very low amount of "volatile matter" and give strong cokes. Yorkshire and Durham coals have higher "volatile matter," and their cokes, while good in quality, are not so good as South Wales cokes. Derbyshire coals, with still higher "volatile matter," yield poor cokes. The relationship between "volatile matter" and coking ability is not a close one, however, and is of no use in accurate work.

Another relationship, closer perhaps than the one just mentioned, is that between coking ability and carbon content of the coal. In this case small differences may be much more important. Coals can be arranged in the following groups: South Wales 92-88 per cent. C., Durham 89-85 per cent. C., Yorkshire 87-83 per cent. C., Derbyshire 85-82 per cent. C. However, several other facts are necessary, such as the origin of the coal, its depth and age, and so on, before carbon content is of much use in foretelling coking power.

The "caking power" of a coal is quite distinct from its "coking power," and is the number of units of an inert material, which unit weight of the coal will bind together. The inert material is, of course, specified in each case. It was supposed that a high caking power meant a high coking ability, but this might not be the case. South Wales coals have very low caking power, and yield the best cokes. Many other coals which have poor coking ability give a very high "caking power." Coke formation thus appears to be rather more complex than mere binding together of the coal substance. It is here that the question of "wetting" of the coal surface by the extruded binding substance is of importance. It is quite possible that a coal with a high "caking power" but a "poor coking ability" possesses an abundance of binding material which has a poor binding action on the coal surface, due probably to some physical factor operating at the coal surface. However, the "caking power" of coals is very useful knowledge when attempts are to be made to blend coals to give better cokes. By blending it is possible for two poorly coking coals to give a good strong coke.

The swelling power of coals in the volatile matter test has also been used as an indication of coking ability. A highly swollen residue usually indicates a strongly coking coal, whereas a shrunken or slightly swollen residue means a non-



coking or poorly coking coal. Here again there are many exceptions. Many coals, particularly the Welsh coals, do not swell appreciably but give strong cokes. The swelling of coals is therefore useful as an indication of coking properties but of little value as a rule.

Foxwell's suggestion (Fuel, 1932, 11, 376) that a good coking coal offers a high resistance to gas flow has also been studied to predict coking ability. It is fairly reliable, but the experimental difficulties are too great to allow of its use as a general test.

Illingworth stated that a good coking coal had to have at least 5 per cent. of Gamma compounds. This, however, while quite useful as a generalisation, is of very little value in assessing coking values.

A method widely used is the Sheffield Laboratory Coking Test. In this method finely crushed coal is heated at 1 deg. C. per min., whilst carrying a load to which is fixed a pointer which marks expansion or contraction. It was discovered that in the majority of cases, at a temperature between 350-400 deg. C., a contraction occurred, continued for 20 deg. C., when expansion suddenly occurred. This attained a maximum below 500 deg. C., and no further movement of the pointer was then observed up to 600 deg. C. By a correlation of the shatter and abrasion indices of oven coke with measurements of contraction and expansion during coke formation in the test described above, it is possible to estimate fairly well the coking ability of the coal employed. Good coking coals have larger percentage expansions than poor coking coals. The most novel feature is that the wider the contraction range and the greater the percentage contraction, the better the coking value of the coal. This method of determination of the contraction ranges and percentage contractions, and expansion ranges and percentage expansions, appears to afford a simple method of assessing the coking ability of coals.

#### EARLY INVESTIGATIONS OF COKE FORMATION.

The swelling and plastic condition of certain coals when subjected to heat was commented on by Percy in his book on "Fuel." Both in Lump form and also in the form of a fine powder certain coals were found to give a coked mass when heated to redness. There were, however, "Non-coking" coals which gave only a very loosely coked residue or in some cases only a powder on heating. Coking and non-coking coals could be blended to give firm cokes, a very useful fact commercially.

De Marsilly (Anon. Chem. Phys., 1862, 66, 167) heated caking coals to 300 deg. C. for periods of 1 to 2 hours. On reheating these coals appeared to have lost their power of caking, and this he concluded was due to the loss of some indefinite "caking principle."

Anderson (Journ. Soc. Chem. Ind., 1898, 17, 107) pointed out that De Marsilly had neglected oxidation of the coal in his preheatings, and showed that oxidation had some effect upon caking power. However, he showed that the caking power of the coal was reduced. This is not conclusive evidence, as it has since been shown by Davis and Place (Fuel, 1925, 4, 295) that CO<sub>2</sub> has some action on the coal substance. Anderson concluded that there were compounds in all coals (since discovered and shown to be chiefly ulmin compounds) which have a detrimental effect on the caking power of these coals.

De Marsilly (Loc. Cit.) extracted coals with various solvents such as chloroform, benzene, ether alcohol, and discovered that the residues after extraction did not yield such coherent masses on heating as did the original coals. This and subsequent work on the extraction of coal led to the use of pyridine as a solvent, Bedson first using it in 1899 (Trans. Fed. Inst. Min. Eng., 1899, 16, 388). Subsequently, extraction by solvents began to play a very important part in the investigation of the coking power of coals.

Baker (Trans. Fed. Inst. Min. Eng., 1901, 20, 159) extracted two Durham coking coals with pyridine. Hutton coal was found to give 20.4 per cent. of extractable material and the residue lost its power of giving a coke. Brockwell coal gave 11.5 per cent. of extractable material and the residue was only very feebly caking.

Clark and Wheeler (J.C.S., 1913, 103, 1704) used a Yorkshire coking coal—Silkstone—and obtained results in accordance with those of Baker. They also investigated the pyridine extract. They found that 30-40 per cent. of it was soluble in chloroform (equivalent to 9 per cent. on the original coal). Thus they had 3 fractions: (1) Alpha fraction (insoluble in pyridine); (2) Beta (soluble in pyridine but not in chloroform); (3) Gamma (soluble in both pyridine and chloroform). The Gamma compounds gave rise to a high percentage of tarry matter on distillation "in vacuo," and this tar on examination proved to consist chiefly of higher paraffins.

If the pyridine-extractable material be mixed with the residue after extraction in the original portions and the mixture subjected to a crucible test, it is found that the caking ability is practically identical with that of the original coal. This fact has led to the view that the pyridine-extractable material is responsible for the caking properties of any coal. (Baker 1901, Bedson 1905, Wahl 1912, Clark and Wheeler 1913).

Illingworth (J. Soc. Chem. Ind., 1920, 39, 133T.) found that only the Gamma compounds soften and melt, and from this fact put forward the view that these compounds were responsible for the softening and plasticity of coking coals. From his experimental work he concludes that at least 5 per cent. of Gamma compounds (having a C/H ratio greater than 10) must be present for a coal to form a coke when heated. He considered that the Gamma compounds melt and in a fluid condition filled the interstices of the coal substance. With increase of temperature these compounds decomposed and the structure of the carbonised and semi-carbonised residue then formed the basis of the coke formed. The Gamma compounds thus acted as a binding material. Illingworth showed also that if a coke formed at 500 deg. C. be crushed, it did not give a coherent mass if heated again, nor did it give any pyridine extract. These two facts he supposed to be due to the destruction of the Gamma compounds in the first coking.

Wedding considered that the destruction of gaseous hydrocarbons during coking led to the deposition of carbon in the coal substance, and so caused coke formation.

Donath ( ~~X~~ ) considered that the molecular rearrangement in the coal substance was the explanation of coke formation.

Seyler (Fuel, 1924, 3, 47) has recorded several examples of excellent cokes made from hard coals, whereas as a general rule it is considered that hard coals are non-coking.

Parr (Fuel, 1925, 4, 49), working with Illinois coal and using phenol as solvent, obtained two fractions, one of which was a non-caking residue, the other a caking extract. He remixed the two portions and the mixture regained the caking ability of the original coal. He has since shown that the phenol extract is more resistant to oxidation than the residue. Consequently loss of caking power by the coal on oxidation is unlikely to be due to oxidation of the extract.

Foxwell (Fuel, 1934, 3, 276) has discovered that a South Wales coal with only 2.8 per cent. of Gamma compounds gave a very good coke, and another coal with 0.1 per cent. of Gamma compounds still gave a fairly coherent residue on heating. On the other hand, a Scotch coal with 6.9 per cent. of Gamma compounds gave a very poor coke on heating, a fact which seems contrary to the conclusions drawn by Illingworth.

If the fractions obtained from a coal by extraction with pyridine and chloroform be mixed and the mixture heated at a rate of 1 deg. C. per min., the coke formed was found by Foxwell to be very powdery. If a very much faster rate of heating was employed, 30 deg. C. in 5 mins., the coke obtained was very similar to that obtained from the untreated coal.

From his results Foxwell concluded that surface tension played a large part in coke formation. In his opinion the first stage was the extrusion of molten material from the interior of the coal which spread on the surface of the particles, globules being formed. These cohered to form a network, the force of expansion in the globules overcoming the force of surface tension which tends to resist alteration of shape. Surface tension effects then become lessened and the process of cell formation, practically complete in the interior of the globules, was carried on at the surface. The fact that the re-mixing of the Alpha, Beta and Gamma fractions (referred to previously) gave a powdery residue on reheating, was explained by supposing that though the original composition of the coal was reproduced, the actual original structure was not regained and consequently extrusion did not take place. Since a coke was formed if the rate of heating is sufficiently rapid, Foxwell supposed that the Gamma compounds were much more fluid under these conditions, the fluid material flowing over the other portions of the coal material and acting as a binding agent. Lack of caking power in certain non-coking coals he explained by the fact that they possess peculiarities of structure rather than that they were deficient in Gamma compounds. These peculiarities prevented extrusion of the Gamma compounds and prevented coking.

Fischer, Broche and Strauch (Brenn. Chem., 1925, 6, 33), using a series of German coals, extracted them with benzene under pressure at 285 deg. C. The complete extracts were found to vary between 2-8 per cent. of the coal, and the extracted residues showed very considerably reduced coking properties. The extracts were very rich in carbon and hydrogen, the hydrocarbon nature being most marked in the extracts from the most strongly caking coals. The extracts from the weakly caking coals were solid and hard, whilst those from the strongly caking coals were soft and malleable. The decomposition temperatures of the two types of extracts differed, being 180-228 deg. C. for those from non-caking coals, and 320-360 deg. C. for those from caking coals. Extraction of the benzene with petroleum ether gave a soluble and insoluble portion. The soluble portion was oily in appearance and termed "Oily Bitumen," the insoluble portion known as "solid bitumen." Fischer concluded that the "oily bitumen" was responsible for the caking of coals on heating, since its proportion in the extract increased with increasing caking power in the original coal. Also, its addition to the extracted coal gave a mixture which caked well but did not swell on heating. He considered that "solid bitumen" was the cause of swelling in coals on heating, since mixtures which contained it gave rise to a swollen product on heating. The "Oily Bitumen"

~~X~~ See W.C. Anderson, Chemistry of Coke, Glasgow, 1906, p 20.



was much richer in carbon and hydrogen than "solid bitumen." Solid Bitumen showed great similarity to the original benzene extracts in their temperatures of decomposition, 176-226 T. for poorly or non-caking, and 320-360 deg. C. for strongly caking coals.

The workers then draw the following interesting conclusion—that the optimum condition for coke formation was that the temperature of initial softening of the coal should coincide with the decomposition temperature of the bitumen. A round figure of 5 per cent. was suggested as the absolute minimum quantity of oily bitumen necessary for complete coking, a conclusion similar to that of Illingworth's. Exhaustive extraction proved that the coals still retained some tar-forming constituents, a fact which led Fischer to assume that tar formation could not be connected with the fusion and caking of a coal. His assumption that the extract contained no tar forming constituents was certainly not justifiable.

Kattwinkel (*Gas und Wasserfach*, 69, 1926, 145) criticised the practical application of the above work and theories of Fischer. Cokes were produced in a by-product oven from coals which by Fischer's theory were non-caking coals. Difference of conditions of large and small scale carbonisation was suggested as an explanation of the above, Fischer's theories being based on results obtained from carbonisation in crucibles.

Sinkinson (*Ind. and Eng. Chem.*, 17, 1, 27-31) based his theory of coke formation on electrical conductivity phenomena, arguing that it is free carbon in a finely divided state which converts coal, a non-conductor, into coke, a conductor. The gases produced upon carbonisation decompose and deposit free carbon in so finely divided a form that cohesive forces come into play and bind the particles into the fundamental coke structure. This argument neglects entirely the plastic condition that is known actually to occur, and which is generally supposed to have a great effect upon the final cell structure of the coke. It conforms to Wedding's idea of deposition of free carbon in the coal mass by hydrocarbon decomposition.

Tideswell (*Fuel*, 1922, 1, 101) described a patent taken out by A. Roberts for the production of a metallurgical coke from a coal generally considered to be non-caking. The coke was obtained by very rapid heating to 600-700 deg. C., the binding constituents being supposed to have the greatest cementing action in this range. The essentials for production of a good coke he concluded were:—

(1) Solid residual particles, which were available in all coals, and (2) a binding material available at the correct time and temperature and also in sufficient quantity. It was also suggested that the binding material might be an intermediate stage, absent in the original coal but formed chiefly from "resinous" constituents. These become plastic between 300 and 500 deg. C., and are decomposed between 600 and 700 deg. C. On decomposition they liberate hydrogen and leave compounds richer in carbon, which act as cementing agents. On raising the temperature higher the only effect is to drive off more volatile matter and to set or harden the coke already formed. Tideswell considered that the amount of the binding material was dependent on two factors and a balance established for each coal. These were: (a) The amount of "resinous material" in the coal, and (b) the percentage of these destroyed before the range in which they exert their binding influence is reached. Volatilisation or oxidation destroys them, and the larger their proportion of the original coal, the greater the amount destroyed. Thus a non-caking coal may have a very small proportion of "resinous" material, but by rapid heating to 600-700 deg. C. very little of this is lost and sufficient remains to bind the coal into a coke.

Bone (*J. Soc. Chem. Ind.*, 1925, 25, 291T.) considered that the chief coking constituent of a coal was a fraction ulmic in type, which was obtained from a benzene extract of coal, and this view is in direct opposition to that of Fischer. Bone, however, used coke breeze and benzene extracts in his carbonisation experiments, whereas Fischer mixed extracted residues and benzene extracts.

Mott (*Fuel*, 1925, 4, 466) criticised Fischer's statement that "solid bitumen" is responsible for the swelling properties of a coal. He pointed out that when the "solid bitumen" in any coal was expressed as a percentage of the coal itself, and not of the total extract, a caking, non-swelling coal had 2.6 per cent., compared with 2.4 per cent. from the most strongly swelling coal. He considered it more desirable to regard the whole extract as being involved in coke formation, and that when the whole extract had a decomposition temperature above a certain limit, swelling most probably would occur. The view that tar is the cementing agent is a development of the above theories, Clark and Wheeler having shown that most of the tar obtainable from any coal have as their origin the Gamma compounds. Also the Gamma compounds, which are frequently regarded as the principal binding agents in the formation of a coke, are soluble in benzene, and therefore will probably include fractions similar in composition to those obtained by Fischer by extraction of coals with benzene under pressure.

Mott advanced the idea that the nature and condition of the solid surfaces over which the binding agent spreads were of great importance, as well as the nature and amount of binding material. Coke formation could be regarded as involving wetting phenomena, and since the wetting agent is of a hydrocarbon nature, wetting would be far more effective on surfaces rich in carbon and



hydrogen or poor in oxygen. This theory is very well supported since the best coking coals are of low oxygen content, whereas coals of high oxygen content are notoriously poorly coking in character. Foxwell's observation that non-coking coals appear to be not merely inert but even to have a negative coking power (as compared, say, with coke breeze) can also be explained by the above wetting theory. Loss of caking power after oxidation was explained by the fact that the Alpha and Beta compounds became "oxyphilic," or possessed of a strong affinity for liquids rich in oxygen. They were thus much less readily wetted by Gamma compounds, which are hydrocarbon in nature and consequently require a "carbophilic" surface before they wet it. Since no wetting occurs in the oxidised Alpha and Beta compounds, the coking power of the coal is negligible.

Damm (Fuel, 1929, 8, 163) found that the caking index was an unreliable guide to the coking properties of a coal, and suggested that some property of the coal constituents responsible for coking was not taken into consideration in the estimation of coking properties by such a determination. He concluded that if the swelling of the coal on coking was zero or so small as to be negligible, the caking index was a reliable criterion, but not otherwise. He determined the amount of swelling and expansion pressures for a series of coals, and concluded that if a good coke is to be obtained a certain swelling pressure, as well as adequate caking properties, is essential.

He also investigated the progress of gasification:—(1) Prior to the temperature of fusion of the coal; (2) from 25 deg. C. below this temperature to 25 deg. C. above it; and (3) after solidification of the coal. He found that in case (1) the caking power of the coal could be very much decreased with a high initial yield of gaseous products. He suggested that the caking index be determined not only for the raw coal but for the coal at the moment of incipient plasticity. The higher the caking index at this point the better the coke produced in practice. Damm concluded that the quicker the rate of heating to the fusion temperature, the less would be the initial gas yield, and consequently the better would be the final coke. From the results of (2) he concluded that the yield of distillation products during the 50 deg. C. range gave some indication of the swelling pressure of the coal. The gas yield in case (3) was important in estimating the quality of the coke produced. He found that the greater the yield of gas after solidification, the more fissured the coke produced. On the other hand, if the gas yield was only small, the contraction of the coal was only slight and the coke adhered to the oven walls.

He concluded that two properties of coals determine the behaviour of coal during carbonisation under pressure (i.e., in a coke oven). These are:—(1) caking properties, (2) swelling properties, which can both be estimated numerically by simple methods. Caking indices give information upon the fusing properties of coals, whilst the swelling properties indicate the pressure applied to the coal during the fused state. An insight into the mechanism of carbonisation is given by an investigation of the distillation during heating. The process of distillation may be divided into three stages, namely, primary distillation, i.e., below the temperature of fusion which indicates the changes in the coal up to fusion; distillation during the fusion stages, which would indicate what is happening to the coal during fusion; whilst the final distillation is important in judging the quality of the coke produced.

By an investigation of this type it should be possible to standardise coking and form sound ideas upon coal blending. Many strongly swelling coals are unsuitable for oven use, owing to their frothing qualities. Other coals which do not swell strongly but give good cokes are unsuitable for oven use owing to the damage they do to the oven walls. By mixing two coals of this type an excellent coal blend, which would give good strong oven cokes, should be produced.

#### MODERN WORK.

Mott (Fuel, 1925, 4, 467) studied coke formation from a new angle, using as a basis for his theories the "surface flow" of solids described by Beilby. Beilby (Aggregation and Flow of Solids, 1921, p. 125) considered that by the application of an external force to the outside surface of any body the surface molecules, to an appreciable depth, gained a temporary degree of freedom which allowed them to take up a new aggregation, which, on removal of the pressure, became permanent. The process he called vitrification, and the new surface aggregation of the molecules conferred on the solid greater rigidity than in the undisturbed state. The force applied can be mechanical, or due to gas pressure, or even due to solvent action.

Mott considered that there were forces called into play when coal was heated which would supply the conditions necessary for vitrification of the coal. Gas pressures inside coal at 400-500 deg. C. may become very large, and it might be that the solid surfaces of the coal flow under these pressures and assume the rigidity of the vitreous state. Then again, solvent action produces surface flow, and as solution is always accompanied by wetting, the extent to which the coal surfaces are wetted by the liquid products of thermal decomposition will be important. There is also actual evolution of gas during the plastic stage of the coke which will produce pressures and cause vitrification. All these factors will

influence vitrification of the coal and have an effect upon the final rigidity of the coke produced. According to this theory, the extent to which vitrification occurs would vary according to the pressure developed in the pores of the coal, and this has been shown to vary with the coking values of a series of coals. It follows that different degrees of vitrification will occur for different coals, the best cokes being produced by greatest vitrification.

With a view to investigating the theory, a series of coals whose carbon content ranged from 80-90 per cent. (on ash free, dry, sulphur free basis) was selected. From each sample, cubes of approximately 1 in. side were cut, and the cubes measured and photographed. The coals were heated in an inert atmosphere at 1 deg. C. per min. from 300 to 600 degs. C. The resulting cokes were photographed, and then sectioned by Rose's method, the pores being filled with plaster of paris, and re-photographed.

It was discovered that the coals placed in order of their alteration in volume gave a series which corresponded roughly with the carbon contents. In general, coals with the highest carbon content gave the most swollen residues, but coals above 90 per cent. in C content were exceptions, e.g., Anthracite. Also, expansion at right angles to the bedding plane was always greater than expansion parallel to the bedding plane.

On examination of the porous structure of the cokes formed, it was discovered that coals which produced the best metallurgical cokes gave large, distorted and disrupted pores. This must be due to high gas pressures developed in the pores during the plastic stage. Also, the better the coke produced the thinner the pore walls, a condition which gives the largest surface and thus allows maximum vitrification. Non-coking coals gave residues on heating which had only small pores or cracks and irregular fractures. It was suggested that in the case of poor coking coals and hard coals the gas pressures produced during the plastic state were very small compared with those of good coking coals, or else the gases formed were very easily released, whereas in coking coals no such release was possible.

In coke formation from crushed particles, wetting phenomena must play an important part in the binding together of the particles to form a coherent mass. Three factors appear to operate in the coking of crushed particles: (1) A suitable quantity of wetting material is needed (probably insufficient in the case of Anthracites); (2) The surface of the coal particles should be of a similar nature to the wetting medium; (3) The coal particles should be packed tightly enough to ensure that the molecular forces of cohesion can come into play.

The conclusions drawn from the above are summarised as follows:—

1. Coke formation primarily depends on the surface flow of liquids under pressure (gas pressures), together with solvent action of the liquid products of thermal decomposition.

When crushed coal is employed, a second phase comes into operation, wetting phenomena being of primary importance. In all cases the greater the gas pressures produced the greater the extent of vitrification and the greater the mechanical strength of the coke produced.

Mott and Shimmura (*Fuel*, 1928, 7, 472-486), in later investigation, subjected a number of moderate and inferior coking coals to similar methods of examination. The series of coals employed had carbon contents of 80 to 85 per cent. Faster rates of heating were also employed, viz., 5 deg. C. per min., and it was discovered the faster the heating the greater the distortion of the coal cube employed.

From these results it was concluded that swelling in coal on heating was in part due to gas pressure, for the more swollen lump coal cokes are found to have large distorted pores. There was also a fairly close relationship between the swelling power of coals, either in lump or crushed form, their carbon contents and their coking power.

Swelling was primarily dependent upon the tar produced during the distillation, and it seemed probable that it was not the amount of tar produced over a critical temperature range, but the ease of wetting of the rest of the coal by the tar. Probably in the case of crushed coal the cohesion of the oil films round the coal particles bound the coal into a cake, and this may be termed the first stage of coke formation. In the second stage there is loss of identity of the coal particles together with formation of pore structure due to swelling.

Burdekin (*Fuel*, 1933, 12, 236) carried on the work of Mott and Shimmura, and collected a series of coals which would complete and test their results.

His results confirmed the fact that the swelling ability of many coals is roughly related to their carbon contents and coking power. The property of swelling, however, varied from one coalfield to another for coals of similar carbon content, and the rule breaks down with carbon contents above 90 per cent. He showed that swelling ceased in the case of a highly swelling coal when the oil had been removed from the coal. Oil, however, does not necessarily cause swelling power, since non-swelling coals yield oil, but this might be due to the poor quality of the oil, or the fact that it did not wet the coal sufficiently well. Since an appreciable gas evolution occurs in the plastic range of non-swelling coals,



swelling cannot be due to gas evolution only. Removal of oil also causes loss in caking power of the coal.

Mott (Fuel, 1933, 12, 184). The heating of coal cubes of 1 in. side at 1 deg. C. per minute in an inert atmosphere has been continued and several interesting facts established. The most strongly swelling coals are those of carbon content, 88-85 per cent. Swelling decreases with increased carbon content above 88 per cent. carbon. Below 85 per cent. carbon the swelling of bright coals is not so great, and below 82 per cent. carbon the non-swelling (and non-coking) coals are found. The swelling of the coal is due to prevention of gas escape. The coals become plastic, pores are formed, and when the internal gas pressure reaches a certain value the pore walls are ruptured and the gas escapes. The higher the carbon content of the coal the higher the internal gas pressure before rupture of the pore walls occurs. Swelling, therefore, is proportional to ease of gas escape. Evidence has been produced since to show that it is probably the wetting action of the liquid products of distillation (the oils) on the residue which restricts gas escape, and that internal gas pressure causes surface flow at so many "internal surfaces" throughout a coal particle that under suitable conditions the coal can behave as a liquid. The Temperature range of swelling was also investigated, and it was found that the temperatures of initial and final swelling were sufficiently close to the temperatures of initial contraction and final expansion of a column of particles of the same coal for these temperatures to be used in further tests on the coal cubes. It was discovered that whereas at the temperature of initial contraction the percentage of oil distilled from the cube was nil, in all cases at the temperature of final expansion 75-90 per cent. of the oil had been distilled. Thus the swelling range of the coal is also the range over which its oil is distilled.

The swelling of a column of crushed particles of the coal was also investigated when heated at a rate of 1 deg. C. per minute. A column of particles was heated under a plunger which had an effective load of 100 grns. At a certain temperature the coal contracts (initial contraction) and then at a still higher temperature swells (initial expansion). At a still higher temperature the expansion ceases to increase (final expansion). With some coals the plunger then remains steady whilst the temperature rises a few degrees and then begins to sink through the coal, finally becoming stationary at a still higher temperature. This temperature is called the solidification temperature of the coal, and it is interesting to notice that plasticity is still evident in the coal above the temperature of final expansion. From the figures obtained the percentage expansion of each coal is found and it is seen that swelling power and carbon content are closely related. It was also noticed that the age of the coal seemed to give it certain qualities, probably because wetting phenomena occurred more easily. The pressure exerted on coals during the heating was also varied, and it was clearly shown that the pressures set up in coking coals by gases were sufficient to explain distortion of the coal. In another series of experiments (*loc. cit.*, p. 379) coal particles were heated at constant volume, and it was discovered that very little gas was given off until a certain temperature was reached, when there was a sudden rush of gas. Poorly coking coals show no sudden release of gas, and in medium coking coals the release is not so marked. The temperature of sudden gas escape was found to correspond quite well with Foxwell's temperature of maximum plasticity.

The fact has been stated that a contraction is first observed when a column of coal particles is heated under a load, whereas if a single particle be heated swelling commences at a fixed temperature and no contraction occurs. The contraction in the first instance is explained as follows: The initial particles of the coal themselves begin to expand just as the cube did. However, oil is extended and the surface tension of this oil draws the coal particles closer together and diminishes the free space between them. It is this fact that causes an initial contraction of the coal. As the swelling of the particles increases it gradually counterbalances the contraction caused by the oil, and at a certain temperature expansion begins. This is the temperature of initial expansion of the column of coal particles. The temperature of initial expansion is also shown to be the temperature at which pores were formed in the coal. Gas pressures are produced in coal which are so high that surface flow is produced and the mass becomes plastic.

Some work has also been carried out on the distillation of coal particles in a stream of gas. Ordinary Gray-King Assay apparatus was used, except that one end of the Assay tube was fitted to allow gas to be passed through it during the heating. Carbon dioxide and steam were the two gases used. It was discovered that more oil could be obtained from a coal than if the ordinary Assay method were used. This is an important fact, as it definitely shows that some oil must necessarily be used in coke formation.



Allinson and Mott (*Fuel*, 1933, 12, 258-268). Earlier work had shown that the swelling of single particles of coal was confined to a comparatively narrow temperature range, during which most of the oil was distilled. At the same rate of heating, the temperature of initial expansion of single particles of coal was shown to be the same as the temperature of initial contraction of columns of particles of the same coal. With single coal particles, swelling began at the same temperature as the evolution of the oil; whilst 75 to 95 per cent. of the total oil was evolved before the temperature which marked the end of swelling of single particles (as well as of columns of particles) was attained. The close relationship between the swelling of a coal and evolution of oil, from single particles, merited a careful study of the same relationship for columns of particles, and this was the object of the above research.

The method devised by Mott and Shimmura (*Fuel*, 1928, 7, 472) was used, together with an improved technique for determining the oil yields, which has been described by Brewin and Mott (*Fuel*, 1933, 12, 239). As this method will be used throughout the present research, a detailed account of it will be given here.

A quantity of coal was freshly ground so as to pass through a 60-mesh sieve, and 25 grams. were charged to a clear silica Gray-King retort so as to occupy a length of 6 inches (see diagram). A small amount of free space was left over the coal in the retort to allow the volatile matter to escape without passing through the column of the coal. The remainder of the free space of the retort was packed with silica distance pieces to reduce the time of contact of the volatile matter with the hot wall of the retort. The side tube of the retort was connected to a condenser (liquor-tube), and a gas-holder. The retort was inserted in the electric furnace when that had attained a temperature of 300 deg. C., and an external resistance was adjusted so that the subsequent rise in temperature was 1 deg. C. per min. The retort was heated to the required temperature, withdrawn immediately, and, after cooling, the yields of tar and liquor were determined. The amount of gas collected was noted at regular intervals throughout a test.

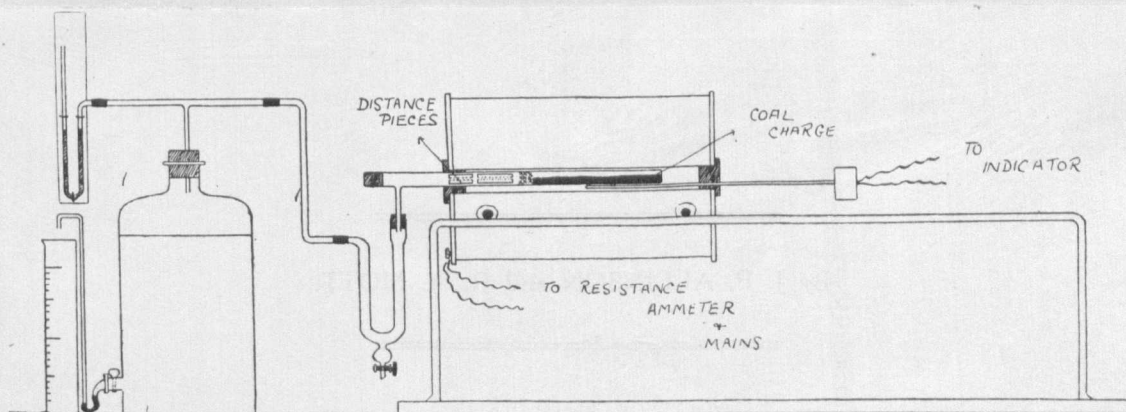


FIG. 1.

Apparatus used for preheating coals to different temperatures.

The solid residue was weighed, ground so as to pass through a 60-mesh sieve. Part of this residue was extracted with ether in a soxhlet extraction apparatus during about 48 hours (until the liquid siphoned was colourless) to determine the amount of oil which had been freed from the coal substance but not distilled. Another part was reheated to 600 deg. C. at a rate of 5 deg. C. rise per min. in a Gray-King assay and the yield of residual oil determined. The amount of residue taken in the reheating test (as in the extraction test) was equivalent to 10 grams of the original coal, allowance being made for the loss of volatile matter during the first heating. The shatter index of the final residue was then obtained.

The ordinary Gray-King assay method of determination of oil and liquor was modified to meet the requirements of this research. The liquor tube, after an assay containing oil and liquor, was washed repeatedly with small quantities of chloroform until the whole of the tar seemed to be removed. The chloroform extract was weighed after evaporation in the usual manner. The residual chloroform in the liquor was then removed by heating the liquor tube in a hot air bath at a temperature of 70 deg. C. for half-an-hour, and passing a stream of carefully dried air through the liquor tube at the same time. Precautions were taken to trap any liquor driven off with the chloroform. The liquor alone was then estimated by difference in weight. This method will also be employed throughout the whole of the present research.

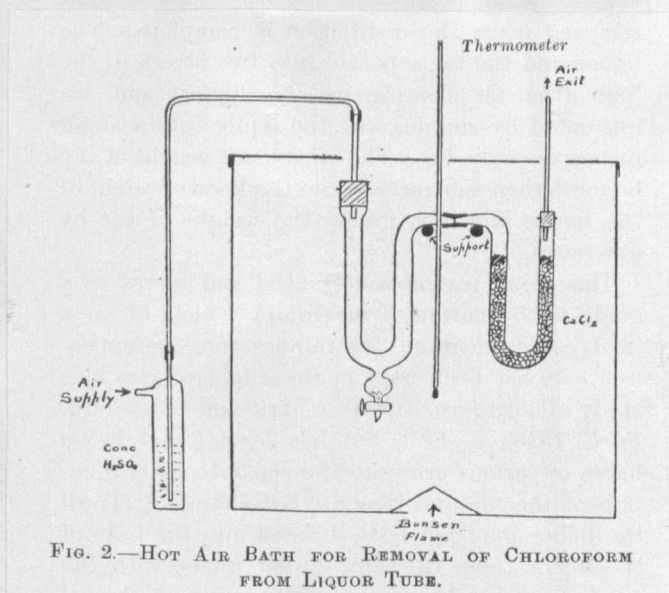


FIG. 2.—HOT AIR BATH FOR REMOVAL OF CHLOROFORM FROM LIQUOR TUBE.

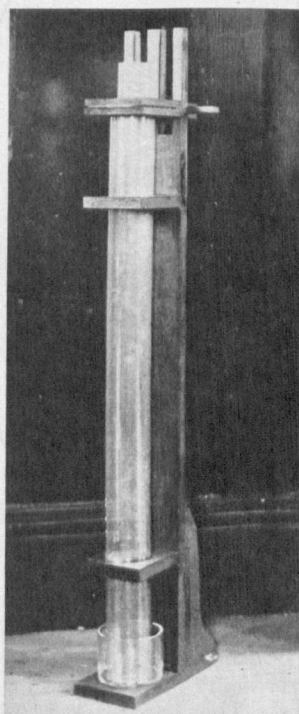


FIG. 1.—PHOTOGRAPH OF "SHATTER TEST" APPARATUS FOR LABORATORY COKES.

The coke is placed in the glass cylinder at the top, resting on a glass plate which is pulled out between two guides to release the coke. After dropping down the 3 ft. glass tube the coke and powder is transferred from the lower glass dish to the upper container for further drops.

The shatter indices of the re-heated residues were obtained using the modified laboratory shatter test apparatus. The residue was weighed after screening power 5.  $\bar{I}$  M.M., and dropped three times down a glass tube 3 feet long. The use of a tube 3 in. in diameter gives a free drop and prevents loss of powder. The tube is fixed in a stand and rests in a shallow flat-bottomed dish. At the top a simple pull-plate release is arranged to allow the material to be dropped through a standard height with no initial velocity. The apparatus is illustrated in the accompanying diagram. After the drops, the residue is screened on different screens and the percentage remaining on each is noted, the per cent. of the original remaining on the 5-mesh screen being recorded as the shatter index of the residue.

A series of coals varying in carbon content from 80-88 per cent. (ash-free, dry basis) were heated to temperatures corresponding to those of initial contraction, initial expansion, and final expansion in the Sheffield Laboratory Coking Test, and to higher temperatures, until 90 per cent. of the available oil of the coal had been distilled. The residues were then reheated to 600 deg. C. in the manner described. The analyses of the coals examined are recorded in Table I., and the results obtained in Table II.



TABLE II.—OIL YIELD ON HEATING COLUMNS OF COAL PARTICLES.

Coal.	Temp. of preheating of column T deg. Cent.	Oil distilled to T deg. Cent. (A per cent.).	Oil freed by pre-heating to T deg. but not distilled (extracted by ether). (B per cent.).	Oil not freed by distillation but freed on re-heating to 600 deg. Cent. (C per cent.).	Total oil to 600 deg. Cent. (A+B+C per cent.).*	Per cent. of total oil distilled at T deg. Cent.
Brockwell (89 per cent. C.)	350	0.3	3.7	5.9	9.9	3
I.C. 349 deg.	395	1.6	3.9	4.0	9.5	17
I.E. 394 deg. C. = 20 per cent.	420	2.6	4.2	2.3	9.1	28
F.E. 417 deg. E. = 172 per cent.	440	4.8	2.6	1.5	8.9	54
	460	6.8	0.4	1.0	8.2	83
	480	7.8	nil	0.8	8.6	91
Busty (88 per cent. C.)	360	0.4	1.1	6.5	8.0	5
I.C. 360 deg.	405	1.1	2.2	4.4	7.7	14
I.E. 405 deg. C. = 20 per cent.	430	2.1	1.1	4.8	8.0	26
	460	6.7	0.3	0.9	7.9	85
F.E. 430 deg. E. = 200 per cent.	480	7.0	nil	0.7	7.7	91
Silkstone (86 per cent. C.)	350	nil	2.8	3.0	5.8	nil
I.C. 347 deg.	400	1.2	3.7	3.6	8.5	14
I.E. 400 deg. C. = 15 per cent.	425	3.1	4.9	1.7	9.7	32
F.E. 422 deg. E. = 100 per cent.	450	7.6	1.1	1.0	9.7	79
	470	8.2	0.5	0.2	8.9	94
Parkgate III (85 per cent. C.)	345	nil	3.6	5.8	9.4	nil
I.C. 342 deg.	395	1.9	3.2	5.0	10.1	19
I.E. 395 deg. C. = 20 per cent.	410	2.7	4.0	4.1	10.8	25
F.E. 412 deg. E. = 129 per cent.	425	4.8	6.1	2.4	13.3	36
	450	9.4	0.7	1.6	11.7	86
	470	10.0	0.3	0.5	10.8	93
Parkgate II (84 per cent. C.)	360	0.5	4.4	8.2	13.1	4
I.C. 357 deg.	400	1.9	4.7	6.6	13.2	14
I.E. 397 deg. C. = 15 per cent.	410	2.5	5.0	5.7	13.2	19
F.E. 408 deg. E. = 119 per cent.	430	6.5	2.1	4.4	13.0	50
	460	10.3	0.6	2.3	13.2	77
	480	12.1	0.2	0.7	13.0	93
Barnsley IV (84 per cent. C.)	365	1.2	2.5	6.4	10.1	12
I.C. 364 deg.	405	2.0	3.3	5.7	11.0	18
I.E. 406 deg. C. = 23 per cent.	420	3.7	4.1	3.3	11.1	33
F.E. 420 deg. E. = 65 per cent.	445	7.9	1.7	1.8	11.4	70
	460	9.0	1.0	1.3	11.3	80
	480	10.4	0.2	0.4	11.0	95
Fenton (83 per cent. C.)	350	nil	3.0	9.4	12.4	nil
I.C. 353 deg.	390	4.1	2.7	6.1	12.9	32
I.E. 392 deg. C. = 14 per cent.	410	5.8	2.5	4.3	12.6	46
F.E. 405 deg. E. = 94 per cent.	430	8.6	1.1	2.5	12.2	70
	460	11.2	0.4	0.9	12.5	90
Swallow Wood (82 per cent. C.)	365	0.2	2.7	6.6	9.5	2
I.C. 364 deg.	390	0.8	2.5	7.3	10.6	8
F.C. 413 deg. C. = 25 per cent.	415	3.1	1.9	6.2	11.2	28
E. = Nil	440	7.5	0.9	2.2	10.6	71
	460	9.7	0.1	0.5	10.3	94
Waterloo (81 per cent. C.)	320	nil	2.3	8.6	10.9	nil
I.C. 320 deg.	390	0.9	2.5	6.8	10.2	9
	415	2.9	1.7	5.4	10.0	29
F.C. 442 deg. C. = 25 per cent.	440	6.0	1.4	1.9	9.3	64
E. = Nil	460	7.9	0.3	1.3	9.5	83
	480	9.0	0.2	0.3	9.5	95
Shafton (80 per cent. C.)	335	nil	2.5	11.2	13.7	nil
I.C. 335 deg.	375	2.9	2.8	7.0	12.7	23
F.C. 411 deg. C. = 26 per cent.	410	7.3	2.7	1.8	11.8	62
E. = Nil	445	11.0	0.4	0.4	11.8	93
Thick (78 per cent. C.)	355	nil	3.7	4.3	8.0	nil
I.C. 307 deg.	380	1.6	2.5	4.1	8.2	20
F.C. 412 deg. C. = 12 per cent.	400	3.2	2.0	3.9	9.1	35
	420	5.6	1.3	1.1	8.0	70
E. = Nil	440	7.6	0.1	0.3	8.0	95
	460	7.9	nil	nil	7.9	100
Main (77 per cent. C.)	335	nil	1.0	6.5	7.5	nil
I.C. 336 deg.	370	0.7	1.1	5.4	7.2	10
F.C. 403 deg. C. = 5 per cent.	405	2.5	1.2	3.1	6.8	37
E. = Nil	425	4.3	0.9	1.7	6.9	62
	460	6.3	nil	0.5	6.8	93
Barnsley IV Hards	395	1.8	0.3	7.4	9.5	19
I.C. 283 deg.	410	2.7	3.6	2.9	9.2	29
F.C. 442 deg. C. = 17 per cent.	435	6.0	0.3	1.5	7.8	77
E. = Nil	460	6.9	nil	0.5	7.4	93

I.C. = Initial contraction; F.C. = Final contraction; I.E. = Initial expansion; F.E. = Final expansion; C = Contraction; E = Expansion; in Sheffield laboratory coking test.

\* Oil obtained on reheating to 600 deg. Cent. the coal which has been preheated to T deg. less the amount extractable by ether.

Note.—Oil yields are calculated on the weight of the original coal.



Coal.	Moisture *	Ash *	Volatile Matter Less		
			Moisture †	Carbon †	Hydrogen †
Brockwell (Durham) .....	1.0	3.7	28.4	88.7	5.00
Busty II. (Durham) .....	0.6	3.6	25.9	88.3	4.90
Silkstone (S. Yorks.) .....	0.8	0.9	35.3	86.0	5.42
Parkgate III. (S. Yorks.) .....	1.0	2.3	37.0	84.8	5.32
Parkgate II. (S. Yorks.) .....	1.4	0.8	36.0	84.2	5.37
Barnsley IV. (S. Yorks.) .....	2.0	1.1	35.2	83.7	5.17
Fenton (S. Yorks.) .....	2.4	0.7	39.1	83.0	5.50
Swallow Wood (S. Yorks.) .....	2.7	1.0	37.1	81.8	5.34
Waterloo (Derby) .....	4.8	1.5	37.1	81.6	5.28
Shafton (S. Yorks.) .....	6.4	5.2	44.0	79.9	5.42
Thick (S. Staffs.) .....	10.2	5.5	40.8	78.9	5.25
Main (Leicester) .....	12.4	5.7	39.5	76.5	5.06
Barnsley Hards .....	2.7	2.8	34.6	85.2	4.97

\* On air dried basis.

† On ash free dry basis.

### OIL ADSORPTION AND EVOLUTION FROM SINGLE PARTICLE AND COLUMNS OF PARTICLES.

It will be noted that, as with single particles, hardly any oil distilled below the temperature of initial contraction of a column of particles under 100 grm. load. On the other hand, at the temperature of final expansion (when for single particles an average of 85 per cent. of the oil had been distilled), less than one-third of the oil distilled from the good coking coals, but considerably more from the poor coking coals of lower carbon content. This difference may be illustrated in Table III.

TABLE III.—PER CENT. OF TOTAL OIL YIELD DISTILLED AT THE TEMPERATURE OF FINAL EXPANSION IN THE SHEFFIELD LABORATORY COKING TEST.

Coal.	From single particles.	From columns of particles.
Carbon content 89 to 84 per c.	Busty .....	26
	Brockwell .....	28
	Parkgate III. ....	25
	Average .....	27
	Silkstone.....	32
	Average .....	27
Carbon content 83 to 77 per c.	Parkgate II. ....	19
	Barnsley IV. ....	33
	Fenton .....	46
	Average .....	28
	Swallow Wood..	71
	Average .....	64
Carbon content 83 to 77 per c.	Waterloo .....	93
	Average .....	84
	Shafton .....	62
	Average .....	51
Thick .....	77	
Main .....	97	
		37

The figures clearly established that the oil produced by decomposition of the coal substance, although readily distilled from the free surface of a single particle, was retained until a much higher temperature by a column of particles. This adsorption or "wetting" was more marked with coals of high carbon content. The difference between coals of high and low carbon content could also be shown by comparison of the percentage of the total oil distilled at an arbitrary temperature, say, 430 deg. C. For the six coals of 89-84 per cent. carbon, the percentage of the total oil distilled was 39 per cent., compared with 70 per cent. for the six coals of low carbon content, and was as high as 81 per cent. for the coals of lowest carbon content, which were definitely non-coking. The temperature at which over 90 per cent. of the oil has been distilled was above 470 deg. C. for the six high rank coals, and above 440 deg. C. for five of the low rank coals.

The adsorption of the oil was shown by the amount extracted by ether from the preheated columns of particles. From single particles, the amount of oil extractable by ether rarely exceeded 2 per cent. (Fuel, 1933, 12, 232), but with columns of particles the amount may be as high as 6 per cent. of the coal substance. It may also be seen that, whilst the coals of 89-84 per cent. carbon content usually adsorbed 4 per cent. or more, the coals of 83-77 per cent. carbon content never adsorbed more than 3 per cent. of oil.

Adsorption of oil was therefore a notable phenomenon during the carbonisation of columns of particles, particularly for coals of high carbon content. The force with which this oil is retained was shown by the fact that the temperature had to be raised 30 or 40 deg. C. (when the rate of gas evolution was almost doubled) before as much oil is distilled from the columns of particles as from single particles.

The difference in behaviour of single particles and columns of particles is illustrated by the following graph, which shows the percentage of the total oil yield obtained at different temperatures.

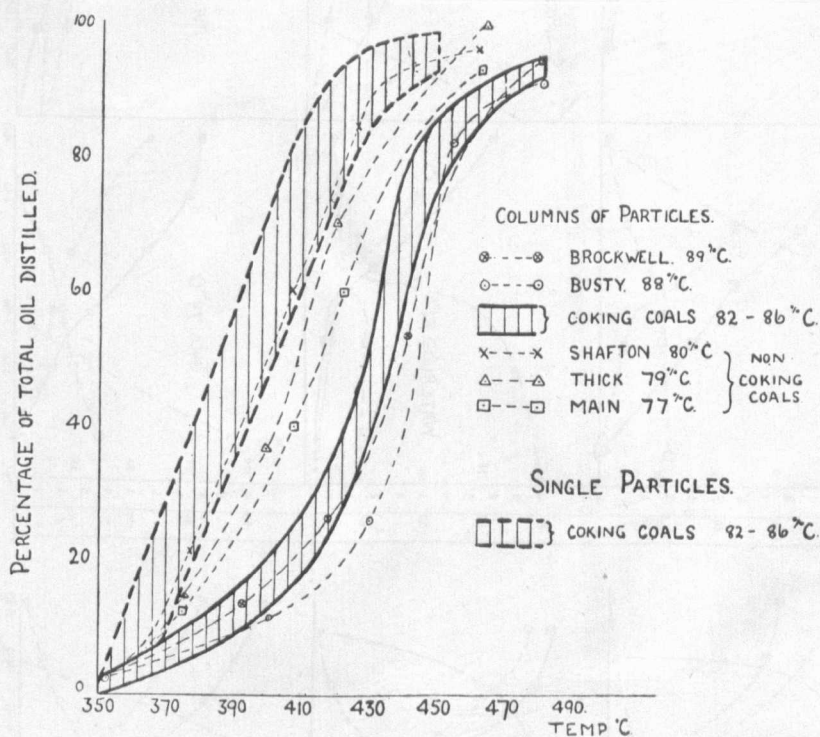


FIG. 2.  
Comparison of oil evolution from single particles and columns of coal particles of different carbon content.

From the single particles there is a regular increase in the amount of oil distilled with increase in temperature. From columns of particles, oil is less easily distilled, this being more marked for the better coking coals of higher carbon content. Non-coking coals as columns of particles tend to behave the same way as single particles.

These results emphasised the importance of considering, when attempting to explain the formation of coke, not only the amount of oil produced and its composition, but the ability of the coal to adsorb this oil.

#### THE RELATIONSHIP BETWEEN OIL AND GAS EVOLUTION.

The amount of oil distilled from the coal, and the amount extractable by ether at different temperatures of preheating were graphed in fig. 3 for the series of coals examined in the crushed condition. On the same graph was (recorded) the evolution of gas and the strength of the coke obtained by reheating the coals, which had already been preheated to the temperature noted on the graph, to 600 deg. Cent. It will be observed that there is a general similarity in the curves for gas and oil evolution. Sometimes oil evolution and gas evolution begin at the same temperature, but the oil evolution may have started before gas is produced though the amount distilled is always small (not exceeding 0.4 per cent.). In only one instance (Main coal) has the oil evolution lagged behind gas evolution, but in this case gas evolution began at a much lower temperature than with the other coals.

Holroyd and Wheeler (Fuel, 1930, 9, 77) showed that during distillation in a vacuum evolution of oil (hydrocarbons and resins present as such in the coal) occurred before active decomposition of the coal, as indicated by a sudden increase in gas evolution. It was evident from the present work that, release of oil from the coal substance having occurred, evolution of gas was necessary to enable more than a very small quantity of oil to be distilled. The curve for gas evolution suddenly changed in direction, with a more rapid evolution of gas at temperatures of about 380 to 430 deg. Cent. (dependent on the coal), the break in the curve of the "adsorbed oil" occurring at approximately the same temperature. As a result of the break in the "oil adsorbed" curve, the "oil distilled" curve was also influenced. The break in the gas curve may be illustrated by the records of gas evolution for two coals of different carbon content as follows:



Brockwell Coal (89 per cent. carbon).																			
Temperature deg. Cent.—	355	360	365	370	375	380	385	390	395	400	405	410	415	420	425	430	435	440	445
Gas c.c. per 5 deg. Cent. rise—	2	2	0	2	0	2	2	0	2	2	2	2	4	4	12	12	18	26	26
Rate of increase per 5 deg. Cent.—	0	—	2	—	2	2	0	—	2	0	0	0	2	0	8	0	6	8	0
Break in gas curve 420–425 deg. Cent. Break in oil adsorbed curve (fig. 2) 430. Break in oil distilled curve (fig. 2) 430.																			
Swallow Wood Coal (82 per cent. carbon).																			
Temperature deg. Cent.—	340	345	350	355	360	365	370	375	380	385	390	395	400	405	410	415	420	425	
Gas c.c. per 5 deg. Cent. rise—	2	2	4	4	4	6	8	10	10	10	12	14	16	22	32	40	50	56	
Rate of increase per 5 deg. Cent.—	0	2	0	0	0	2	2	2	0	0	2	2	2	8	10	8	10	6	
Break in gas curve 400–405 deg. Cent. Break in oil adsorbed curve 405–410 deg. Cent. (fig. 2). Break in oil distilled curve 405 deg. Cent. (fig. 2).																			

The agreement of the breaks in the gas and oil curves was good for all coals of 82 per cent. carbon and over, but with Fenton coal, and the three coals of lowest carbon content, the breaks were not well defined. The results in fig. 3 show clearly the dependence of oil evolution on the release of gas. The relationship between oil and gas evolution may be studied further by reference to figs. 4 and 5. In fig. 4 the oil evolution is shown for the series of coals over the range 400 to 460 deg. Cent., the results being plotted as the percentage of the total oil evolution from each coal to avoid undue crossing of the curves. It will be seen that the curves arranged themselves fairly well in the order of the carbon content of the coals. There were two groups of curves, the lower including eight of the nine coals of high carbon content, and the upper including the three coals of lowest

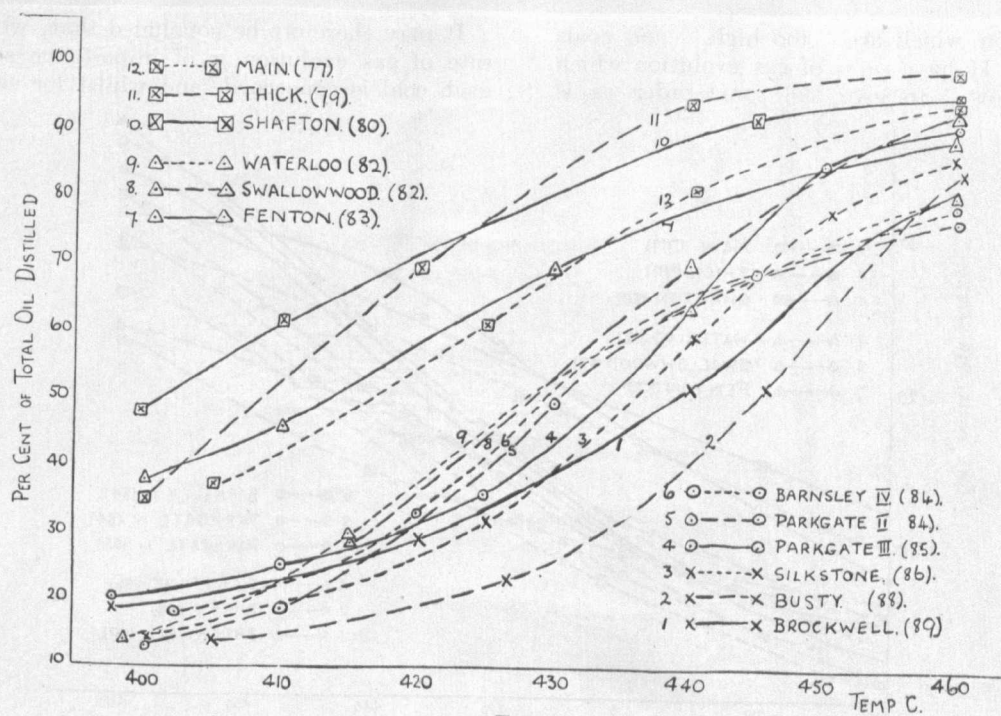


FIG. 4.  
Percentage of total oil yield distilled at different temperatures, from a series of columns of coal particles.  
(Figs. in brackets are approximate carbon contents.)

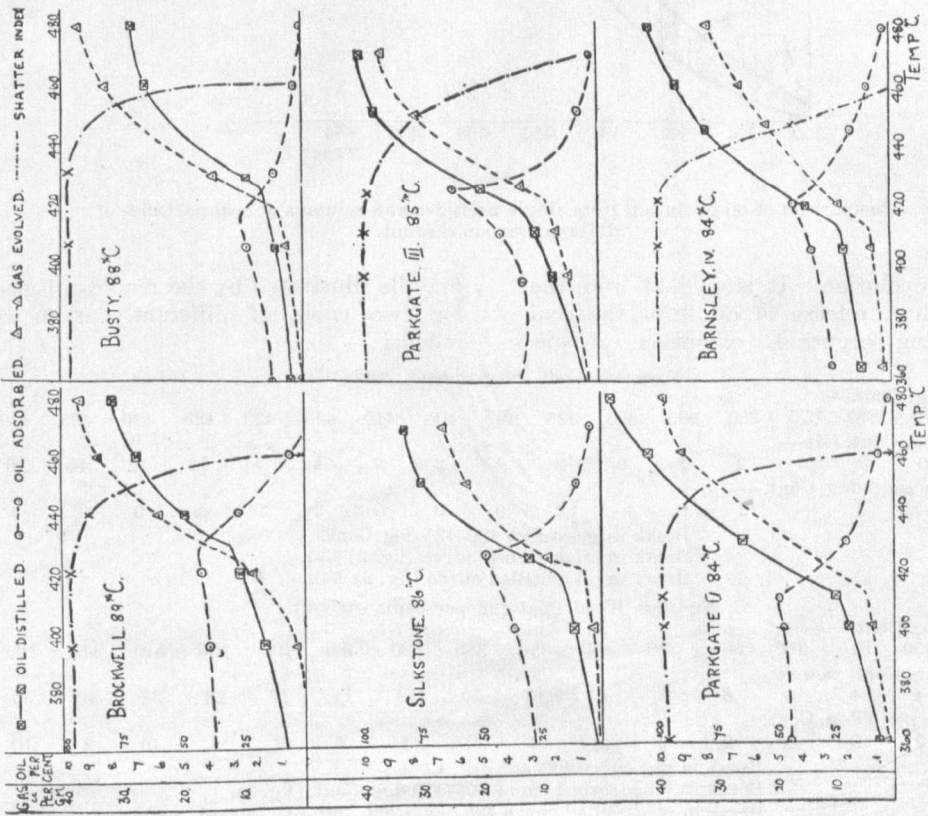
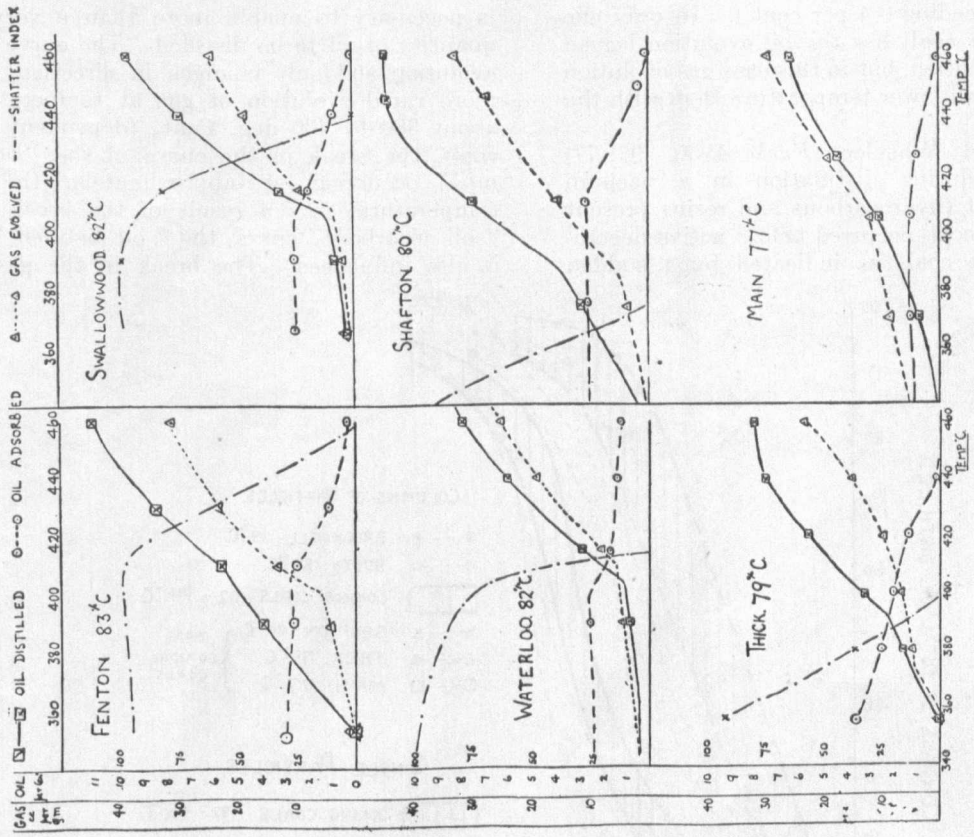


FIG. 3.  
 Comparison of gas and oil evolution from columns of particles of a series of coals heated at a rate of 1° rise per min. to different temperatures and free to expand.  
 (c = carbon content.)



carbon content, and one other (Fenton). The four coals of highest carbon content (89 to 86 per cent.) gave curves which are convex to the abscissa. The next four coals (Nos. 5, 6, 8 and 9) gave curves which were at first convex to the abscissa, and then became concave above about 420 deg. C. The upper group of curves, referring to coals mainly of low carbon content, were concave. The difference between the evolution of oil from the different types of coal was therefore strongly marked, the ready evolution from the three non-coking coals (Nos. 10, 11 and 12) being noteworthy. Coal No. 7 is a coking coal, although of inferior quality.

Fig. 5 shows the gas evolution from the series of coals over the same range. The gas evolution was not so dependent on the rank of the coal as was the oil evolution. The curves group together more closely, but there were still two distinct groups. The upper group included coals Nos. 7, 10 and 12 (as in fig. 4), but coal No. 11, which was included in the upper group of curves in fig. 4, now appeared at the bottom of the lower group of curves (fig. 5). Moreover, the coals of high carbon content, Nos. 1 and 2, appeared almost at the top of the lower group of curves in fig. 5.

The relative positions of the different curves in figs. 4 and 5 were compared at different temperatures, as in Table IV.

TABLE IV.  
RELATIVE ORDER OF COALS AS REGARDS EVOLUTION OF GAS AND OIL.

Order of curves for gas evolution. (Fig. 5.)				Order of curves for oil evolution (Fig. 4.)				
Temp.				Temp.				
420 deg.	430 deg.	440 deg.		420 deg.	430 deg.	440 deg.		
3	3	11	.....	2	2	2	} Group I., 89-86 p.c. C.	
6	11	3	.....	3	1	1		
2	6	6	.....	1	3	3		
11	2	8	.....	4	4	4	} Group II., 85-84 p.c. C.	
4	9	9	.....	5	5	5		
9	8	2	.....	6	6	6		
1	4	4	.....	8	8	9	} Group III., 83-82 p.c. C.	
5	1	1	.....	9	9	8		
8	5	5	.....	12	12	7		
12	12	12	.....	7	7	12	} Group IV., 80-77 p.c. C.	
7	10	10	.....	11	10	10		
10	7	7	.....	10	11	11		

Considering the coals in groups of three, it was noticed that, at a temperature of 440 deg. Cent. the curves for oil evolution were in a regular order, and at the lower temperatures this order was only affected by the interchange of coals Nos. 7 and 12. It was therefore concluded that, between temperatures of 420 and 440 deg. Cent. under the conditions of these experiments, the rate of oil evolution was directly related to the rank of the coal, being low for coals of high rank and high for coals of low rank.

It was not possible to draw the same conclusions for gas evolution over the temperature range during which maximum oil evolution occurs (see fig. 2). Coals Nos. 1, 2, 5 and 7 had rates of gas evolution which were "too high," and coals Nos. 8 and 11 had rates of gas evolution which were "too low" to give the same order as was found for oil evolution. Remembering the relationship found for oil and gas evolutions for each coal (fig. 3), it was probable that the unusually high rate of oil evolution from coal No. 7 was due to the unusually high rate of gas evolution from that coal over the range 420-440 deg. Cent., and caused the displacement of the oil evolution curve in fig. 4. It was noteworthy that coal No. 7, which grouped with the coals of lowest carbon content in figs. 4 and 5, behaved like them in giving curves for gas and oil evolution in which there were no pronounced breaks. On the other hand, the rate of oil evolution for coal No. 11 was the maximum of the series (fig. 4) at a temperature of 440 deg. Cent. when the gas evolution was the lowest.

If the rate of gas evolution from single particles had been very much greater than from columns of particles over the range when most of the oil is distilled from single particles, fig. 2 would not have the significance here suggested, namely, that the oil is adsorbed in columns of particles. Tests were therefore made with single particles of Silkstone and Partgate III coal which were heated in a Gray-King assay at a rate of 1 deg. Cent. per min. to determine the rate of gas evolution. Each particle weighed about 10 grm. The rates of gas evolution were, however, similar to those found for columns of particles of the same coals. The rapid evolution of oil from single particles cannot therefore be explained by a more rapid evolution of gas than is found for columns of particles.

It was therefore concluded that, whilst the rate of gas evolution was of importance so far as each coal was concerned, and whilst for each coal a sudden

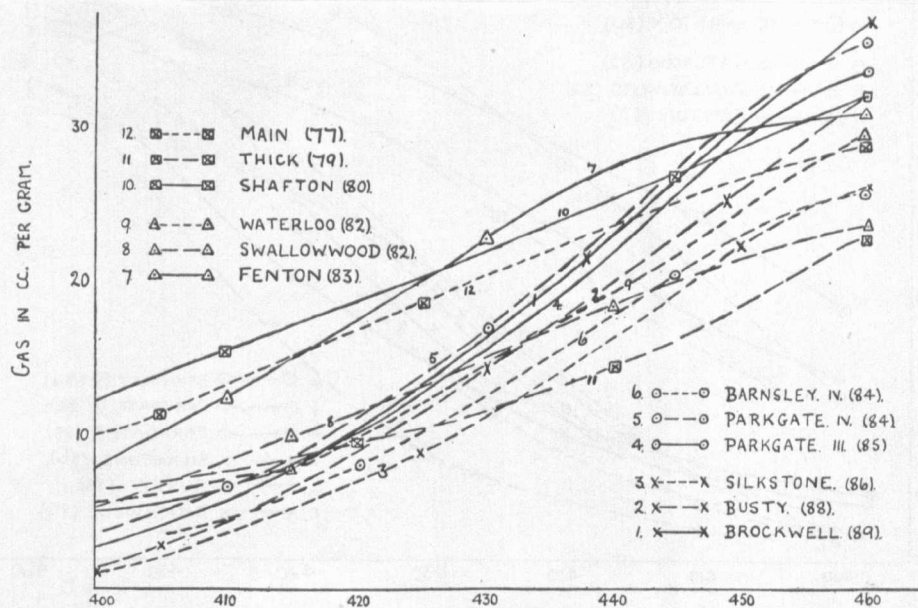


FIG. 5.  
Rate of gas evolution at different temperatures, from a series of columns of coal particles.

increase in the rate would cause a sudden increase in the evolution of oil, the rate of oil evolution was not dependent solely on the rate of gas evolution, but another factor, namely, the ability of the coal to adsorb oil, was important. The converse action of oil in influencing the evolution of gas was shown by fluctuations in the rate of gas evolution from high carbon coals over the temperature range when marked distillation of oil was occurring.

#### THE INFLUENCE OF OIL ON COKE FORMATION.

The tests previously described demonstrated the adsorption of oil by coal when heated as columns of particles, the adsorption being greater for good coking coals of high carbon content (over 84 per cent.). Whilst the amount of oil adsorbed by coals of high carbon content attained a maximum of over 4 per cent. at a temperature of about 420 deg. Cent., that adsorbed by coals of low carbon content began to decrease at a temperature of 400 deg. Cent. (a temperature which generally marks the beginning of true plasticity), and was only 1 or 2 per cent. at a temperature of 420 deg. Cent. The retention of oil over the range 400 to 420 deg. Cent. under the experimental conditions therefore distinguished coking coals from non-coking coals, and since this temperature range was also the range when the columns of particles swelled (see Table II.), the phenomena of oil adsorption and swelling were related, probably as cause and effect.

Although swelling and coke formation were not dependent on the total amount of oil a coal would yield on carbonisation, a deficiency of oil would prevent coke formation. This is shown in fig. 6, which gives the "shatter index" of the cokes produced by heating to 600 deg. Cent., at a rate of 5 deg. Cent. per min., coals which have been previously heated at a rate of 1 deg. Cent. per min. to the series of temperatures noted in Table IV. Shafton coal preheated to 335 deg. Cent. (when no oil was distilled) gave on reheating to 600 deg. Cent. a coke of shatter index 99.5, a hard product; when the same coal had been preheated to 375 deg. Cent. (when 2.9 per cent. oil was distilled) and then reheated to 600 deg. Cent. the product was a non-coherent powder. Coals of higher carbon content could be heated to higher temperatures before they lost the ability to form a hard coke on reheating. Fig. 6 shows that, as the carbon content of the coal increased the temperature of preheating required to make the residue a non-coherent on reheating also increased. The Yorkshire coking coals of 86 to 83 per cent. carbon content gave non-coherent residues in a carbonisation test after being preheated to 450 deg. to 460 deg. Cent. For coals of lower carbon content, from which only inferior cokes can be produced in practice, the temperature of preheating which just gave a non-coherent residue in the re-heating test, fell rapidly and was under 400 deg. Cent. for the non-coking coals Shafton and Thick.

The relationship between the amounts of oil remaining in the coal after preheating to particular temperatures (and therefore obtained on reheating to 600 deg. Cent.), and the hardness of the coke produced in the latter operation could be judged from the results in Table V.

The division lines in Table V. were drawn to mark the limits enclosing (a) cokes with shatter index over 90, (b) cokes with shatter index less than 60.



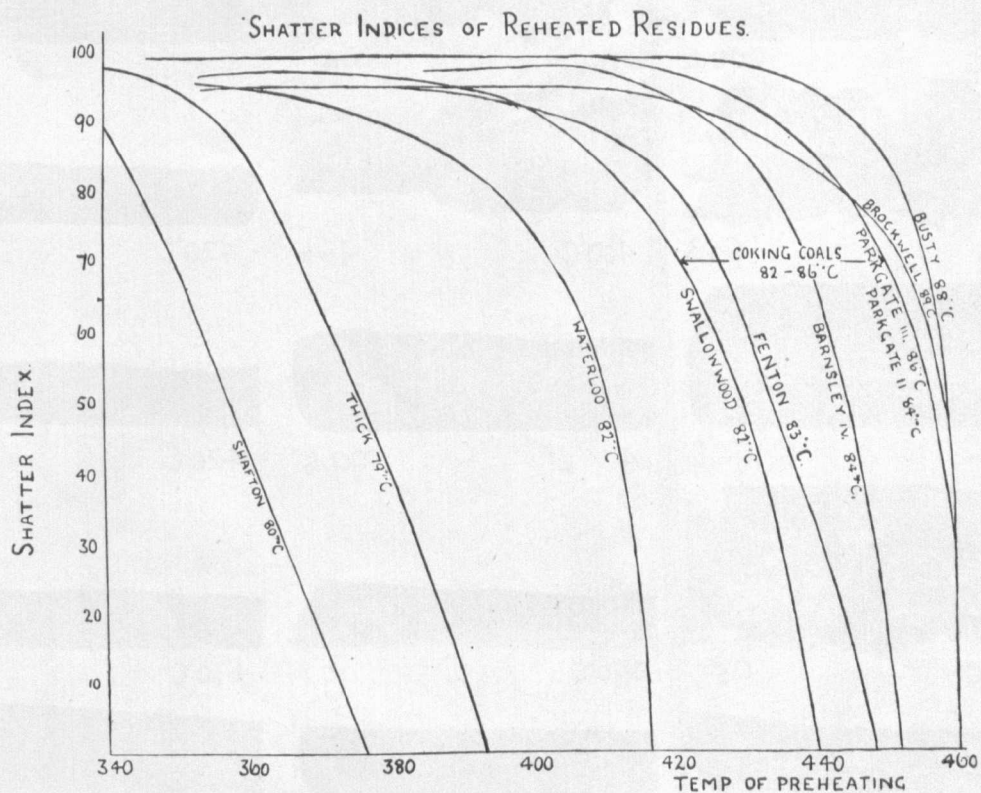


FIG. 6.  
Shatter Index of Cokes prepared by reheating to 600°C, coals which have been previously preheated to different temperatures.

From these figures it was concluded that:—

- (1) Coals over 85 per cent. carbon begin to give poorer cokes when 2 to 3 per cent. of oil remains.
- (2) Coals of 84 to 82 per cent. carbon begin to give poorer cokes when 4 to 9 per cent. of oil remains.
- (3) Coals of 80 to 79 per cent. carbon begin to give poorer cokes when 7 to 12 per cent. of oil remains.

In general the amount of oil which was required to give cokes of over 90 shatter index increased from 4 per cent. for coals of 89 to 85 per cent. carbon to 5 per cent. for coals of 84 per cent. carbon, to 7 per cent. for a coal of 83 per cent. carbon, to 9 per cent. for coals of 82 per cent. carbon and to 12 per cent. for a coal of 80 per cent. carbon. The amount of oil required for good coke formation therefore varied with the rank of the coal, being relatively low for coals of high carbon content, but rising rapidly when the carbon content of the coal fell below 84 per cent. Since it had previously been shown that only coals which are capable of adsorbing about 4 per cent. of oil on preheating to 420 deg. Cent. yield good cokes in practice, and that non-coking coals were incapable of adsorbing this quantity from the natural oil produced by the coal on distillation, it followed that addition of "foreign" oil might be necessary to enable a coke to be made from a coal which was normally non-coking.

TABLE V.—THE EFFECT OF RESIDUAL OIL ON COKE QUALITY.

(Shatter index of cokes obtained by reheating to 600 deg. Cent. coal previously preheated to T deg.; amounts of oil recovered on heating from T deg. Cent. in brackets).

Preheating temp. (T deg. Cent.).	400	410	420	430	440	450	460
Brockwell (89 per cent. C.)	96 (7)	96 (7)	95 (7)	94 (6)	89 (4)	70 (3)	Nil (2)
Busty (88 per cent. C.)	94 (7)	96 (7)	97 (7)	97 (6)	94 (4)	83 (2)	Nil (1)
Parkgate IV (85 per cent. C.)	99 (9)	98 (8)	98 (7)	94 (5)	85 (3)	76 (2)	Nil (1)
Parkgate II (84 per cent. C.)	99 (11)	99 (11)	99 (8)	98 (6)	92 (5)	75 (3)	Nil (2)
Barnsley IV (84 per cent. C.)	99 (9)	99 (9)	99 (7)	93 (5)	70 (4)	30 (3)	Nil (2)
Fenton (83 per cent. C.)	99 (8)	99 (7)	85 (6)	60 (5)	40 (3)	15 (2)	Nil (1)
Swallow Wood (82 per cent. C.)	98 (9)	87 (8)	65 (6)	30 (4)	Nil (3)	—	—
Waterloo (82 per cent. C.)	75 (9)	35 (7)	Nil (6)	—	—	—	—
Shafton (80 per cent. C.)	65 (12)*	Nil (7)	—	—	—	—	—
Thick (79 per cent. C.)	65 (7)†	Nil (5)	—	—	—	—	—
Main (77 per cent. C.)	—	Nil (5)	—	—	—	—	—

\* Temperature of preheating 350 deg. Cent.

† Temperature of preheating 370 deg. Cent.





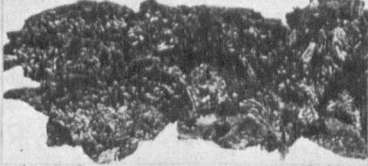
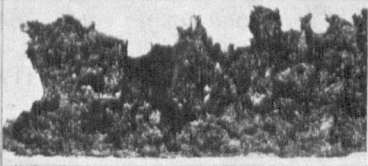
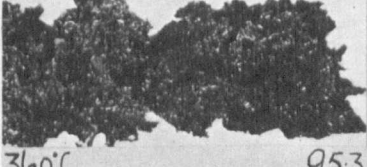
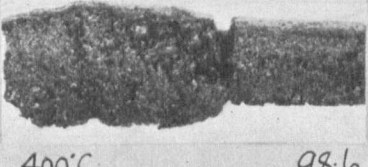
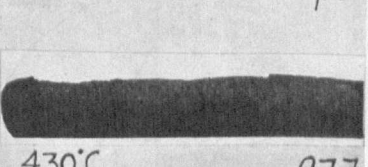
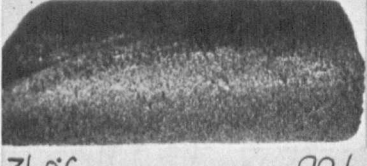
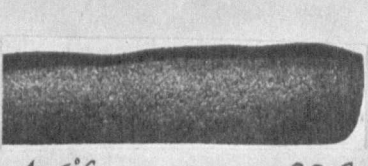
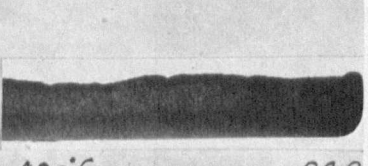

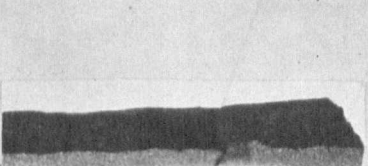
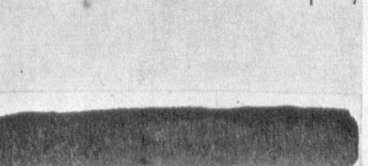
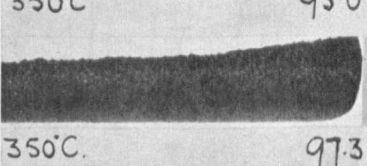
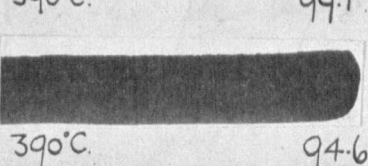
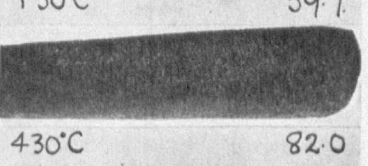
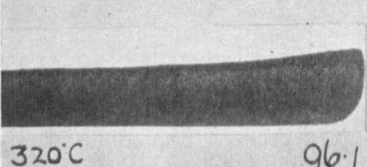
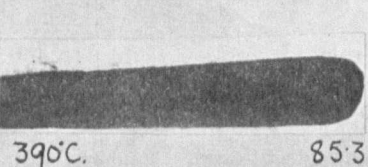
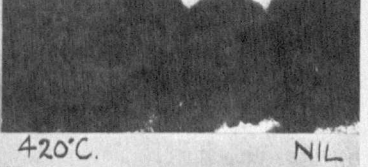
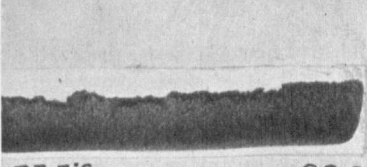
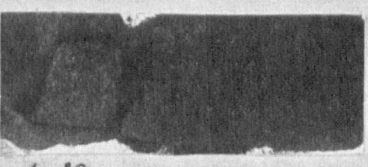

BROCKWELL, 89 per cent. C.	 350°C	96.5	 420°C	95.0	 440°C	89.0
BUSTY, 88 per cent. C.	 360°C	96.2	 405°C	94.1	 430°C	91.8
PARKGATE II, 84 per cent. C.	 360°C	95.3	 400°C	98.6	 430°C	97.7
BARNSELY IV, 84 per cent. C.	 360°C	99.6	 405°C	99.8	 420°C	98.9
FENTON, 88 per cent. C.	 350°C	95.0	 390°C	99.1	 430°C	59.7
SWALLOWWOOD, 82 per cent. C.	 350°C	97.3	 390°C	94.6	 430°C	82.0
WATERLOO, 82 per cent. C.	 320°C	96.1	 390°C	85.3	 420°C	NIL
SHAFTON, 80 per cent. C.	 335°C	99.5	 410°C	NIL	 420°C	NIL

PLATE I.

The Effect of Preheating Coals to Different Temperatures on their swelling and coking power. (The cokes were obtained by reheating to 600°C, coals which had been preheated to the temperatures noted. The shatter index is recorded to indicate the hardness of the coke.)



Photographs of the coked residues obtained on reheating heated coals to 600 deg. Cent. were given (Plate I.) from which the decrease of swelling power with decrease in carbon content or increase in temperature of initial preheating could be noted.

#### SUMMARY AND CONCLUSIONS.

(1) A series of coals varying in carbon content from 89 to 77 per cent. on the ash-free, dry basis were examined, and particular attention devoted to the part played by the oil distilled from the coal on its coking phenomena.

(2) It was shown that, at the same rate of heating, the oil evolution from columns of particles of coals began at the same temperature as from single particles of the same coal. The temperature of initial oil evolution coincided with that of initial continuous gas evolution which occurred at about the softening temperature of the coal as determined in the Sheffield Laboratory Coking Test.

(3) The oil was not distilled from columns of particles so rapidly as from single particles. For coals of 82 to 86 per cent. carbon content, 90 per cent. of the oil from single particles was distilled over the range 350 to 430 deg. Cent., but the corresponding range for columns of particles was 350 to 470 deg. Cent. was therefore one of the causes of difference in swelling power of coals.

(4) The slower oil evolution from columns of particles was due to adsorption of the oil distilled from one particle on the surface of adjacent particles. The adsorptive power for oil of different coals was directly related to its carbon content, and therefore the rate of oil evolution from different coals over the plastic range was directly related to the carbon contents of the coals, being lower for coals of high carbon content.

(5) The rate of gas evolution over the plastic range was not directly related to the carbon content of the coal. Evolution of gas was necessary to carry off oil, and a sudden increase in the rate of gas evolution caused an increase in the rate of oil evolution.

(6) Coals which were strongly swelling (and good coking), of over about 84 per cent. carbon content, generally adsorbed over 4 per cent. of oil (expressed on the coal) at a temperature of 420 deg. Cent., whilst poor-swelling and non-swelling coals, of under about 83 per cent. carbon content, adsorbed only 1 to 2 per cent. of oil at the same temperature. The varying ability to adsorb oil was therefore one of the causes of difference in swelling power of coals.

(7) The quantity of oil necessary to allow a good coke to be made varied with the rank of the coal, being about 4 per cent. for coals of 89 to 95 per cent. carbon, but up to twice as much for coals of 83 to 82 per cent. carbon and up to three times as much for coals of 80 per cent. carbon.

The preceding work has given a definite basis upon which to commence the study of the influence of oil addition upon the coking properties of coal. If by some means we can add an oil which is retained by the coal substance after preheating to 420 deg. C., to give a total of more than 3.0 per cent. of the coal, it seems feasible to assume that we might be able to confer coking ability upon coals which heated by themselves fall in the non-coking or inferior coking class, or to increase the coking ability of the coking coals. According to the "wetting" theory of coke formation the extruded oil by reason of its "physico-chemical forces" spreads over and wets the whole of the coal surface, the wetted coal forming a strongly coking mass. In coking there must then be two factors: (1) Possession of this "extruded oil"; (2) ability of the coal surface to be "wetted" by it. In various types of coals we might have:

	Type of Coal.
1. Sufficiency of suitable oil and a surface possessing suitable adsorbing properties.	Strongly coking.
2. Sufficiency of suitable oil together with a surface which is not so strongly adsorbing.	} Coals of inferior coking ability.
3. Insufficiency of suitable oil together with a strongly adsorbing surface.	
4. There may be both insufficiency of suitable oil, and the surface may be incapable of adsorbing oil.	Definitely non-coking.

N.B.—The oil must be "suitable" or capable of being adsorbed. Many coals give sufficient oil on distillation, but this seems incapable of being adsorbed.

The object of the research will be to add oils of various types to different classes of coals, and to study the effects of this oil addition upon the coking abilities of the coal. Strongly coking coals would appear to have a sufficiency of oil and it is anticipated that little will be learned from these. In the case of the non-coking coals and coals of inferior coking quality, however, it is hoped that these coals can be converted to coking coals. It seems reasonable to expect, in the light of the previous work, that if an oil-coal mixture can be produced, which will retain at least 3.0 per cent. of extractable oil after preheating to 420 deg. C., that this mixture should possess coking properties similar to those of coking coals. In the case of the non-coking coals (No. 4), it is not anticipated that any great improvement in coking ability will be effected. The problem of "inactive" surface seems much more difficult than that of "insufficient" oil, and it is too much to hope that oil addition can possibly influence the activity of the coal surface.

## INTRODUCTION. THE PRODUCTION OF OIL-COAL MIXTURES.

It was decided in the previous research that the temperature of preheating which gave the maximum of information with regard to the coking properties of any coal was 420 deg. C. This, of course, is an average temperature, the average being obtained from results of heating non-coking and poorly-coking coals rather than from strongly-coking coals. It was apparent that coking ability depended upon the amount of oil freed but not distilled at 420 deg. C. This oil apparently plays some important part in coke-formation, and retention of it in sufficient quantity at 420 deg. C. is a characteristic of coking coals. If there is an insufficiency of oil at 420 deg. C. in any coal, the continued heating of the coal to 500 deg. C., or higher temperatures, will not result in a strong coke. This insufficiency can perhaps be supplied by mixing the coal before heating with some oil which will give the necessary quantity of oil at 420 deg. C. There are two problems: (1) Choice of a suitable oil; (2) adequate mixing of the coal and oil to give a mixture which will behave in the desired manner. In the first problem it is at once suggested that the nature of the oil added should be similar to that distilled from strongly-coking coals. Durham coals all swell strongly on heating, and release a coal tar, which is usually a very viscous liquid. Since this tar comes from coals very suitable for coke-making, its employment in this research seems very obvious. However, we must not lose sight of the fact that it might be the coal surface that is detrimental to coke formation, that it might not have the ability to adsorb the distilled oil and be bound into a mixture suitable for coking. The natural oil of the coal might be eminently suitable as a binding medium, but might be present in insufficient quantity, and if more were added might form a very satisfactory coke when reheated. Consequently the oils distilled from non-coking and weakly-coking coals might be just as suitable for mixing with coals as those from strongly-coking coals. We cannot eliminate any oils that are coal products in our research.

One of the characteristics that distinguishes coking from non-coking coals is carbon content. Coking coals usually contain a larger percentage of carbon than non-coking coals. Coking coals—that is to say, those employed in coking practice—contain from 84-91 per cent. C., Poorly-coking coals contain 82-84 per cent. C., and below 82 per cent. C. coals are usually non-coking. If we have two coals of similar carbon content, their ability to coke is generally proportional to their hydrogen contents, the one containing more hydrogen forming a stronger and more swollen coke than the one with less. Thus we have suggested another method of improving coking power by oil addition. The addition of liquid hydrocarbons to coal will give a coal-oil mixture, and the more the hydrocarbon added, the greater will become the percentage of hydrogen in the mixture. It will therefore be interesting to add hydrocarbon oils to poorly-coking and non-coking coals with a view to studying the effect produced upon the percentage of oil freed but not distilled at 420 deg. C. and on the coke produced. The percentage of oxygen in a coal also tells us something of its coking power. The lower the percentage of oxygen in a coal, the better it cokes. South Wales and Durham coals contain very little oxygen. South Yorks. coals contain rather more and are correspondingly less strongly coking. Other coals, such as those of Derbyshire, are less strongly coking and have more oxygen. It is a well known fact that allowing a coal to absorb oxygen by standing in air considerably lessens its ability to form a coke. Some Derbyshire coals, when stored in a bunker over a week-end lose their coking power. Consequently, the lower in oxygen content the oils used, the better would seem the chance that they would improve the quality of the coke produced from the coal with which they are mixed.

In short, the only criterion of the oil used will be the improving effect it has upon the percentage of oil retained by the coal at 420 deg. C. The whole question seems to be one of physico-chemical action. If the oil by virtue of its interfacial tension, or by molecular attraction "wets" the coal so that on heating to 420 deg. C. the oil extruded is retained and not distilled, then it has a beneficial effect. It may be that the oil is of the type necessary to "wet" the coal for successful coke formation, it may be that its presence helps to retain the inherent oil of the coal up to 420 deg. C., and this inherent oil remains to perform its correct function in coke formation. Or it may be that by its success in wetting the coal mass that the oil removes oxygen in the form of air from the coal, and thus removes also the retarding effect of this oxygen upon coke formation. It would seem from the fact that oil is to be retained at 420 deg. C. that the oil should have a boiling point which is fairly high, say in the neighbourhood of 300 deg. C., and also that the oil employed should contain as high a percentage of hydrogen and as little oxygen as possible.

The second problem was that of suitable mixing of the coal and oil, in order to obtain a product in which the oil was distributed uniformly over the surface of the coal, and to ensure that the spreading was carried out without any great loss of the oil chosen. It was decided to obtain the coal-oil mixture by



agitating the coal with the oil in a suitable medium, called for convenience "Trenting," after P. E. Trent, who used a similar method for coal cleaning purposes. The medium was water, as this could easily be removed from the coal-oil mixture by air drying. The coal used was ground to pass 60 mesh size, and a known weight placed together with excess of water in a small glass churn. The mixture was agitated for a few minutes to ensure complete wetting of the coal by the water. The required quantity of oil to be added was then run in from a measuring vessel such as a burette, and the whole then agitated for a considerable time. The coal-oil mixture floated to the top of the water, and when complete separation appeared to have been effected, the coal-oil mass was removed and freed from water by pressure-filtration. The coal-oil mixture was then allowed to air-dry overnight and subjected to the usual preheatings and reheatings.

After a few experiments had been carried out, several facts became apparent. It was found that coking coals were flocculated more readily than non-coking coals, the separation into the coal-oil layer being more quickly effected and more complete. If complete separation was required with a non-coking coal, very much more oil had to be added, in some cases separation into a clear-cut coal-oil layer never being obtained before free oil was observed on the surface of the water. The viscosity of the oil used was very important, some oils being far too viscous to be used in the normal manner. Either the water had to be hot, or they had to have their viscosity lowered by the introduction of some light oil. Later in the research it was decided to preheat mixtures of coal and oil produced by spraying a thin layer of the coal with an oil jet, but in the majority of the earlier experiments agitation in water was always employed.

The first investigations were carried out using Hamstead Thick Coal and low temperature oil from Parkgate coal (obtained by carbonising the coal in preheated steam, and approximating therefore to a primary oil), the temperatures of preheating varying from 360 deg. C. to 460 deg. C. This was done in order to observe the effect of oil addition over a wide temperature range, and to confirm that the selection of a temperature of 420 deg. C., based on tests without oil addition was correct under the new conditions.

#### **THE ADDITION OF OIL TO A NON-COKING COAL.**

Hamstead Thick coal (South Staffordshire) is a non-coking coal of 79.0 per cent. Carbon Content. There is no break in the curve of its "oil distilled during preheating," and under no circumstances does it form a swollen residue on reheating.

The coal was ground to pass 60 mesh and 25 gm. was agitated in water with 2.5 c.c. of oil measured from a burette. The specific gravity of the oil was previously ascertained to be approximately 1. The mixture was agitated for half-an-hour, when it was observed that complete separation of the coal-oil layer was accomplished. There had also been some separation of the coal substance, a portion of the coal falling to the bottom of the churn. The coal-oil mixture was removed, filtered and air-dried overnight, giving a dry powder. 20 gm. were preheated to 360 deg. C. at 1 deg. C. per minute, the oil and liquor evolved being determined, the residue crushed to pass 60 mesh and reheated to 600 deg. C. at a rate of 5 deg. C. per minute. Part of the preheated residue was extracted with ether in a soxhlet apparatus for 60 hours, and the extracted oil weighed. Further tests were made, using in all cases a 10 per cent. oil-coal mixture, and temperatures of preheating of 380 deg. C., 400 deg. C., 420 deg. C., and 440 deg. C. The results were then compared with those obtained with the coal alone. Further tests were made using 30 per cent. of oil, the temperatures of preheating being 380 deg. C., 420 deg. C., and 440 deg. C., and finally a 50 per cent. coal-oil mixture was prepared and preheated to 410 deg. C.

It was discovered in this last experiment that the coal was more than saturated with oil. A pasty mass was obtained which retained water to a far greater extent than the other mixtures. If pressure filtration was employed, oil as well as water was drawn off. Consequently, the mixture was allowed to air-dry overnight and used. Apparently too much oil could be added, and in further work steps were taken merely to add a sufficient quantity to give adequate mixing and separation. The results are recorded in Table I.

TABLE I.

The effect of Adding Low Temperature Oil to Hamstead Thick Coal (C. 79 per cent.), on the oil extracted, and Shatter Index.

## A.—USING 10 PER CENT. OF OIL.

Oil extracted from preheated coal in Soxhlet.						
Temp. of Preheating deg. C.	360	380	400	420	440	460
Coal alone .....	3.7	2.4	1.7	1.3	0.08	Nil
+ 10 per cent. of Oil .....	5.3	4.8	3.0	2.0	0.10	Nil
Shatter Indices of "Cokes" on reheating preheated residues to 600 deg. C.						
Coal alone .....	93.0	36.0	Nil	Nil	Nil	Nil
+ 10 per cent. of Oil .....	86.2	66.8	52.6	Nil	Nil	Nil

## B.—USING 30 PER CENT. OF OIL.

Oil extracted from preheated coal in Soxhlet.				
Temp. of Preheating deg. C.	360	380	420	440
Coal alone .....	3.7	2.4	1.3	0.08
+ 30 per cent. of Oil .....	7.1	6.9	2.7	0.6
Shatter Indices of "Cokes" on reheating preheated residues to 600 deg. C.				
Coal alone .....	93.0	36.0	Nil	Nil
+ 30 per cent. of Oil .....	84.7	72.0	Nil	Nil

## C.—USING 50 PER CENT. OF OIL.

Oil extracted from preheated coal in Soxhlet.	
Temp. of Preheating .....	420 deg. C.
Coal alone .....	1.3
+ 50 per cent. of Oil .....	3.9
Shatter Index of coke on reheating preheated residue to 600 deg. C.	
Coal alone .....	Nil
+ 50 per cent. of Oil .....	78.0

These results show that the oil addition is very effective if the temperatures of preheating do not exceed 400 deg. C. The oil extracted by ether in the soxhlet from preheated coal, that is, freed in, or retained by, the coal substance from the added oil, has been increased from 1.7 to 3.0 per cent. in the case of a 10 per cent. oil-coal mixture at 400 deg. C. The coal can be made to give a reasonably firm coke up to temperatures of preheating of 420 deg. C., whereas the coal alone loses its power of coke-formation after preheating to 380 deg. C. Thus it is established that the addition of oil by suitable methods has a beneficial effect upon the coking qualities of the coal, but that this effect is rapidly reduced by increase in the temperature of preheating. There is a limit to the amount of oil which can be added, but the more oil added, the higher the amount retained on preheating to 420 deg. C.

The next series of experiments was conducted in a similar manner, using the same oil and a coal which is of an inferior coking quality—Barnborough Barnsley Coal (carbon content 81.6 per cent.). This coal gives a weak coke, but is poorly swelling. A 15 per cent. oil-coal mixture was preheated to 360 deg. C., 380 deg. C., 400 deg. C., 420 deg. C., and 440 deg. C., and the usual extractions and reheatings carried out. The oil added was found to have a beneficial effect upon coke formation. Even when the temperature of preheating was 440 deg. C., a coke was formed although the preheated residue only gave 1.1 per cent. of extractable oil. At 420 deg. C. the coke formed was quite firm although non-swollen, and had a shatter index of 88.

TABLE II.

The effect of adding 15 per cent. of Parkgate Low Temperature Oil to Barnborough Barnsley Coal (C. 81.6 per cent.)

Oil extracted from preheated coal.					
Temp. of Preheating deg. C. ...	360	380	400	420	440
Coal alone .....	3.1	3.0	2.7	2.4	Nil
+ 15 per cent. of Oil .....	6.5	6.5	4.6	3.0	1.1
Shatter Index of final coke.					
Coal alone .....				65.0	Nil
+ 15 per cent. of Oil .....	98.0	89.0	99.0	89.0	17.0

## THE ADDITION OF OIL TO COALS VARYING IN CARBON CONTENT.

Since the coking properties of Barnborough coal showed remarkable improvement after oil addition, it was decided to experiment with a series of coals embracing non-coking, poorly coking, and strongly coking coals, varying in carbon content between 77 per cent. and 86 per cent. These were treated as before with 15 per cent. of Parkgate Low Temperature Oil and preheated to 420 deg. C., following the usual routine. The coals were:—

	C. Content.		C. Content.
R. M. Silkstone .....	86.0	Swallow-Wood Soft .....	81.8
R. M. Parkgate .....	84.8	Waterloo .....	81.6
R. M. Barnsley .....	83.7	Shafton .....	79.9
Fenton .....	83.0	Ellistown Main .....	76.5

These coals had been previously investigated and the amount of oil retained at 420 deg. C. determined.



TABLE III.

The effect of adding 15 per cent. of Parkgate Low Temperature Oil to a series of coals.

Temperature of Preheating, 420 deg. C.

1. OIL RETAINED.								
Carbon Content of Coal	86.0		83.0	82.4	81.8	81.6	79.9	76.5
Coal alone	4.9		3.7	2.4	2.0	1.7	2.0	0.9
+ 15 per cent. of Oil	4.8		4.0	3.0	3.8	2.2	1.8	0.6
N.B.—Barnsley Hard Coal was also used to complete the series which had been examined in the previous research.								
2. OIL DISTILLED ON REHEATING TO 600 DEG. C., AT 5 DEG. C. PER MIN.								
Carbon Content of Coal	86.0	83.0	82.4	81.8	81.6	79.9	76.5	
Coal alone	1.5	2.7	4.8	5.0	1.4		1.9	
+ 15 per cent. of Oil	3.6	5.3	4.7	4.7	3.35		2.6	
3. SHATTER INDICES OF REHEATED RESIDUES.								
Carbon Content of Coals	86.0	83.0	82.4	81.8	81.6	79.9	76.5	
Coal alone		70.0	65.0	82.0	Nil	Nil	Nil	
+ 15 per cent. of Oil	98.0	99.0	89.0	98.0	13.0	15.0	Nil	

From these results it is clear that the improvement in the case of the coking coals is only slight. The strongly coking R.M. Silkstone Coal shows no improvement, although it shows more oil distilled upon reheating to 600 deg. C. In the case of R.M. Parkgate and Barnsley coals the improvement is slight but noticeable, the final residue being more swollen, and more oil being distilled upon reheating to 600 deg. C. It is with the poorly coking coals, carbon content 81-83 per cent. that the most noticeable improvement takes place. Barnborough coal (c. 81.6 per cent.) was improved, and Fenton coal (c. 83 per cent.), another coal of inferior coking quality, is also greatly improved. The amount of oil freed in the coal substance, but not distilled is increased from 1.5 per cent. to 4 per cent.

According to our criterion of coking coals, namely, more than 3.0 per cent. of oil freed but not distilled, Fenton coal can be classed with the coking coals, if mixed with 15 per cent. of Parkgate Low Temperature Oil. In the case of the non-coking coals, Ellistown Main and Waterloo, there may be an improvement effected, but it is too slight to be recognised in the coke, or in the oil freed but not distilled. The oil distilled on reheating to 600 deg. C. at 5 deg. C. per minute is increased, and this may mean that some improvement is taking place.

It may be that the coking coals have a sufficiency of oil and their surfaces are capable of retaining this oil in such a fashion that they require no external aid in the form of added oil. In the case of the non-coking coals it may be that their surfaces are incapable of retaining oil and that the oil they contain is unsuitable for the purpose of coking, the slight improvement effected being due to the substitution of a better oil for the oil already in the coal. However, in the case of the poorly-coking coals we might have a situation ideally suited to the improvement of coking power by oil addition. It may be that the poorly-coking coals are really coking coals denied the opportunity of exercising their proper function. The oil they contain may be unsuitable or insufficient for coke formation, or it may be unsuitable to the surface that their coal substance offers. The added oil may either fill the deficiency of shortage of oil, or may be an oil suitable to be adsorbed by the surface presented at 420 deg. C. In any case, it seems that the most suitable coals to form the basis for a systematic study are the poorly-coking coals as represented by Fenton (C. 83.0) and Barnborough Barnsley (C. 81.4). The amount of oil added is also an important factor. Up to the present a proportion of the oil added appears to have evaporated whilst drying overnight. Consequently in future experiments 10 per cent. by weight of the coal will be the amount of oil added in all experiments until notice is given of an alteration in this quantity. In the next series of experiments Fenton and Barnborough coal will be treated with different types of oils, and the oil-coal mixtures preheated in all cases to 420 deg. C. This should give some idea of the nature of the oils which play the greatest part in coke formation, and perhaps give some idea of the function of both the retained oil and the coal substance in the formation of coke.

### THE ADDITION OF OIL TO POORLY-COKING COALS.

The coals chosen were Fenton (83.0 per cent. C.) and Barnborough Barnsley (C. 81.4 per cent.). Fenton possesses the better coking qualities, and its behaviour upon preheating has been previously studied, and the results show it to be a weakly swelling coal. The curve for oil distilled at various temperatures is practically a straight line, and the total oil yield is quite high, but at 420 deg. C. at least 50 per cent. of this oil has been distilled.

The curve for the oil extracted for various temperatures of preheating (Allinson and Mott ) shows no maximum as in the case of the strongly-coking coals, but shows a steady decrease from the temperature at which it is "freed" in the coal, to that when at least 9.0 per cent. of the oil has been distilled. At 360 deg. C. the oil "extractable" is about 3.0 per cent., but has dropped to 2.5 per cent. at 420 deg. C. On preheating to 360 deg. C. and reheating to 600 deg. C. a swollen residue is obtained, but at 420 deg. C. the residue is scarcely coherent. If we are to improve the coking ability of Fenton coal we must increase the oil extractable at 420 deg. C. by at least 0.5 per cent. If we are to convert it into a good coking coal considerably more than 3.0 per cent. of oil must be extractable at 420 deg. C. Since Barnborough coal is still less strongly coking than Fenton, the increase of oil extractable at 420 deg. C. must be even greater.

### RELATIVE VALUES OF OILS FOR IMPROVING COKING POWER.

TABLE IV.

The effect of adding 10 per cent. of different oils and solids on the amount of oil adsorbed on preheating to 420 deg. C., and on the Shatter Index of the preheated coal, reheated to 600 deg. C.

COAL—FENTON, C. 83.0 PER CENT.			BARNBOROUGH, C. 81.4 P.C.		
Oil added.	* Oil adsorbed. Per cent.	† Shatter Index of coke.	Oil added.	* Oil adsorbed. Per cent.	† Shatter Index of coke.
None	3.0	70.0	None	2.4	65.0
<i>B.P.</i> Langley Park Tar in Benzene	3.2	93.6	Langley Park Tar in Benzene	3.5	99.2
Pitch in Pentane	7.3	91.6	Pitch in Pentane	5.8	99.4
Manvers Main Tar	4.0	99.4	Manvers Main Tar	4.0	99.0
Anthracene Oil	4.0	99.4	Anthracene Oil	6.2	99.4
<i>79</i> Benzene	7.0	97.6	Benzene	3.5	99.2
<i>80</i> Cyclohexane	4.4	96.1	Cyclohexane	3.0	99.2
Phenol	4.5	96.8	Phenol	4.0	96.4
Paraffin Wax in hexane	5.6	94.3	Paraffin Wax in hexane	5.0	99.9
Pentane	4.6	99.1	Pentane	3.3	99.4
Tetra-hydro naphthalene	3.4	99.8	Tetra-hydro naphthalene	2.5	96.9
Hexane	3.7	99.6	Hexane	3.5	99.4
Creosote Oil	4.3	99.4	Creosote Oil	3.6	98.2
Amylene	4.6	99.2	Amylene	3.5	98.6
Ortho-Cresol	4.5	99.0	Ortho-Cresol	3.9	98.6
<i>80</i> Cyclohexane	3.5	99.0	Cyclohexane	2.7	98.9
Cumar Resin	3.6	98.4	Cumar Resin	3.7	98.0
Pitch	5.4	98.2	Pitch	4.6	99.8
Naphthalene	3.2	97.8	Naphthalene	2.4	98.2
Anthracene	5.3	95.6	Anthracene	5.0	94.2
Low-Temp. Tar	4.5	95.8	Low-Temp. Tar	2.8	95.6
Anthraquinone	1.9	25.6	Anthraquinone	2.0	Nil
Parallac Resin	1.9	Nil	Parallac Resin	2.0	Nil

\* On preheating the oil-coal mixture to 420 deg. C. at 1 deg. C. per minute.

† Obtained by crushing the coal preheated to 420 deg. C., and reheating to 600 deg. C. at 5 deg. C. per minute.

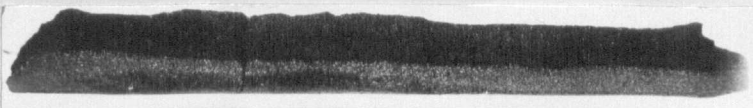
The usual procedure was carried out, both coals being ground to pass 60 mesh, mixed with water and then agitated with 10 per cent. of oil. In some cases solids such as pitch and wax were added, and in these cases the requisite amount of solid was intimately mixed with the ground coal. The mixtures were then preheated to 420 deg. C. at 1 deg. C. per minute, part of the residue extracted with ether in a Soxhlet to determine the extractable oil, and part reheated at 5 deg. C. per minute to 600 deg. C. The residues were photographed and their shatter indices obtained.

The oils employed were chosen to give as wide and comprehensive a series as possible. Several coal tar oils were obtained and used in their natural state or mixed with solvents in order to give solutions capable of addition to the coal by agitation in water. The oils used were:



COALS WITH VARIOUS "COAL BY-PRODUCTS"

FENTON.



70.0

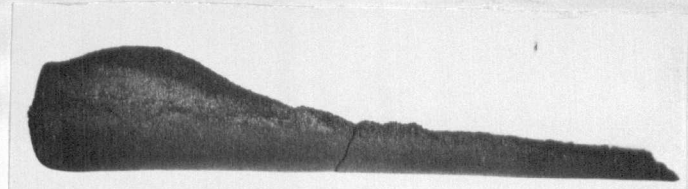
BARNSLEY. B. M.



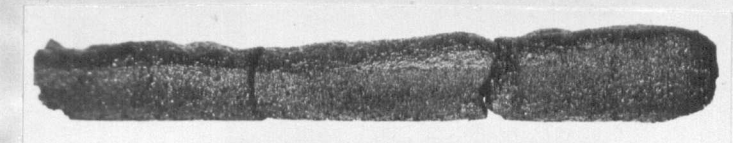
65.0



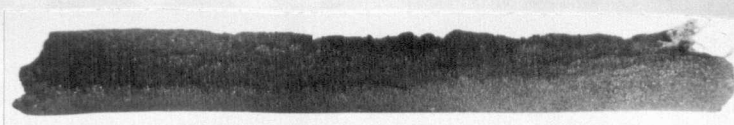
PARKGATE LOW TEMPERATURE TAR. 92.6



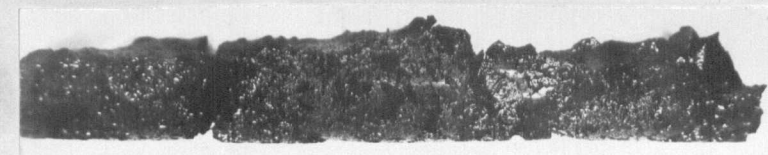
88.7



WIGAN SIX FOOT TAR. 95.8



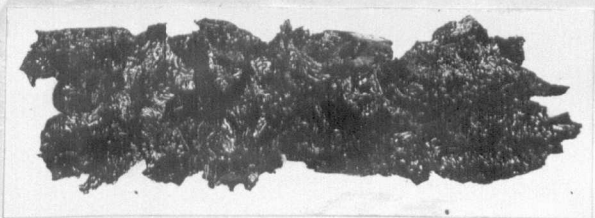
94.6



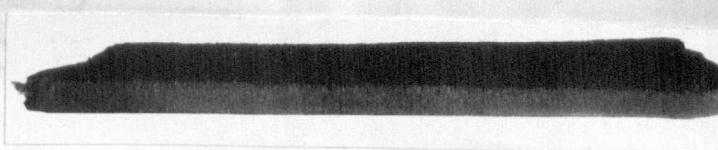
M. M. COKE OVEN TAR. 99.4



99.0



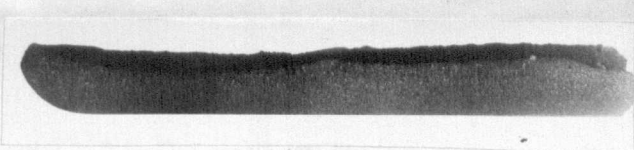
L. P. TAR IN BENZENE. 93.6



99.2



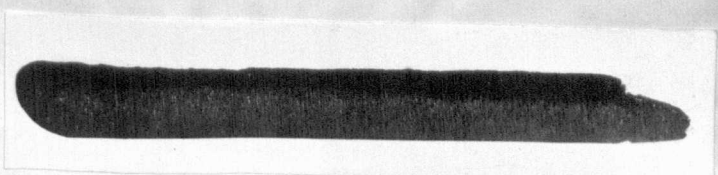
CREOSOTE OIL 99.4



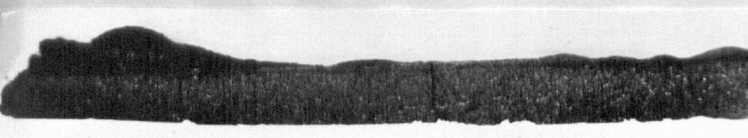
98.2



M. M. ANTHRACENE OIL 99.4  
(B. Pt > 360°C)



99.4



COAL TAR PITCH. 98.2



99.8

COALS TOGETHER WITH SEPARATE INGREDIENTS OF GOAL TAR

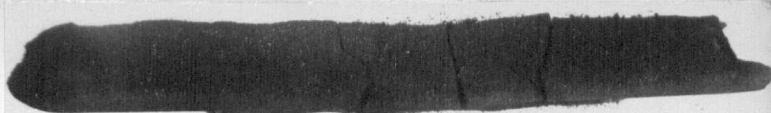
FENTON.

BARNESLEY. B.M.



COALS ALONE

70.0

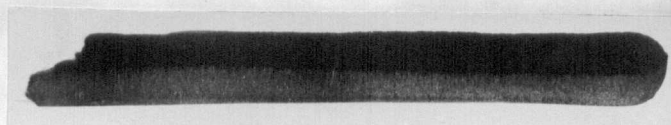


65.0

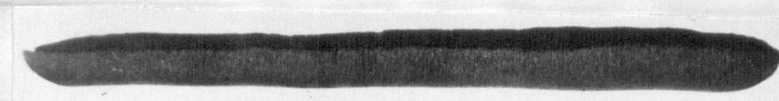


BENZENE

97.6



98.6

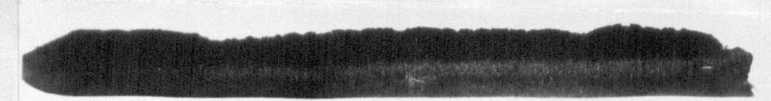


NAPHTHALENE

97.8

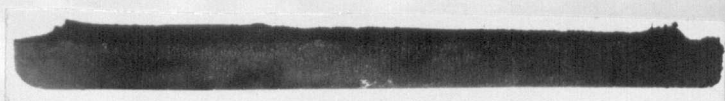


98.2

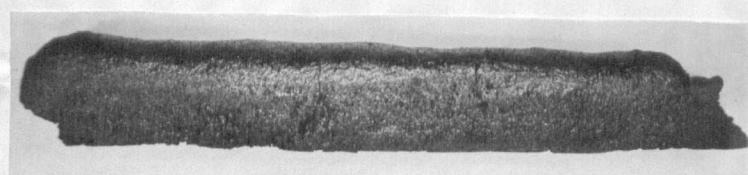


ANTHRACENE

95.6

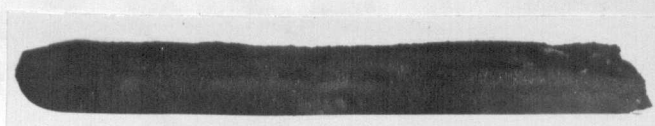


94.2

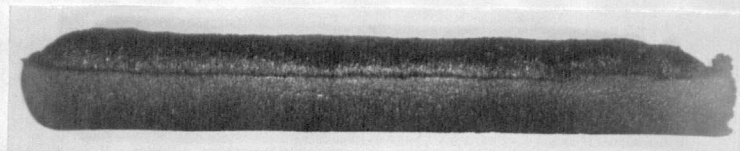


PHENOL

96.8

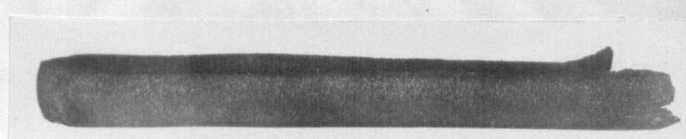


96.4



O-CRESOL

99.0



98.6

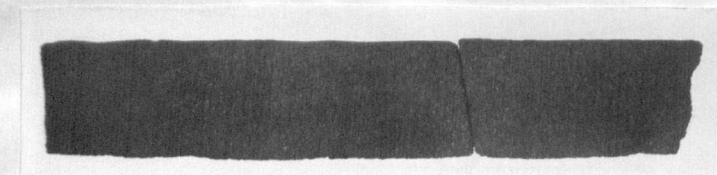


CUMAR RESIN  
(LOW OXYGEN)

98.4

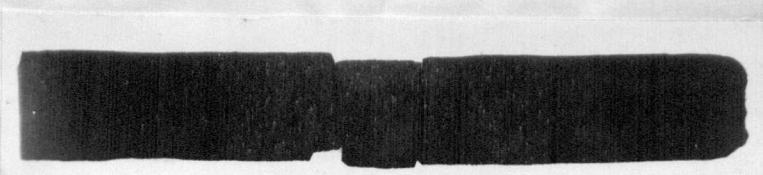


98.0

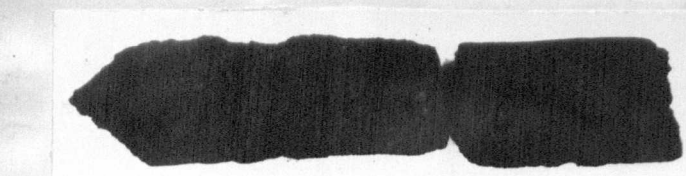


PARALAC RESIN  
(HIGH OXYGEN)

NIL

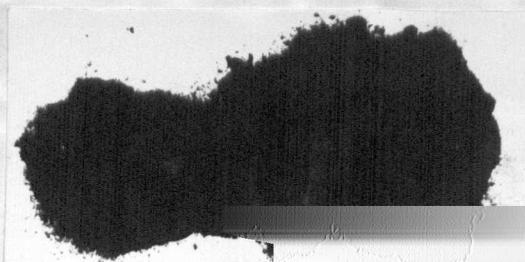


NIL



ANTHRAQUINONE

25.6



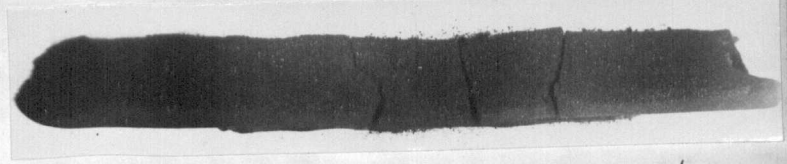
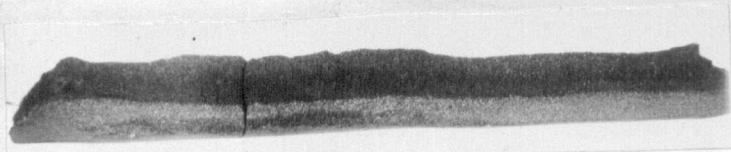
NIL.



COALS TOGETHER WITH VARIOUS HYDROCARBONS.

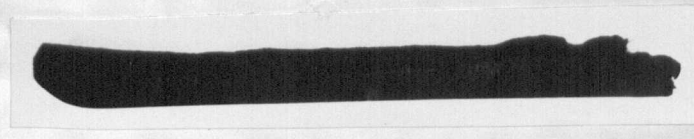
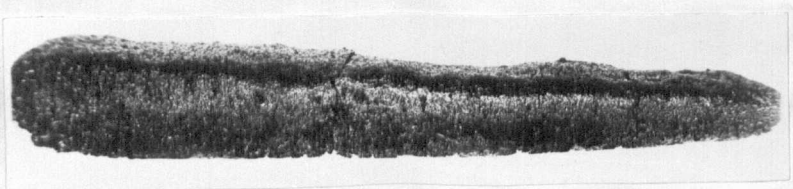
FENTON.

BARNESLEY. B. M.



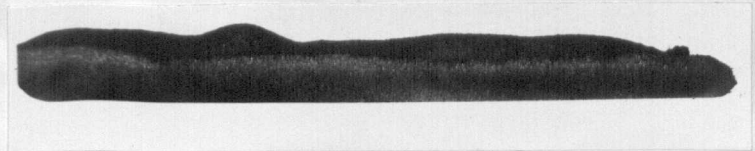
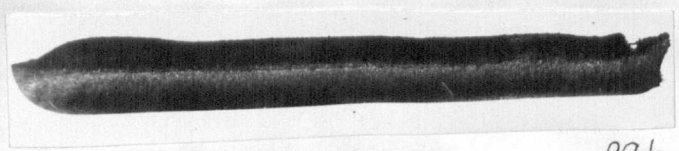
COALS ALONE. 70.0

65.0



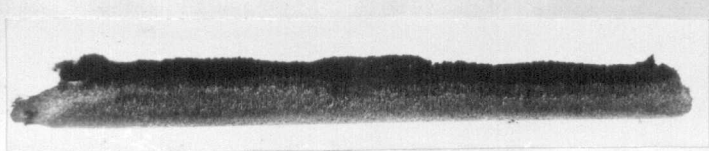
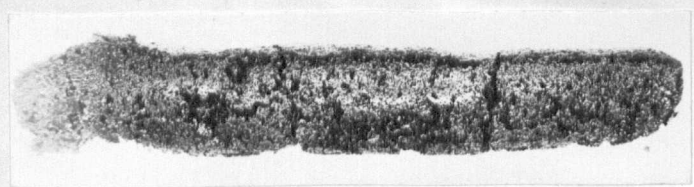
PENTANE. 99.9

99.4



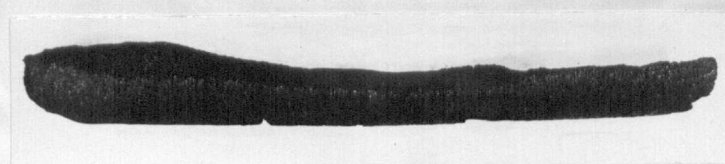
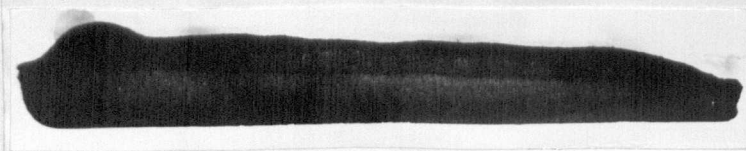
HEXANE. 99.6

99.4



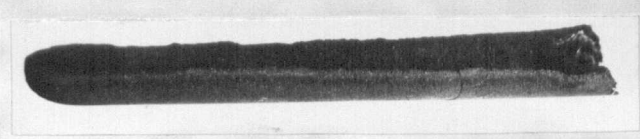
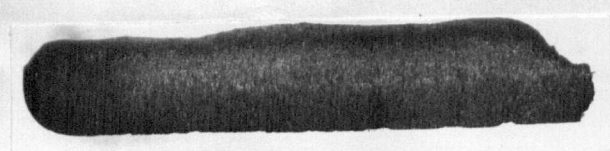
PARAFFIN WAX IN HEXANE. 94.3

99.9



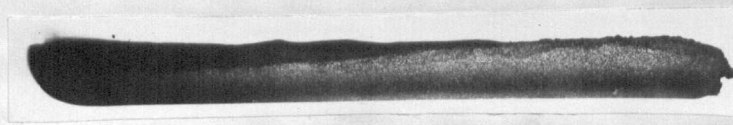
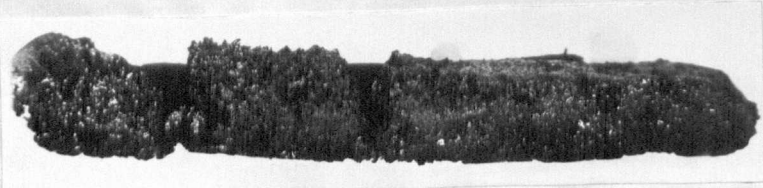
AMYLENE. 99.2

98.6



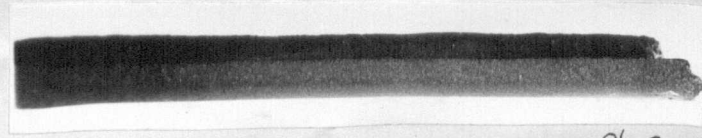
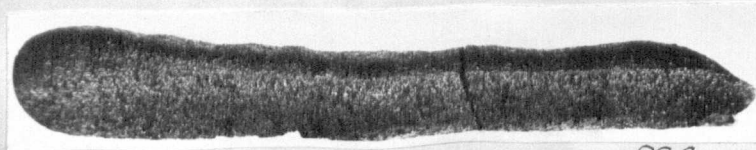
CYCLOHEXANE. 99.0

98.9



CYCLOHEXENE. 96.1

99.2



TETRA-HYDRO-NAPHTHALENE. 99.8

96.9

1. Langley Park Tar. Coke-oven tar from a strongly-coking coal.
2. Manvers Main Tar. Coke-oven tar from a Yorkshire coking coal.
3. Wigan 6 foot Tar. A "primary" low temperature tar.
4. Manvers Main anthracene oil.

These gave a series of coal tar oils. Pitch, the ultimate product of the distillation of coal tar, was also finely ground, mixed with the two coals, and used in experiments. Several pure hydrocarbons were also added, to see if they had any effect upon coking ability. Pentane, hexane, cyclohexane, cyclohexene, amylene, tetrahydro-naphthalene and paraffin wax were all added, although at the time it was anticipated that the addition of such low boiling oils must have little effect.

Two resins were added, one low and one high in oxygen content. Anthraquinone was also used, it being assumed that it was equivalent to anthracene together with added oxygen, in the hope that this would shed light on the part played by oxygen. Coal tar derivatives were also added, either as oils or solids. Benzene was added by agitation in water, whereas naphthalene, anthracene, phenol, and ortho-cresol were mixed as solids. All these bodies are definite components of high-temperature tars. One or two experiments were carried out using mixtures such as pitch in pentane, and paraffin wax in hexane, but unfortunately this study of binary mixtures could not be pursued far.

#### SUMMARY OF RESULTS.

The results, as shown in Table IV., considered as a whole are illuminating. In every case the quality of the coke produced has been improved. The shatter index of Fenton coal after preheating to 420 deg. C. is 70.0, whilst that of Barnborough is 65.0. In all cases of the oil additions carried out, these indices have been improved, until they are in the neighbourhood of 100.0. For Fenton coal the amount of oil extractable by ether at 420 deg. C. has also been improved, and in one or two cases this improvement has been so marked as to be singular, from 2.5 per cent. to figures more than twice that amount. The best impression of the improvement can perhaps be obtained from the photographs of the preheated residues (Plates I., II., III.). At 420 deg. C. the coals by themselves both gave crumbly residues which still retained the identity of the original coal particles. The cokes from all the oil-coal mixtures, particularly in the case of Fenton coal, had lost the identity of the original coal particles and formed pores, and given cokes similar in every way to those obtained under similar conditions from the strongly-coking Durham coals.

#### FENTON COAL.

##### 1. WITH THE COAL TARS.

In the case of all the coal tars added, with the exception of Langley Park tar (added in hot water), the shatter index of the resulting coke is approximately 100.0, and the percentage of oil extractable at 420 deg. C. is increased. With Langley Park tar the figure for the shatter index is 93.6, this figure being lower than the true value on account of the expanded nature of the coke which has formed large pores whose walls are thin and easily broken. The extractable oil had increased to 3.2 per cent., a figure in keeping with that of a strongly-coking coal. With Manvers Main tar the shatter index is 99.0, the coke being less expanded than with Langley Park tar and consequently being stronger, whilst the extractable oil has increased to 4.0 per cent. Manvers Main anthracene oil gives similar results, except that the extractable oil reaches the high figure of 6.0 per cent. Wigan 6 foot tar also gives great improvement, the shatter index being 99.4, and the extractable oil 4.5 per cent., but in this case the coke is not so expanded, the pores formed being much smaller. Pitch gives a greatly expanded residue with large pores, and the extractable oil has increased to 5.4 per cent.

##### 2. DERIVATIVES OF COAL TARS.

In the case of benzene, a liquid boiling at 78 deg. C., it was fairly reasonable to expect very little improvement, since it would be supposed that all the benzene would boil off long before 420 deg. C. However, the final coke had a shatter index of 97.6, being expanded with large pores, whilst there was as much as 7.0 per cent. of extractable oil. Anthracene and naphthalene both give marked improvements, the cokes formed being very little expanded but nevertheless very strong. The extractable oil is increased to 5.3 per cent. and 3.2 per cent., respectively. Phenol and ortho-cresol are both oxygen-containing bodies, so improvement was scarcely anticipated. However, both gave expanded cokes with fairly large pores, and both have the amount of extractable oil increased to 4.5 per cent.

##### 3. PURE HYDROCARBONS.

With pure hydrocarbons whose boiling points are comparatively low, we should expect them all to be distilled unchanged during the preheating, and to have very little effect upon the final coking conditions. As in the case of benzene, this diagnosis proved to be incorrect. The shatter indices of the final cokes were approximately 100, and in most cases the cokes were expanded and showed



evidence of pore formation. For pentane the shatter index had increased to 99.9 and the extractable oil to 4.6 per cent. The other hydrocarbons, hexane, cyclohexane, cyclohexene, amylene, and tetrahydronaphthalene, which were chosen with a view to discovering the effect of the addition of straight chain, ring, saturated and unsaturated types of hydrocarbons, improvements similar to those with pentane, were obtained. In no case was the percentage of extractable oil lowered, or did the quality of the coke fail to improve.

#### 4. OTHER ADDITIONS OF OILS.

The experiments with oxygenated bodies, i.e., parallac resin and anthraquinone, in which it was anticipated there would be less improvement than in the case of the allied compounds, cumar resin, and anthracene, gave surprising results. These compounds were definitely detrimental to coke formation, the final cokes being scarcely coherent and the percentage of extractable oil being reduced to 1.9 per cent., equivalent in fact to making the coal non-coking. On the other hand, the mixtures of pitch in pentane and paraffin wax in hexane gave great improvements, the improving effects of each alone seeming to combine when used together. Pitch in pentane gave a highly swollen residue and the percentage of extractable oil had increased to 7.3 per cent. Paraffin wax in hexane gave a strong swollen coke and the extractable oil had increased to 5.6 per cent.

### BARNBOROUGH COAL.

#### 1. ADDITION OF COAL TARS.

For Barnborough coal the improvement effected is scarcely so noticeable as with Fenton. It seems difficult to give Barnborough coal the property of expansion, and most of the cokes, although strong and showing pores, are still unswollen. All have shatter indices of 99-100.

Barnborough coal preheated to 420 deg. C. gives a final coke with a shatter index of 65.0, and has 2.4 per cent. of extractable oil. Langley Park tar in benzene gives 2.65 per cent., Manvers Main tar 4.1 per cent., Manvers Main anthracene oil 4.6 per cent., Wigan 6 foot tar 2.85 per cent., and Pitch 4.65 per cent. of extractable oil. In all these additions we find evidence of improvement in the coking ability of the coal.

#### 2. COAL TAR PRODUCTS.

The coal tar products gave much improvement, though this was perhaps not so noticeable as with the coal tars themselves. The extractable oil is again increased in all cases save that of the addition of naphthalene, and here there is evidence that the coke is improved. The cokes are all non-swollen but are firm and have improved shatter indices. Naphthalene gives 2.4 per cent. of extractable oil, similar to that of the coal alone, but the shatter index of its coke is 98.2. The shatter indices of the cokes from the addition of anthracene, benzene, phenol and ortho-cresol are all 99-100, and the extractable oil is in all cases increased.

#### PURE HYDROCARBONS.

In the case of Fenton coal with pure hydrocarbons we find a definite improvement in coking ability. With Barnborough coal this is also the case, the improvement being slight, but nevertheless definite. The shatter indices of the cokes are again 98-100, whilst the cokes themselves are strong, showing definite evidence of pore formation, although being non-swollen. The oil extractable at 420 deg. C. improves in all cases, but never to more than 3.6 per cent., which from the 2.4 per cent. of the coal alone, gives a 50 per cent. improvement.

#### OTHER RESULTS.

The results with the oxygenated compounds parallac resin and anthraquinone confirm the results obtained with Fenton coal. In both cases the final residue is in powder form, all coking properties of the coal being removed, its shatter index being nil. The percentage of oil extractable at 420 deg. C. has decreased from 2.4 per cent. to 1.9 per cent.

The results of the addition of mixtures to Barnborough coal were just as surprising as with Fenton coal. The percentage of extractable oil was increased by more than 100 per cent. in each case, whilst the cokes produced were swollen, having enlarged pores. Barnborough coal with pentane alone gives 3.3 per cent. of extractable oil at 420 deg. C., whereas with pitch in pentane it gives 6.0 per cent., an even greater increase than with Fenton coal.

#### DISCUSSION OF RESULTS.

The series of experiments, the results of which have just been outlined, have greatly strengthened the theory that the coking properties of poorly-coking coals can be improved by mixing these coals with oils. In every experiment attempted (except those with parallac resin and anthraquinone) improvement was achieved. Both coals were converted to the equivalent of strongly-coking coals, their percentage of oil extractable at 420 deg. C. being increased into the range of the good-coking coals, whilst the cokes produced are all strong and in many cases swollen. It was, of course, expected that the coal tars themselves would

give some improvement, and this hope was more than justified by the results. The coal tar products presented less possibility. The probability was that the function of the coke formation was fulfilled by one particular portion of the coal tar, some high boiling oil, or series of oils present, and that removal of this would result in removal of all the coke forming properties of the tar. Particularly in the case of benzene and its homologues it was anticipated that these would have very little improving effect. Benzene boils at 78 deg. C., and any benzene added would be expected to be distilled long before the temperature of 420 deg. C. in the preheating was reached. How, then, could the benzene possibly be present during the reheating to aid the formation of coke from the coal? Benzene, however, was a surprisingly potent agent, and the benzene-coal mixtures gave increased figures for oil extraction at 420 deg. C., and greatly improved cokes. Benzene must, then, be retained in the mixtures to temperatures much higher than 78 deg. C. It may be that the benzene is adsorbed by the coal surface, and forms loosely bound chemical compounds as propounded by Langmuir. This might release oil on the coal surface, which could perform its natural function in binding together the coal particles and assisting coke formation, whereas it would otherwise be employed by being adsorbed on the coal surface in chemical combination. It may, of course, be that benzene itself is retained and is part of the oil extractable at 420 deg. C., and that this oil is benzenised and rendered most suitable to coke formation. This, however, is taking a particular view of the case, and as most oils and allied compounds added improve the coke quality, it seems to point rather to the view that the benzene addition releases a certain "latent" part of the oil which is then free to perform its natural function in coke formation. It also supports the theory that coal surface plays an important part in coke formation. So long as the surface is free (no benzene has been added) it either reduces the power of the retained oil, or will not hold sufficient oil to enable a true coke to be formed. When the benzene attaches itself to the surface it reduces the effective area, and thus enables more oil to perform its function in coke formation. Pentane boils at 33 deg. C. Indeed it is so volatile that it evaporates almost completely during its addition, and much more than the requisite 10 per cent. must be added in order to give a good separation of coal-pentane and water. Pentane, however, gives results which are not quite so good as those of benzene, but, nevertheless, are quite sufficient to identify it as having a definite beneficial influence.

It is possible, of course, that both benzene, pentane, and all the other added materials displace the air layer which will be present on the surface of the crushed coal, and so enable the freed oil to act much more successfully. In this case the added oil is merely a latent factor and plays no part in coke formation save that of removing some inhibiting factor. In every case, however, there is more oil distilled on reheating at 5 deg. C. per minute to 600 deg. C., so that the added oil seems to play a more important rôle than that of a "spectator" which merely removes a gas film from the surface of the coal substance. However, the importance of the surface during coking seems to be emphasized by these experiments, and the function of the added oil in either occupying or preparing the surface of the coal is one explanation of its value.

In the case of hexane and cyclohexane the ring compound seems of less value than the straight chain compound. On the "surface" idea this can be explained. The molecule of cyclohexane is not capable of orientating itself on the coal molecule as closely as the straight chain molecule and consequently cannot occupy as much surface as the straight chain molecule. This might be an explanation of its rather lower efficiency. On the other hand, the configuration of the benzene molecule is similar to that of the molecule of cyclohexane and the benzene molecule is very effective. On the other hand, naphthalene and anthracene are not so effective, and their molecules have a larger bulk than that of benzene.

The inhibitive qualities displayed by the oxygenated Parallac resin and anthraquinone are of great significance. It was stated in the introduction that the percentage of oxygen in any coal was usually a criterion of its coking qualities, the higher the oxygen content the less strongly coking the coal. This apparently applies also to the added oil. Cumar and parallac resins are similar to those obtained during extraction experiments from coal. The only difference in the two is the high oxygen content of the parallac resin (36.0 per cent.). Yet cumar resin improves coking properties of the Fenton and Barnborough coal, whereas parallac resin practically destroys the coking properties already present. Anthracene and anthraquinone are similarly related and give similar results. In both cases the quantity of oil distilled upon reheating the preheated residues is quite large, sufficient to enable us to conclude, with lack of contrary evidence, that the residues should give good cokes. However, in both cases the amount of extractable oil has decreased to a value lower than that of the coals alone under similar conditions. Again, we have several possible explanations of this. The oxygen of the added oil might communicate itself to the oil already present in the coal, perhaps the mixture of added oil and inherent oil might so orientate itself that the bulk of the oxygen molecules were on the outside. These molecules might



be unable to spread over the coal surface and consequently the oil would not form a binding agent, so destroying all chance of coke formation, even though previously inherent oil possessed possibilities in this direction. The oxygen molecules of the added oil might themselves attack the surface of the coal and render it unsuitable to oil adsorption, or by increasing the oxygen content of the coal substance render it definitely less capable of coking than it was previously. In any case, these two experiments serve to show that oxygen has a definite inhibitive effect upon coke formation.

It is interesting to notice the effect of addition of two other substances in which the oxygen was differently combined. Phenol and cresol both contain oxygen, combined in "enol" form, whereas in parallac resin and anthraquinone the oxygen was combined in the "keto" form. These two groupings are =O and —O—H, so that we see in the case of the keto group the oxygen is capable of attaching itself directly to the coal molecule, whereas in the enol form the connection must be made through the H atom. This appears to make all the difference, and it will be interesting to ascertain if this factor recurs with other oxygenated compounds.

The result of these investigations into the influence of various oils upon the coking power of Fenton and Barnborough coals has furnished a lot of interesting information, and provided a basis for further research. Obviously swelling power is an important factor in coke formation, and indeed the oil retained at 420 deg. C. together with the ability of the preheated residue to give a swollen coke on reheating will form the criteria upon which the success of future experiments will be based. Further knowledge is required of the behaviour of coals with rather poorer-coking properties than those of Fenton and Barnborough. Some of the oils previously used can be discarded and only those giving the better results used. The coal tar oils themselves must be employed, together with benzene and perhaps one pure Hydrocarbon such as pentane or Tetrahydronaphtholene. The coals will have carbon contents of 80-82 per cent., and will be chosen from those already investigated in the previous work as far as is possible. Shafton, Waterloo, Swallow-wood soft, Hamstead thick, and two other coals which are on the fringe of the coking coals, Hatfield Main Barnsley and High Hazel coal, will be used.

#### THE ADDITION OF SPECIAL OILS TO A RANGE OF POORLY-COKING COALS.

The coals chosen were:—

Coal.	Carbon content.
1. Swallow-wood Soft .....	81.8 per cent.
2. Waterloo .....	81.6 per cent.
3. Barnsley Hatfield Main .....	81.6 per cent.
4. Tupton No. 5 Jerries	
5. Shafton .....	80.0 per cent.
6. Hamstead Thick .....	77.0

In all cases the oils employed were:—

- (a) Langley Park tar in benzene.
- (b) Manvers Main tar.
- (c) Benzene.
- (d) Tetrahydronaphthalene.

The coals were ground to pass 60 mesh, agitated in water and 10 per cent. of the oils added, after preheating to 420 deg. C. at 1 deg. C. per minute. Part of the residue was extracted with ether in a Soxhlet, and part was reheated at 5 deg. C. per minute to 600 deg. C.

The results are recorded in Table VII., but are scarcely so outstanding as was the case for Fenton and Barnborough coals. In no single instance was any swelling obtained on reheating. Thus one of our standards of improvement has disappeared, and the only ones left are the shatter indices of the cokes and the amounts of oil extracted from the preheated residues. In almost every case, however, we have an appreciable increase in the percentage of oil freed but not distilled at 420 deg. C.

Hamstead coal, which only contains 77 per cent. C., and when heated alone to 420 deg. C. yields 1.3 per cent. of extractable oil, has this amount increased to 3.0 per cent. on addition of the various oils. The cokes formed also show improvement, but in no case is the residue truly coked, the original particles of the coal never losing their identity and merely being bound together in the "coke." This binding, however, certainly occurs in the cases in which the oil is added, whereas in the case of Hamstead coal by itself, when reheated after previously preheating to 420 deg. C., the resulting mass is a powder with a shatter index of nil. The oil obtained upon redistillation to 600 deg. C. is also improved from 2.4 to 6.0 per cent. on oil addition, so that it must be binding the preheated residue in some fashion. Since we know that the oils would, if the surface were responsive, yield a satisfactory coke, it is probable that the inability of Hamstead

coal to form a coherent residue is due to the coal substance. The possibility is that the surface is too highly oxygenated, or perhaps the external molecules are orientated in such a fashion that the adsorption of the oil by them is physical, and on reheating this oil is merely distilled and plays no part in coke formation.

In the case of Waterloo coal we find a similar state of affairs. Again, after oil addition, the coal displays no ability to lose its identity and become a true coke upon reheating to 600 deg. C., but on the other hand the coal particles are bound together and do form a coherent residue, which, though soft, is nevertheless compact. The amounts of oil extractable by ether are also increased in all cases, and it is surprising that the low boiling oils show a larger increase than the higher boiling coal tars. This was confirmed by adding pentane to Waterloo coal when the amount of extractable oil increased from 1.5 per cent. to 4.1 per cent. Shafton coal has a very low carbon content, and the improvement is not so noticeable.

The residue from Shafton coal alone after preheating to 420 deg. C. has a shatter index of nil, and the shatter indices of all the oil-coal mixtures are low. Langley Park tar in benzene gives a residue with a shatter index of 37.9, and here again the coal is not coked, the coal particles merely being bound together to form a soft coherent residue. The increase in the extractable oil is low, but is definite.

Barnsley Hatfield Main coal is nearer to the coking coals, and shows much more decided improvement. With the two coal tar products it gives cokes which have shatter indices greater than 95 and which have been truly coked and not merely an aggregate of sintered particles. The low boiling hydrocarbons gave improved cokes, but not so much improved as in the case of Fenton and Barnborough coals.

Swallow-wood Soft Coal has been previously studied and gave 2.0 per cent. of extracted oil when pre-heated to 420 deg. C. by itself. This figure is greatly improved on addition of oil, being almost doubled in two cases. Apparently Swallow-wood Soft Coal is capable of being improved, possibly because its carbon content of 82 per cent. shows it to be nearer to the range of coking coals than Barnsley Hatfield Main. It is in point of fact only very slightly inferior to Fenton coal, but even so no swelling was obtained in the coked residues. However, the Shatter Indices were raised from 50.0 to 90, and the cokes showed evidence of pore formation.

The other coal employed was an unfamiliar one, Tupton No. 5 coal, from the Derbyshire coalfield. This is a coal on the fringe of the coking range, being only slightly inferior to Swallow-wood Softs in the nature of its coked residues. The amount of extracted oil after preheating to 420 deg. C. from the coal itself was only 1.6 per cent., whilst the residue on reheating is in powder form. It shows good improvement with the coal tars added, but less improvement than was expected with the pure hydrocarbons. The extracted oil is increased by 2.0 per cent. to more than double the original figure in the first case, but only by 0.5 per cent. in the second. The coked residues are very similar to those obtained from Shafton coal, being soft and coherent, but having no pores. The residues, after reheating to 600 deg. C., have low but definite shatter indices.

The general impression obtained from these experiments is that the effect of oil addition diminishes with carbon content from Fenton Coal (C. 83 per cent.) down to Hamstead Coal (C. 77 per cent.). The nearer a coal is to the coking range, the more it has its coking properties improved by addition of oils. Fenton and Barnborough coals, as we have seen, can be converted into moderately good coking coals by the addition of oil. Barnsley Hatfield Main, Swallow-wood Soft, and Waterloo are noticeably improved, more especially by coal tars themselves than by pure hydrocarbons with comparatively low boiling points. Tupton No. 5, Shafton, and Hamstead coals show practically no improvement in the coked residues, but some improvement in amount of oil extracted at 420 deg. C., the improvement again being most pronounced in the case of the coal tars, with the exception of Waterloo coal which has this behaviour reversed. The lower the carbon content of these coals, the higher the oxygen content, confirming the significance of oxygen content in coke formation. The low "wettability" of the coal particles may explain the inability of coals of low carbon content to form suitable cokes themselves, or to adsorb oil to form good cokes. It may be that:—

(1) The coal particles have surfaces which are unsuitable (perhaps from oxygen molecules in ketonic form on the surface) for oil adsorption, and the coal is thus unable to retain either its inherent oil or any added oil.

(2) The surfaces retain their air or oxygen film so strongly that the oils are unable to displace this, or the surface tension between coal-oil is unable to overcome that between air-coal.

(3) The surfaces will retain oil, but in an amount insufficient to enable the oil-coal mixture to give a good coke upon reheating. Quite possibly there is a definite amount of oil required to satisfy the coal surface, and then a further



amount is necessary to ensure good coking, it being this further amount which the coal is incapable of retaining.

TABLE VII.  
THE ADDITION OF SPECIAL OILS  
TO A RANGE OF POORLY-COKING COALS.

	Oil adsorbed at 420 deg. C.	Shatter Index of coke.
WATERLOO (C. 81.6 %).		
Coal alone .....	1.5 %	Nil
+ Pentane .....	4.1 %	38.0
+ Manvers Main Tar .....	2.2 %	64.0
HAMSTEAD THICK (C. 77 %).		
Coal alone .....	1.3 %	Nil
Langley Park Tar .....	3.5 %	48.0
Manvers Main Tar .....	3.4 %	44.0
SWALLOW-WOOD SOFTS (C. 81.8 %).		
Coal alone .....	1.6 %	65.0
Tetrahydronaphthalene .....	4.0 %	89.2
Langley Park Tar .....	4.1 %	92.6
TUPTON JERRIES (C.		
Coal alone .....	1.6 %	Nil
Langley Park Tar .....	3.6 %	68.0
Tetrahydronaphthalene .....	2.1 %	19.0
SHAFTON (C. 80.0 %).		
Coal alone .....	2.5 %	Nil
+ Benzene .....	2.8 %	15.0
+ Langley Park Tar .....	2.0 %	37.9
HATFIELD MAIN, BARNSLEY (C. 81.6 %).		
Coal alone .....	3.1 %	59.6
+ Langley Park Tar .....	5.2 %	98.2
+ Manvers Main Tar .....	3.0 %	95.3

It was thought probable that some light would be thrown upon this problem of the effect of coal surface if a quantitative study of the behaviour of one oil was carried out when mixed with a poorly coking coal capable of improvement, and a non-coking coal which was not improved by oil addition. The coals chosen were Fenton (C. 83.0) and Shafton (C. 80.0) and the oil added was benzene.

## THE REACTION OF BENZENE WITH COKING AND NON-COKING COALS ONPREHEATING TO 420 DEG. C.

As was previously stated, the coals employed were Fenton (C. 83 per cent.) and Shafton (C. 80 per cent.), the former being a poorly-coking coal, the latter a definitely non-coking coal. Benzene had previously been added to these two coals in the usual manner, and then the usual preheating and reheating had been carried out. In the case of Fenton coal 7.0 per cent. of extracted oil was discovered instead of the usual 2.5 per cent., whereas in the case of Shafton coal 2.8 per cent. was discovered instead of the usual 2.0 per cent.; in one case the increase was very marked, but in the other, small. The present work is to trace, if possible, step by step, the course taken by the benzene, and so gain some idea of the work it is performing in the one case, and why it is unable to perform this work in the other case. Consequently, we shall need some means of estimating benzene in (1) the coal itself in order to obtain the amount added; (2) in the various oils distilled and extracted during the experiments; and (3) in the gas given off which might contain benzene distilled in the pure state.

Benzene estimation in the case of the coal-benzene mixture can be obtained by washing out the benzene from a known weight of coal at a low temperature (10 deg. C) and estimating either the benzene obtained or the coal left. The benzene in the gas can be removed by active charcoal, and recovered by distillation. The chief difficulty lay in estimating the benzene in the various oils distilled and extracted. Several methods were explored, and finally it was decided that the best results would be obtained by adsorption in Manning's reagent (2 per cent. Silver Sulphate in conc  $H_2SO_4$ ) which quantitatively absorbs unsaturated and aromatic hydrocarbons.

Much spade work had to be done before the problem could be properly attacked. The oils had to be dissolved in a suitable solvent for the estimation, one which would be totally unaffected by Manning's reagent on bubbling through it. Ether, the solvent used previously in the extractions, was of course quantitatively absorbed by the reagent, and several other solvents were used before it was found that chloroform would be suitable. This chloroform was specially dried and distilled before use so as to eliminate as much error as possible. It was found that in all cases there was a very slight gain in weight due to chloroform passing through the bubbler together with the oil, and allowances were made for this gain. The method of estimation of unsaturated and aromatic hydrocarbons by Manning's reagent was as follows:—

A weighed quantity of the oil to be estimated was dissolved in chloroform and then vaporised in a current of nitrogen, passed through the absorbing reagent, the weight of which was determined. About 1.0 gram. of oil was used, and the amount of unsaturated and aromatic bodies was determined by the gain in weight of the absorbent.

Thus in any oil it is possible to determine the amount of unsaturated and aromatic bodies in that oil. In any one of the estimations carried out in the present research we have had first a preliminary reheating to 420 deg. C., and then a reheating to 600 deg. C. Three quantities of oil have been obtained: 1, oil distilled during the preheating and collected in the liquor tube; 2, oil extracted by ether in a soxhlet apparatus from this preheated residue and known as extracted oil; 3, oil distilled during the reheating and again collected in the liquor tube. Consequently in any experiment we require 3 estimations of unsaturated and aromatics.

If we are to investigate the effect of the benzene added to any coal, we must first require a quantitative estimation of the unsaturated and aromatic hydrocarbons in the oils and gases obtained when the coal is heated by itself. This gives the basis on which any increase or decrease in unsaturated and aromatic bodies can be detected when the treated coal is examined in a similar manner.

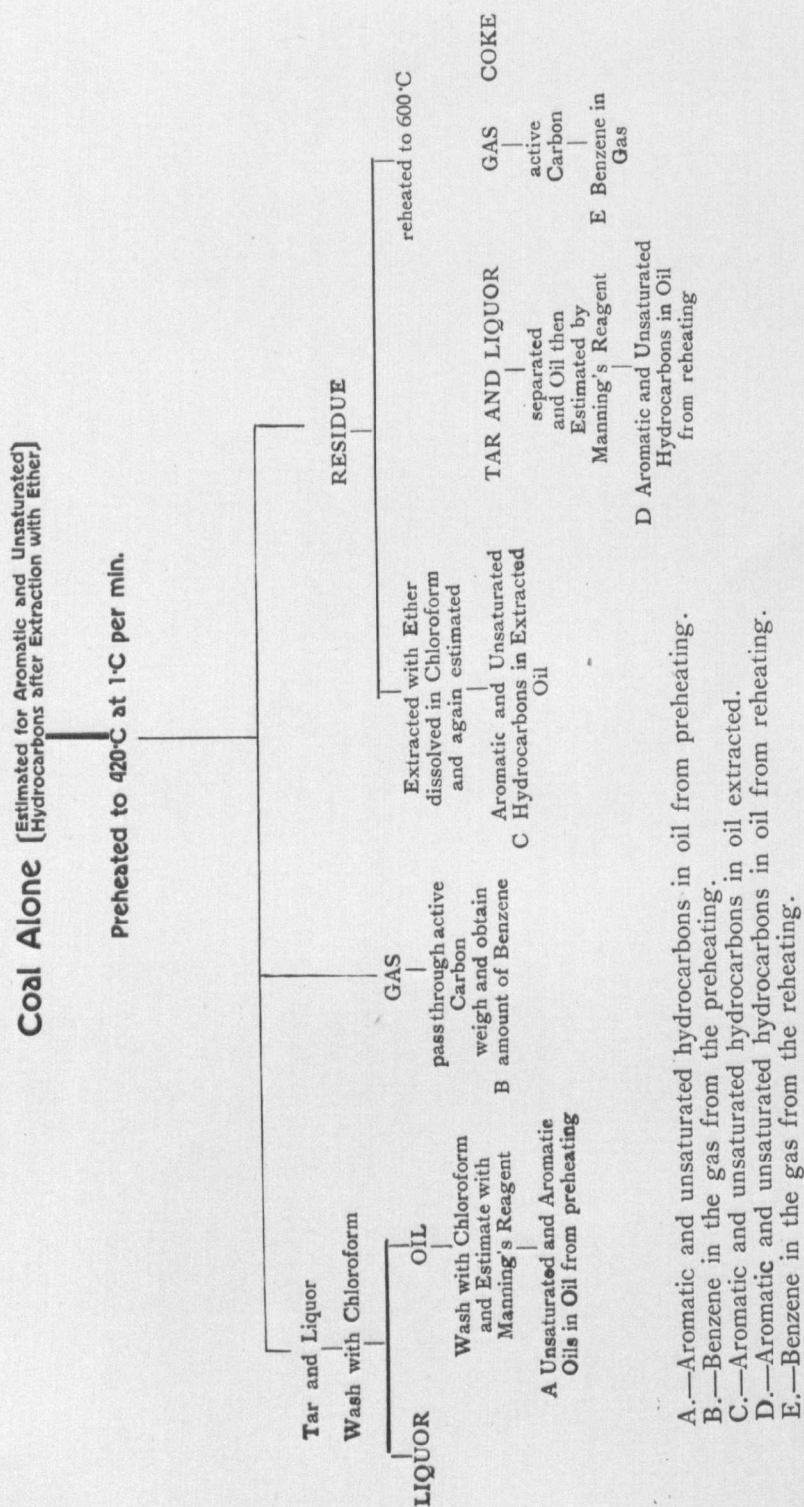
The estimation of any one coal may be described as follows: First the coal itself is preheated to 420 deg. C. at 1 deg. C. per minute, and the oil distilled carefully collected in an ice-cooled receiver. The residue is extracted with ether in a soxhlet apparatus, and another portion is distilled to 600 deg. C. at 5 deg. C. per minute, the oil "distilled" again being collected in a cooled receiver. In both heatings the gas is passed first through Calcium Chloride to dry it and then through weighed active charcoal to estimate the amount of benzene in it. The oils from the two distillations are dissolved in as little chloroform as possible and freed from liquor, and are then bubbled through Manning's reagent in order to estimate the percentage of unsaturated and aromatic hydrocarbons.

The extracted oil first has the ether distilled off, then is weighed, dissolved in as little chloroform as possible and the unsaturated and aromatic hydrocarbons again estimated by absorption in Manning's reagent.

The coal was then agitated with water and excess of benzene was added to ensure complete saturation, excess water removed by pressure filtration, and left to dry overnight. Some of the dry benzenised coal was extracted in a soxhlet with ether, and the extracted oil dissolved in chloroform and estimated by



Manning's reagent. (N.B.—A blank test was carried out on the coal itself and the amount of oil extracted by ether in a soxhlet obtained.) This gave the amount of benzene in the benzenised coal, assuming that the benzene did not chemically attack the coal at the temperatures employed, namely, 20 deg. C. The benzenised coal was then preheated and reheated, and the distilled and extracted oils again estimated for aromatic and unsaturated hydrocarbons. The benzene in the gas was again estimated by means of the gas filter of active charcoal. The whole system can be shown thus:—



The coal is then treated with benzene, a similar table obtained for the benzenised coal, and from the results obtained a balance sheet showing the behaviour of the added benzene can be made out:—

1. The amount of benzene added can be determined from the estimations carried out on the two coals before preheating.

2. The excess of unsaturated and aromatic hydrocarbons in extracted and distilled oils from the benzenised coals can be obtained by difference, and the whole of the difference is assumed to be due to benzene.

3. The excess benzene in the gases from the preheating and reheating can also be obtained by the difference in the weight of active carbon.

The results are recorded in Table VI.

### THE ADDITION OF BENZENE TO FENTON AND SHAFTON COAL.

TABLE VI.  
FENTON COAL.

	Unsaturated & Aromatic Hydrocarbons in coal.	Benzene in gas from preheating.	Benzene in gas from reheating.	Unsaturated & Aromatics in extracted oil.	Un. & Arom. in oil from preheating	Un. & Arom. in oil from reheating.
Coal alone .....	0.6	0.31	1.70	0.21	0.58	0.3
Coal + Benzene ...	4.0	0.29	1.70	0.30	0.10	0.9
Excess Benzene ...	3.4	—	—	0.09	0.42	0.6

### SHAFTON COAL.

Coal alone .....	0.4	0.55	1.30	0.6	0.30	0.47
Coal + Benzene ...	4.6	1.50	1.20	0.66	3.30	0.50
Excess Benzene ...	4.2	0.95	—	0.06	3.00	0.03

From these results we see that Fenton coal gives a mixture of benzene and coal containing 3.4 per cent of added benzene—an unexpectedly low figure, since at least 15 per cent. of benzene was added, showing the high evaporation during agitation. During the preheating experiments about 0.5 per cent. of benzene is accounted for in the extracted and distilled oils. There remains 2.9 per cent. of benzene which is not distilled, even at 420 deg. C., and which does not seem to be free in the oil extracted from the preheated residue. During the reheating another 0.6 per cent. is accounted for, making a total of 2.3 per cent. of benzene, which seems to have been absorbed in some way so as to lose its identity.

In the case of Shafton coal, the coal-benzene mixture again contains a low percentage of benzene, namely, 4.2 per cent.

During the preheating experiments as much as 3.95 per cent. of the added benzene is removed in the gas and the distilled oil, which means that practically the whole of the benzene, within the limits of experimental error is accounted for. In the preheating experiments only .05 per cent. of excess benzene is discovered, and this again is within the limits of experimental error. In the extracted oil the increase in aromatic and unsaturated hydrocarbons is only from 0.6 per cent. to 0.66 per cent., again within the limits of experimental error.

To account for the results, we can say that for Shafton coal benzene seems to be added in such a manner as to be totally removed during the preheating experiments. The oil-coal mixture must be a loose physical combination, capable of being broken down by the application of heat. There seems to be no definite evidence of excess benzene in either the oil extracted at 420 deg. C., or in that from the reheating. In the case of Fenton coal we have a different state of affairs. Very little benzene seems to be distilled in the preheating to 420 deg. C. About 0.3 per cent. of the added 3.4 per cent. is found in the oil from the preheating, but the benzene in the gas is unaltered. There remains approximately 3.0 per cent. of added benzene to account for, and it would naturally be expected that this would be found in the oil extracted from the preheated residue. This shows an increase of 0.1 per cent., an increase well within the limits of experimental error. Nor in the reheating experiments is the natural yield of benzene obtained. About 0.6 per cent. of the remaining 3 per cent. of benzene is accounted for in the distilled oil, and none in the gas from the reheating. There remains 2.4 per cent. of benzene, that is, about 70 per cent. of the 3.4 per cent. added, that cannot be accounted for, a result quite different from that obtained in the case of Shafton coal.

In these statements of the distribution of the added benzene, several assumptions have been made and these may now be re-considered. We assumed that the aromatics and unsaturated hydrocarbons obtained from the coal heated by itself will be repeated in the benzenised coal, and that any increase will therefore be due to the benzene added. This assumption seems to be fairly well justified in the case of the Shafton coal, when practically the whole of the benzene is distilled in the preheating and in all probability comes over unchanged. In the case of Fenton coal, however, 70 per cent. of the benzene is unaccounted for.



This may be due to chemical combination of benzene on the coal surface, and subsequent breakdown of the coal molecule to yield oils which are not even aromatic but saturated in nature, since no increase in aromatic or unsaturated oils is detected. On the other hand, it is possible that introduction of benzene has inhibited production of certain aromatic constituents of the oil distilled, and the fact that only a small increase of aromatics and unsaturates in the distilled oil is obtained is due to a balance obtained by increase in benzene and decrease in aromatic and unsaturated constituents due to benzene addition.

It was also assumed that increase in the benzene in the gas is determined by increase in weight of the active carbon, which is known to be a non-selective absorbent. It seems fairly logical, however, that since benzene is added, and is a fairly volatile oil, that the increase will be due to benzene, since the increase was discovered to take place in the first evolution of gas up to 100 deg. C., and the gas was of a similar nature from both coal alone and benzenised coal at temperatures above 300 deg. C.

Efforts were made to ascertain the amounts of benzene in the distilled oils. Nitrations of these oils were carried out, and it was discovered that the increase in the case of Shafton coal could be accounted for as benzene, the amount of di-nitro-benzene produced being increased as was expected. In the case of Fenton coal, the oils seemed very similar, that is they seemed to give similar amounts of benzene in both the oils from the coal alone and the benzenised coal. There was a slight excess in di-nitro-benzene from the oil distilled in preheating from the benzenised coal, but this was almost to be expected. It seems fairly safe to assume therefore that:—

- (1) The whole of the benzene added to Shafton coal is loosely combined and distilled unchanged in the preheating.
- (2) The benzene added to Fenton coal is so intimately associated with the coal that it must be involved in some chemical change on preheating, in which it loses its identity and is not distilled unchanged as benzene.

#### CONCLUSIONS.

From the results obtained in the quantitative estimation of the benzene-coal mixtures we find much support for theories which have been hitherto tentatively suggested. Fenton coal seems to adsorb benzene and with this adsorption gives an improved percentage of retained oil, and also, a point which has not previously been stressed, an increased oil yield on reheating. This latter increase corresponds quite closely to the benzene added. There is, of course, the improvement in the quality of the coke produced, Fenton coal being converted into a good coking coal. It is interesting to notice that there is an improvement of from 2.5 per cent. to 7.0 per cent. of oil retained but not distilled, and the amount of benzene added is almost similar—3.4 per cent. Yet the majority of the benzene is converted into some oil which is not aromatic in nature since the amount of aromatic and unsaturated hydrocarbons in this oil is practically unaltered, there being a small increase which is readily accounted for by the increased amounts of oil dealt with. Shafton coal shows a complete inability to retain its benzene upon heating, practically the whole of it being distilled over unchanged in the preheating, and the majority being distilled before the temperature reaches 300 deg. C.

It would seem obvious that the benzene in the case of Fenton Coal is bound by some chemical means and that this union is strengthened by heating; whereas in the case of Shafton coal the union between coal and benzene is of a loose physical nature easily ruptured by heat. What, then, is the reason that for two coals differing only by 3 per cent. in carbon content, both being related to the non-coking coals, one should adsorb benzene to give a mixture similar to the good coking coals, whereas the other adsorbs benzene in such a loose fashion as to give it back unaltered when heated to a comparatively low temperature. The explanation of the problem must lie in the different surfaces of the two coals. The surface of Shafton coal, whilst being capable of adsorbing benzene to the extent of 4.2 per cent., must not be capable of combining with this benzene. Probably the surface contains a large percentage of the oxygen molecules of the coal, and these will only combine physically with the benzene. Possibly the surface is not at all active but is in a passive condition. With Fenton coal the union of coal surface and benzene must definitely be chemical. According to the Langmuir theory the molecules orientate themselves on the surface of the coal and combine with it if suitable conditions are satisfied, and these conditions must exist in the case of Fenton Coal. The benzene probably attaches itself to unsaturated molecules on the surface, and during the preheating a molecular rearrangement takes place adsorbing the benzene and resulting in the formation of new saturated components. Thus the benzene loses its identity completely and new oil compounds are formed which facilitate coke formation and which probably have stronger tendencies to be adsorbed on the surface of the coal giving an intimate coal-oil mixture similar to that produced by preheating a coking coal. The question of coking seems to be resolving itself upon (1) suitable coal surface, (2) suitable oils for adsorption on this surface and giving a mixture capable of giving a good coke upon heating.

### THE EFFECT OF FUSAIN ON COKE FORMATION.

It is well known that strongly-coking coals will give a coke with an even higher shatter index, if they are mixed with a small percentage (less than 5 per cent.) of fusain or coke breeze. It might be that the addition of fusain dilutes the coal-oil mixture produced upon heating, to ideal proportions for coke making. On the other hand, the fusain might retain, over the coking range, oil which would otherwise be distilled, and unable to play its correct function in coking. Thus the coal-oil mixture over the coking range would contain a higher percentage of oil, and give a better coke.

An attempt was made to investigate the oil-retaining power of fusain at temperatures over the coking range. Clay Cross Slurry (Derbyshire), containing 80 per cent. of fusain under 60 mesh size, was preheated as usual to 420 deg. C. at 1 deg. C. per minute, part was extracted with ether and part reheated to 600 deg. C. at 5 deg. C. per minute. It was then agitated in water with several oils and the same heatings and extractions carried out.

In all cases the coal-oil mixtures were flocculated. The oils employed were Langley Park tar in benzene, benzene, and pitch. The benzene was hand mixed to prevent loss on agitating in water so that at least 10 per cent. was added.

In no case was a coherent residue obtained, and the gas yield in all cases was very low.

The results are recorded in Table VII.

#### THE OIL RETAINING POWERS OF FUSAIN (Slurry containing 80 per cent.).

RESULTS.—Coal used, Clay Cross Slurry, 45 AS. (80 per cent. Fusain).

Oil added.	Oil extracted from			Shatter Index, etc.
	Preheating, etc.	Oil from preheated residue.	Oil from reheating, etc.	
Slurry Alone .....	1.04	1.3%	3.2	} NIL
Langley Park tar in benzene	4.6	1.9	3.3	
+ Benzene .....	2.4	1.2	2.7	
+ Pitch .....	2.0	1.95	3.3	

There was an increase of 0.6 per cent. of extractable oil when the slurry treated with Langley Park tar in benzene was heated to 420 deg. C., despite the fact there was no increase in the total oil on reheating. In the case of benzene the amount of extractable oil and the total oil from the mixture preheated to 420 deg. C. is lower. Although these results are not very definite, it is still possible to draw some conclusions from them. The Langley Park tar and pitch obviously give some type of oil to the fusain, which takes the place of the "inherent" oil, and which is extractable by ether. This oil may be that which plays the important part in coke making. In the case of benzene there is no increase. One of the conclusions in the case of Fenton coal was that benzene was adsorbed, and released some of the coke forming oil to play its correct function when it would otherwise have been lost. Thus we can conclude that the surface presented by fusain is incapable of retaining benzene and thereby releasing oil extractable by ether, whereas for Langley Park tar and pitch, both of which are high boiling compounds, either the fusain surface is capable of adsorbing these oils and thereby releasing its inherent oil, or the Langley Park tar and pitch are only partially distilled at 420 deg. C., and the remaining oil is extractable by ether and gives the increase shown. If this latter were the case we should expect a similar increase in the oil distilled to 600 deg. C., which would be in the neighbourhood of 4.0 per cent., instead of 3.3 per cent., and the fact that this increase is not proved points to the oils taking the place of inherent oils and not merely being only partially distilled. In the case of benzene the oil on reheating is less than 3.2 per cent. This may be due to part of it being distilled over with the benzene at a temperature lower than usual, conditions similar to those of "steam distillation" being established.

The results of these experiments are not very conclusive. They certainly lend some support to the suggestion that fusain has the ability to retain oil in coking, but the evidence is rather indefinite. It is quite true that if a coal contains a high percentage of fusain it is poorly or non-coking, and has a much greater tendency to oxidation. The inhibitive effect of this fusain may be to employ oil during heating which otherwise would be playing an important part in coke formation, but further tests are required with smaller concentrations of fusain to elucidate the phenomena.

### THE INFLUENCE OF OILS ON SWELLING POWER.

It has been pointed out that there are three ways of establishing the coking power of any coal that are employed in the present investigation:—1, the shatter index of the coke produced; 2, the amount of "retained" oil at 420 deg. C.; and 3, the swelling power of the coal or the ability of the coal to give a swollen residue. Up to the present this last method has been neglected except by photographic records of the coked residues, and it was decided to use a more definite method of investigation, using the Sheffield Laboratory Coking Test, in which a column of particles is heated under load and the swelling of the particles noted.

The results give the temperature of initial contraction, the temperature of initial expansion, of final expansion, and also the percentage contraction and



expansion of the coal. A series of experiments was commenced, using Barnsley Hatfield Main coal (82.0 per cent. C.), mixing it with various oils and carrying out a Sheffield Laboratory coking test. It was assumed that this expansion would be simply related to the expansion of the coal when heated in a Gray-King assay apparatus. Benzene was added in quantities varying between 1 and 10 per cent., by hand. The results are recorded in Table VIII.

TABLE VIII.

THE EFFECT OF ADDING VARYING AMOUNTS OF BENZENE TO COAL TESTED IN THE SHEFFIELD LABORATORY COKING TEST.

	Percentage	1 per	2 per	3 per	4 per	6 per	10 per
	of benzene.	Coal alone.	cent.	cent.	cent.	cent.	cent.
	Deg. C.	Deg. C.	Deg. C.	Deg. C.	Deg. C.	Deg. C.	Deg. C.
Initial Contraction °C. ....	343	344	344	343	345	348	342
Initial Expansion °C. ....	392	395	397	400	400	400	400
Final Expansion °C. ....	417	418	420	422	420	420	423
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Percentage Expansion ...	34	44	74	102	95	82.5	85

A very definite increase in swelling power is obtained on adding benzene to the coal. The maximum increase seems to occur between additions of 3-4 per cent of benzene. The temperature of initial expansion also increases uniformly, from 392 deg. C. with the coal alone to 400 deg. C. in the mixture giving the maximum expansion and then remains constant.

The experiments were continued using different oils and the following coals: High Hazel (C. 81.5), Shafton (C. 79.9), and Barnsley Hards, all inferior to Hatfield Main in coking ability. Tetrahydronaphthalene, cyclohexane, pentane, and benzene were added to the coals in amounts of 5 per cent., and the results are recorded in Table IX.

TABLE IX.

THE EFFECT OF ADDING 5 PER CENT. OF VARIOUS OILS TO COALS TESTED IN THE SHEFFIELD LABORATORY COKING TEST.

Temperature.	Coal alone.	Plus			
		Benzene.	Cyclohexane.	Tetrahydro naphthalene.	Pentane.
Deg. C.	Deg. C.	Deg.	Deg.	Deg.	Deg.
HATFIELD MAIN.					
Initial Contraction .....	343	346	360	343	344
Initial Expansion .....	392	400	397	405	395
Final Expansion .....	417	421	427	427	419
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Percentage Expansion.	34	88	30	47	35
HIGH HAZEL.					
Initial Contraction ....		329	378	365	367
Initial Expansion .....		403	417	418	411
Final Expansion .....		438	437	441	430
Percentage Expansion.		40	46	15	6
SHAFTON.					
Initial Contraction .....		352	364	352	364
Initial Expansion .....		407	412	411	413
Final Expansion .....		432	435	437	430
Percentage Expansion.		35	53	30	Nil
BARNSELY HARDS.					
Initial Contraction .....		364	375	368	380
Initial Expansion .....		425	450	428	435
Final Expansion .....		425	450	428	435
Percentage Expansion.		Slight	Nil	Nil	Nil

The results show that the improvement in swelling power is not as marked in High Hazel and Shafton coals as in Hatfield Main Barnsley coal. In no case is the Shafton or High Hazel coal improved to the extent that 1 per cent. of benzene improves Hatfield Main coal, even though 5 per cent. has been added. It is also noticeable that benzene gives by far the best results in the case of Hatfield Main coal, pentane having little or no effect, whilst those for Tetrahydronaphthalene and cyclohexane are not very good. In the case of the other coals, all the oils seem to give a similar slight improvement. These results, although indefinite in themselves, are conclusive enough to establish the fact that the swelling power of these poorly-coking coals is definitely improved by oil addition. There is another factor, too, which is even more significant.

THIS IS "THE EFFECT OF ADDED OIL ON 'WEATHERING'."

It is well known that crushed coals deteriorate upon standing in air. Their swelling power decreases, and their coking power also decreases. In the case of strongly-swelling coals the decrease is not very noticeable, but is neverthe-

less important. In the case of the Derbyshire coals, their coking power decreases so rapidly that standing for a week-end is often sufficient to render them useless for coking. This deterioration is a very important factor in coking ability, and it is entirely due to atmospheric oxidation. If air can be excluded on storage their coking and swelling power is not decreased. This at once suggests another advantage of oil addition, an advantage which has hitherto been ignored. The function of the oil is to spread over the surface of the coal, excluding the air layer from the coal surface. Consequently any coal, thoroughly mixed with oil, should offer an oil surface to the air. This would mean that the coal is protected, and therefore no matter how long it stands, so long as it retains sufficient of the added oil to cover its whole surface, it should suffer no deterioration in either swelling or coking properties.

The preliminary investigation was attempted with the coal-oil mixtures whose swelling powers have just been determined, Hatfield Main, Shafton and High Hazel coals with benzene, Tetrahydronaphthalene and cyclohexane. The mixtures were allowed to "weather," or to stand in the air for one month, and the swelling power was redetermined in the Sheffield Laboratory C. Test. The coals themselves were found to have lost entirely their power of swelling after a period of 1 to 15 days.

TABLE X.  
THE EFFECT OF OILS IN REDUCING LOSS OF SWELLING POWER BY OXIDATION.

Coals treated with 5 per cent. of oil. Swelling powers.

A.—FRESHLY TREATED.

Coal.	+				Coal alone. Per cent.
	Benzene. Per cent.	Cyclohexane. Per cent.	Tetrahydro naphthalene. Per cent.	Pentane. Per cent.	
Hatfield Main .....	88	30	47	35	34
Shafton .....	35	53	30	Nil	
High Hazel .....	40	46	15	6	

B.—Standing in air for 1 month.

Hatfield Main .....	63.0	10	20	5	Nil
Shafton .....	1.0	Nil	Nil	Nil	Nil
High Hazel .....	35.0	10	10	Nil	Nil

Hatfield Main Barnsley treated with benzene retains most of its swelling power after one month, but in the other cases the swelling power of the mixture is inferior to that of the freshly treated coal. Shafton, a non-coking coal, loses its swelling power with all the oils except benzene, and here the expansion is so small as to be within the limits of experimental error. However, untreated Shafton coal only has a swelling power of 2 per cent., and this disappears if left to weather one day, so that the figure for the treated coal may have some significance. High Hazel coal, intermediate between Hatfield Main and Shafton, shows intermediate properties. Untreated High Hazel coal loses its swelling power in 5 days, whereas the treated coals, except in the case of pentane, show positive results after one month's "weathering." It was discovered that addition of benzene helped H.M. Barnsley coal to retain its original swelling power of 34 per cent. (for the coal alone) for ten weeks, whereas the untreated coal lost all swelling power in twelve days. High Hazel coal treated with benzene retained some swelling power (10 per cent.) for six weeks, whereas the coal alone lost all swelling power in five days. Shafton coal with benzene retained swelling power (10 per cent.) for three weeks, whereas the coal alone lost its swelling power in one day.

Ability of a coal to retain its swelling power over long periods is an important factor in coke formation, as it is often impossible to coke freshly-mined coal. It is fairly obvious that the volatility of the added oil will play an important part in this case, the more volatile the oil the more easily will it be removed during "weathering." On the other hand, the attraction of the coal for the oil and the strength of the coal-oil bonds (if we assume the union to be chemical and not physical) will play an important part. It was decided to carry out a full series of experiments over a period of three months in order to investigate the effect of the addition of oil upon the "weathering" of Hatfield Main Barnsley coal, and to use oils varying in volatility.

#### THE "WEATHERING" OF HATFIELD MAIN COAL TREATED WITH DIFFERENT OILS.

A series of oils, obtained during the distillation of Iranian crude oil, and two coke oven tars were selected as offering a suitable selection of commercial oils differing considerably in volatility. 5 per cent. of oil was added with agitation in water, and part of the treated coal was employed in the usual preheating and reheating experiments, another part was subjected to "weathering," and expansion tests were carried out at various times. The first expansion test was carried out as soon as the coal-oil mixture had dried, and the other tests at intervals of one month. The results are recorded in Table XI.



TABLE XI.  
RESULTS.—PETROLEUM FRACTIONS AND COAL TAR OILS ADDED  
TO HATFIELD MAIN BARNSELEY COAL.

Oil added.	% oil				Shatter Index.
	Percentage distilled on		% oil on		
	expansion in S.L.C.T.	preheating. to 420 °C.	% oil extracted.	% oil on reheating to 600 °C.	
	Per cent.	Per cent.	Per cent.	Per cent.	
Coal alone .....	30	4.8	1.7	6.9	68.7
Aviation Spirit .....	95	8.8	2.3	8.0	97.1
Straight run Benzine .....	84	5.8	2.35	8.0	93.2
Kerosene .....	68	6.8	2.5	8.0	97.0
Crude Oil .....	86	8.4	2.0	7.35	95.1
Gas Oil .....	60	8.4	1.8	7.1	91.2
Shell-Mex Gas Oil .....	90	5.8	2.3	9.5	94.7
Light Diesel Oil .....	85	7.5	2.8	9.2	99.3
Fuel Oil .....	62	9.7	1.7	5.8	82.6
Langley Park tar in benzene	100	3.6	2.7	10.0	95.3
Manvers Main Tar .....	105	8.8	3.0	7.3	96.5

In the case of the coal alone, only 1.7 per cent. of oil can be extracted after preheating to 420 deg. C., whilst the coked residue on reheating has a shatter index of 68.7, is soft and retains its identity, i.e., there is no pore formation. For the treated coals, in no case does the Shatter Index of the coke from the reheating ever have a value less than 80. With fuel oil and gas oil there seems to be little improvement, though the Shatter indices are in the neighbourhood of 90. In all the other cases the amount of "retained" oil is increased to between 2—3 per cent., and the Shatter indices of the cokes produced are always between 95-100. In several cases there is evidence of pore formation and, with Langley Park tar, a slight swelling of the coked residue. The coal tars seem to give slightly better results than petroleum oils. It is interesting to notice that the very volatile "Aviation spirit" gives a much better improvement than several much less volatile oils, such as the fuel oil and the gas oil. Apparently volatility is not such an important factor as we should expect, and this result bears out the results previously obtained using Barnborough and Fenton coals with pentane.

The original swelling power of the coal is 30 per cent., and in no instance is the swelling power of the coal-oil product ever less than 60 per cent. With the addition of the coal tars it has increased to 100 per cent., and the oil-coal mixture has the swelling power expected from a good coking coal. If we examine the figures for the "adsorbed oil" and the "swelling powers" of the coal-oil mixtures a very significant fact is observed. The greater the improvement in the amount of adsorbed oil the greater usually is the improvement in the swelling power in the S.L.C.T. With fuel oil and gas oil, which scarcely increase the amount of oil retained at 420 deg. C., the swelling power of the coal rises to 60 per cent. Addition of coal tars, which cause an increase in "adsorbed oil" from 1.7 to 3.0 per cent. raises the swelling power of the coal to 100 per cent. The other oils are intermediate, giving similarities in the amounts of "adsorbed oil" and in the swelling power of the coal. The only anomaly appears to be kerosene, which gives 2.5 per cent. of adsorbed oil, whilst the swelling power is only 68 per cent., instead of the expected 90 per cent.

This similarity cannot be a coincidence, and is very significant. It means that the oil retained on the coal surface must have some very definite effect upon the swelling of the coal, if indeed it is not absolutely responsible for it. If this is so we have established a definite criterion of coking ability, i.e., the amount of oil it retains at 420 deg. C., which is adsorbed on the coal surface, but which can be extracted by ether. The shatter indices of the cokes formed agree with the above table, that is, the coals with expansions more than 80 per cent. form cokes with shatter indices more than 90, whereas, in the case of the Gas oil and Fuel oil, which have lower swelling powers, and a lower amount of "adsorbed oil," the shatter indices are noticeably lower. Coupled with the knowledge obtained in the quantitative estimation of benzene addition to Shafton and Fenton coals, we can now consider the evidence of coke formation thus far obtained:—

1. The coal surface determines the ability of the coal to adsorb oil and retain it at 420 deg. C., so that it can be used by the coal in coke formation.
2. The swelling power of the coal determined in the S.L.C. Test is a very important factor in coke formation.

On addition of oil this swelling power is proportional to the retention of the added oil. Since this retention is also proportional to the suitability of the coal surface to retain added oil (1), the swelling power must be directly dependent upon coal surface, and we again arrive at the conclusion that the most

important factor in coke formation, is the condition of the surface of the coal particles, whether or not they are able to retain liberated oil, either by physical or by chemical means.

The experiments on the "weathering" of these mixtures of Hatfield Main coal and Petroleum oils were conducted over a period of three months, a determination of the swelling power in the S.L.C. Test being made after 2, 4, and 12 weeks. The mixtures were allowed to stand with as much of the surface of the coal as possible exposed to air which was continually moving. The results are recorded in Table XII.

TABLE XII.  
THE EFFECT OF ADDED OILS ON THE WEATHERING OF HATFIELD MAIN COAL AND ON ITS SWELLING POWER IN THE S.L.C. TEST.

Oil added.	Original value.	2 weeks.	4 weeks.	12 weeks.	Time till swelling power falls to NIL.
None .....	30	5	Nil	Nil	
Langley Park Tar .....	105	—	81	54	26 weeks
Manvers Main Tar .....	102	—	71	46	16 weeks
Diesel Oil .....	85	80	35	14	14 weeks
Aviation Spirit .....	95	32	11	Nil	
Straight run Benzine ...	85	30	14	Nil	
Shell Mex Gas Oil ...	90	—	72	18	} 14 weeks
Crude Oil .....	86	79	72	29	
Kerosene .....	68	56	27	15	13 weeks
Gas Oil .....	62	50	18	5	} Just over 12 weeks
Fuel Oil .....	60	56	10	3	

The results show very clearly the beneficial effect of the added oil on the retention of swelling power of the coal when exposed to the air over long periods. The coal itself loses its original swelling power of 34 per cent. in exactly 15 days. At the end of this time the oxidation that has taken place has completely removed all swelling of the coal, and its value as a coking coal has disappeared. Addition of oil in all coals improves the swelling power of the coal, but this improvement must be retained over long periods. In the case of the coal tars, the coal still retains more than 70 per cent. of its original swelling power. Even after three months, a period which is as long as most coal would be stored before coking, the swelling power is higher than that of freshly-ground coal by itself. We find, however, that volatility now plays an important part. Aviation spirit loses its effect in just over three weeks, and at the end of six weeks the coal is non-swelling. Straight-run Benzine also loses its effect rapidly, and leaves a non-swelling coal within six weeks. The other oils gave intermediate results. Crude oil, and Shell Mex gas oil approximate in their effect most nearly to the coal Tars, but once deterioration sets in, these coal-oil mixtures lose their swelling power rapidly. Most of the mixtures at the end of three months have a swelling power less than 10 per cent., and are practically useless for coking purposes.

Considering the results as a whole, we can conclude that an important factor in coal storage has been discovered. In all cases addition of oil not only has a beneficial effect upon swelling power, and consequently upon the coking power of coal, but also has a very important effect on the ability of coal to retain its swelling power over longer periods. It inhibits oxidation to such a degree in some cases that the coal retains a considerable swelling power at the end of three months. The fact that only 3-5 per cent. of oil is necessary in these mixtures to give the optimum results in improvement in swelling power, means that the film of oil on the coal is very thin. This film, however, is very resistant to oxidation, and adheres very tenaciously to the coal. Volatility of the oil added now becomes important, since a volatile oil in a constantly-changing atmosphere must necessarily evaporate more quickly than a less volatile oil. It would seem that the oil was attached to the coal in some manner as to give very strong bonds, and this fact points to the union being chemical rather than physical.

#### A COMPARISON OF DIFFERENT METHODS OF ADDING OIL.

A few experiments were carried out, using Fenton coal with several oils, hand mixing instead of the usual agitation in water being employed to obtain a coal-oil mixture. The mixtures were treated in exactly the same way as the oil mixtures, and the results are recorded in Table XIII. Fenton coal had its swelling power determined, and its deterioration upon being allowed to stand in a constantly-changing atmosphere was investigated.



TABLE XIII.  
COMPARISON OF RESULTS OBTAINED BY ADDING OIL DIRECTLY  
AND BY AGITATION IN WATER TO FENTON COAL.

Oil added.	Expansion in S.L.C. Test.	Oil distilled to 420°.	Oil extracted from pre- heated coal.	Oil distilled on reheating to 600 °C.	Shatter Index of residue.
Coal alone .....	50%	4.5	3.0	8.0	70.0
Langley Park Tar in Benzene:					
Trented .....	130%	4.5	3.2	10.8	93.6
Added by hand .....	80%	7.5	3.5	10.4	98.4
Manvers Main Tar:					
Trented .....	94%	11.6	4.0	12.2	97.6
Added by hand .....	50.0%	8.0	4.45	8.9	99.0
Iranian Crude Oils:					
Trented .....	80.0%	10.9	3.9	12.0	99.4
Added by hand .....	50%	11.9	3.6	8.9	98.6
Benzene:					
Trented .....	102%	3.0	7.0	11.7	97.6
Added by hand .....	67%	7.7	3.9	7.6	99.0

The results show that "treating" gives better results than hand mixing. Increase in swelling power is greater for treating than for hand mixing, the improvement usually being at least 50 per cent. This points to the fact that a far more intimate mixing is obtained by treating, and for hand mixing we probably have an excess of oil at one point and an insufficiency at another. The cokes, too, show the same differences. Those obtained by "treating" are swollen, and give evidence of pore structure. Those obtained by hand mixing have high shatter indices but are non-swollen, although they all show pore structure. The percentage of "adsorbed oil" is very similar in most cases, except with Benzene, but the oils obtained by redistillation to 600 deg. C. are higher in the case of the treated mixtures.

Weathering tests carried out with Fenton coal and oils mixed by hand gave the results shown in Table XIV.

TABLE XIV.

Oil added.	Value when			
	originally mixed.	2 weeks.	4 weeks.	12 weeks.
None .....	52	17	5	Nil
Langley Park tar in benzene ...	80	78	74	62
Manvers Main tar .....	50	50	45	36
Iranian Crude Oil .....	50	50	40	13
Benzene .....	67	66	36	Nil

The coal-oil mixtures were prepared by hand mixing, so that the results may be expected to be inferior to those obtained by agitation in water. In the cases of the two coal tars the swelling powers even after three months' weathering are considerable, sufficient to enable good cokes to be formed on preheating to 420 deg. and reheating to 600 deg. C. In the case of Iranian crude oil the effect is not so noticeable. The swelling power falls very slowly for the first six weeks, and then more rapidly until at the end of three months it is only 13 per cent. Benzene is by far the most volatile of the added oils, and here again we see the effect of volatility. At the end of two weeks the effect of the Benzene is scarcely diminished. Then after about 24 days it suddenly begins to diminish rapidly, until at the end of six weeks it has vanished. The persistence of the influence of Langley Park tar is amazing. At the end of six months the mixture still retains quite an appreciable swelling power, and at the end of three months it has scarcely deteriorated at all. The Fenton coal itself lost practically all its swelling power in one month; when heated at the end of this period gave much lower oil yields than when freshly ground, and also gave a coked residue in powder form.

#### THE TREATMENT OF DERBYSHIRE COALS.

The influence of the addition of oil on the coking and weathering properties of certain Derbyshire coals was investigated. The coals chosen were Tupton No. 7 coal (C. 81.9), Tupton No. 5 coal (C. 82.1), No. 6 Soft coal from the hard seam (C. 82.0), No. 2 Threequarter (C. 83.1), No. 2 coal, and No. 5 Main coal. (81.8' C)

For two of these coals, namely, Tupton No. 7 and Tupton No. 5, the oil was added with agitation in water as well as by hand mixing, but for the others hand mixing only was used. The coals were ground to pass 60 mesh, mixed with 4 per cent. of the oil, part was preheated and the usual investigation

carried out, and part was set aside to weather and the swelling power was determined at intervals of two weeks. All these coals are from Derbyshire seams, and all are in the band of poorly-coking or non-coking coals. They all possess certain coking qualities, but these disappear if the coals are left exposed to air oxidation for as short a period as a week-end.

In the present investigation hand mixing was mostly employed. At first it was thought that efficient mixing of coal and oil might be obtained by spraying a thin layer of the crushed coal with an oil-spray. It was discovered, however, that rapid evaporation took place, and it was probable that the oil added had lost some of the lighter boiling fractions and changed in character during the addition. It was found that fairly efficient mixing could be obtained by hand, the oil being added to the ground coal and the mixture stirred until the coal lost its brown colour and gave the characteristic appearance of oil-coal mixtures. The results obtained are given in Table XV.

TABLE XV.  
ADDITION OF OILS TO DERBYSHIRE COALS.  
TUPTON No. 7:—

Oil added.	Per-cent. expansion in the S.L.C. Test.	Oil distilled on preheating to 420° C.	Oil extracted.	Oil distilled on reheating to 600.
None .....	7%	3.6	1.6	5.2
Trented + Langley Park Tar in benzene .....	67.5	5.0	4.6	9.3
Hand mixed + Langley Park Tar in benzene .....	62.0	8.4	3.7	8.4
Trented + Manvers Main tar...	25.0	7.4	2.0	7.7
Hand mixed + Manvers Main tar .....	19.0	10.4	2.1	7.8
Trented + Derbyshire tar .....	10.0	7.2	2.3	6.6
Hand mixed + Derbyshire tar	5.0	8.4	2.7	5.9
Trented + Iranian Crude Oil...	13.0	9.2	3.1	7.7
Hand mixed + Iranian Crude Oil .....	12.0	7.2	3.4	7.8
TUPTON No. 5:—				
Coal alone .....	Nil	3.1	0.9	7.6
Trented + Langley Park Tar in benzene .....	56	6.2	2.7	6.8
Hand Mixed + Langley Park Tar in benzene .....	48	6.7	2.5	6.7
Trented + Manvers Main Tar	20	7.8	2.35	6.3
Hand mixed + Manvers Main Tar .....	11.5	7.8	2.1	6.6
Trented + Derbyshire Tar ...	19	7.2	2.6	7.1
Hand mixed + Derbyshire Tar	16.1	6.8	3.9	7.8

These results confirm those obtained with Hatfield Main coal. In practically every case the figures are better for "treating" than for hand mixing, although in the case of these Derbyshire coals the discrepancies are not so large. The expansion is usually a little higher, very little in some cases, whilst the oil adsorbed is also very slightly higher, except in two cases. There seems little difference in the results of the two methods of oil addition (except that hand mixing requires more oil which is distilled up to 420 deg. C.), and this difference can be accounted for by the fact that treating ensures a more complete and more uniform oil film on the surface of the coal. In every case of oil addition we find improvement both in the expansion in the Sheffield Laboratory coking test, and (more noticeably) in the case of the "adsorbed" oil. In the case of Tupton No. 7 coal, which has a small original expansion, the amount of oil "adsorbed" from the coal-oil mixtures is similar to that of the coking coals. Langley Park tar has the best effect on the expansion of the coal, Manvers Main tar and Iranian crude oil are almost similar in effect, whilst Derbyshire tar a poor effect, scarcely any improvement in the expansion being obtained. It is noticeable that the better coking the coal from which the tar is produced, the better its effect. The other coals, No. 6 soft coal No. 2 Threequarter coal, No. 2 coal and No. 5 Main coal, were hand mixed with the above oils, and similar experiments conducted with the results recorded in Table XVI.



RESULTS—TABLE XVI.

No. 6 SOFT COAL:—

Oil added.	Per cent. expansion.	Per cent. oil to 420 °C.	Per cent. oil extracted.	Per cent. oil to 600 °C.
None .....	Nil	3.8	0.9	5.4
Langley Park tar in benzene	6.5	4.4	2.9	7.8
Manvers Main tar .....	Nil	5.6	5.3	8.1
Derbyshire tar .....	Nil	6.8	4.6	9.3
Iranian crude oil .....	Nil	5.7	3.0	6.1

No. 2 THREEQUARTER COAL:—

Coal alone .....	10	3.1	2.0	9.1
Langley Park tar in benzene	49.0	5.2	3.4	8.5
Manvers Main tar .....				
Derbyshire tar .....	43.0	6.8	3.6	7.0

No. 2 COAL:—

Coal alone .....	75	5.0	3.2	7.1
Langley Park tar .....	95	4.6	4.1	9.55
Manvers Main tar .....				
Derbyshire tar .....	80	7.6	3.8	7.9

No. 5 MAIN COAL:—

Coal alone .....	15	4.5	3.25	6.5
Langley Park tar .....	50	8.0	4.2	6.5
Manvers Main tar .....				
Derbyshire tar .....	33	10.2	3.7	5.9

On examining these results we find that the added oil is having a beneficial effect. The first coal, No. 6 Soft coal, is a very poorly-coking coal, being similar to Shafton coal in having no expansion in the Sheffield Laboratory Coking Test, and only giving 0.9 per cent. of retained oil at 420 deg. C. Only the addition of Langley Park tar gives the coal any swelling power, and this is only very slight. The amounts of retained oil, however, are increased to at least 3.0 per cent. in all cases, and the cokes produced in the reheatings are all coherent, whereas that from the coal alone has a shatter index of nil.

The other three coals all have a definite swelling power of their own, No. 2 coal being similar to Fenton coal, the other two, No. 2 Threequarter and No. 5 Main coal, being more like Hatfield Main or High Hazel coal. No. 2 coal shows its improvement by oil addition best in the coked residues. In the case of Langley Park tar a slight swelling is found, whilst in all cases there is evidence of pore formation. Derbyshire tar does not seem to improve this coal to a great extent. The other two coals, No. 2 Threequarter and No. 5 Main, show a good improvement in swelling power, the effect of Derbyshire tar being larger than was expected. It might be that these coals have a deficiency of their own natural oil, and when this is made up by adding this oil, they become coals similar to No. 2 coal. The amounts of adsorbed oil are increased, and the amounts extracted from most of the coal-oil mixtures after preheating to 420 deg. C. are similar to those from a good coking coal. Nevertheless, despite these improvements, we never, except in the one case mentioned, find any swelling in the final coked residues, so that these coals are not so adaptable to improvement by oil addition as either Fenton or Barnborough coals. This is probably on account of their higher oxygen content, and also the higher water content of all the Derbyshire coals. The presence of water in the coals themselves might interfere with the function of the added oil, especially if the orientation of the water molecules is hostile to the added oil molecules.

The weathering experiments gave very satisfactory results. All the coals, with the exception of No. 2 coal, had low expansions (in two cases there was none at all), and these were lost very rapidly. Tupton No. 7 coal which had an expansion of 7-10 per cent. when freshly ground had lost this expansion within 12 hours when left exposed to the air. No. 2 Threequarter coal and No. 5 Main coal, when ground to pass 60 mesh and left for air oxidation, both lost their expansion within three days. No. 2 coal, with an original expansion of 75 per cent., had no expansion at the end of a fortnight, and that of the coal in the lump had fallen in this time to 48 per cent. The figures for the coals and the coal-oil mixtures are given in Table XVII.

TABLE XVII.

## No. 7 TUPTON:—

Oil added.	Percentage expansion in the S.L.C.T.	Expansion after 2 weeks.	Expansion after 4 weeks.	Expansion after 12 weeks.
None .....	9	Nil	—	—
Langley Park tar, tressed ...	67.5	52	25	Nil
Langley Park tar, by hand ...	62	32	10	Nil
Manvers Main tar, tressed ...	25	10	Nil	—
Manvers Main tar, by hand ...	19	Nil	—	—
Derbyshire tar, tressed .....	10	10	Nil	—
Derbyshire tar, by hand .....	5	Nil	Nil	—
Iranian crude oil, tressed .....	13	5	Nil	—
Iranian crude oil, by hand ...	12	Nil	Nil	—

## No. 5 TUPTON:—

Coal alone .....	Nil	Nil	Nil	—
Langley Park tar, tressed ...	56	40	16	Nil
Langley Park tar, by hand ...	48	15	Nil	—
Manvers Main tar, tressed ...	20	5	Nil	—
Manvers Main tar, by hand ...	11.5	Nil	Nil	—
Derbyshire tar, tressed .....	19	5	Nil	—
Derbyshire tar, by hand .....	16	Nil	—	—

In the case of these two coals, tressing seems much more efficient a method of preventing atmospheric oxidation. Some of the tressed coals give expansions in some cases at the end of one month, whereas in most cases the hand mixed oil-coal mixtures have lost their expansion at the end of a fortnight. Since the coals themselves lose their swelling power in three days, however, in every case oil addition has a decided improving effect upon the "weathering" of the coals. The fact that tressing gives the better results bears out the previous work and strengthens the argument that it ensures a uniform and more complete film of oil being distributed over the surface of the coal.

In the case of the other Derbyshire coals, hand mixing was employed. The results of the weathering tests of these coals are given in Table XVIII.

TABLE XVIII.

## No. 6 SOFT COAL:—

Oil added.	% Expansion.	2 weeks.	4 weeks.	12 weeks.
None .....	Nil	Nil	—	—
Langley Park tar in benzene	6.5	5.0	Nil	—
Manvers Main tar .....	Nil	—	—	—
Derbyshire tar .....	Nil	—	—	—
Iranian crude .....	Nil	—	—	—

## No. 2 THREEQUARTER COAL:—

None .....	10	Nil	—	—
Langley Park tar in benzene ...	49	34	10	—
Manvers Main tar .....	32	5	Nil	—
Derbyshire tar .....	43	10	Nil	—

## No. 2 COAL:—

None .....	75	Nil	—	—
As for .....	95	80	54	15
No. 2 Threequarter Coal .....	85	76	22	Nil
Derbyshire tar .....	81	37	9	Nil

## No. 5 MAIN COAL:—

Coal alone .....	15	Nil	Nil	Nil
As for .....	50	45	17	Nil
No. 2 Threequarter Coal ...	45	40	5	Nil
Derbyshire tar .....	36	10	Nil	Nil

The results are not so good as was hoped, the increase in swelling power never being retained for a longer period than one month, except in the case of No. 2 coal, which had an original swelling power of 75 per cent. Nevertheless, Tupton No. 2 coal and Langley Park tar at the end of a fortnight shows a swelling power of 80 per cent., whereas that of the ground coal has disappeared absolutely, and that of the lump coal has fallen to 48 per cent. No. 6 Soft coal seems definitely non-coking, and only in the case of Langley Park tar is any swelling power obtained, this persisting at first but disappearing at the end of three weeks. No. 2 Threequarter coal has its swelling power of 10 per cent. increased by all the added oils, remarkably so in the case of Derbyshire tar, as was previously noticed. Only the Langley Park tar mixture retains its swelling power to any great extent, and at the end of one month all the mixtures are non-



swelling with this single exception. No. 5 Main coal has an original swelling power of 15 per cent. which disappears in under three days. The added oils all increase this to approximately 50 per cent., and the Langley Park tar mixture is again the most resistant to weathering. At the end of a month this retains 17 per cent. swelling power, but this disappears in another seven days. Derbyshire tar seems in all cases to improve the swelling power, but this improvement is not so lasting as is the case with the other two tars. Tupton No. 2 coal, by addition of Langley Park tar, seems to be converted into a good coking coal, insomuch that it is capable of retaining its swelling power for a much longer period than any of the other coals. At the end of one month it still has a swelling power of 54 per cent., which is as much as that of Fenton coal when freshly ground.

The results are as was expected, although the weathering of the oil-coal mixtures is more rapid than previous work led us to believe. When the peculiarly rapid weathering of the ground coals, the high percentage of oxygen in the coals, and the high percentage of inherent water, are considered, perhaps the results are not so disappointing as was thought. They bear out the previous work on improvement of coking quality, and also show improvement in swelling power and resistance to weathering..

#### MISCELLANEOUS EFFECTS OF ADDING OILS TO COALS.

Several facts were noticed during the course of the preceding experiments which were not mentioned previously, so as not to withdraw attention from the more important issues. The gas yields of the various oil-coal mixtures, the effect of trenting upon the ash content of the coal, and upon the liquor content of the coal, the composition of the oil-coal mixture and the effect of oil addition upon its ultimate analysis, were all points which were examined and several interesting facts observed.

#### ASH CONTENT.

The ash content of the coal in the case of trenting was expected to be reduced. The original work by P. E. Trent dealt at length with this subject. It was found that the coal that was flocculated upon the surface of the water in company with the oil had a much smaller ash content than that which sank. The sunken portion, which was discovered to be always less than 10 per cent. of the original coal when the coal was so thoroughly trented as to give a good separation, was found to contain a high percentage of ash, and the coal in the oil-coal layer had a corresponding decrease in ash content. A few experiments were carried out during the present investigation whilst the Derbyshire coals and Shafton coal were being trented. The original ash content of the coals was known and that of the oil added. The ash content of the dried coal-oil mixture was determined, and it was found that a very appreciable fall in ash content had occurred. In addition to improving the qualities of the coal as a coking agent, the coal had been cleaned, as shown in Table XIX.

TABLE XIX.

#### REDUCTION OF ASH CONTENT BY "TRENTING."

SHAFTON COAL—	Ash content.
Coal alone .....	5.2%
+ Benzene .....	3.8%
+ Pentane .....	4.0%
+ Langley Park tar in benzene .....	4.7%
TUPTON No. 7—	Ash content.
Coal alone .....	1.4%
Langley Park tar in benzene .....	0.9%
Manvers Main tar .....	1.0%
Derbyshire tar .....	1.0%

#### LIQUOR CONTENT.

The liquor content of the coal was also studied. It would naturally be expected that by trenting the ground coal in water with the added oil, the water content of the mixture would be much higher than that of the coal alone. It is well known that the percentage of moisture in washed coal is usually in the neighbourhood of 10 per cent., whereas in the unwashed coal it probably is 1 to 4 per cent. This added moisture would naturally be a drawback during coking operations, since an increased quantity of heat would be necessary to expel it. It was discovered, however, that if the coal-oil mixture was dried by pressure filtration and then allowed to air dry for 12 hours, that the liquor content of the coal-oil mixture was approximately that of the original coal. In many cases, especially those coals which are known to contain much loosely-bound moisture (c.f. Hamstead Thick), the liquor content of the coal-oil mixture is often less than that of the original coal, as follows:—

Hamstead coal to 420 deg. C. gives 17.25 per cent. liquor.

Hamstead coal—Parkgate Low Temperature oil at 410 deg. C. gave 8.7 per cent. liquor; at 440 deg. C. gave 9.5 per cent. liquor.

This is with 15 per cent. of oil added, but it is found that if more oil is added the coal-oil mass becomes more retentive of moisture and the liquor content increases.

Some figures for Fenton and Barnborough coals are given in Table XX. which show that in some cases, especially in the case of the higher boiling oils, diminution in liquor content can be obtained by Trenting.

TABLE XX.  
LIQUOR DISTILLED TO 420° C. WITH OIL-COAL MIXTURES OF FENTON AND BARNBOROUGH COALS.

Oil added.	Liquor contents to 420° C.	
	Barnborough.	Fenton.
None .....	5.7	3.9
Langley Park tar .....	3.8	2.3
Manvers Main tar .....	3.4	2.5
Manvers Main anthracene oil .....	4.4	3.3
Creosote oil .....	5.0	3.6
Hexane .....	5.5	3.7
Amylene .....	4.3	3.7
Cyclohexane .....	5.0	3.4
Pentane .....	6.3	3.5
Benzene .....	8.5	4.1

In the case of the Derbyshire coals the results are not so promising. The coals themselves yield about 8 per cent. of liquor when heated to 420 deg. C., and in the majority of cases the coal-oil mixtures yield about 10 per cent. Since the majority of the liquor from Derbyshire coals seems distilled below 300 deg. C., an experiment was performed to investigate whether this liquor had any inhibitive effect upon the oil added. The coal was ground to pass 60 mesh and carefully preheated at 1 deg. C. per minute to 300 deg. C. The residue was then ground to pass 60 mesh and treated with Langley tar, and the coal-oil residue resulting preheated and reheated as usual. The coal (Tupton 7 coal) treated quite well, but after reheating to 600 deg. C. the coke was still non-swollen, with evidence of pore formation. The amount of adsorbed oil had risen from 4.6 per cent. to 5.0 per cent., and the amount redistilled on reheating from 9.3 per cent. to 9.8 per cent. The swelling power was raised from 67.5 per cent. to 85 per cent., but what is more important was the increased ability of the coal to maintain its swelling power and coking ability over longer periods. At the end of three months the coal-oil mixture still had a swelling power of 25 per cent., whereas the swelling power was lost completely in six weeks in with of the normal treatment when the liquor had not previously been distilled. The results are recorded in Table XXI.

TABLE XXI.  
TUPTON No. 7 COAL WITH LANGLEY PARK TAR IN BENZENE.

	Swelling power in the S.L.C. Test. Per cent.	Oil				
		Percentage of oil on pre-heating to 420 deg. C. Per cent.	extracted after pre-heating to 420 deg. C. Per cent.	Oil distilled on heating to 600 deg. C. Per cent.		
		Coal alone .....	Nil	3.0	1.6	5.2
		+ Normal oil addition ... Preheated to 300 deg. C. and then oil added	67.5	5.0	4.6	9.3
	85.0	4.9	5.0	9.8		

COAL COMPOSITION.

The composition of the coal-oil mixtures was investigated, using Tupton No. 7 and Tupton No. 5 coals. It was thought at one time that introduction by trenting of oils high in Hydrogen content would increase the Hydrogen content of the coal, and so place it nearer in type to the coking coals. Combustion experiments were carried out on dried samples of Tupton No. 7 and No. 5 coals, and also upon mixtures of these coals treated with various oils.

The results calculated to the dry-ash free bases are recorded in Table XXI.

TABLE XXII.  
THE COMPOSITION OF OIL-COAL MIXTURES.

TUPTON No. 5 COAL—	Carbon content.		Hydrogen content.	
Coal alone .....	82.1		5.28	
Langley Park Tar .....	82.42		5.30	
Manvers Main Tar .....	82.30		5.31	
Derbyshire Tar .....	82.2		5.30	
A.P. Crude Oil .....	82.1		5.27	
TUPTON No. 7 COAL—				
Coal alone .....	81.9		5.27	
Langley Park Tar .....	82.2		5.29	
Manvers Main Tar .....	82.0		5.30	
Derbyshire Tar .....	82.0		5.28	
A.P. Crude Oil .....	81.9		5.27	

It can be seen that there is very little improvement in the carbon and hydrogen contents of the coals.



## SUMMARY OF RESULTS.

The object of the present research was originally to study the influence of oil addition upon the coking properties of coal. It is unfortunate that as the work has progressed the field of research has widened enormously, and left many gaps in the results which rendered them somewhat incomplete. It has been attempted, as far as possible, to investigate new problems as they arose, with the result that the scope of the work has extended.

To study the influence of the addition of oil upon coking properties it was first necessary to know something of the part played by the oil inherent in the coal during coking. A preliminary investigation had been made upon the distillation of oil from crushed coal particles, a range of coals embracing coking, poorly-coking, and non-coking, being employed. Their carbon contents ranged from 89 per cent. in the case of Busty coal, which was very strongly coking, to 76.5 per cent. in the case of Ellistown Main coal, which was very definitely non-coking. From the graphs of the total oil distilled at various temperatures of preheating it was possible to establish definite curves for each type of coal. The difference between the types of coal seemed to be the ability of the coking coals to release but retain oil to much higher temperatures than the non-coking coals. The latter released their oil at comparatively low temperature, when it seemed to dissociate itself from the coal substance and distil normally. With the coking coals the oil was released but retained by the coal throughout the swelling range of that coal. It was discovered that the break point in the oil distillation graph was approximately 420 deg. C., and it was decided to adopt the standard of 3.0 per cent. of retained oil at 420 deg. C. to distinguish coking coals. Here was the basis for oil addition to coal. If by oil addition a coal could be made to retain 3.0 per cent. of oil at 420 deg. C. it should become coking. Oil addition was accomplished by "treating," i.e., adding the oil to the coal in water and agitating the mixture—and then the oil-coal mixtures were preheated and reheated in the usual manner.

First a series of coals was treated (a similar series to that employed in the primary investigation), and it was discovered that the greatest effect was produced in the cases of the coking coals of inferior quality. The strongly-coking coals seemed to have a sufficiency of oil and adsorbed very little more. The non-coking coals seemed incapable of improvement by any oil, but those coals which gave weak cokes, coals with a carbon content of 81-84 per cent., showed great improvement, and were taken as the basis for further work. Fenton and Barnborough coals were employed, both of these being on the fringe of the coking coals, and these were treated with a fairly wide series of oils of different types. Considerable improvement was effected in their coking qualities, firm cokes being produced, and in the case of Fenton coal, pore formation was accomplished. It was significant, however, that oxygenated bodies with ketonic linkages destroyed whatever coking ability the coals previously had, this being the only case in which the coke quality did not improve.

The effect of low-boiling oils was found to be similar to that of tars in improving coking ability. Benzene, Pentane, Tetrahydronaphthalene and Hexane all gave much improved cokes in the reheated residue. This led to the next step in the research, when an attempt was made to study quantitatively the effect of the addition of benzene. Estimation of unsaturated and aromatic hydrocarbons was made at every stage in the preheating and reheating, and two coals, one definitely improved (Fenton) and one not improved (Shafton) were employed. The results lent support to the theory that Benzene is chemically adsorbed by the coal substance in the case of Fenton coal, but only loosely bound in the case of Shafton coal. It also confirmed the opinion that one of the most important factors in coking was the surface of the coal.

It was then decided to study the effect of oil addition upon the swelling power of coal. Swelling power is a very important factor coke formation, since the ability of the coal to swell upon heating gives strength to the coke when it is used in coking practice. Experiments were carried out upon the effect of the addition of oil on swelling power, and it was found that this invariably increased. It was observed that there was a connection between ability to retain oil and swelling power—as the percentage of oil retained at 420 deg. C. increased, so the swelling power increased. It was also noticed that a certain quantity of oil added gave maximum swelling power, and any excess of this quantity gave no further increase. A very important by-product to the work on swelling power came to light in these expansion tests. It was found that a coal-oil mixture retained its swelling and coke-forming power over much longer periods than crushed coal alone. Some Derbyshire coals, when allowed to stand in air by themselves, lost their coking power in a few days. This retention of swelling power meant an extension of as much as three months before their ability to give a coke on heating had disappeared.

On the whole, very gratifying results have been obtained. They point to the inferior coking coals, with carbon contents of 81.84 per cent., as most improved by oil addition. Quite a number of coals of this type have been examined and are all definitely improved, some of them so much as to give pore formation in the resulting cokes. If we add to the ability of a coal to retain more than 3.0 per cent. of oil at 420 deg. C., the power to give a swollen residue on reheating, we have a definition of a coking coal, and the results of this research at least seems to have established this.

## DISCUSSION OF RESULTS.

From the results obtained there seems no doubt as to the improvement to the coking ability of many coals if a suitable oil be added. In the case of the strongly-swelling and strongly-coking coals this improvement is not very marked, whilst there are some coals of such low carbon content and of such inferior quality that no oil has any noticeable improving effect. However, for those coals whose coking performance is moderate or poor, we have a very marked effect, which usually depends upon the type of oil employed. Coals of 81.5-83.5 per cent. carbon content are usually weakly swelling and of inferior coking quality. They can be converted into coals comparable in type with those of 83.5-86 per cent. C. content when they are mixed with certain oils, the most important of which are the crude coal tars. It is noticeable, too, that increase in coking ability usually means considerable increase in swelling power, and if with any one oil addition a graph be drawn of increased swelling power against carbon content, there is practically no increase of swelling power to 81.0 per cent. C., a very marked increase between 81.5 and 83.5 per cent. with a maximum at 82.5-83.0 per cent., and above 84 per cent. very little increase, gradually decreasing with increasing carbon content. In all cases trenting of the powdered coal in a water medium gave much better results than either hand mixing or spraying of the coal—indeed, trenting of the coal seems to give a very intimate coal-oil mixture in which the oil is probably bound to the coal substance chemically rather than physically. The work established the fact that swelling of the coal on reheating, coupled with the ability of the coal substance to retain at least 3.0 per cent. of its oil at a temperature of 420 deg. C., were the main factors in coke formation, and if any coal had these two attributes it usually was a good coking coal. For coals of between 81.5-83.0 per cent. C. content, varying increases in both the swelling power and the "oil retained" at 420 deg. C. could be effected by oil addition, and the quality of the cokes produced was dependent upon the ability of the added oil to promulgate coke formation. The crude coal tars gave the best results, which, as would be expected, depended chiefly upon the source of the coal tar. Durham Tar, which is distilled from strongly-coking coals, gave better results than Yorkshire Tar from moderate coking coals, which in turn gave better results than Derbyshire Tar from poorly-coking coals. The fact that Derbyshire Tar will improve coking ability seems to point to deficiency in oil being a factor of inability of some coals to form a coke. Yet some Durham coals retain very little oil at 420 deg. C., so apparently the quality of the Tar is a factor too. The ability of the coal surface, or its reactivity, is undoubtedly of great importance. If the surface is inert it is unable to retain oil, and no matter how much oil is added it will not be retained. Coals with these inert surfaces are probably the definite non-coking coals, whose coking performance is not improved upon oil addition. As for the gradual change from non-coking to coking coals, say from 81.5 to 89 per cent. C. content, this surface factor probably plays a very important part. As the C. content increases, so the ability of the coal surface to retain oil, that is oil suitable to coke formation, increases, and so coking ability increases. What it is that alters upon the surface of the coal seems obscure, because carbon itself cannot be made into a coking mass by trenting with a suitable oil. It is interesting too that certain low-boiling oils, with boiling points less than 100 deg. C., considerably improve coking ability. It was shown how the identity of benzene added to Fenton coal by trenting was completely lost, whereas that added to Shafton coal (which was non-coking) seemed loosely bound and easily removed by distillation. The condition of the surfaces of the Fenton coal and the Shafton coal must be quite different, and that of Fenton must be much more reactive.

The effect of the addition of oxygenated oils was rather astonishing. Two resins were added to various coals, Cumar resin which contained about 3 per cent. and Parallac resin which contained 36 per cent. oxygen. In all cases where expected Cumar resin improved the coke quality, whereas Parallac resin destroyed what coking ability the coal originally had. Anthracene and anthraquinone were similarly related, and acted in a similar manner, anthraquinone, the oxygenated body, destroying the previous coking ability of the coal. However, Phenol and Cresol, which contain oxygen, improved both the swelling power and the oil retained at 420 deg. C., and gave greatly improved cokes. Apparently the manner in which the oxygen is linked in the molecule is of the utmost importance, and the ketonic linking is definitely detrimental to coke formation. However, much more information must be obtained upon this point before any conclusions can be drawn.

One important fact was discovered whilst examining the effect of oil addition upon swelling power, when the duration of the improvement was studied. It was found that the presence of oil on the coal substance greatly lengthened the life of its "swelling power." Coals which lost their swelling power in a few days retained it after oil addition for several weeks. Often after two months storage they had a swelling power much higher than that of freshly ground coal. This improvement in the "weathering" capabilities of coals is certainly of great



importance, for many Derbyshire coals lose their coking ability if stored over a week-end.

In these experiments it has been shown that in many cases, almost always those of coals of inferior and poor coking ability, varying amounts of improvement can be effected by oil addition to the coal. It has also been shown fairly conclusively that upon addition the oil mixes intimately with the coal substance and seems to lose its identity. It may be that upon coking, cracking of the oil in question occurs, leaving a residue of activated carbon which acts as a binding agent, and that this is the factor upon which the whole of successful coking depends. If the oil is not distilled until temperatures higher than 420 deg. C., this supposition certainly might hold, because severe cracking of the oil should begin to occur at this temperature. The more severe the cracking the more gas and light oils are formed together with coke, but since the temperature factor has been constant throughout, the character of the original oil must determine the resultants. It might be a very profitable line of research to examine the behaviour of various oils on cracking—to study the resultant cokes and also the oils formed, and at the same time to examine the effect these oils have upon poorly-coking coals.

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