CV.—*Studies in the Composition of Coal. The Resolution of Coal by Means of Solvents.*

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As the result of systematic researches initiated in 1912, which have followed since 1915 the scheme outlined by Stopes and Wheeler (*Rep. Brit. Assoc.*, 1916), we can now express the " analysis " of a coal in a form which indicates its properties more clearly than the usual " proximate " and " ultimate " analyses. For example, the characters of the four component bands of the Hamstead coal, a markedly banded bituminous coal, can be expressed in the following manner :

	Per cent. by weight.			
	Ulmin compounds.	Organised plant entities.	Hydro-carbons and resins.	General character of plant entities.
Vitrain	96	Nil.	4	—
Clarain	92	5	3	Cuticles and spore exines.
Durain	83	15	2	Cuticles, spore exines, and woody tissues.
Fusain	20	80	Nil.	Woody tissues.

In these analyses, certain resin-like compounds, which cannot be definitely classed as resins, present in the coals in small quantity, have been ignored.

Other researches have dealt, and are dealing, with the constitution of the ulmin compounds and the organised plant entities (see, *e.g.*, Tideswell and Wheeler, J., 1922, **121**, 2345; Legg and Wheeler, J., 1925, **127**, 1412; Francis and Wheeler, *ibid.*, p. 2236). The present research is concerned with that portion of a normal bituminous coal which can be extracted by organic solvents, the sometimes incorrectly named " resinous " portion.

In many bituminous coals there are inclusions of resinous matter, usually on the cleavage planes, which can be separated mechanically and are thus readily examined (see Wigginton, *Fuel*, 1926, **5**, 476). With these we are not at present concerned. The substances extractable from a normal bituminous coal by organic solvents presumably contain the remains of oils, fats, and waxes of the original coal-forming plants, in addition to resins and their degradation products disseminated throughout the coal mass, such as the microscopic rods preserved *in situ* in what are known to have been resin-containing cells (see White and Thiessen, *U.S. Bureau of Mines*, Bull. 38, 1913; Francis and Wheeler, J., 1926, 1410). All such substances, although they could not have formed more than a small proportion of the plants of coal-measure times, would yet, owing to their resistance to decay, survive and proportionately increase in amount while the plant material was accumulating and partly decaying in the early stages of coal formation.

Although this " resinous " portion forms but a small fraction of a bituminous coal, it is an important constituent technically, by reason of the properties it confers on the coal; and it is of considerable scientific interest in relation to the origin, mode of formation, and constitution of coal.

A critical survey of the more important work carried out before 1918 on the action of solvents on coal has been given by Stopes and Wheeler in their monograph " The Constitution of Coal " (London, 1918), reprinted, with additions by Dr. F. V. Tideswell bringing it up to date, in " Fuel in Science and Practice," Vol. III, 1924. Therein the value of pyridine, first suggested by Bedson (*Trans. Inst. Min. Eng.*, 1899, **16**, 388) as a means of resolving the coal conglomerate, was emphasised. Clark and Wheeler had found (J., 1913, **103**, 1704) that when the pyridine extract of a bituminous coal was treated with chloroform or benzene, up to 10% (on the original coal) dissolved. This fraction, soluble in both pyridine and chloroform, differed markedly in properties from the bulk of the coal, and from a consideration of those properties Clark and Wheeler concluded that their treatment had made " a complete, or nearly complete, separation between the resinous constituents and the degradation products of the celluloses of which coal is conglomerated " (*loc. cit.*, p. 1706). The portions of a bituminous coal (α), insoluble in pyridine, and (β), soluble in pyridine but insoluble in chloroform or benzene, were found to be of the same type, differing mainly in their behaviour towards pyridine, whilst both were quite distinct from (γ), the portion soluble in both pyridine and chloroform. Clark and Wheeler had termed the fractions (α) and (β) " cellulosic " or, alternatively, in conformity with a nomenclature used by Lewes (*J. Roy. Soc. Arts*, 1911, **60**, 135), " humic " compounds. Stopes and Wheeler (*loc. cit.*, p. 41) pointed out that, until the composition of these groups of compounds had been more definitely ascertained, it was desirable to use less dogmatic terms than " cellulosic " and " resinic," and proposed the non-committal labels α, β, and γ, which are now commonly used.

Jones and Wheeler (J., 1916, **109**, 707) summarised the information then available regarding the γ-compounds, which they considered to be derived mainly from the gums, resins, and starches of the original coal-forming plants. They are clearly a mixture of several classes of compounds. Jones and Wheeler (J., 1914, **105**, 140) had obtained from them, by the solvent action of pentane, crystals of paraffin wax (heptacosane), m. p. 55—59°, amounting to 0·10% on the original coal. We have now attempted further to resolve the mixture into simpler components by suitable solvents.

EXPERIMENTAL.

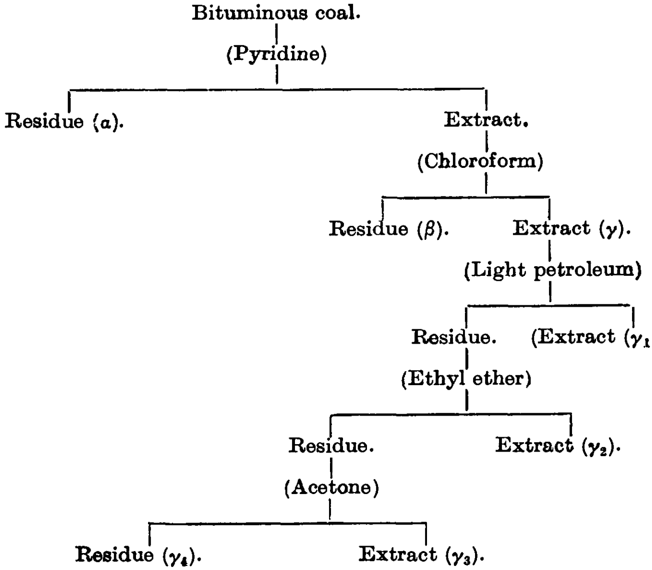
The γ-Compounds.—Supplies of the γ-compounds from the different coals were obtained by extraction with pyridine at its boiling point, followed by treatment of the extract with boiling chloroform. The action of pyridine on coal is often regarded as that of a reagent rather than a solvent. Harger (*J. Soc. Chem. Ind.*, 1914, **33**, 389) appears to have been the first to suggest that it effects "a process similar to depolymerisation." This view, for which no evidence has been adduced, has been adopted by later workers, notably by Illingworth ("Researches on the Constitution of Coal," London, 1921), but cogent reasons for rejecting it have been advanced by Tideswell (*Fuel*, 1922, **1**, 246). The work of Pearson (*J. Soc. Chem. Ind.*, 1923, **42**, 241) supports the view that pyridine is a solvent which resolves mechanically the colloidal mass of coal.

The first resolution of the coals in this research was by pure dry pyridine. The coals, dried and ground to pass a 10- and remain on a 60-mesh sieve, were extracted in large Soxhlet apparatus of special design. These and all subsequent extractions were carried out in an atmosphere of nitrogen. When extraction was complete, the solution was concentrated on a glycerol-bath and poured into a mixture of equal parts of concentrated hydrochloric acid and water. The mixed β- and γ-compounds were precipitated as a dark brown powder. This was filtered off, washed with dilute acid and with hot water, purified by steam distillation, and dried in a vacuum at 100°. In this way all but a trace of pyridine was removed.

The extraction of the γ-compounds by chloroform was completed in from 10 to 14 days. After removal of the solvent, the extracts were obtained as reddish-brown, brittle solids, m. p. 95—100°.

Resolution of the γ-Compounds.—In preliminary tests to determine the most suitable solvents with which to effect the resolution of the γ-compounds, acetone, ethyl ether, and light petroleum were found to be the most satisfactory. Ethyl alcohol tended to produce colloidal dispersion and therefore was not used.

With the particular sample of γ-compounds used in the preliminary experiments, acetone dissolved 85—90%, ethyl ether 70%, and light petroleum 33%. In the scheme of resolution finally adopted, the least effective solvent, light petroleum, was used first, the residue was extracted with ether, and any material then remaining was treated with acetone. The full scheme of resolution of the coals was as follows :



The fractions so obtained have distinctive properties, shortly to be described, which enable a judgment to be formed as to the character and origin of the groups of compounds each contains. We have made no attempt to isolate pure compounds, since a comprehensive research with this end in view is being carried out on a coal from Upper Silesia by Hofmann and Damm (see preliminary account, *Brennstoff-Chem.*, 1922, **3**, 73; 1923, **4**, 65).

In conformity with the nomenclature introduced by Stopes and Wheeler, the several fractions of the γ-compounds have been labelled, for convenience in reference, γ_1, γ_2, γ_3, and γ_4. A large number of bituminous coals have been resolved according to this scheme. In each instance the respective fractions have the same characteristics. It will therefore suffice here to record the results of examination by these means of one coal, a typical South Yorkshire coking coal from the Parkgate seam. This will be referred to as Parkgate A. The clarain portion only of the seam was examined. Its analysis is recorded in Table I.

By treatment with pyridine and chloroform, the proportions of α-, β-, and γ-compounds obtained were 75·8, 17·3, and 6·9%,

TABLE I.

Analysis of Parkgate A Clarain.

Proximate.	
Moisture	3·18%
Ash	1·23%
Per cent. on ash-free, dry coal.	
Volatile matter, other than moisture	38·83
" Fixed carbon "	61·17

Ultimate.	
Per cent. on ash-free, dry coal.	
Carbon	83·60
Hydrogen	5·46
Oxygen	6·75
Nitrogen	1·72
Sulphur	2·47

respectively. Further resolution of the γ-compounds, in the manner described, gave the results recorded in Table II.

TABLE II.

Resolution of γ-Compounds. Parkgate A Clarain.

	% of total γ-compounds.	% of coal.	Ultimate analysis.			
			C.	H.	S.	O + N.
Soluble in light petroleum (γ_1)	33	2·30	83·90%	9·00%	0·74%	6·36%
Soluble in ethyl ether (γ_2)	37	2·54	82·72	6·90	0·91	9·47
Soluble in acetone (γ_3)	12	0·83	79·00	5·70	0·89	14·41
Insoluble in acetone (γ_4)	18	1·23	80·00	5·90	1·10	13·00

The nitrogen contents of the fractions were not determined quantitatively, since minute traces of pyridine were sometimes retained by them. Each fraction could be completely redissolved in the cold solvent.

Examination of Fraction γ_1.—Extraction of the γ-compounds with light petroleum was completed in 14 days. The extract removed during the first few hours consisted entirely of hydrocarbons. As the extraction approached completion, the extract became darker in colour owing to the solution of some resinous matter. The total extract was a white, crystalline substance mixed with a certain amount of red oil. On drying in a vacuum, a reddish-brown material of the consistency of vaseline, mobile at temperatures above 80°, was obtained. On dissolving this material in ether and washing successively with dilute acid and alkali, traces of bases and fatty acids (volatile in steam) were obtained.

The remainder of the oxygenated compounds, forming 20% of the γ_1-fraction, were separated by Robinson's method (J., 1925, **127**, 768). They were resinous, dark red compounds, m. p. 90—95°, free from nitrogen and sulphur, completely soluble in cold chloroform, and of composition : C, 84·21 ; H, 7·31 ; O, 8·48%.

The rest of the γ_1-fraction consisted of saturated and unsaturated hydrocarbons in nearly equal amounts, and was similar to the neutral oils investigated by Hofmann and Damm (*loc. cit.*). The saturated hydrocarbons were obtained as a light yellow, faintly fluorescent oil having the characteristic odour of paraffins. Analysis gave: C, 87·4; H, 11·13; O, 1·47%, showing that hydrocarbons of other than straight- or branched-chain structure were present.

Fraction γ_1, 33% of the total γ-compounds, was thus found to consist of: Saturated hydrocarbons, 40; unsaturated hydrocarbons, 40; and resins, 20%.

Examination of Fraction γ_2.—The residue after the γ_1-compounds had been removed was a brown powder. This on extraction with ethyl ether (which was complete within 3 or 4 days) and evaporation of the solvent, yielded a brick-red powder, m. p. 100—110°. Small quantities of acids and pyridine bases were removed and the powdered extract was then shaken with a dilute solution of sodium bisulphite with a view to remove aldehydes and ketones. Neither of these groups of compounds was present.

Continuing the examination according to Tschirch's scheme for the separation of resin acids, the washed material was saponified in benzene solution with 10% alcoholic potassium hydroxide. A portion, 15% of the total fraction, dissolved, forming a dark red solution from which a light brown, flocculent powder was precipitated on acidification with hydrochloric acid; it was a mixture of phenols and acids (Found: C, 75·5; H, 5·9; O, 18·4%). These were separated by bubbling carbon dioxide through a sodium hydroxide solution of the mixture. There were thus obtained four fractions: *Precipitated by carbon dioxide,* (1) a brown solid; (2) a red oil extracted by ether. *Not precipitated by carbon dioxide,* (3) an oily acid volatile in steam; (4) a solid, non-volatile acid.

Fraction (1) formed 80—85% of the total saponifiable material. It consisted of a mixture of complex phenols soluble in hot alcohol, from which they were obtained on evaporation of the solvent as a brick-red powder (Found: C, 75·6; H, 6·3; O, 18·1%). Neither the mixture of the phenols themselves nor that of their benzoyl derivatives (which were brown powders) had a sharp m. p. Fraction (2) was a red oil having a powerful odour of limonene.

Fraction (3) was present in small quantity only. It was a volatile unsaturated acid. Fraction (4), 15·20%, was a mixture of acids from which insoluble silver, iron, and barium salts were obtained. Benzoyl chloride, both in pyridine and in aqueous alkaline solution, effected benzoylation. The acids were therefore hydroxy-acids.

The saponifiable portion of the γ_2-fraction thus consisted of phenols and hydroxy-acids in the form of esters, similar to the resin esters, or " resines " and " resinols," of Tschirch. The unsaponifiable portion was a dark red solid, m. p. 90—100°, free from nitrogen and sulphur (Found : C, 84·0 ; H, 7·2 ; O, 8·8%). In composition and general properties it closely resembled the resin separated from the γ_1-fraction. Tests showed that the oxygen it contained was not present in carboxylic, ketonic, aldehydic, or alcoholic grouping, but formed, presumably, a non-reactive bridged linkage. In its general inertness towards reagents, the substance was similar to the class of resins that Tschirch has termed " resenes."

Fraction γ_2, 37% of the total γ-compounds, was thus found to consist mainly of resins and resin-degradation products.

Examination of Fractions γ_3 and γ_4.—The residue from extraction with ethyl ether was a dark brown powder (m. p. 280—300° without decomp.). Acetone dissolved 40%, but the two fractions—γ_3, acetone-soluble, and γ_4, acetone-insoluble—were similar in composition (see Table II) and general properties. Both fractions were insoluble in alcoholic potassium hydroxide. Their resemblance to each other, and their dissimilarity from the γ_1 and γ_2 fractions, is best brought out by the results of destructive distillation and regulated oxidation, which will now be described.

Destructive Distillation of the Fractionated γ-Compounds.—One g. of each fraction was distilled in a small horizontal retort of Jena glass connected to an automatic Sprengel mercury pump. The retort was heated by an electric furnace, the temperature being raised slowly through intervals of 100° up to 450° and then of 50° to 600°. At each stage, the temperature was maintained constant until gases ceased to be evolved, a high vacuum being maintained, and the gases collected during each interval were analysed separately. The results are summarised in Table III.

TABLE III.

Destructive Distillation of Fractions of γ-Compounds.

A. Yields at 600°.

Fraction.	Total volatile matter, %.	Tar and oil, %.	Gas (c.c. per g.).
γ_1	(Distilled over unchanged below 300°.)		
γ_2	61·7	46·0	96·6
γ_3	48·3	13·0	140·5
γ_4	41·0	16·7	185·0

B. Gas analyses (%).

(Total gas over the range 15—600°.)

Fraction.	CO_2.	Higher olefines.	C_2H_4.	CO.	H_2.	Paraffins.
γ_2	5·2	2·0	1·0	6·5	32·5	54·4
γ_3	5·7	2·1	1·0	6·8	62·7	21·7
γ_4	6·2	2·3	1·7	9·5	52·0	28·2

The major portion of the tar from fraction γ_2 distilled between 200° and 300°. It consisted almost entirely of hydrocarbons. The residue was a dark brown, lustrous, intumescent mass, insoluble in chloroform. It will be seen that the gases evolved up to 600° contained a high proportion of paraffins.

The tars obtained from fractions γ_3 and γ_4 contained small quantities of phenols. The gases contained a high proportion of hydrogen and are thus dissimilar from the gases yielded by fraction γ_2. They more closely resemble the gases obtained from the β-fraction of the coal.

Oxidation of the Fractionated γ-Compounds.—Chemical analysis and the results of destructive distillation have thus shown the existence in the γ-compounds of three main types of constituents: hydrocarbons, resins, and a third group which has some of the characteristics both of resins and of coal-ulmins. The coal-ulmins, as exemplified by the β-compounds in particular, are readily oxidised, whereas the resins are not. We sought, therefore, to differentiate between the four γ-fractions by determining their relative ease of oxidation by hydrogen peroxide and dilute nitric acid.

Oxidation by hydrogen peroxide. One g. of each γ-fraction, as a fine powder, was treated under identical conditions with boiling hydrogen peroxide during 50 hours. The amount and character of the residues were then determined. The results are summarised in Table IV.

TABLE IV.

Oxidation of Fractionated γ-Compounds by Hydrogen Peroxide.

Fraction.	Residue, %.	Solubility of residue in KOH, %.	Analysis of residue.
γ_1	100	Nil.	
γ_2	90	Nil.	C, 78·1; H, 5·7; O, 16·2.
γ_3	Trace.	100	
γ_4	20	60	C, 70·8; H, 4·7; O, 24·5.

Fraction γ_1 was not affected by the treatment, but the more prolonged action of hydrogen peroxide removed the resinous material that this fraction contains, leaving hydrocarbons. Fraction γ_2 became lighter in colour and gradually lost its solubility in ether and in chloroform as it increased in oxygen content (compare Francis and Wheeler, J., 1925, **127**, 119). Fraction γ_3 reacted violently with each addition of hydrogen peroxide and was ultimately oxidised completely to water and oxides of carbon. Fraction γ_4 was not so reactive as γ_3, but was much more readily oxidised than γ_1 and γ_2. Much of the residue after oxidation was soluble in alkaline solutions, from which a brown, flocculent precipitate was obtained on acidification.

Oxidation by nitric acid. Since it was desired to avoid nitration, 30% nitric acid was used, 2·5 g. of the materials being boiled with 100 c.c. of the acid under reflux. Fraction γ_1 was not examined.

Fraction γ_2, which was rendered completely soluble in alkalis after 30 hours' treatment, showing that it contained no hydrocarbons, gave a copious evolution of nitrous fumes, and imparted a dark red colour to the nitric acid. The soluble acids (10%) did not contain picric acid. They were not further examined. The insoluble oxidation products (90%) were purified by washing with distilled water, dissolution in ammonia, and reprecipitation, as a reddish-brown powder, by dilute acid; further treatment with 30% nitric acid did not affect the composition (Found: C, 67·0; H, 4·6; O + N, 28·4%). The silver and copper salts of the acids were prepared and from combustion of the latter the equivalent was found to be 250.

Fractions γ_3 and γ_4 were treated together. The treatment, which was completed sooner than with fraction γ_2 and was accompanied by much frothing, rendered them completely soluble in alkalis. It was noted that the acids soluble in 30% nitric acid (10%) did not contain picric acid, but no further examination of them was made. The insoluble acids contained C, 60·9; H, 3·9; O + N, 35·2%, the composition remaining unchanged after further treatment with 30% nitric acid (Found: equiv., by combustion of copper salt, 268). As with similar products from fraction γ_2, benzene polycarboxylic acids were absent.

Whilst oxidation by hydrogen peroxide disclosed a difference in character between the γ_2- and the γ_3- and γ_4-fractions, oxidation by nitric acid shows a resemblance between all three fractions and a dissimilarity from coal-ulmins, such as the β-compounds from the same coal, which are rendered completely soluble in 30% nitric acid by prolonged treatment and yield both picric acid and benzene polycarboxylic acids (Francis and Wheeler, J., 1925, **127**, 2245).

We are in some doubt as to how the γ_3- and γ_4-fractions should be classed. The main bulk of any bituminous coal consists of groups of ulmin compounds, differing from each other according to the degree of condensation and dehydration they have experienced and differing, in consequence, as regards the extent to which they undergo colloidal dispersion in organic liquids. Just as the α-compounds are not dispersed in pyridine (whilst the β-compounds are), the β-compounds are not dispersed in chloroform; and it seemed possible that the γ_3- and γ_4-fractions might be ulmins that had been colloidally dispersed in chloroform.

In support of this suggestion, their low yield of tar and high yield of hydrogen on distillation in a vacuum, and their ease of oxidation by hydrogen peroxide, all relate them to the β-compounds. On the other hand, they melt, without decomposition, at temperatures no higher than do many resin inclusions from bituminous coals. No ulmins that we have examined, whether synthetic or of natural occurrence, melt on heating—all decompose without fusing. Moreover, their presumed dispersion in chloroform (no ulmin compounds are soluble in chloroform) indicates that they have undergone less change during the coalification process than the β-compounds. They should therefore be more readily oxidised. They are not; and, moreover, their products of oxidation by nitric acid are such as are yielded by resins rather than by ulmins.

On the whole, we consider the γ_3- and γ_4-fractions to be more nearly akin to the resins, representing perhaps the degradation products of some intermediate stage in the production of resins in the plant metabolism, such as gives rise to, *e.g.*, the tannins.

We therefore specify the various fractions of the γ-compounds from a bituminous coal as follows :

γ_1 (soluble in light petroleum) : Mainly hydrocarbons. In the example described, some 20% of resins were also present.

γ_2 (soluble in ethyl ether) : Resinols, resines, and resenes.

γ_3 and γ_4 (insoluble in ethyl ether) : Resin-like.

It may here be noted that the resins which occur macroscopically in bituminous coals are rarely of the same degree of solubility as modern resins, and the usual resin solvents, such as ether, alcohol, and benzene, do not dissolve them completely.

We have been surprised not to obtain direct evidence, in any of the coals that we have examined, of the presence of waxes (esters of fatty acids and alcohols). In the cuticles of modern plants, waxes invariably coat or permeate the cutin layer, whilst the cuticles that form so large a proportion of the Russian papierkohle have about 4% of wax associated with them (Legg and Wheeler, Safety in Mines Research Board Paper No. 17, 1925). Such waxes are particularly resistant to bacterial decay and one would expect them therefore to accumulate in the coal-forming deposits. The explanation of their absence is probably to be found in the behaviour of the montan wax of brown coals on being heated. Montan wax is a mixture of resins with carboceric and montan acids ($C_{27}H_{54}O_2$) both free and esterified with tetracosanol and ceryl and myricyl alcohols. The wax does not contain free hydrocarbons in any quantity, but it begins to decompose at about 200°, yielding solid and liquid hydrocarbons (Schneider and Tropsch, *Ges. Abh. Kennt. Kohle*, 1917, **11**, 28). It may be, therefore, that a portion of the free hydrocarbons found in bituminous coals (fraction γ_1) represents the waxes originally present.

As examples of the fractionation of the γ-compounds of other coals, we may record the following (Table V). The coals are arranged in order of their carbon contents, the results obtained with Parkgate A being included for comparison.

TABLE V.

Fractionation of γ-Compounds.

(Percentages on ash-free, dry coal.)

	γ_1.	γ_2.	γ_3.
1. Vermilion County, Illinois, U.S.A. C, 76·7; H, 5·8.	2·13 (C, 86·0; H, 9·2.)	2·67 (C, 79·8; H, 6·3.)	1·20 (C, 80·3; H, 6·3.)
2.* Ayr Hard. C, 78·5; H, 5·9.	1·92	2·43	2·92
3.† Hamstead, Staffs. C, 79·3; H, 5·3.	1·06 (C, 85·9; H, 9·4.)	2·95 (C, 80·6; H, 6·5.)	0·98 (C, 79·7; H, 5·5.)
4.* Blackband. C, 79·5; H, 5·5.	2·37	2·85	2·28
5.* Top Hard. C, 80·1; H, 5·5.	1·61	2·40	2·62
6.† Wigan Six Feet. C, 82·0; H, 5·5.	2·92	1·57	3·67
7.† Parkgate B1, S. Yorks. C, 83·4; H, 5·5.	1·50 (C, 86·1; H, 9·3.)	1·75 (C, 84·0; H, 6·4.)	1·75
Parkgate B2, S. Yorks. C, 83·2; H, 5·8.	1·60 (C, 86·2; H, 9·2.)	4·20 (C, 84·0; H, 6·7.)	1·40 (C, 80·2; H, 5·9.)
8.† Ten Feet, Staffs. C, 83·4; H, 5·4.	2·30	2·16	4·34
9.† Parkgate A, S. Yorks. C, 83·6; H, 5·4.	2·30 (C, 83·9; H, 9·0.)	2·54 (C, 82·7; H, 6·9.)	2·06 (C, 79·5; H, 5·8.)
10.† Silkstone, S. Yorks. C, 83·6; H, 5·4.	2·26	1·52	5·14
11.† Arley, Lancs. C, 84·3; H, 5·4.	1·52	2·30	5·18
12.† Busty (Tudhoe), Durham. C, 85·1; H, 5·4.	1·72 (C, 88·4; H, 9·0.)	2·59 (C, 86·1; H, 6·5.)	3·68 (C, 84·4; H, 5·7.)
13.† Busty (Beamish Mary), Durham. C, 87·8; H, 5·4.	1·35	1·56	5·91

* Durain portion. † Clarain portion. The Hamstead clarain contained a high proportion of vitrain streaks.

The Parkgate samples B1 and B2 (No. 7 in Table V) are of particular interest. They were chosen from a section of the seam taken about 12 miles from Parkgate A, as representing the upper and lower clarain bands in that seam. This seam is a good example of a banded coal in which the several bands are of considerable thickness and can be mined separately. Since the several bands have distinctive properties, this is often desirable. The seam is characterised throughout the S. Yorkshire coal-field by the existence of a broad (1—2 ft.) central durain band with equally broad clarain bands above and below it (see Evans, " The Correlation of the Parkgate Seam," *Trans. Inst. Min. Eng.*, 1926, **71**, 451). The lower clarain band in this section differs from the upper in containing many bright bands in which, under the microscope, resin rods can be distinguished amongst the woody structures. Their presence has markedly increased the proportion of fraction γ_3 extractable from the coal. It is perhaps necessary to point out that, in records of a study of the chemical constitution of a banded bituminous coal, the character of the band investigated should be specified.

It was at one time held that a certain proportion of γ-compounds in a coal was essential if a good commercial coke was to be made from it (Illingworth, *J. Soc. Chem. Ind.*, 1920, **39**, 133T). This is probably true, in general, but it has long been realised that a measure of the quality of the coke that could be obtained from a coal was not given by its content of γ-compounds. This is not surprising in view of the varying proportion in which the several fractions, each having different characteristics, are present in the γ-compounds of different coals, as shown in Table V. The determination of the effectiveness of the several γ-fractions in causing the agglutination of the remainder of the coal during the process of coking throws considerable light on their properties. Coking tests were made on blends of the coal residues, left after extraction, with each one in turn of the γ-fractions from the same coal, in the proportions in which they originally existed. The blends were made by dissolving the extracts in chloroform and immersing the residues in the solutions. After being allowed to soak during several hours, the solvent was removed by evaporation in a vacuum. Throughout the operations, care was taken to avoid oxidation of any of the ingredients of the blends, since oxidation of any one of them adversely affects the quality of the coke yielded (compare Parr and Hadley, *Univ. Illinois Bull.*, 76, 1914). The test employed was that commonly used when attempting to assess the coking-value of a coal, *viz.*, the standard crucible test for the determination of " volatile matter " (" Interim Report on Methods of Analysis of Coal, 1923," Fuel Research Board, Survey Paper No. 2, H.M. Stationery Office). As an example of the results, we may quote those obtained when the coal used for the tests was Parkgate A clarain, which gives a good quality coke in practice. The following observations were made :

A blend of the separated α-, β-, and γ-compounds, in the proportions in which they were obtained from the coal, gave a hard, well-sintered coke-button of nearly the same character as did a sample of the original coal, showing that the α- and β-compounds had not suffered any material change during their separation.

A blend of the α- and β-compounds with only the γ_1-fraction gave in most of the tests a hard, well-sintered coke-button. A rather friable residue was occasionally obtained, which may be attributed to the fact that it is difficult to obtain satisfactory admixture of the extracted coal and this oily extract—there is a tendency for the extract to remain on the surface of the coal and to be volatilised during the coking test before it has been able to exert its agglutinating action. All such tests necessarily suffer from the fact that they do not reproduce exactly the original conditions of existence of the extracted material within the coal substance.

A blend of the α- and β-compounds with the γ_2-fraction gave a hard, well-sintered, and slightly swollen coke-button.

A blend of the α- and β-compounds with either the γ_3- or the γ_4-fraction gave a barely coherent residue, easily powdered between the fingers.

A discussion of the conditions necessary for the production of a good commercial coke would be out of place in this journal, but it may be said that, with regard to the composition of the coal, success does not rest solely on the use of a coal containing a sufficiency of some " coking principle." In so far as the presence of a " coking principle " is necessary, the conclusion can be drawn from this research that the agglutinating medium during coke-formation consists of the resins and hydrocarbons contained in the coal or is yielded by those resins and hydrocarbons during the early stages of heating in the coke-oven.

The Treatment of Bituminous Coals with Benzene.

Under atmospheric pressure, boiling benzene removes very little from most bituminous coals, but under higher pressures it apparently dissolves more. The most important researches in which this method of treating coal has been employed are those of Fischer, Broche, and Strauch (*Brennstoff-Chem.*, 1924, **5**, 299; 1925, **6**, 33), following preliminary experiments of Fischer and Gluud (*Ges. Abh. Kennt. Kohle*, 1916, **1**, 54), who found that at a pressure of 50 atms. (b. p. of benzene about 288°), a bituminous coal yielded, after several treatments, as much as 6·7% of extract.

Fischer, Broche, and Strauch have indicated an important relationship between the character of the substances extractable by benzene under pressure and that of the coal treated, which may throw light on the character of the coalification process. Briefly, they suggest that their work shows that with increasing geological age of the coals the ratio of free hydrocarbons to resins increases, whilst the decomposition temperatures of the resins are raised.

We considered it important to institute a comparison between the substances obtained by resolving a coal with pyridine and chloroform and what may be termed "pressure-benzene" extracts such as those described by Fischer, Broche, and Strauch. We therefore carried out experiments on a number of bituminous coals in a similar manner. As a preliminary, we wished to know the effect, if any, of preheating a bituminous coal in an inert atmosphere at 250—280° on the amount of extractable matter it would subsequently yield to benzene or chloroform in the cold, Harger (*loc. cit.*) having stated that preheating at as low a temperature as 200° has the effect of greatly increasing the amount soluble in chloroform. We therefore sought this information from Mr. H. Berry, of the staff of the Fuel Research Board, who has been carrying out such experiments, and we have the permission of the Director of Fuel Research to quote some of his results (see Table VI).

TABLE VI.

The Effect of Preheating Bituminous Coal on its Solubility in Chloroform and Benzene. (H. BERRY.)

Extractable matter (% on ash-free, dry coal).

Coal.	Parkgate Brights.*		Parkgate Hards.†		Barnsley Brights.*		Barnsley Hards.†	
Solvent.	$CHCl_3$.	C_6H_6.	$CHCl_3$.	C_6H_6.	$CHCl_3$.	C_6H_6.	$CHCl_3$.	C_6H_6.
Without preheating.	1·45	0·37	1·39	0·50	0·73	0·31	1·15	0·59
After preheating at 200°	1·01	0·41	1·56	0·73	0·86	0·15	1·45	0·53
After preheating at 250°	2·75	0·54	2·72	0·71	1·20	0·30	2·37	0·34
After preheating at 350°	5·88	1·35	4·63	1·61	5·15	0·68	4·44	1·27

* *I.e.*, clarain and vitrain. † *I.e.*, durain.

It would thus seem that a change in a bituminous coal, which may be decomposition of some ingredient, is effected by heating at temperatures higher than 200°. In the work on the coking power of coal by Fischer, Broche, and Strauch (who were well aware of this effect of preheating), its incipient decomposition was of little moment, but we were anxious to remove the extractable matter unchanged, for comparison with the γ-compounds. Our first pressure-benzene extractions were therefore made at 200°.

The coals were ground to pass a 10- and remain on a 40-mesh sieve, and were dried in a vacuum. The extractions were carried out in an autoclave in an atmosphere of nitrogen, 4 or 5 successive treatments of each coal with pure benzene being made. After removal of the benzene, the extracts were obtained as dark brown, viscous solids. The following results, obtained with Parkgate A clarain, can be regarded as typical.

Treatment of Parkgate A Clarain with Benzene.—(*a*) *At* 200°. The extract amounted to 5·96% of the coal. This was fractionated according to the scheme adopted for the γ-compounds, and yielded :

	% of coal.
Soluble in light petroleum.	2·22 (C, 85·0; H, 9·0.)
Soluble in ethyl ether.	2·02 (C, 84·0; H, 6·8.)
Insoluble in ethyl ether.	1·72 (C, 82·5; H, 5·95.)

In physical character and general chemical properties the substances were similar to the corresponding fractions of the γ-compounds.

These results should be compared with those recorded in Table II, from which it will be seen that the pressure-benzene extraction at 200° has removed all the hydrocarbons but has left a proportion of the resins and resin-like substances undissolved. These were removed from the coal residue in the autoclave by extracting it in a Soxhlet apparatus with pyridine and treating the extract with chloroform, 1·1% of soluble material being obtained. This was partly soluble in ethyl ether, the proportions, expressed as percentages on the original coal, being : ether-soluble, 0·66 (C, 82·0 ; H, 6·8%), and ether-insoluble, 0·44 (C, 80·0; H, 6·2%). The total amount extracted from the Parkgate A clarain by treatment with benzene at 200°, followed by resolution with pyridine and chloroform, was thus 7·06%, a figure which compares closely with the percentage of γ-compounds (6·9) obtained from this coal by direct resolution with pyridine and chloroform.

(*b*) *At* 285°. In order to compare our results more closely with those of Fischer, Broche, and Strauch, we now extracted a sample of the same coal with benzene at 285°, using 6 successive treatments in the autoclave. The extract amounted to 7·3% on the ash-free, dry coal. It was fractionated with light petroleum and ether and yielded (per cent. on the original coal) : soluble in light petroleum, 2·55 (C, 85·4; H, 9·2); soluble in ether, 1·97 (C, 84·2; H, 7·3); insoluble in ether, 2·78 (C, 79·4 ; H, 5·8). Resolution of the residual coal from the autoclave with pyridine and chloroform yielded a small quantity of material (about 0·7% on the coal) completely soluble in ether.

The higher temperature of extraction thus appears to have caused decomposition of part of the resins, with the result that the proportions of hydrocarbons and resin-like material insoluble in ether have been increased. Some other part of the coal-substance also seems to have been decomposed. A direct comparison of the different fractionations (Table VII) will make this clear.

TABLE VII.

	Resolution by pyridine and chloroform.	Pressure-benzene extraction.	
		at 200°.	at 285°.
Soluble in light petroleum (hydrocarbons).	2·30[*] (C, 83·9; H, 9·0.)	2·22 (C, 85·0; H, 9·0.)	2·55 (C, 85·4; H, 9·2.)
Soluble in ethyl ether (resins).	2·54 (C, 82·7; H, 6·9.)	2·02[†] (C, 84·0; H, 6·8.)	1·97[†] (C, 84·2; H, 7·3.)
Insoluble in ethyl ether (resin-like substances).	2·06 (C, 79·5; H, 5·8.)	1·72[‡] (C, 82·5; H, 5·6.)	2·78 (C, 79·4; H, 5·8.)
Total.	6·90	5·96	7·30

[*] Contains 20% of resins, owing to prolonged Soxhlet extraction.

[†] On adding the ether-soluble fractions (0·66 and 0·7%, respectively) obtained on resolving the residue from the autoclave with pyridine and chloroform, these figures become 2·68 and 2·67%, respectively.

[‡] On adding the ether-insoluble fraction (0·44%) obtained on resolving the residue from the autoclave with pyridine and chloroform, this figure becomes 2·16.

The method used by Fischer, Broche, and Strauch to fractionate their pressure-benzene extracts was to pour them into light petroleum, causing separation of insoluble solids, which they termed *Festbitumen.* On filtering these off and evaporating the light petroleum, viscous oils (*Ölbitumen*) were obtained. From our results it will be realised that this method effected a separation of the hydrocarbons from the resins and the resin-like compounds, probably a better separation than in our experiments, since our prolonged extraction with light petroleum in a Soxhlet apparatus dissolved some of the resins. Particular interest therefore attaches to their deduction that the former increase in amount, at the expense of the latter, with the geological age of the coal. The principal data on which this deduction is founded are recorded in Table VIII.

In conformity with the higher proportions of hydrocarbons removable from the older coals, their pressure-benzene extracts as a whole were more mobile, the most mobile being that obtained from a Ruhr anthracite (not included in Table VIII). The results certainly suggest a gradual increase in the proportion of hydrocarbons contained in the coal as the process of coalification proceeds, if it is considered that no thermal decomposition has occurred at the high temperature of extraction employed. We can make no statement on this point regarding the German coals, but we can affirm that with all the British coals we have tested appreciable decomposition takes place, hydrocarbons being produced at the expense of resins (see, *e.g.*, Table VII). Apart from this disadvantage, we cannot

TABLE VIII.

Treatment of Different Coals with Benzene at 285°.

(Fischer, Broche, and Strauch.)

	Percentages on ash-free, dry coal.		
Description of coal.	Total extract.	Hydrocarbons (Ölbitumen).	Resins and resin-like compounds (Festbitumen).
Dilsburg, Saar.	1·98	1·04	0·94
C, 74·3; H, 5·3.	(C, 84·5; H, 7·9.)	(C, 89·3; H, 9·6.)	(C, 87·0; H, 6·5.)
Lohberg, Ruhr.	4·60	2·48	2·12
C, 79·3; H, 5·6.	(C, 87·6; H, 7·0.)		
Altenwald, Saar.	4·56	2·55	2·01
C, 85·5; H, 6·7.	(C, 86·3; H, 6·7.)		
Dudweiler, Saar.	7·76	5·10	2·66
C, 86·5; H, 5·2.	(C, 87·9; H, 6·7.)		
Prosper, Ruhr.	7·45	(Not determined.)	
C, 88·3; H, 5·2.	(C, 91·3; H, 6·9.)		
Osterfeld, Ruhr.	5·0	3·40	1·60
C, 89·5; H, 5·8.	(C, 91·6; H, 6·9.)		
Thyssen, Ruhr.	7·60	5·10	2·50
C, 90·3; H, 5·4.	(C, 88·5; H, 6·7.)	(C, 92·2; H, 7·2.)	(C, 89·6; H, 6·1.)

regard pressure-benzene extraction as a satisfactory method of resolving British bituminous coals, for it does not appear to be equally effective with all. For example, the Hamstead clarain, which was found to contain 5·0% of γ-compounds on resolution with pyridine and chloroform, only yielded 1·6% of extractable matter to benzene at 200° and 4·5% at 285°. At the latter temperature, marked thermal decomposition took place.

Fischer, Broche, and Strauch's method of pressure-benzene extraction has been employed for several coals by Bone, Pearson, and Quarendon (*Proc. Roy. Soc.*, 1924, *A*, **105**, 608). Having poured the benzene extract into light petroleum, the last-named authors fractionated the *Ölbitumen* with benzene-free light petroleum and the *Festbitumen* with ethyl alcohol, thus obtaining four portions which they describe as follows : " (I) A yellowish-brown, non-nitrogenous portion soluble in light petroleum. (II) A nitrogenous reddish-brown solid, of low softening point, soluble in a mixture of 4 parts of light petroleum and 1 part of benzene. (III) A non-nitrogenous resinous portion. (IV) A group of nitrogenous bodies of ' humic ' type " (*loc. cit.*, p. 613).

The main reason for describing fraction IV as " humic " (a synonym for ulmic) appears to have been that it contained 1·1—1·5% of nitrogen. Be that as it may, this fraction should correspond with our γ_3- and γ_4-fractions, if ethyl alcohol were an effective solvent for coal-resins. In our experience, this seemed doubtful. We therefore subjected pressure-benzene extracts of the Parkgate A clarain to fractionation according to a variant of Bone, Pearson, and Quarendon's scheme, with the following results :

Extraction with Benzene.—(*a*) *At* 200°. Total extract, 6·00. Soluble on pouring into light petroleum, 2·00; soluble in ethyl alcohol, 0·90; insoluble in ethyl alcohol, 3·10, all as % on the ash-free, dry coal. The alcohol-soluble fraction was similar in character to the ether-soluble fraction obtained from the pressure-benzene extract at 200° previously described, but was less in quantity (see Table VII). The fraction insoluble in ethyl alcohol was now extracted with ethyl ether, resins amounting to 1·4% of the coal dissolving.

(*b*) *At* 285°. Total extract, 7·29. Soluble on pouring into light petroleum, 2·30; soluble in ethyl alcohol, 1·00; insoluble in ethyl alcohol, 3·99, all as % on the ash-free, dry coal. On extracting the alcohol-insoluble material with ether, resins amounting to 1·22% of the coal dissolved.

These results are summarised in Table IX and should be compared with those given in Table VII.

TABLE IX.

Fractionation of Pressure-Benzene Extracts of Parkgate A Clarain.

(% of ash-free, dry coal).

	Extracted at 200°.		Extracted at 285°.	
Soluble in light petroleum.	2·00 (C, 86·2; H, 9·1.)		2·30 (C, 85·9; H, 9·4.)	
Soluble in ethyl alcohol.	0·90 (C, 83·2; H, 6·75.)	2·30	1·00 (C, 83·4; H, 6·8.)	2·22
Soluble in ethyl ether.	1·40 (C, 84·5; H, 6·9.)		1·22 (C, 84·5; H, 7·2.)	
Insoluble.	1·70 (C, 82·6; H, 6·0.)		2·77 (C, 80·1; H, 5·9.)	

The fraction of the Parkgate A clarain which would be described by Bone, Pearson, and Quarendon as "humic" (fraction IV) thus contained about 30—45% of resins; the remainder was what we have termed resin-like.

The research of Bone, Pearson, and Quarendon, like that of Fischer, Broche, and Strauch, deals with the probable importance of the various fractions of the pressure-benzene extracts as regards the coking power of the coals containing them. We propose to discuss this subject in detail in a communication to a technical journal, but may here note that Bone, Pearson, and Quarendon correlate the coking power of a coal with its content of that portion of the pressure-benzene extract (at about 285°) insoluble in light petroleum and ethyl alcohol (their " Fraction IV "). We have shown that this fraction (in the coals that we have examined) consists of two classes of compounds—resins, soluble in ethyl ether, and compounds, allied to the resins, insoluble in that solvent. " Fraction IV," from the Parkgate A clarain, contains about 30% of ether-soluble and 70% of ether-insoluble compounds, but in this material from other bituminous coals the proportions are different. Apart from general considerations regarding the coking process, into which we need not here enter, it is therefore difficult to attach value to an apparent relationship between the coking power of a coal and its content of such indefinite constituents (or, in part, products of thermal decomposition).

The observations of Fischer, Broche, and Strauch on the change in character of the substances extractable from a coal with its geological age, or degree of coalification, seem to us to require, and to merit, amplification. We have therefore undertaken an examination of a series of coals, from the same seam, of increasing carbon content, adopting the method of resolution described in the first portion of this paper.

Much of the information contained in this paper was obtained during the course of an investigation that we are carrying out for the Safety in Mines Research Board, to whom we are indebted for permission to utilise it. Our thanks are also due to Mr. A. L. Godbert for a number of the data employed.

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