CCCXC.—Studies in the Composition of Coal. The Rational Analysis of Coal.

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A RATIONAL analysis of any coal can be given in terms of the proportions of free hydrocarbons, resinous compounds, organised plant entities, and ulmin compounds that it contains (see, e.g., Cockram and Wheeler, J., 1927, 700), for these are the principal ingredients of the coal substance and they have characteristic properties. Such an analysis is not sufficient, however, to specify completely the quality of the coal, for the ulmin compounds, of which it is mainly composed, are not identical in character in all coals. We have, in fact, shown (J., 1925, 127, 2236) that the properties of the ulmin compounds, which exist in all coals, from lignites to anthracites, are modified by progressive changes in molecular arrangement. When first formed by the decay of vegetable tissues, the ulmins are readily soluble in alkaline solutions, but the further the "coalification" of the material proceeds the less is its natural content of soluble ulmins and the less easily can such ulmins be " regenerated " by oxidation processes (see Safety in Mines Research Board, Paper No. 28, 1926).

Coals can differ from each other in respect of (1) the proportions and (2) the properties of their ingredients. There is sufficient evidence, which cannot be detailed here, that the chemical compositions of the free hydrocarbons, resinous compounds, and organised plant entities (e.g., spore exines and cuticular tissues) do not vary much whether those bodies form part of a lignite, a bituminous coal, or a semi-anthracite. Certainly they do not vary sufficiently to account for the wide differences in properties of such coals. On the other hand, the composition of the ulmin compounds does vary widely, dependent upon the coals from which they are obtained, by reason of differences both in the external groupings of the large and complicated molecule and in its internal, or nuclear, structure.

A preliminary study of a series of coals suggested that a measure of the difference in character as between the ulmin compounds of two coals could be obtained by determining their reactivity; for example, as regards oxidation, from the proportion rendered soluble in alkalis after their subjection to limited oxidation under standard conditions. Such a measure, a "reactivity index" for the ulmins, should be sufficient, in addition to a rational analysis, to specify a coal so that its general properties would be discernible.

We have tested this suggestion by the examination of a series of coals from the same seam, the Pittsburgh seam of the United States of America. Some of the samples were obtained through the courtesy of Dr. David White, of the U.S. Geological Survey, who himself collected them; others were collected by one of us in person. The advantage of carrying out a study of this kind on coals from the same seam lies in the elimination of a possible complication due to wide differences in character of the vegetation from which the coals were formed.

The Pittsburgh seam extends conformably over wide areas in Pennsylvania, Ohio, West Virginia, and Maryland, and the coal varies in carbon content from 78% at its westernmost limit, where it is a sub-bituminous coal (Seyler's ortho-per-lignitous) to 90% in the Georges Creek region of Maryland, where it is a semi-anthracite (Seyler's sub-meta-bituminous). When the coal measures of the Allegheny formation were deposited, there existed over these areas a vast coastal plan, or an area of subsidence, upon which a series of almost continuous stretches of vegetation accumulated, each in turn to be gradually covered by detrital matter carried by the encroachment of water (see White, Bull. 38, U.S. Bureau of Mines, 1913). The Pittsburgh seam, which lies above the coals of the Allegheny formation, was formed under similar conditions. The variations in composition of the seam would thus appear to be due mainly to changes in temperature and pressure caused by earth movements during the coalification process.

In addition to the Pittsburgh seam, coals were collected from the lignite fields of Montana, North Dakota, and Wyoming, from the bituminous fields near Price, in Utah, and from the Yampa Valley in Colorado, where local earth movements have transformed coals of comparatively recent formations into semi-anthracites. With the coals of the Pittsburgh seam, the earth movements responsible for their regional metamorphism were those resulting in the Alleghenv mountains, the greatest upheavals being in the George's Creek district of Maryland (e.g., the Ocean coal) and the least in Ohio (e.g., the Bailey's Mills coal). In Montana and North Dakota, the earth movements which caused the change of rank of the coals were those which formed the Rocky Mountains. In places where the uplift of the mountains was not felt, as in North Dakota, the coal is a lignite. There is a general tendency for the rank of the coal to increase in a westerly direction (toward the Rocky Mountains), whilst it is highest in the neighbourhood of local upheavals.

The method of examination, in addition to the usual forms of analysis and the determination of the proportions of the principal ingredients, has been to measure the reactivity with oxygen of the ulmin constituents. This has been done both directly, from the amount of oxygen combining with them in a given time, and indirectly from the rate of production of alkali-soluble ulmins under standard treatment with an oxidising agent. It has been found that the order of reactivity of the ulmins as measured by each method is substantially the same. In Table I the rational analyses of the coals examined are recorded, together with their carbon contents. A "reactivity index" for the ulmins (obtained as described in the experimental part of this paper) is also included, and the coals are arranged (those of the Pittsburgh seam being grouped together) in two groups of decreasing reactivity.

In the rational analyses, the hydrocarbons and resins have been grouped together. These are oil-yielding constituents of high hydrogen content, and their presence in the coal in suitable amount affects (but is not wholly responsible for) its coking power. There is no general relationship between the quantity of hydrocarbons and resins extractable from a coal and its age or degree of coalification; nor is this to be expected, since the concentration, in the original coal-forming materials, of the substances that yielded them must have been to a certain extent accidental. Their quality also (e.g., in the Pittsburgh seam) is but little altered by such changes of conditions as have had a marked effect on the ulmins.

TABLE I.

Rational Analyses of Coals.

	1000	ondi anarysi	., /0.		
	Hydro- carbons	Organised		Reactivity	Carbon, %, on
NT (1			TT1		ash-free,
					dry coal.
					$78 \cdot 9$
					81.1
Elm Grove	6.4			56.7	81.1
Monongah†	$5 \cdot 0$		84.7	47.0	83.3
Irwin	$3 \cdot 9$	8.0	88.1	45.0	84.5
Revere*	3.5	9.2	87.3	42.5	86.1
Greensburg	4.5	15.3	80.2	41.5	86.7
Trotter	3.7	$15 \cdot 1$	81.2	39.6	87.6
Revere†	$7 \cdot 8$	10.4	87.3	31.2	85.2
Martin	7.4	13.0	79.6	30.2	84.8
Scotch Hill	$4 \cdot 4$	8.7	86.9	29.2	85.2
Berkley	1.0	13.8	85.2	20.0	87.6
Jamison	$3 \cdot 2$	8.8	88.0	16.0	86.5
Vogele†	$2 \cdot 3$	13.3	84.4	14.0	86.6
Vogele*	1.6	2.7	$95 \cdot 7$	12.0	87.4
Seal†	2.7	12.5	84.8	10.0	89.1
Ocean*	< 1	9.5	89.5	5.0	89.0
* Bottom part	of seam.		† Top 1	part of seam.	
(Wvodak	3.8	$5 \cdot 1$	91.1	80.0	71.9
	4.9	14.4	80.7	71.2	78.4
Hotchkiss	3.4	1.3	95.4	70.0	73.4
. Milk River	3.8	3.8	92.4	68.5	$73 \cdot 4$
Pinnacle	4.1	12.4	83.5	55.3	79.1
Owl Creek		5.3	91.0	54.3	77.0
S King		7.0	87.3	53.2	80.7
Gantar					78.4
					74.6
					81.5
Sunnyside	5.7	4.0	90.3	48.0	82.5
	Monongah† Irwin Irwin Revere* Greensburg Irotter Trotter Revere† Martin Berkley Jamison Vogele† Vogele† Sealt Ocean* Revere* Wyodak Martin Wadge Hotchkiss Martin Ocean* King Owl Creek Gantar Colstrip Castlegate Colstrip	$\begin{array}{c} & \begin{array}{c} & & & & & & & & & & & & & & & & & & &$	$\begin{array}{c} Hydro-carbons & Organised \\ and & plant \\ resins. & entities. \\ Bailey's Mills* 5·4 & 8·7 \\ Skillcross 3·1 & 9·7 \\ Elm Grove 6·4 & 7·6 \\ Monongah† 5·0 & 10·3 \\ Irwin 3·9 & 8·0 \\ Revere* 3·5 & 9·2 \\ Greensburg 4·5 & 15·3 \\ Trotter 3·7 & 15·1 \\ Revere† 3·7 & 15·1 \\ Revere† 3·7 & 15·1 \\ Revere† 3·7 & 16·4 \\ Martin 7·4 & 13·0 \\ Scotch Hill 4·4 & 8·7 \\ Berkley 1·0 & 13·8 \\ Jamison 3·2 & 8·8 \\ Vogele† 2·7 & 12·5 \\ Ocean* 2·7 & 12·5 \\ Ocean* <1 & 9·5 \\ * Bottom part of seam. \\ \hline \begin{array}{c} Wyodak 3·8 & 5·1 \\ Wadge 4·1 & 12·4 \\ Owl Creek 3·7 & 5·3 \\ King 5·7 & 7·0 \\ Gantar 4·0 & 9·2 \\ Colstrip 2·2 & 11·5 \\ Castlegate 5·8 & 11·6 \\ \end{array}$	$\begin{array}{c} \mbox{carbons} & \mbox{Organised} \\ \mbox{and} & \mbox{plant} \\ \mbox{plant} \\ \mbox{Name of coal.} & \mbox{resins.} & \mbox{entities.} & \mbox{Ulmins.} \\ \mbox{Bailey's Mills*} & 5\cdot4 & 8\cdot7 & 85\cdot9 \\ \mbox{Skillcross} & & 3\cdot1 & 9\cdot7 & 87\cdot2 \\ \mbox{Elm Grove} & & 6\cdot4 & 7\cdot6 & 86\cdot0 \\ \mbox{Monongah}^{\dagger} & & 5\cdot0 & 10\cdot3 & 84\cdot7 \\ \mbox{Irwin} & & 3\cdot9 & 8\cdot0 & 88\cdot1 \\ \mbox{Revere*} & & 3\cdot9 & 9\cdot2 & 87\cdot3 \\ \mbox{Greensburg} & & 4\cdot5 & 15\cdot3 & 80\cdot2 \\ \mbox{Trotter} & & 3\cdot7 & 15\cdot1 & 81\cdot2 \\ \mbox{Revere}^{\dagger} & & 7\cdot4 & 13\cdot0 & 79\cdot6 \\ \mbox{Scotch Hill} & & 4\cdot4 & 8\cdot7 & 86\cdot9 \\ \mbox{Berkley} & & 1\cdot0 & 13\cdot8 & 85\cdot2 \\ \mbox{Jamison} & & 3\cdot2 & 8\cdot8 & 88\cdot0 \\ \mbox{Vogele}^{\dagger} & & 3\cdot2 & 8\cdot8 & 88\cdot0 \\ \mbox{Vogele}^{\dagger} & & 2\cdot3 & 13\cdot3 & 84\cdot4 \\ \mbox{Vogele}^{\ast} & & <1 & 9\cdot5 & 89\cdot5 \\ \mbox{* Bottom part of seam.} & ^{\dagger} \mbox{Top } \\ \mbox{Wadge} & & 3\cdot8 & 3\cdot8 & 92\cdot4 \\ \mbox{Milk River} & & 3\cdot8 & 3\cdot8 & 92\cdot4 \\ \mbox{Milk River} & & 3\cdot7 & 5\cdot3 & 91\cdot0 \\ \mbox{King} & & 5\cdot7 & 7\cdot0 & 87\cdot3 \\ \mbox{Gantar} & & 4\cdot0 & 9\cdot2 & 86\cdot8 \\ \mbox{Colstrip} & & 2\cdot2 & 11\cdot5 & 86\cdot3 \\ \mbox{Castlegate} & & 5\cdot8 & 11\cdot6 & 82\cdot6 \\ \end{tabular}$	$\begin{array}{c} \hline Hydro-carbons Organised and plant index of and plant index of Name of coal. resins. entities. Ulmins. ulmins. (Bailey's Mills* 5·4 8·7 85·9 61·5 Skillcross 3·1 9·7 87·2 58·8 Elm Grove 6·4 7·6 86·0 56·7 Monongah† 5·0 10·3 84·7 47·0 Irwin 3·9 8·0 88·1 45·0 Revere* 3·5 9·2 87·3 42·5 Greensburg 4·5 15·3 80·2 41·5 Trotter 3·7 15·1 81·2 39·6 Revere† 3·2 8·8 88·0 16·0 Vogele† 2·7 12·5 84·8 10·0 Ocean* <10 13·8 85·2 20·0 Jamison 3·2 8·8 88·0 16·0 Vogele† 2·7 12·5 84·8 10·0 Ocean* <10 9·5 89·5 5·0 * Berkley 1·6 2·7 9·5 7 12·0 Seal† 2·7 12·5 84·8 10·0 Ocean* <10 9·5 89·5 5·0 * Bottom part of seam. † Top part of seam. $$ Ring 4·0 9·2 86·8 55·3 0 Owl Creek 3·7 5·3 91·0 54·3 $$ Si 2·1 Colstrip 2·2 11·5 86·3 50·5 $$ Costelgate 5·8 11·6 82·6 49·0 $$ Pinnacle 5·8 11·6 82·6 49·0 $$ Pin$

Rational analysis, %.

They remain soluble in organic solvents, for example, except in that part of the seam that has been subjected to extreme tectonic disturbance, as in the Westmoreland and Somerset Counties of Pennsylvania and the George's Creek region of Maryland. In the samples obtained from these regions (the Vogele, Berkley, and Ocean Mines, Table I), the proportions of chloroform-soluble material have greatly diminished, and it can be assumed that the effects of the violent earth movements have been either to remove part of the hydrocarbons and resins (by distillation) or to render them insoluble.

Similarly, there is no connexion between the degree of coalification of the seam and the proportion of organised plant entities that it may contain. In the Pittsburgh seam the proportions of these bodies (which other researches have shown to be extremely resistant to decay and to the processes of coalification) vary at haphazard between 3 and 16%, dependent no doubt, as with the resins, on their original, accidental, concentration in the coalforming materials. The spore exines and cuticular tissues, which form the bulk of the morphologically organised plant entities, are of high hydrogen content and are oil-yielding constituents of the coal, the oils consisting mainly of paraffins and unsaturated hydrocarbons.

Regarding these non-ulmic organic constituents as impurities, it is desired to trace a relationship between the "reactivities" of the ulmin constituents and the chemical compositions of the coals as determined by ultimate analysis. It will be understood that, since the proportions of the non-ulmic constituents, of higher hydrogen content than the bulk of the coal, vary between rather wide limits (4.6-23.2%) in the Pittsburgh seam), any such relationship can only be partial. The percentage of carbon, being high throughout the series of coals, should be least affected by the presence of varying quantities of materials of high hydrogen content. Table I shows that there is, in fact, a general relationship between the carbon content of the coal as a whole and the "reactivity" of the ulmins it contains, a relationship which is remarkably close when, in addition to the fact that the ultimate analysis shows no more than the mean carbon content of all the organic constituents of the coal, it is remembered that the accuracy of coal analyses, calculated, as is usual, on an ash-free, dry basis, suffers from the fact that the inorganic impurities differ in composition and amount from the ash they yield on incineration. For these reasons we consider the "reactivity index" of the ulmins to be a better measure of the degree of coalification than the carbon content of the coal as a whole can be, though the latter may often be a sufficiently close measure. For example, if care be taken to choose only the vitrain portion of a seam, the fact that this portion can readily be freed from all but a small percentage of mineral matter and is essentially free from spore exines and cuticles, causes the analysis to be nearly representative of the ulmin constituents alone. Thus, in Table II a comparison is made between the carbon contents of four coals and those of the vitrains separated from them. It will be seen that the "reactivity index" of the ulmins corresponds with the carbon content of the vitrain from the coal rather than with that of the coal as a whole.

What we have termed the "degree of coalification" of a coal is sometimes (following David White, e.g., U.S. Bureau of Mines, Bull. No. 38, 1913) termed its "rank," a coal of lowest rank being one in which the processes of coalification (in whatever way induced, *i.e.*, whether by time, temperature, or pressure) have had least result, and a coal of highest rank one in which such processes have

TABLE II.

		, on ash-free, dry coal.	Reactivity index of
Name of coal.		Vitrain portion only.	ulmins.
Trotter	87.6	85.4	39.6
Revere (bottom)	86.1	85.9	42.5
Revere (top)	$85 \cdot 2$	86.5	31.2
Jamison	86.5	87.2	16.0

been the most effective. We have shown elsewhere (loc. cit.) that the external groupings of the ulmin molecules are modified with increasing rank of the coal. The present work affords additional evidence of this. From the results in Table III, which records the amounts of oxygen that combined with the coals at 150° (one method of determining the reactivity of the ulmins), it will be seen that the ratio between the oxygen that remained combined with the coal and the total consumed increases as the rank of the coal increases. In order that a given quantity of oxygen shall combine with an ulmin of low rank (forming acidic groupings), a greater total quantity must be consumed than with a high-rank ulmin. presumably because the nuclear groupings of the ulmin molecule of low rank are of smaller mass in comparison with that of the external groupings. These external groupings are the first points of attack by the oxygen (yielding water and oxides of carbon), and they confer high reactivity on the low-rank ulmins.

As the rank of the ulmins increases, the amount of oxygen that must combine with them, forming acidic groupings which confer on them solubility in alkaline solutions, also increases, whilst the ratio C: O in the soluble ulmins produced becomes greater (see Table III). This suggests that the nuclear structure of the ulmin molecules increases in magnitude with their rank, and that polymerisation or condensation takes place during the coalification process.

An important inference to be drawn from the examination of the Pittsburgh seam is that all coal ulmins which have the same "reactivity index" are alike in constitution and properties. Exceptions are apparent amongst coals of younger formations, explicable by reason of the widely distant geological periods during which the coal-forming materials accumulated, but there seems no reason why coals from the upper (and, perhaps, the middle) carboniferous period should differ materially in character from those of the Pittsburgh seam. For any such coal, a determination of the "reactivity index" of the ulmins, together with an estimation of the principal ingredients, should give more valuable information as to its properties than other forms of analysis. We are accumulating such data with regard to a number of British coals, using the methods now to be described.

EXPERIMENTAL.

For convenience, the coals are identified by the name of the mine at which the seam is worked. The positions of the mines are recorded in Table VI. The Pittsburgh seam varied in thickness from 4 to 10 ft., the others from 6 to 80 ft. With few exceptions (recorded in Table I), the samples, of about 10 lb. weight, were taken from the middle of the seam at a newly-exposed face. The blocks of coal were immediately wrapped in sheets of lead foil to prevent exposure to the air. In the laboratory, the coarsely ground samples were dried in a vacuum oven and extracted with pyridine in large Soxhlet apparatus in an atmosphere of nitrogen, and the γ_1 - and γ_2 -fractions separated by treatment with chloroform. The α - and β -compounds were then dried in a vacuum at 105°, ground, and sieved. All the oxidation experiments were made on samples so treated.

Rate of Oxidation.—To determine the rates of oxidation of the samples, 10 g. of each, sieved so as to pass a 100- and remain on a 200-mesh sieve (Tyler U.S. standard), were placed in glass tubes in a constant-temperature oven at 150° , and pure dry air was drawn through them for several weeks. The time taken for complete conversion of the coal ulmins into alkali-soluble compounds varied with the character of the coals, being as long as 40 weeks for those of highest carbon content. The quantities of water and oxides of carbon formed during the reaction were measured, as well as the changes in weights of the coals. The amounts of oxygen that remained combined with the residues, and the total oxygen consumed, could thus be estimated. The results for the first two weeks are recorded in Table III, the amounts of oxygen being expressed in c.c. per g. of ulmins free from unoxidisable plant entities and mineral matter.

So far as the coals of the Pittsburgh seam are concerned, their carbon contents follow closely the rates of oxidation of the ulmins, but amongst the other coals there are notable exceptions. For example, the ulmins of Colstrip coal react with less oxygen in a given time than do those from Wadge coal, though the carbon content of the former coal is the lower by 4%. There are possibilities of experimental error with such low-rank coals, both in the analyses, because of their high moisture contents, and in the measurements of rates of oxidation, because their avidity for oxygen might cause them to absorb appreciable quantities during their preliminary treatment. From superficial examination of these coals, however, one would judge the Colstrip to be of lower rank than the Wadge, the former having the dark brown, streaky appearance characteristic of sub-bituminous coals, and the latter being a brilliant black.

2973

TABLE III.

Atmospheric Oxidation.

Volumes of oxygen consumed (c.c. per g. of coal ulmins). Temp., 150°. After 1 week After 2 weeks

20	After 1	week.	After 2	weeks.	, T	,
	Total	Com- bined	Total	Com- bined	Analy soluble	vsis of ulmins.
Name of coal.	con- sumed.	with coal.	con- sumed.	with coal.	C, %.	н, %.
Bailey's Mills		89	352	109	$63 \cdot 2$	3.1
Skillcross	243	72.5	319	95.5		<u> </u>
Elm Grove	236	89	310	109	$63 \cdot 1$	3.5
Monongah	228	83.5	305	104	63.6	3.3
Delmont	228	67	298	88		
Greensburg	$\bar{202}$	68	266	88	68.1	3.0
Martin	198	72	258	88.5	69.5	3.0
Revere (bottom)	196	67	264	90	68.6	3.0
Scotch Hill	194	67	261	86.5	66.3	3.3
Revere (top)	193	58			67.7	3.3
Trotter	193	58	256	78	68.9	2.8
Jamison	190	67	246	86	70.2	3.4
Vogele (top)	152	72	222	106	69.6	$2 \cdot 9$
Berkley	146	49	203	69	71.9	$2 \cdot 9$
Seal	137	50	196	74.5	$72 \cdot 1$	$2 \cdot 9$
Vogele (bottom)	136	59	193	78.5		·
Ocean	79	36	120	45.5	72.6	$2 \cdot 9$
Wyodak	331	$69 \cdot 5$	411	71.5	60.8	$2 \cdot 9$
Knife River	320	54	390	68	63.5	3.0
Milk River	308	65	372	67.5	59.7	$2 \cdot 9$
Wadge	285	71	391	97.5	62.7	3.0
Hotchkiss	274	52.5	327	55	61.5	$3 \cdot 1$
King	264	70	344	80.5	$63 \cdot 4$	3.0
Pinnacle	262	65	388	97		
Colstrip	259	64	356	88.5	62.0	3.0
Gantar	259	78.5	335	93.5	$62 \cdot 1$	$3 \cdot 0$
Castlegate	259	84	347	109	$65 \cdot 2$	$2 \cdot 0$
Sunnyside	254	60	327	75	$65 \cdot 6$	$3 \cdot 1$
Owl Čreek	245	66	327	73	61.2	$2 \cdot 9$

Rate of Formation of Soluble Ulmins.—(a) By atmospheric oxidation. Samples were exposed in thin layers in an air-oven at 150° for several weeks. At the end of each week 1 g. of each was withdrawn and extracted during $\frac{1}{2}$ -hour with 150 c.c. of a boiling 1%potassium hydroxide solution. The solutions were filtered while hot, and the ulmins precipitated by hydrochloric acid, filtered through tared papers, washed, dried, and weighed.

The results are recorded in Table IV. In order to compare the reactivities of the coals, it is convenient to calculate the times taken for 50% production of soluble ulmins, figures readily obtainable from the data recorded with an accuracy within 1%. The coals are arranged on this basis in Table IV in order of decreasing activity. The order is substantially the same as that given by their rates of oxidation (Table III), and it will be noticed that those coals, of the younger formations (Colstrip, Owl Creek, and

Gantar), which were there placed low in order of reactivity (for their carbon contents) are again so placed.

One marked discrepancy between Tables III and IV is caused by the Knife River coal, which was one of the youngest studied. In appearance it resembled dark brown wood, the seam containing complete tree trunks. When mined, its content of soluble ulmins was 24%, but on drying at 104° this was reduced to 4% (despite the fact that about 35% of moisture was driven off). Even this moderate temperature, therefore, caused either dehydration or condensation of the ulmin molecules, an effect which heating in air at 150° would no doubt intensify, despite the fact that soluble ulmins were simultaneously formed by oxidation. With such coals the rate of formation of soluble ulmins during atmospheric oxidation cannot be used as a measure of their rank.

TABLE IV.

Atmospheric Oxidation.

The rate of formation of soluble ulmins.

		Percent	age for	mation	of solu	ıble ulı	mins.		required for 50% form-
Time in weeks	í1	2	3	4	6	8	10	n	ation.
Name of coal									
Bailey's Mills		31.5	77.5		100				390
Skillcross	17	31	76			100*			395
Elm Grove		30	75		100				410
Monongah		24.5	72		100				425
Delmont		27.5	57.5	76	100		_		430
Greensburg		27	57			100			475
Trotter		26.5	54	75	100				480
Martin		20	52.5			100			495
Revere (bottom)		22	51		100		`		505
Revere (top)		19	$45 \cdot 5$	80		100			520
Scotch Hill		12.6	42		100				550
Jamison			21.5	55		100			650
Vogele (bottom)				16	72		100		915
Vogele (top)				16.5	69.5		100		925
Berkley	—			11.5	63			100	980
Seal					29	43	67†	100	1120
Ocean							<u> </u>	50	1800
* 7 w	eeks.					†	9 wee	ks.	
Wyodak	64	82	100 .						140
Hotchkiss	64	91	100						140
Milk River	56.5	94	100	—					150
Colstrip	37	82	100						225
Wadge	32	85		100					240
Owl Creek	17	51	77		100				332
Gantar	16	51	68.5		100				332
King	16.5	50	74.5	100			—		334
Castlegate	19	50	72	88	100				334
Pinnacle	17	49		90.5	100				340
Sunnyside		30.5	61.5	81	100				417
Knife River	20	40.5	60.5	1					468

2975

Hours

(b) By chemical oxidants. After a number of chemical oxidising agents had been tried, the most suitable was considered to be a mixture of hydrochloric acid and potassium chlorate (Hoffmeister's reagent). With this reagent a measure of the reactivity of the ulmins can be obtained fairly rapidly. The coals, freed from hydrocarbons and resins as previously described, were ground so as just to pass through a 150-mesh (Tyler U.S. standard) sieve, care being taken to avoid the production of fine dust. Several 0.5-g. samples of each of the treated coals were heated with 50 c.c. of \tilde{N} -hydrochloric acid and different weighed amounts of potassium chlorate in stoppered pressure bottles (370 c.c. capacity) in a bath of boiling water, during 6 hours. The bottles were allowed to cool over-night before being opened, and their contents were then filtered and the proportions of insoluble material determined. In recent work, this method has been modified in minor details.

A convenient measure of the reactivity of the coal ulmins, as determined by chemical oxidation, is given by the calculated percentage production of soluble products caused by 0.5 g. of potassium chlorate, such as is recorded in Table I as the "reactivity index." Such determinations may not be as accurate as those given by atmospheric oxidation, but they are more readily obtained, and for that reason we have chosen them for use in our table of "rational analyses." They are sufficiently accurate for practical purposes. This method of measuring the reactivity of the coal ulmins (see Table V) arranges the coals in nearly the same order as do the methods employing atmospheric oxidation, the younger coals, Colstrip, Owl Creek, and Gantar, again proving exceptions to the general relationship between reactivity and carbon content.

Determination of Hydrocarbons and Resins.—For some of the determinations, the usual method of separating the γ_1 - and γ_2 compounds (see Cockram and Wheeler, *loc. cit.*) was simplified. The coals were extracted with pyridine in Soxhlet apparatus, in an atmosphere of nitrogen, during 16 hours. The pyridine solution was concentrated to small bulk, excess of chloroform added, and the pyridine neutralised with dilute hydrochloric acid, thus causing precipitation of the insoluble β -compounds and the dispersed γ_3 and γ_4 -compounds. The γ_1 - and γ_2 -compounds, in solution, were estimated by evaporating off the chloroform and weighing.

Determination of Organised Plant Entities.—When the production of soluble ulmins is effected by atmospheric oxidation of the coals (freed from hydrocarbons and resins) at 150° , the determination of the proportion of organised plant entities is straightforward, for they, together with any mineral matter, constitute the residue remaining insoluble in alkaline solutions when the oxidation has

TABLE V.

Chemical Oxidation.

Percentage formation of soluble ulmins. Weight of KClO₃ used.

Name of coal.	0.25.	0.50.	0.75.	1.00.	1.25.	2.50.
Bailey's Mills	31.5	61.5				
Skilleross	30.0	$58 \cdot 8$				
Elm Grove	29.0	56.7				
Monongah		47.0	65.7			
Delmont		45.0	67.1			—
Revere (bottom)		42.5	57.9			
Greensburg		41.5	57.7			-
Trotter	Following	39.6	54.9			
Revere (top)			51.0	61.5		
Martin		30.2	50.0			
Seotch Hill			49.0	60.5		
Berkley					56.5	
Jamison				46.1		-
Vogele (top)		<u> </u>			49.0	
Vogele (bottom)					$44 \cdot 3$	
Seal					41.5	-
Ocean	—	_	—	-		66 ·0
Wyodak	48 •1	80.0			_	
Wadge	$39 \cdot 5$	71.2				
Hotchkiss	44.6	70-0				
Knife River	33.5	70.0				
Milk River	42.7	68.5				
Pinnacle	30.0	55.3				
Owl Creek	30.0	$54 \cdot 3$				—
King	30.0	$53 \cdot 2$	$64 \cdot 6$			
Gantar	25.0	$52 \cdot 1$				
Colstrip		50.5				
Castlegate		49 •0	$63 \cdot 8$			
Sunnyside	—	48.0	60.7		—	

been carried to completion. This takes several weeks, however, and some more convenient method of estimation is essential. As the result of extensive tests in comparison with the results obtained by atmospheric oxidation, the following procedure, which gives reasonably accurate estimations, was adopted.

A sample (0.5 g.) of the coal (freed from hydrocarbons and resins) was boiled during 7 hours under a reflux condenser with one or other of the solutions specified in the accompanying table, according to its carbon content.

Carbon content of coal	Oxidising solution.						
(% on ash-free, dry basis).	Nitric acid, c.c.	Water, c.c.	KClO ₃ , g.				
< 79	37.5(N)	12.5	Nil				
79-83	50 (N)	Nil	,,				
8386	30 (2N)	20	0.5				
86-88	35~(2N)	15	0.75				
88-89	40 (2N)	10	1.0				
89-90	50 (2N)	Nil	$3 \cdot 0$				

The ash-free material insoluble in potassium hydroxide solution after this treatment was estimated to be the resistant plant entities. With all the coals tested, the estimations showed fair agreement with those obtained by atmospheric oxidation of the coals.

This work has been carried out for the Safety in Mines Research Board in co-operation with the United States Bureau of Mines. We wish gratefully to acknowledge, in particular, the help given us by Dr. David White, by the staff of the U.S. Geological Survey, and by the analytical staff of the Bureau of Mines Experiment Station at Pittsburgh.

SAFETY IN MINES RESEARCH LABORATORIES, SHEFFIELD. [Received, August 21st, 1928.]

APPENDIX.

TABLE VI.

Coal Analyses.

	Moist-	dry coal.		Ultima	ate an	alysis, 9	%, on	
	ure, %,			ash-free, dry coal.				
	as re-	Volatile						
Coal.	ceived.	matter.	Ash.	С.	$\mathbf{H}.$	N.	s.	
Bailey's Mills*	$2 \cdot 0$	$43 \cdot 8$	13.5	78.9	$5 \cdot 9$	$1 \cdot 3$	4.4	
[Barnesville, Ohio]								
Elm Grove	$2 \cdot 2$	41.4	4.5	81.1	$5 \cdot 3$	$1 \cdot 6$	$3 \cdot 2$	
[Wheeling, W. Virg.]								
Skilleross, No. 2	$3 \cdot 0$	$42 \cdot 4$	$7 \cdot 8$	81.1	$5 \cdot 6$	$1 \cdot 4$	4.4	
[Wheeling, W. Virg.]								
Monongah, No. 63†	1.6	38.0	$4 \cdot 6$	83.3	$5 \cdot 6$	$1 \cdot 9$	0.6	
[Fairmont, Pa.]								
Irwin Strip	$1 \cdot 0$	$38 \cdot 5$	$5 \cdot 4$	84.5	$6 \cdot 0$	1.8	$2 \cdot 4$	
[Delmont, Pa.]	<u> </u>	00.1	- 0		~ ~		0.0	
Martin	0.4	39.1	$5 \cdot 6$	84.8	2.0	ca.1.5	0.9	
[Fairchance, Pa.]	0 7	91.0	0 7	050	~ ~	1.0	0.0	
Revere†	$3 \cdot 5$	31.6	8.7	85.2	$5 \cdot 5$	$1 \cdot 9$	0.8	
[Uniontown, Pa.]	1.2	94.9	3.6	85.2	$5 \cdot 2$	1.3	1.0	
Scotch Hill	1.2	$34 \cdot 2$	3.0	80.7	0.7	1.9	1.0	
[Newburg, W. Virg.] Revere*	3.6	30.6	5.9	86.1	5.4	1.8	0.7	
	9.0	30.0	9.9	00.1	9.4	1.0	0.1	
[Uniontown, Pa.] Jamison, No. 20	0.5	31.8	5.6	86.5	5.6	ca.1.5	0.8	
[Pleasant Unity, Pa.]	00	51 0	00	000	00	04.10	00	
Vogele†	$2 \cdot 9$	24.5	12.7	86.6	$5 \cdot 2$	1.9	2.5	
[Ligonier, Pa.]	- •							
Greensburg, No. 2	0.8	33.7	3.0	86.7	5.5	ca.1.5	0.9	
[Greensburg, Pa.]								
Vogele*	3.6	$24 \cdot 8$	14.3	87.4	$5 \cdot 4$	1.9	1.8	
[Ligonier, Pa.]								
Trotter	0.6	30.9	$6 \cdot 0$	87.6	6.7	ca.1.5	0.8	
[Connellsville, Pa.]								
Berkley	$3 \cdot 7$	20.6	10.3	87.6	$5 \cdot 0$	1.9	1.7	
[Meyersdale, Pa.]	·					• •	0.0	
Ocean†	0.8	17.5	6.3	89.0	4.7	$1 \cdot 9$	0.9	
Ocean† [Midland, Maryland]	o –	21 0	- 0	00.1	~ 1		10	
Seal [†]	$2 \cdot 7$	21.6	7.8	89.1	$5 \cdot 1$	$2 \cdot 1$	$1 \cdot 0$	
[Meyersdale, Pa.]								

* Bottom part of seam.

† Top part of seam.

TABLE VI (contd.).

	Moist- ure, %,			Ultimate analysis, %, on ash-free, dry coal.				
Coal.	as re- ceived.	Volatile matter.	Ash.	Ĉ.	н.	N.	s.	
Wyodak	31.1	43.7	7.7	71.9	5.4	$1 \cdot 2$	0.6	
[Gillette, Wyoming] Knife River [Beulah, N. Dakota]	35.0	41.9	7 ·0	72.9	4 ·9	1.1	1.1	
Milk River	26.4	38.2	9.6	$73 \cdot 4$	5.4	1.7	0.7	
[Chinook, Montana] Hotchkiss [Sheridan, Wyoming]	22.2	42.7	$5 \cdot 6$	73.4	6 ·0	1.3	0.6	
Colstrip	$25 \cdot 8$	39.8	8.0	$74 \cdot 6$	5.3	$1 \cdot 2$	0.9	
[Colstrip, Montana] Owl Creek [Gebo, Wyoming]	12.9	39.6	6.6	77.0	5.7	1.7	0.6	
Wadge	$9 \cdot 9$	40.4	$5 \cdot 2$	78·4	$5 \cdot 1$	1.9	$1 \cdot 2$	
[Routt Co., Colorado] Gantar [Roundup, Montana]	15.0	36.3	5.4	78 •4	5.3	1.4	0.5	
Pinnacle	$9 \cdot 2$	39.5	$2 \cdot 9$	$79 \cdot 1$	5.7	$1 \cdot 8$	0.6	
[Routt Co., Colorado] King, No. 1 [Hiawatha, Utah]	5.7	$43 \cdot 9$	4 ·9	80.7	$5 \cdot 8$	1.5	0.9	
Castlegate, No. 2	3.7	40 ·9	5.6	81.5	5.5	1.3	0.3	
[Castlegate, Utah] Sunnyside, No. 1 [Sunnyside, Utah]	3.8	40·3	2.8	82.5	5.8	1.8	1.0	