

All of these facts are in harmony with the concept that in methanol lignin units related to propylbenzene are joined in chains, while in soda lignin cyclization has taken place during the process of isolation. Hydrogen over copper chromite cleaves the bond between successive C<sub>9</sub> units in

methanol lignin, while with soda lignin the action of hydrogen is largely limited to hydrogenation of unsaturated rings and the hydrogenolysis of hydroxyl, methoxyl and cyclic ether linkages, since the rings are stable toward hydrogenolysis.

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[CONTRIBUTION FROM THE GEOCHEMICAL SECTION OF THE ILLINOIS STATE GEOLOGICAL SURVEY]

## The Oxidizing Power of Illinois Coal. I. The Reaction with Titanous Chloride<sup>1</sup>

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High volatile bituminous coals such as those found in Illinois are known to deteriorate rather rapidly upon exposure to air. This deterioration is particularly evident in the loss of coking properties<sup>3</sup> and in the diminution of calorific value.<sup>4</sup> The purpose of the present work was to investigate the initial stages of this atmospheric oxidation.

It has been shown that finely divided lignite possesses oxidizing power,<sup>5</sup> and the observations of Francis<sup>6</sup> upon spontaneous combustion suggest that weathered coal contains an active oxidizing agent. It has been postulated that organic peroxides play an important role in the mechanism of spontaneous ignition of coals.<sup>7,8</sup>

Although charcoals have been shown to possess oxidizing ability,<sup>9</sup> it does not necessarily follow that similar activity exhibited by coal is of the same nature, since bituminous coals contain little, if any, free carbon.<sup>10,11</sup>

**Preparation of Samples.**—Samples were collected by chipping coal from a freshly exposed face directly into a special stainless-steel ball mill. The cylindrical portion of this mill was 7.6 cm. i. d. and 20.3 cm. long; conical ends carrying needle valves were provided to facilitate the replacement of air by an inert gas. Flint pebbles were used. The pulverized coal was removed from the mill, passed through a 100-mesh sieve and portions placed in

ground glass capped weighing bottles in an air-tight handling box containing a carbon dioxide atmosphere. Determinations of oxidizing power were made upon unexposed samples and upon samples exposed to air or oxygen at room temperature for various lengths of time.

**Determination of Oxidizing Power.**—A weighed sample of approximately 1 g. of coal, 150 ml. of boiled distilled water, 5 ml. of concentrated hydrochloric acid and a few drops of 2% aqueous Aerosol-OT<sup>12</sup> were placed in a titration bottle swept with a stream of oxygen-free nitrogen. A measured quantity of 0.02 to 0.03 *N* titanous chloride was added, and the excess titrated with standardized ferric chloride,<sup>13</sup> approximately 0.01 *N*. The end-point was detected potentiometrically. A blank determination was run, and the difference between the amounts of ferric chloride used in the two titrations gave the oxidizing power of the coal used. The results are shown graphically in Fig. 1; all but two points (second point for C-2102 and third point for C-2094) were obtained by averaging two or more duplicate determinations. The results of duplicate determinations showed an average deviation from the mean of 0.0023 milliequivalent per gram.

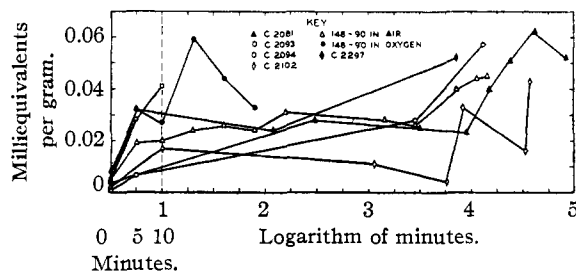


Fig. 1.—Change of oxidizing power of coals with increased time of exposure to air.

**Effect of Mechanically Entrained Air.**—Determinations made using powdered silica in place of coal indicated that mechanically entrained oxygen had a negligible oxidizing action upon the titanous chloride.

**Effect of Soluble Ferric Compounds.**<sup>9,14</sup>—The determinations of the oxidizing power of coal C-2297 were

(12) Kindly provided by the American Cyanamid and Chemical Corporation.

(13) Rieche, "Alkyl Peroxide und Ozonide," T. Steinkopff, Dresden-Blasewitz, Germany, 1931, pp. 14, 23, 29, 31, 39, etc.

(14) Mayers, *THIS JOURNAL*, **55**, 2435 (1933).

(1) Presented before the Division of Gas and Fuel Chemistry at the Detroit meeting of the American Chemical Society, Sept. 12, 1940. Published with the permission of the Chief of the Illinois Geological Survey.

(2) Associate Chemist and Research Assistant, respectively.

(3) G. Thiessen, "Coke from Illinois Coals," Illinois State Geol. Survey Bull., **64**, p. 51 (1937).

(4) S. W. Parr, *Univ. Illinois Eng. Expt. Sta. Bull.*, **97**, pp. 14 ff. (1917).

(5) Ashmore and Wheeler, *J. Chem. Soc.*, 1405-1408 (1933).

(6) Francis, *Fuel*, **17**, 363-372 (1938).

(7) Erdmann and Stoltzenberg, *Braunkohle*, **7**, 69-73 (1908).

(8) F. Fischer, *Ges. Abhandl. Kenntnis Kohle*, **4**, 443-457 (1920).

(9) Lamb and Elder, *THIS JOURNAL*, **53**, 157-158 (1931).

(10) Bone and Himus, "Coal, its Constitution and Uses," Longmans, Green & Co., New York, N. Y., 1936, p. 181.

(11) Sinkinson, *J. Chem. Soc.*, **117**, 843 (1920).

paralleled by ferric iron determinations upon solutions obtained by leaching coal samples with hydrochloric acid of the same concentration for the same time, filtering out the coal and titrating the filtrates with standard titanous chloride, using thiocyanate as the indicator. The results are given in Table I.

TABLE I

COAL C-2297: COMPARISON OF OXIDIZING POWER OF COAL WITH THAT OF THE FERRIC SALTS EXTRACTED THEREFROM

Time of exposure to air	Oxidizing power (milliequivalents per g. of coal used)	
	Coal	Soluble Fe <sup>+++</sup>
0	0.0079 <sup>a</sup>	0.0025
5 min.	.032	.0024
2 hrs.	.024	.0027
5 days	.052	.0020

<sup>a</sup> Single determination; all other values are averages of two determinations.

was not possible in the limited space of the handling box. The coal collected as drill cuttings (C-2102) became noticeably warm during drilling; this heating may have modified the properties of the coal and thus contributed to the erratic results obtained thereon.

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TABLE II

## ANALYTICAL DATA, ILLINOIS COALS

Lab. no.	County	Seam	"As received" basis			Ash- and moisture-free basis					Remarks
			Moisture	Ash	C	H	N	O	S		
C-2081	Franklin	6	7.2	5.9	80.96	5.16	1.76	9.18	2.94	Chipped from fresh face, predominantly clarain	
C-2093	Vermilion	7	9.8	6.1	80.39	5.80	1.38	9.73	2.70	Chipped from fresh face	
C-2094	Vermilion	7	8.6	6.4	80.62	5.85	1.54	8.72	3.27	From interior of a block taken from tippie	
C-2102	Washington	6	7.3	4.9	79.05	5.90	1.22	9.62	4.21	Drill cuttings	
C-2297	Vermilion	7	11.6	3.3	80.29	5.77	1.49	9.36	3.09	Chipped from selected bright area on fresh face	

Analytical data are listed in Table II.

**Discussion**

The precision of the measurements was sufficient to establish the general trend of change in oxidizing power of these coals, *i. e.*, that unexposed coal had negligible oxidizing action; this "active oxygen" content increased rapidly during the first few minutes of exposure to air and more slowly thereafter. Some of the irregularities in this increase may have been due to the fact that complete and thorough mixing of the sieved samples

**Summary**

Illinois coals which have been exposed to air or oxygen show a small but definite ability to oxidize titanous chloride.

This oxidizing power is gained very rapidly when freshly ground coal is exposed to air.

Neither the magnitude nor the rapid increase of this oxidizing power can be accounted for entirely by the presence or the formation of soluble ferric compounds in the coal.

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