

PREPARATION OF HUMIC ACIDS FROM ILLINOIS COAL

G. R. YOHE AND C. A. HARMAN*

Humic acids are complex, high molecular weight colloidal substances. They form dark brown solutions in aqueous alkalis, from which they separate as highly hydrated, brown flocculent precipitates upon acidification. They are products of certain types of plant decomposition, and may be obtained from such materials as decayed wood, peat, and brown coals by alkali extraction. Bituminous coals, which do not yield these alkali soluble materials directly, may become good sources of humic acids after being subjected to partial oxidation.

Humic acids have been recognized by many investigators^{1, 2, 3, 4} as a rich source of information concerning the constitution of coal. Various methods have been utilized for preparing them by partial oxidations of coal. Those reported have included oxidation with nitric acid,^{5, 6, 7} sulfuric acid,^{7, 8} potassium permanganate,^{9, 10} hydrogen peroxide,⁹ and atmospheric oxygen.¹¹ Pure oxygen has been used on coals suspended in aqueous alkalis,¹² and electrolytic oxidation^{13, 14} has been reported. The oxidations using air appear to be the most convenient for the production of humic acids in large quantities.

The problem of preparing a quantity of humic acids from vitrain, the brilliant, jet-black portion of coal, arose in connection with another investigation. For purposes of comparison, the methods used have been applied also to the other banded ingredients of coal, which have been described¹⁵ as follows: clarain is glossy and finely laminated, durain (commonly called "splint") is dull gray and laminated, and fusain is the very friable mineral charcoal. The coal used in the present work was obtained from the Herrin No. 6 seam in Franklin County, Illinois. Vitrain was isolated by subjecting —4, +8 mesh coal to float-sink separation in a benzene-carbon tetrachloride mixture of sp. gr. 1.30. The floating portion was again treated with a mixture of sp. gr. 1.28; giving a "sink" fraction (C-2108) and a "float" fraction, which was handpicked to remove dull

pieces (C-2092). The clarain, durain and fusain were hand-selected at the mine. Analyses of the vitrain samples are given in table 3.

Oxidation of citrain with *N* nitric acid gave a 70 per cent yield of humic acids, but the method was abandoned because it introduces nitrogen into the product.^{9, 16, 17}

Dry Air Oxidation of Coal.—An experiment with air oxidation, in which the powdered coal was placed in a well-ventilated electric oven at 150° C., showed that the coal "heated" spontaneously. The following procedure eliminated this difficulty. One hundred grams of vitrain (C-2092), 30 gm. each of durain and clarain, all ground to pass a 200-mesh sieve, were placed in separate shallow pans in an electric oven at 110° C. The temperature was raised gradually (ca. 5° per day), and at the end of one week it was set at 150° C. and kept there for 3 weeks. The coal samples were stirred daily, and at the end of the oxidation period two 10 gm. samples of each coal were digested for 15 minutes with 500 cc. of boiling 5 per cent sodium hydroxide. The coal residues were washed free of alkali-soluble humates by decantation; the residues were recovered and the solutions clarified by centrifuging, first with a type 1-C International centrifuge (1,750 r.p.m., centrifugal force about 600 times gravity), then with a Sharples supercentrifuge (50,000 r.p.m., centrifugal force about 63,000 times gravity). The sodium humate solutions were acidified with hydrochloric acid and the precipitated humic acids washed several times by stirring with water, centrifuging and decanting. Both the coal residues and the humic acids were finally transferred to filter papers and air-dried. The amounts of coal residue and the yields of humic acid obtained are given in table 1.

Air Oxidation of Coal Suspended in Hot Aqueous Alkali.—The powdered coal samples were suspended in dilute sodium hydroxide (50 cc. per gm. of coal) in 1 liter round-bottomed flasks fitted with reflux condensers. A moderate stream of air was bubbled into the bottom of each

* Associate Chemist and Research Assistant, respectively, Fuels Division, Geochemical Section, Illinois State Geological Survey, Urbana. Published with permission of the Chief.

TABLE 1—DRY AIR OXIDATION OF COAL

Description of Sample	Products from 10 g oxidized coal (grams)		Yield of Humic acid (Per cent)
	Coal residue	Humic acids	
1. Durain.....	3.7	6.3	63
2. Durain.....	3.8	5.9	59
3. Clarain.....	1.4	8.2	82
4. Clarain.....	1.4	8.3	83
5. Vitrain (C-2092).....	0.5	9.6	96
6. Vitrain (C-2092).....	0.6	9.6	96
7. Vitrain (C-2092).....	0.5	9.5*	95

* A 30-minute NaOH digestion was used in isolating this yield.

TABLE 2—OXIDATION OF COAL IN ALKALINE SUSPENSION

Type of Sample	Period of Oxidation (Days)	Yield of Humic Acid		
		As rec'd. basis		Dry-ash free basis (Per cent)
		Grams	Per cent.	
1. ^a Vitrain (C-2108).....	6 ^d	1.1	11	11
2. ^a Vitrain (C-2108).....	8 ^e	6.0	60	61
3. ^a Vitrain (C-2108).....	24 ^f	7.2	72	73
4. ^b Vitrain (C-2108).....	7	0.3	2	2
5. ^b Vitrain (C-2108).....	14	2.6	17	17
6. ^b Vitrain (C-2108).....	21	12.5	83	84
7. ^c Vitrain (C-2108).....	7	0.3	3	3
8. ^c Vitrain (C-2108).....	21	6.8	68	69
9. Fusain.....	21	<0.1	<1	
10. Fusain.....	21	<0.1	<1	
11. Durain.....	21	0.7	7	
12. Durain.....	21	1.6	16	
13. Clarain.....	21	1.6	16	
14. Clarain.....	21	3.3	33	

^a 60 mesh samples used; all others were 200 mesh.

^b 15 g samples were used; all others were 10 g.

^c 10% NaOH used; all others were 5% NaOH.

^d Three 2-day periods; new NaOH for each period.

^e Two 4-day periods; new NaOH for each period.

^f Three 8-day periods; new NaOH for each period.

TABLE 3—ANALYTICAL DATA

Type of Sample	Moisture	Ash	Dry-ash free basis				
			C	H	O	N	S
1. Vitrain.....	5.4	2.2	81.96	4.98	10.23	1.65	1.18
2. Vitrain.....	8.1	2.1	81.74	5.10	10.23	1.98	0.95
3. Oxidized vitrain.....	3.9	1.4	68.99	2.98	25.18	1.77	1.08
4. Humic acid.....	8.4	1.0	71.27	3.60	22.86	1.56	0.71
5. Humic acid.....	8.3	0.8					
6. Humic acid.....	7.0	2.5					

Description of samples:

1. Vitrain from No. 6 coal, Franklin Co., sp. gr. < 1.28; Lab. No. C-2092.

2. Vitrain from No. 6 coal, Franklin Co., 1.28 < sp. gr. < 1.30; Lab. No. C-2108.

3. Sample (1) air oxidized 3 weeks at 150° C; Lab. No. C-2117.

4. Combined sample of crude, air-dried humic acids, obtained from experiments 1-8, table 2; Lab. No. C-2110.

5. Combined sample of humic acids, obtained from experiments 9-14, table 2.

6. Combined sample of humic acids, obtained from experiments 1, 3 and 5, table 1.

flask and the temperature maintained at $95^{\circ} \pm 5^{\circ} \text{C}$. At the end of the oxidation period the reaction mixtures were diluted and the residual coal removed as in the dry air oxidations. The humic acids were precipitated with hydrochloric acid, recovered by centrifuging and filtering and air-dried. The yields are shown in table 2.

Discussion.—The inconsistent results obtained by the oxidations in sodium hydroxide suspension may be due in part to differences in effectiveness of agitation by the air streams introduced into the reaction mixtures. The use of hot alkaline solutions for the prolonged periods of time resulted in pronounced etching of the pyrex flasks used.

In all cases except fusain, the separation and washing of the alkali insoluble residue was difficult. This residual matter settled slowly, even in the International centrifuge, and upon attempted filtration either went through the filter or clogged the paper to such an extent that filtration was impossible. The difficulty of this separation was greater with the samples oxidized in sodium hydroxide suspension, and may have contributed to the variations in the yields of humic acids obtained.

The alkaline humate solutions were apparently colloidal; they showed the Tyndall effect even after being put through the Sharples supercentrifuge.

The humic acids formed bulky, flocculent precipitates. Effective washing was difficult because of their tendency to disperse colloiddally in pure water; it was necessary to acidify the final portions of wash water with a few drops of hydrochloric acid to prevent this dispersion. After centrifugal settling humic acids had a dark brown to black color and a jelly-like consistency. They dried to jet black, friable solids resembling vitrain.

Summary and Conclusions.—Humic acids have been prepared from the banded ingredients of Illinois coal by dry air oxidation at 150°C ., and by bubbling air through a sodium hydroxide suspension of the coal at 95°C .

The dry air oxidation has proved more satisfactory from the standpoint of yields obtained and reproducibility of results. It is decidedly more convenient to carry out, and minimizes the possibility of contaminating the products with silicates removed from glass vessels by prolonged hot alkali treatment.

Vitrain can be converted almost completely to humic acids, clarain and durain yield smaller amounts, while fusain is resistant to this oxidation under the conditions used.

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