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Some Properties of Cuticle-Derived Components of Coal*
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The chemical and physical characteristics of any coal seam or portion of a seam are determined by the chemical and physical characteristics of the constituent parts called macerals or phyterals. Vitrinite, derived from the cell walls of the contributing plants, predominates in most coals; while micrinite, resinite, exinite, and fusinite make up only minor amounts of most coals. An above average amount of any of these latter four constituents in a coal sample will result in that sample being classed as chemically and physically abnormal when compared to typical coals from the same vicinity.

Among the coal ingredients which normally constitute a minor part of a coal seam, are the remains of plant cuticles (which are classed with the exinites). Cuticle is a wax-like covering on leaves and young twigs, and serves to deter dessication of these succulent tissues. Cutin, the constituent material of cuticles, is formed by the atmospheric condensation and oxidation of fatty acids which migrate to the surface of the plants (Weaver and Clements, 1938). Cuticles are essentially resistant to bacterial and chemical destruction when deposited in swamp conditions and thus are preserved in an essentially unaltered condition in most peat deposits. Van Krevelen and Schuyer (1957, p. 241), as well as other authors, indicate that exines (of which cuticle is one) are less affected by dynamic metamorphism than ligno-cellulosic constituents and thus tend to retain their distinctive identities well into the bituminous rank coals. Thus, in high-volatile bituminous coals, cutinite is chemically distinct from the associated vitrinites. It seems best to refer to cuticular remains in coal as "cutinite," (Stopes, 1935) as they have been altered, if only slightly, from the original cutin.

Legg and Wheeler (1925, 1929) conducted the first modern analyses of present-day and fossil cuticles. By analysing cuticles from Agave (a highly cutinized, semi-tropical plant) Legg and Wheeler determined that cuticle consists of four major components, three of which are respectively soluble in boiling water, alcohol, and cuprammonia solution. The residue, after extracting the above soluble constituents, represents 60 percent of the weight of the original cuticle and was referred to as "cutin," the basic cuticle substance. Ultimate analyses of the dissolved fractions indicated their compositions to be:

Water soluble -	carbon	48.7	hydrogen	6.7	ash	28.8
Alcohol soluble (waxes) -		79.1		13.1		10.8
Cuprammonia soluble (cellulose) -		44.1		6.4		2.0
Cutin residue -		67.1		9.9		2.8

Treatment of the residue (cutin) yielded two semi-liquid acids, the formulae for which Legg and Wheeler calculated to be $C_{26}H_{50}O_6$ and $C_{13}H_{22}O_3$; and two solid acids, one with a melting point of 107-108°C, thought to be phloionic acid, and the other with a melting point of 88-90°C, to which no name was assigned.

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Matic (1955) was "... concerned with the separation, isolation and structure of the acids constituting the ether soluble fraction obtained on saponification of cutin from *A. americana* L.". Matic succeeded in isolating 5 acids, all of which he named with their respective organic terms. He concluded that "in the light of evidence presented, it is quite clear that the cutin acids reported on previously (Fremy, 1859, 1881, 1885; Legg and Wheeler, 1925, 1929) were not pure compounds, but mixtures with the possible exception of Legg and Wheeler's 'phloionic' acid which was probably impure phloionolic acid"

Legg and Wheeler (1929) also analysed cuticles isolated from several coals. Russian Papierkohle samples were treated with NH_4OH to remove the ulmins and the cuticles were then mechanically separated from any remaining undissolved ulmins. Ultimate analyses of the concentrated cutinite indicated: carbon 73.9, hydrogen 11.4, nitrogen 1.1, sulphur 2.1, and ash 13.4 percent. They felt that fossil cuticles (cutinite) contain neither water solubles nor cellulose, although they undoubtedly do contain waxes. Roelofsen (1952) after optically studying cuticles, also concluded that after severe extractions (which we might consider partly analogous to biogenic coal formation) cuticles still contain waxes. Legg and Wheeler (1929) also isolated cuticles from an English durain by oxidizing and subsequently removing the ulmins with NH_4OH . The durain contained; carbon 83.0 and hydrogen 5.5 percent, whereas the isolated cuticles (cutinite) contained; carbon 65.2 and hydrogen 7.4, ash 4.9 percent, and traces of nitrogen and sulphur.

Analyses conducted by Edwards (1947) on hand picked cuticles (cutinite) from pockets in the Yallourn brown coal of Australia, indicate the following composition; carbon 70.4, hydrogen 7.6, nitrogen 0.45, sulphur 0.20, oxygen 21.64, and ash 0.6 percent. The coal from which these cuticles were obtained had a fuel ratio (FC/VM) of; about 0.9, while the cuticles had a fuel ratio of about 0.25.

Legg and Wheeler (1929) subjected Agave cutin, Papierkohle cutinite, and durain derived cutinite to destructive distillation in a vacuum apparatus. The results are presented as Table 1. The low distillate yield of the durain cutinite may be partially attributable to the method of obtaining the cuticle, that is, by severe oxidation and treatment with NH_4OH , to remove ulmins. Oxidation is known to reduce tar yields of coals (Schmidt, 1945, p. 666).

Table 1
Distillation of Cutin (from Legg and Wheeler, 1929)

<u>Properties of Oils</u>	<u>Plant Cutin</u>	<u>Papierkohle Cutin</u>	<u>East Kirkby Durain Cutin</u>
First appearance °C	280	265	350
Main evolution °C	300 - 350	300 - 350	350 - 370
Yield percent by weight	60	40	20
Analysis percent			
Saturated Hydrocarbons	38	25	11
Unsaturated Hydrocarbons	trace	33	22
Aromatic Hydrocarbons	16	9	22
Phenolic and Acidic Oils	26	10	1
Oxygenated Compounds	8	16	22
Ether soluble resin	4	3	11
Chloroform soluble pitch	7	3	11

In 1958, a coal seam containing abnormally abundant cuticle derived components was discovered in Indiana. (See Heavel and Guennel, in manuscript). Chemical analyses of cutinite from this "paper coal" were instigated at the Indiana Geological Survey. Mechanical weathering of the paper coal, removed much of the vitrinite in which the cuticles were embedded. Several grams of pure cutinite were concentrated by disaggregation of the coal in water and hand-picking pieces of cutinite. In order to check the results obtained from analysing this sample, several more samples of relatively pure cutinite were obtained by dissolving the weathered vitrinite of the paper coal in a dilute KOH solution. Petrographic analyses of these latter samples indicated that they still contained between 10 and 20 percent vitrinite. Results of their analyses could thus be calculated to a vitrinite-free basis. Analyses of the cutinite were, in most cases, standard coal analyses rather than organic chemical analyses. No attempts were made to determine molecular constituents. The results of the analyses of the cutinite concentrates from Indiana paper coal and the results of analyses conducted by several other investigators on other cutinite concentrates are presented, along with results of several control sample analyses, as table 2. A description of the samples follows:

Sample No.	Description
1	Channel sample of weathered paper coal
2	Grab sample of weathered paper coal - analysed by U. S. Bureau of Mines Laboratory - results courtesy of Dr. J. M. Schopf, United States Geological Survey
3	Coal lying 15 feet below paper coal
4	Coal V. sample used for control in retort
5	Pure cutinite - hand-picked from disaggregated paper coal
6,7,8	Cutinite concentrates obtained by treating paper coal with KOH
9	Cutinite from Australian lignite (Edwards, 1947)
10	Cutinite from Russian paper coal (Legg and Wheeler, 1929)
11	Cutinite from durain (Legg and Wheeler, 1929)
12	Cutinite from HVC bituminous coal (Kosanke, 1952)

Table 2 - Analyses of Cutinite and Control Samples

Samp. No.	Sample Description	Moist.		Ash		VM		BTU		S.		H.		C.		N.		O.	
		AR	Dry	Dry	DAF	AR	DAF	DAF	DAF	DAF	DAF	DAF	DAF	DAF	DAF	DAF	DAF	DAF	DAF
1	Paper coal	14.3	14.9	65.5	8896	12203	0.62												
2	Paper coal	5.0	25.6	60.2	8690	12280	0.5	7.1	69.6	1.4	21.4								
3	Lower coal	14.7	7.7	42.8	11411	14499													
4	Retort control	14.0	7.2	44.4	11360	14232	4.23	5.4	78.9	1.7	9.8								
5	Pure cutinite	11.0	10.7	84.7	13320	16730	0.21	8.1	74.7	0.7	16.3								
6	Cutinite conc.	5.4	14.9	79.2	11372	14134	0.45	8.2	74.5	1.2	15.6								
7	Cutinite conc.	6.7	13.3	77.4	11258	13906	0.62	8.0	74.9	1.3	15.3								
8	Cutinite conc.	7.4	11.2	77.1	11510	14050	0.17	7.7	73.4	1.3	17.5								
9	Lignite cutinite	6.1	0.6	79.0	NA*	NA	0.20	7.6	70.4	0.45	21.64								
10	Russian Paper coal	NA	13.4	NA	NA	NA	2.1	11.4	73.9	1.1	11.4								
11	Durain cutinite	NA	4.9	NA	NA	NA	Tr.	7.8	68.5	Tr.	23.3								
12	HVC bit.cutinite	17.0	Tr.	NA	NA	NA	NA	6.3	74.5										

*Data not available

The analyses of sample 5 best show the characteristics of cutinite from the Indiana paper coal. The ash content appears to be exceptionally high when cognizance is taken of the fact that there is little, if any, mineral matter in the sample. All, or almost all, of the 10.7 percent dry ash is inherent ash; that is, it is actually a part of the plant tissue. Semi-quantitative spectrographic analyses indicate that over 30 percent of the ash is CaO and less than 5 percent is Al₂O₃. Much of the remainder is probably silica, although the techniques used did not allow its determination.

The amounts, in percent of cutinite ash, of trace and minor elements, determined spectrographically, are (abundances in earth's crust, in parentheses, from Mason, 1952): B - 0.14(0.0003), Cr - 0.066(0.02), Ge - 0.01(0.007), Fe - 0.78(5.0), Pb - 0.01(0.0016), Mn - 0.044(0.1), Mg - trace(2.1), Mo - 0.01(0.0015), Ni - 0.01(0.008), P - 1.0(0.12), Sn - 0.08(0.004), Ti - 0.11(0.44), V - 0.01(0.015), Zn - 0.059(0.013), and Y - 0.02(0.0028). Ash content and ash properties of any coal ingredient are, however, functions of swamp environment and plant type. The present results, therefore, are not necessarily indicative of ash content and ash properties to be found in all cutinite (note sample 12). The high ash content of the Indiana paper coal does, however, point out the importance of inherent or non-mineral matter ash in certain coal ingredients.

The volatile matter content of cutinite is very high. On the basis of analyses performed by the Indiana Geological Survey during the last 4 years on over 400 samples of Indiana coals, the average volatile matter content of Indiana coal is 47.9 percent (daf). The paper coal cutinite contains almost 85 percent dry, ash-free volatile matter. As samples 6, 7, and 8 are not pure cutinite, their volatile matter contents are somewhat lower than 85 percent. In order to check this figure of 85 percent, the amount of cutinite in samples 6, 7, and 8 was determined. Thin-sections of pelletized portions of these samples were analysed petrographically, and samples 6, 7, and 8 were found to contain, respectively, 82, 84, and 90 percent cutinite; the remainder was vitrinite. No mineral matter was visible although the higher ash content of samples 6 and 7 indicate that they probably contained some adventitious mineral matter.

Vitrinite from coal wherein the cutinite has a volatile matter content of 85 percent, should have a volatile content of about 40 percent. This value was obtained by extrapolating the figures given by Van Krevelen and Schuyer (1957) in their Table X, 1, P. 239. The total dry, ash-free volatile matter of a sample containing vitrinite and exinite is the sum of the volatile matter derived from each of the constituents. Therefore, the following equation was set up: $VM\% \text{ (vitrinite)} + VM\% \text{ (exinite)} \times 100 = \text{Total VM as daf\% of sample.}$

By substituting the respective amounts for vitrinite and exinite determined microscopically, 40 percent for VM of vitrinite, and the respective total VM in each sample one arrives at figures of 88.0, 84.2 and 81.3 percent for the volatile matter content of the exinite in samples 6, 7, and 8 respectively. The average of these three is 84.5 which corresponds quite well with the figure of 84.7 percent determined on pure cutinite (sample 5).

When one realizes that the calorific value of coal is normally inversely proportional to the total volatile matter content, the results of calorimetry of cutinite are somewhat surprising. The figure of 16,780 Btu/lb for sample 5 (daf basis) represents an average of several determinations, and is felt to be fairly accurate. The authors found it somewhat difficult to reconcile the relatively low calorific values for samples 6, 7 and 8 with the calorific value of sample 5 (pure cutinite), even if it is assumed that the vitrinite in samples 6, 7, and 8 has no heating value, which probably is not true. It is probable that the treatment of the samples with KOH affected their heating value, but not their volatile matter yields. The calorific value of cutinite is apparently higher than the calorific value of associated coals subjected to the same metamorphism and consequently of the same "rank." An interesting point raised by this fact is that the coal ingredients containing the most volatile matter (exinite) and the least volatile matter (fusinite) have higher calorific values than vitrinite (which has intermediate volatile matter content) from the same coal.

The present ultimate analyses indicate that cutinite contains a high proportion of hydrogen, which is reflected in the high volatile matter yields. Van Krevelen and Schuyer (1957) have prepared graphs to represent the carbon, hydrogen, and oxygen relationships of typical macerals. Four of these graphs have been reproduced (and extended when necessary) as Plate 1 and the results of the cutinite analyses (including those

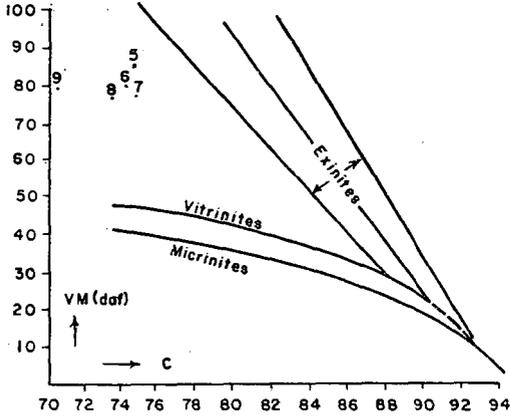


Figure 1

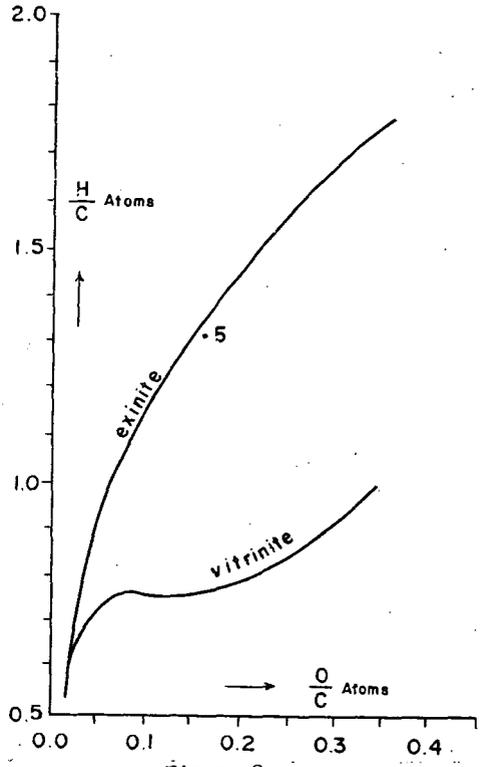


Figure 2

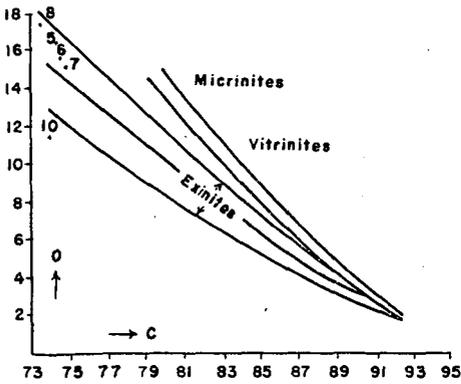


Figure 3

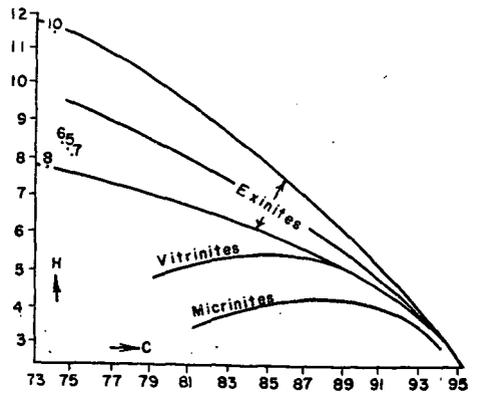


Figure 4

Graphs from Van Krevelen and Schuyer (1957)
Points from present data, Edwards (1947), and Legg and Wheeler

of Edwards (1947) and Legg and Wheeler (1929)) are superposed on the graphs. The points are numbered to correspond to the sample numbers in table 2. All of the points fit into the exinite areas except those on fig. 1, which plots volatile matter against carbon. Even sample 5, which is pure cutinite, is well outside the exinite lines, suggesting that the exinite area should curve downward in the lower carbon region, as do the lines for micrinite and vitrinite. Only the point for sample 5 is placed in fig. 2 (which plots the ratio of atomic hydrogen and atomic carbon against the ratio of atomic oxygen and atomic carbon). The fact that the point for sample 5 falls almost on the median line for the exinites tends to substantiate both the graph and our assumption that sample 5 is pure cutinite.

Because coals containing abnormally high proportions of exinite may serve as sources of petroleum substitutes, distillation assays were conducted on the cutinite samples to determine the types of yields which could be expected from the exinite fraction of coals.

The method used to determine distillation yields was patterned after the Fischer-Schraeder low temperature carbonization method with modifications of apparatus to utilize the equipment on hand. A retort 6" long was machined out of a stainless steel rod that was 1" in diameter. The retort chamber was tapered for ease of coke removal and holds a maximum coal charge of 3 grams. The charged retort was connected to the tar distilling flask with a copper tubing which during carbonization was wrapped with a heating tape that reached a temperature of approximately 400°C. A "U" tube containing anhydrous calcium chloride was attached to the tar distilling flask to absorb any water that may have escaped the tar distilling flask. The tar distilling flask was immersed in ice water. The light oil tube attached to the calcium chloride tube was a conventional 100 mm. "U" tube stuffed with glass wool and was immersed to its side arms in dry ice and acetone. During carbonization no attempt was made to measure the volume of gas that was evolved. The first noticeable condensation in the tar distilling flask was between 52° - 80°C. Visible vaporous volatiles were given off from 200° - 250°C and the first drop of tar was noticed at 450°C. In all instances, gas stopped evolving around 760°C. The retort was allowed to reach 950°C and was held at this temperature for 7 minutes. The retort was heated by means of a Hoskins FA120 Furnace which was attached to a temperature controller, permitting temperatures to be controlled with a fair degree of accuracy. This furnace is recommended for volatile determinations by A.S.T.M.-D-271. The time consumed for the entire experiment was approximately 1 hour.

The results are shown in Table 3. Sample number 4, a sample of Indiana coal V, was first run as a control or standard sample. Thin-sections of this sample indicate it to be a typical vitrinitic coal with several percent of exinite and several percent of opaque matter. About 11 percent of the dry, ash-free sample was precipitated as tar, ammonia, and light oil. The cutinite concentrates (samples 6, 7, and 8; insufficient material was left of sample 5 to run tar assays) yielded over four times this amount.

Table 3 - Distillation Yields of Cutinite Concentrates

Samp. No.	Char. DAF	Tar DAF	Lt. Oil DAF	Gas DAF	Tar Calculated			
					1	2	3	4
4	66.3	10.5	0.6	21.9	13.2	17.9	14.8	18.0
6	26.5	58.6	0.2	11.3	53.5	45.3	49.4	39.7
7	24.8	53.4	0.5	19.0	50.5	43.5	45.5	38.5
8	22.1	48.2	1.6	23.2	45.5	40.6	43.0	36.3

1 Francis (1954) tar and oil = $eH 1.5 \times 5.48$ where eH is H over 3.6
 2 Selvig and Ode (1944) tar = $0.697X + 0.0031X^2 - 6.4$ where $X = VM - (1.3 \times 0)$
 3 Selvig and Ode (1944) tar (for cannel coals) = $12.3 (H_2 - 4.2)$
 4. Selvig and Ode (1957) tar = $(0.783 \times VM) - (0.96 \times 0) - 7.3$

The amount of dry, ash-free char produced averaged about 1.18 times the amount of dry, ash-free fixed carbon in the original sample; meaning that some of the original material driven off as volatile matter in the proximate analyses is retained in the char of the assays. The yields of char shown in Table 3 represent only the organic portion of the char (percentage of ash in char was determined experimentally) as the percentage of the dry, ash-free charge. The yield of tar shown in Table 3 represents distilled volatiles less moisture (from proximate analysis) calculated as percent of dry, ash-free charge.

The calculated tar yields shown in Table 3 were obtained from several formulae suggested by the respective authors as means to estimate tar yields from proximate and ultimate analyses data. Although there appears to be no constant factor relating the yields obtained with those estimated, the general relationship of highest to lowest yields from samples 6 through 8 in both the experimental and calculated results suggests that the experimentally determined yields are probably correct. The experimental yields are, except for sample 4, all higher than the estimated yields, probably as a function of the high final temperature used. It might be noted that the tar yields are apparently inversely related to the amount of petrographically determined cutinite in samples 6, 7 and 8. It is felt that this apparent anomaly is a function of sample treatment, and consequently all of the yields would be even higher if pure, untreated cutinite was utilized.

Summary:

Analyses of the cuticle-derived component (cutinite) of Indiana paper coal which lies in an area containing high-volatile C and high-volatile B bituminous coals indicate that cutinite exhibits the following characteristics:

1. High ash content - analyses of other cutinite samples by other investigators suggest, however, that ash content varies from only a trace to over 16 percent, and is dependent upon swamp environment and plant type.
2. High volatile matter content - The apparent volatile matter content appears to be about 85 percent of the dry, ash-free cutinite.
3. High calorific value - Dry, ash-free cutinite was determined to contain over 16,000 Btu/lb.
4. Carbon, hydrogen and oxygen contents - Ultimate analyses indicate that hydrogen is abundant in pure cutinite, attaining a value of approximately 8 percent. The results of all of the ultimate analyses fall within the "exinite" areas of the graphs prepared by Van Krevelen and Schuyer (1957) to show the characteristics of macerals.
5. Tar, oil and coke assays - Tar yield was exceptionally high, averaging over 50 percent of the dry, ash-free sample.

One of the properties of cutinite is that of yielding high proportions of condensable tars. Gas yields differed little from yields of normal coals of the same rank.

Unquestionably, coal containing a high proportion of cutinite, if it is not associated with equally high proportions of opaque matter, would serve as an ideal raw material for the extraction of tars and oils. Such coals should, wherever possible, be utilized for this purpose.

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