Paramagnetic Resonance in Coals

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Paramagnetic resonance absorption in coals has been attributed by Bennet, Ingram and others[1] to free radicals which are associated with a broken bond in the condensed aromatic structure. Contrary to this, facts have been discovered which appear to suggest another possibility. First, pyridine extracts of coal show less

1) J. E. Bennet, D. J. E. Ingram and J. G. Tapley, *J. Chem. Phys.*, **23**, 215 (1955).

TABLE I
ANALYSIS OF COALS USED

Source	Moisture	Ash	d. a. f. base %		O+N+S + error
			C	H	
Rich Rum	0.68	7.90	82.95	5.77	11.28
Mathics Bituminous	0.78	8.17	83.16	6.17	10.67
Monongalia	0.58	5.72	83.31	5.97	10.72
Elkhorn	0.82	3.13	83.39	5.80	10.81
Jerry Fork	0.92	5.81	84.46	5.55	9.99
Grichton	0.72	3.79	86.20	5.33	8.47
Bergoo	0.53	5.29	86.60	5.37	8.03
Denise	0.84	5.90	88.95	4.79	6.26
Maryland Shapy	1.00	9.19	89.08	5.03	5.89
Mammoth Anthracite	1.05	13.68	89.44	3.95	6.61
Indian Ridge	0.11	5.24	90.11	5.14	4.75
Primrose Anthracite	0.43	9.35	90.32	4.13	5.55
Nakagō (Japan)	13.32	3.96	74.33	5.26	20.41
Yūbari (Japan)	1.13	2.67	84.85	6.16	8.99
Yatake (Japan)	1.11	2.74	89.55	4.86	5.59
Uonuki (Japan)	1.68	1.80	91.16	3.97	4.87

but distinct paramagnetic resonance[2]. If the paramagnetic substance be actually due to a broken bond, possibly it might be destroyed by some physical changes. Secondly, both violanthrone and violanthrene[3], which have similar aromatic chemical composition to coal but no broken bonds show distinct paramagnetic resonance absorption.

Recently a suggestion has been advanced that the resonance absorption in coals may be due not to the unpaired electrons present in free radicals or broken bonds but to the unpaired π electrons in the triplet state[4]. On the other hand, Austen and Ingram et al. have emphasized again that the resonance absorption in coals is due to the free radicals formed by breakage of bonds round the edge of the carbon clusters or originated in the formation of defects in the ring packing and not to the exited triplet state[5]. Still evidence is lacking to make a decisive choice between the two views. In the present paper a trial will be described which was done in the above connection.

Experimental Material and Method

Twelve American coal specimens are kindly provided by Dr. K. Inouye who is staying at Pennsylvania State University. All of these samples have been kept in the fresh state: During the storage and transportation the samples were sealed in an atmosphere of nitrogen, and contact with air was avoided as far as possible. Four Japanese specimens were chosen for the sake of comparison. Chemical analysis of the samples used is shown in Table I.

The observation of resonance absorption were carried out for each specimen treated in two different ways: (a) a sample sealed under vacuum and (b) the same kept in air. The measurements were made by use of a microwave of 3.2 cm. wave-length at room temperature[6]. The signal intensity was determined in comparison with diphenylpicrylhydrazil (DPPH). Paramagnetic susceptibility per gram thus obtained is recorded in Table II.

TABLE II
PARAMAGNETIC SUSCEPTIBILITY OF COAL
(10^{-8}c g s per gram)

Specimen	In vacuum	In air
Rich Rum	0.67	1.36
Mathics Bituminous	0.58	0.77
Monongalia	0.70	0.87
Elkhorn	1.03	0.73
Jerry Fork	0.93	0.60
Grichton	1.12	0.93
Bergoo	0.64	0.78
Denise	1.86	1.57
Maryland Shapy	1.16	2.02
Mammoth Anthracite	4.20	2.55
Indian Ridge	1.16	1.68
Primrose Anthracite	3.65	2.36
Nakagō (Japan)	0.40	0.37
Yūbari (Japan)	0.28	0.82
Yatake (Japan)	1.23	2.32
Uonuki (Japan)	3.90	3.39

2) Y. Yokozawa, I. Miyasita, M. Kugo and K. Higasi, This Bulletin, **28**, 536 (1955).
3) Y. Yokozawa and I. Tatsuzaki, *J. Chem. Phys.*, **22**, 2087 (1954).
4) H. Honda and K. Ōuchi, *Fuel*, **36**, 159 (1957).
5) D. E. G. Austen and D. J. E. Ingram, *Brennstoff Chemie*, **39**, Sonderausgabe, 25 (1958); D. E. G. Austen, D. J. E. Ingram and J. G. Tapley, *Trans. Faraday Soc.*, **54**, 400 (1958).
6) Y. Yokozawa and I. Tatsuzaki, *Bull. Res. Inst. Appl. Elec.*, **6**, 111 (1954).

Results and Discussion

As pointed out by Ingram[7] the action of oxygen on the paramagnetic absorption was found to be important. If broken bonds be responsible for paramagnetic resonance, one may expect that the admission of air would destroy free radicals and the signal intensity in air would become weaker than that in vacuum. The result of experiment was more complicated than expected*. In half of fresh coals the absorption intensity decreases in the presence of the oxygen, while in the remaining half it even increases. If the fresh coals actually be abundant in free radicals of broken bonds, the trends of this oxygen influence would be hard to understand.

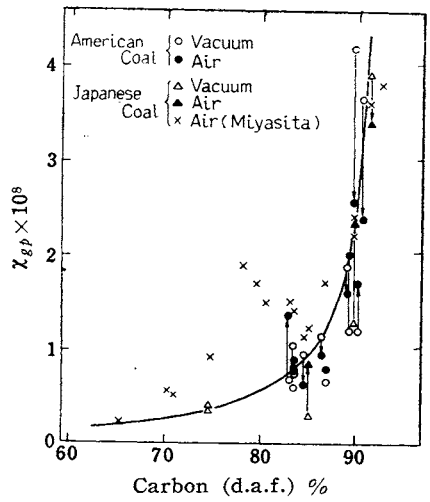

Fig. 1

In Fig. 1 the paramagnetic susceptibility of coal is plotted against the carbon content (d. a. f.). For the sake of comparison, Miyasita's[8] values are recorded in the same graph—in the latter case the samples were dried at 105°C and were measured mostly in air. Again it will be seen that there is no abnormality in resonance intensity for the fresh American coals.

Remembering that the "freshness" of coal is a matter of comparison, one may not be entitled to deny the theory of broken bonds solely on the basis of the present observation. Still it strongly suggests that further critical examination on that theory should be desirable.

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7) J. E. Ingram, *Disc. Faraday Soc.*, **19**, 179 (1955).

*) Measurements were made also on the oxidized products of four specimens obtained by heating at 150°C for 1, 2 and 3 hours. Each of them was found to be paramagnetic and the signal intensity was of the same order with that of the original sample.

8) I. Miyasita, Dissertation of Hokkaido University for the degree of doctor of science (1957); see also I. Miyasita and Y. Yokozawa, *Bull. Res. Inst. Appl. Elec.*, **7**, 162 (1955).