Dielectric Investigation on Coals. III. On a Variety of Coals

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Introduction

A preceding paper[1] has shown that by a method using mixture of powdered coal and paraffin wax, the dielectric constant of coal could be estimated with fair precision of ±10 per cent. It has been pointed out that almost the same amount of deviation is to be found when testing different samples of the same specimen.

The present article deals with the dielectric constant data obtained by using the mixture method on a variety of Japanese coals and on five coals from foreign sources.

1) K. Higasi, I. Miyasita and Y Ozawa, This Bulletin, **30**, 546 (1957).

Experimental

Coal samples here examined do not include all the types of Japanese coals, but are representative caking coals produced in Japan. Some of the conclusions reached for them will be applicable to all other Japanese coals. Foreign coals are chosen from among those which have been imported to certain iron works in Japan. Chemical analyses of all these coal specimens are recorded in Tables I and II.

The coal samples were reduced to fine powders, thoroughly dried at 105°C in a vacuum, and then mixed with melted paraffin wax[1]. The volume

TABLE I

PROXIMATE ANALYSES

Coal No.	Source of Sample	Moisture	Ash	Volatile matter	Fixed carbon	Total sulfur
A1	Yubari No. 2—10	1.38	4.71	51.44	42.47	—
B1	Mayazi No. 1a	0.97	1.80	43.38	53.85	—
B2	Mayazi No. 2	0.72	1.61	47.37	50.30	—
B3	Mayazi No. 3	1.11	2.26	47.29	49.34	—
C1	Sunagawa No. 2	1.02	4.35	44.63	50.00	—
C2	Sunagawa No. 3	0.83	6.85	38.67	53.65	—
C3	Sunagawa No. 4	2.65	4.68	48.65	44.02	—
C4	Sunagawa No. 8	1.20	2.54	46.26	50.00	—
C5	Sunagawa No. 9	2.30	3.61	57.06	37.03	—
C6	Sunagawa No. 10	1.78	8.93	52.76	36.53	—
C7	Sunagawa No. 11	1.13	6.36	42.83	49.68	—
D1	Yatake	1.11	2.94	21.29	74.86	0.65
E1	Taihei (lignite)	12.86	5.84	45.33	35.97	0.76
E2	Tempoku (brown coal)	12.80	1.52	35.62	50.06	0.77
F1	India	—	14.96	27.65	57.39	—
F2	Pocahontas, Western (U. S. A.)	—	7.33	22.00	70.67	—
F3	Pocahontas (U. S. A.)	—	5.92	18.60	75.48	—
F4	Pocahontas (U. S. A.)	—	4.85	19.30	75.85	—
F5	Durham (England)	0.85	1.70	26.14	71.31	—

TABLE II

ULTIMATE ANALYSES (dry, ash-free basis)

Coal No.	Source	C%	H%	O%	N%	S%
C3	Sunagawa No. 4	82.09	6.21	10.26	1.36	0.09
C7	Sunagawa No. 11	81.84	5.50	10.75	1.59	0.32
D1	Yatake	89.4	4.86	3.06	1.88	0.64
E1	Taihei	65.1	4.93	28.42	0.93	0.62
E2	Tempoku	70.2	4.74	23.4*	1.10	0.6
F1	India	88.03	5.28	4.69	1.66	0.34
F4	Pocahontas	87.99	4.98	5.17	1.51	0.35
F5	Durham (England)	89.31	4.31	—	—	—

* Estimated from (O+S)% 23.96 on the assumption S% 0.6.

fraction of the coal was kept as 0.56 of the whole part.

The dielectric measurements[2] were made at room temperature with a Q meter for the frequency range of 50 Mc/s to 100 kc/s, and with an impedance bridge for the range of 10 kc/s to 300 c/s.

The results of measurements are collected in Tables III and IV. Dielectric constants, ε' and loss factors, ε'' without parenthesis all refer to the paraffin-wax mixtures of 56 vol % coal. Figures in parentheses show the dielectric constants of the coals themselves which were obtained by the use of the following mixture formula due to Bottcher[3].

$$\frac{\varepsilon'-\varepsilon'_1}{3\varepsilon'}=v_2\,\frac{\varepsilon'_2-\varepsilon'_1}{\varepsilon'_2+2\varepsilon'} \qquad (1)$$

in which ε', ε'_1, and ε'_2 are the dielectric constants of the mixture, the paraffin wax and the coal particles, respectively, and v_2 is the volume fraction of the coal particles in the mixture.

When the mixture has an appreciable loss factor, the application of Eq. (1) becomes questionable. For instance, the mixture with the British sample (F5) has ε'' 0.284 at the frequency of 1 kc/s. To check errors arising from this, a general equation for complex dielectric constant $\varepsilon^*=\varepsilon'-j\varepsilon''$ derived from Eq. (1) was employed for comparsion's sake. By putting $\varepsilon^*=4.79-0.284j$ in this modified equation, the following values of the coal were obtained: $\varepsilon_2^*=7.36-0.664j$ in contrast to $\varepsilon_2'=7.37$ obtained from Eq. (1) (See Table IV). This one example will illustrate well the validity of other approximate calculations on Eq. (1).

As the error due to conductivity is very important, a further check was made by the use of an equation presented by Lewin[4]. The results were: $\varepsilon^*=4.79-0.284j$ gives $\varepsilon_2^*=7.96-0.895j$

2) I. Miyasita and K. Higasi, This Bulletin, **30**, 513 (1957).

3) C. J. F. Böttcher, *Rec. trav. chim.*, **64**, 47 (1945); and cf. ref. 1) above.

4) L. Lewin, *J. Inst. Elec. Engrs.*, **94**, 65 (1947).

TABLE III

DIELECTRIC CONSTANTS (ε') AND LOSS FACTORS (ε'') OF JAPANESE COALS*

(Paraffin-wax mixture, coal 56 vol %)

Coal No.		300 c	1 kc	10 kc	100 kc	1 Mc	10 Mc
A1	ε'	3.36 (4.21)	3.32 (4.12)	3.30 (4.08)	3.27 (4.02)	3.24 (3.96)	3.24 (3.96)
	ε''	0.0333	0.0212	0.0144	0.0087	0.0115	0.0083
B1	ε'	3.24 (3.96)	3.24 (3.96)	3.24 (3.96)	3.22 (3.92)	3.19 (3.86)	3.16 (3.79)
	ε''	0.0256	0.0193	0.0135	0.0088	0.0080	0.0068
B2	ε'	3.29 (4.06)	3.28 (4.04)	3.26 (4.00)	3.25 (3.98)	3.22 (3.92)	3.22 (3.92)
	ε''	0.026	0.0198	0.0154	0.0109	0.0082	0.0080
B3	ε'	3.28 (4.07)	3.24 (3.96)	3.24 (3.96)	3.22 (3.92)	3.19 (3.86)	3.15 (3.77)
	ε''	0.0242	0.0176	0.0145	0.0113	0.0097	0.0085
C1	ε'	3.39 (4.27)	3.36 (4.21)	3.36 (4.21)	3.31 (4.10)	3.30 (4.08)	3.30 (4.08)
	ε''	0.0309	0.0252	0.0170	0.0089	0.0131	0.0112
C2	ε'	3.29 (4.06)	3.28 (4.04)	3.24 (3.96)	3.22 (3.92)	3.18 (3.84)	3.17 (3.81)
	ε''	0.0312	0.022	0.019	0.0135	0.0100	0.0065
C3	ε'	3.11 (3.69)	3.08 (3.63)	3.06 (3.59)	3.05 (3.58)	3.04 (3.56)	3.02 (3.52)
	ε''	0.0180	0.0135	0.0103	0.0097	0.0072	0.0059
C4	ε'	3.34 (4.17)	3.32 (4.12)	3.28 (4.04)	3.26 (4.00)	3.24 (3.96)	3.24 (3.96)
	ε''	0.0242	0.0161	0.0147	0.0114	0.0096	0.0095
C5	ε'	3.42 (4.33)	3.34 (4.17)	3.32 (4.12)	3.21 (3.90)	3.19 (3.86)	3.17 (3.82)
	ε''	0.0570	0.0407	0.0290	0.0153	0.0154	0.0128
C6	ε'	3.44 (4.37)	3.40 (4.29)	3.37 (4.23)	3.37 (4.23)	3.32 (4.12)	3.31 (4.10)
	ε''	0.0320	0.0190	0.0132	0.0099	0.0086	0.0099
C7	ε'	3.36 (4.21)	3.34 (4.17)	3.29 (4.06)	3.28 (4.04)	3.25 (3.98)	3.22 (3.92)
	ε''	0.0407	0.0272	0.0168	0.0080	0.0097	0.0098
D1	ε'	3.08 (3.55)	3.07 (3·53)	3.02 (3.43)	3.01 (3.41)	3.03 (3.45)	3.00 (3.40)
	ε''	0.034	0.0248	0.0126	0.0097	0.0053	0.00306
E1	ε'	3.76 (4.83)	3.73 (4.78)	3.61 (4.56)	3.59 (4.52)	3.55 (4.45)	3.44 (4.24)
	ε''	0.115	0.0904	0.0482	0.0421	0.043	0.0428
E2	ε'	3.64 (4.61)	3.62 (4.58)	3.57 (4.48)	3.58 (4.50)	3.52 (4.38)	3.46 (4.27)
	ε''	0.031	0.0284	0.023	0.0248	0.0256	0.0312

* Values in parenthesis refer to ε' of coals themselves.

while $\varepsilon^*=4.79-0.00j$ gives $\varepsilon_2^*=7.99-0.00j$. Again there is hardly any significant difference between the values of ε'_2, i. e. 7.96 versus 7.99.

A comparison of the values of Tables III and IV would reveal that the coals from foreign sources here examined exhibit entirely different dielectric behavior from the Japanese coals. In all of them strong frequency dependence of dielectric properties is found which is not so pronounced in most of the Japanese specimens.

The ε' values of Japanese coals generally show slight increases at the lower frequency side. Among them two samples E1 and E2 of higher oxgen contents may be noted, since they have a little higher value in ε' and show somewhat noteworthy dependence of ε'' upon frequency.

TABLE IV

DIELECTRIC CONSTANTS (ε') AND LOSS FACTORS (ε'') OF COALS* FROM FOREIGN SOURCES
(Paraffin-wax mixture, coal 56 vol %)

Ccal No.		300 c	1 kc	10 kc	100 kc	1 Mc	10 Mc
F 1	ε'	4.93 (7.69)	4.62 (6.98)	4.12 (5.84)	3.91 (5.37)	3.74 (5.00)	3.60 (4.71)
	ε''	0.53	0.419	0.285	0.149	0.097	0.0588
F 2	ε'	4.62 (6.98)	4.43 (6.53)	4.11 (5.81)	4.04 (5.66)	3.82 (5.18)	3.68 (4.87)
	ε''	0.315	0.236	0.187	0.115	0.0867	0.0760
F 3	ε'	4.66 (7.07)	4.41 (6.48)	4.14 (5.88)	3.96 (5.48)	3.82 (5.18)	3.66 (4.83)
	ε''	0.318	0.246	0.151	0.116	0.0902	0.0688
F 4	ε'	4.66 (7.07)	4.48 (6.64)	4.14 (5.88)	3.97 (5.51)	3.81 (5.16)	3.66 (4.83)
	ε''	0.359	0.262	0.171	0.123	0.0948	0.0768
F 5	ε'	5.01 (7.88)	4.79 (7.37)	4.44 (6.55)	4.22 (6.06)	3.97 (5.51)	3.82 (5.18)
	ε''	0.327 [0.775]	0.284 [0.664]	0.196 [0.448]	0.143 [0.321]	0.120 [0.264]	0.0936 [0.203]

* Values in parenthesis are ε' of coals and those in square bracket refer to ε'' of the coal concerned.

The behavior of ε'' of E1 and E2 is entirely different from other Japanese coals. Definite increase in ε'' with increasing frequency is found in these samples as was found in Tempoku brown coal[2], indicating the existence of some dispersion which is probably due to the rotation of OH groups.

As a general trend there is observed a slight increase of ε'' at the lower frequency side in most of the Japanese coals. No definite explanation can be offered for this phenomenon. Possibly it may be due to the presence of impurities such as trace of water which forms a conducting phase*.

Discussion

Having obtained rather ample data of dielectric constants of coals, either directly determined in a previous study[2] or indirectly estimated in the present research, it was thought of interest to make some comparison between the dielectric constant and other properties of coal.

To begin with, the change of the dielectric constant with carbon-content (dry, ash-free) will be examined. As the observed dielectric properties are not independent of the frequency of the measurement**, two graphs of ε' vs. C % plots are drawn for two representative frequencies, 1 kc/s and 1 Mc/s (Figs. 1 and 2).

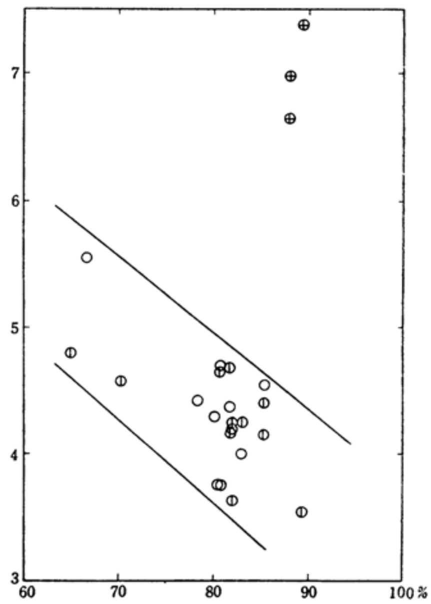

Fig. 1. Dielectric constants measured at frequency of 1 kc/s of coals of various carbon contents. ○, determined directly on Japanese coals; ⦶, estimated from powdered mixtures on Japanese coals; ⊕, ditto on foreign coals.

Among the widely scattered points there appears to be a general trend of increase in dielectric constant with decrease in carbon-content.

According to the infra-red absorption

* See for instance, C. P. Smyth, "Dielectric Bahavior and Structure," McGraw-Hill Book Co., New York (1955), p. 191.

** The curves in Fig. 3 illustrate different types of dependence of the dielectric constant upon the frequency.

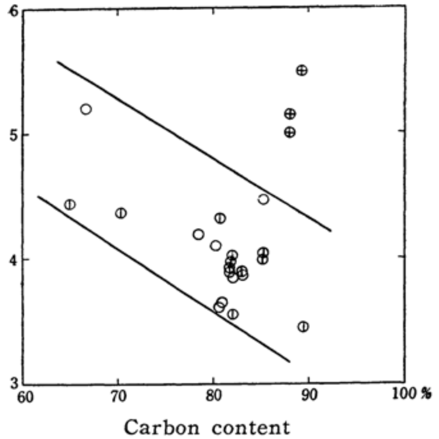

Fig. 2. Dielectric constants measured at frequency of 1 Mc/s of coals of various carbon contents. ○, ⦶ and ⊕, the same with Fig. 1.

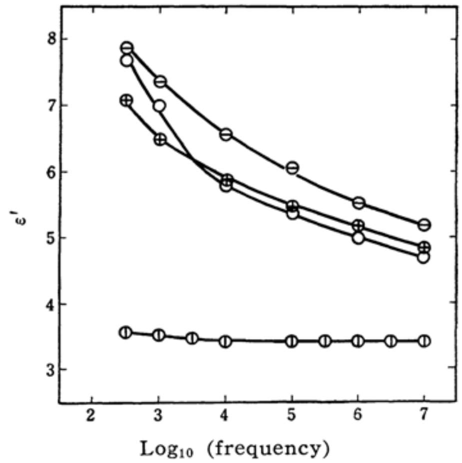

Fig. 3. Dielectric constant-frequency curves of high rank coals. ⦶, Yatake (Japan); ○, Indian coal; ⊕, Pocahontas (U. S. A.); ⊖, Durham (U. K.).

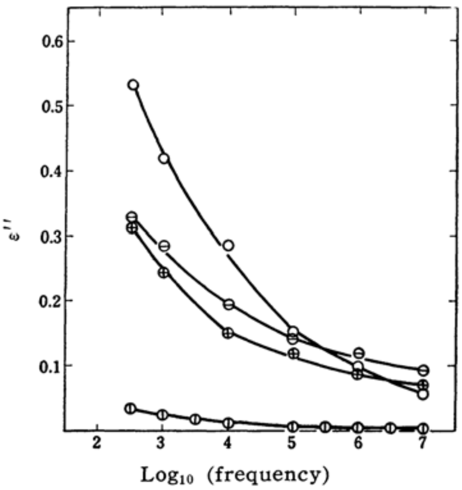

Fig. 4. Loss factor-frequency curves of powdered mixtures of high rank coals. ⦶, ○, ⊕ and ⊖, the same with Fig. 3.

studies[5,6] the intensities of bands concerning oxygen-containing groups of coal constituents, especially of the bonded OH at near 3.3 μ, appear to decrease as the oxygen-content decreases. These intensities become greater in the low rank coals of which the carbon-contents are in the range from 78 to 84 per cent. They fall in the higher rank coals, especially over 89 per cent carbon coals.

The oxygen-containing groups which appear to be rich in the low rank coals are provided with large electric moments. If the rotation of these polar groups is possible to a certain extent, they would make effective contributions to the dielectric constant.

Consequently it would be reasonable to conclude that the lower rank coals have the higher dielectric constants on account of the higher content of polar groups such as OH or CO.

In the range of carbon 88 to 90 per cent, very remarkable differences are recognized between the dielectric constants of foreign coals and of the Japanese coal here examined (See Fig. 1). The change in ε' of these coals with frequency is shown in Fig. 3. The value of Yatake coal (C % 89.4) is low and almost independent of frequency, while others (F1, F4 and F5) show pronounced anomalous dispersion: the dielectric constants greatly decrease with increasing frequency.

Regarding the foreign coals it will be of interest to examine the relation between the loss factor and frequency. In Fig. 4 ε'' values of the mixtures of coal and paraffin wax are shown. In each of them a steep rise of ε'' value is found in the lower frequency region. This also makes a remarkable contrast to the almost flat curve of Yatake coal.

Non-dispersive character is not limited to Yatake coal. Most of the Japanese bituminous coals (C % 80–87) may be regarded as lacking in anomalous dispersion*

5) J. K. Brown, *J. Chem. Soc.*, 744 (1955).
6) R. A. Friedel and J. A. Queiser, *Anal. Chem.*, **28**, 22 (1956).

* There is found an increase in ε'' values at the low frequency side, but as compared with values of coals from foreign sources the magnitude of this increase is small so that possibly it may be attributed to the presence of impurities.

(See the results for A1, B1–3, C1–4, C6–7 and D1 in Table III and data of previous reports[1,2]. Their dielectric constants are generally low — their dielectric properties in general resemble those of ordinary electric insulators.

It may be worth while to cite the results of infrared absorption studies on Japanese coals recently reported by Kozima and his co-workers[7]. The ratio of C_{arom}—H to C_{aliph}—H on the same specimens of Japanese coals, A1 and D1, of the present study was determined by them*. It was pointed out then that the ratio of Yatake coal (C % 89.4) was four times larger than that of Yubari coal (C % ca. 85.5). This remarkable difference, however, is not reflected in the dielectric constant (See Table III).

According to the above facts the following views would be offered. They are not merely of presumptive evidence based only upon the present results.

1) The high ε' values of foreign coals are due to the condensed aromatic structures with pi-electrons[8]. As described by van Krevelen and his co-workers[9] the influence of electric conductivity is evident. The loss factor-frequency curves in Fig. 4 are of the shape to be expected for a system of semi-conductor particles densely packed in an insulating medium[10,11].

2) Japanese high-rank bituminous coals as represented by Yatake coal appear to have rather different structures from the foreign coals. They are relatively poor in condensed aromatic structures. Possibly they are rich in hydroaromatic rings or in alkyl side chains[12].

Summary

By using a method of paraffin-wax mixture dielectric constants were determined for a variety of coals including five specimens from foreign sources. It was found that dielectric constants of lower rank coals are generally higher than those of bituminous coals of higher rank. Large difference in dielectric behavior was detected among the coal specimens (C % 87–90) from different sources. The present dielectric measurement supported the view that the nature of Japanese coals is particular as compared with European and American coals.

The writers wish to thank Professor G. Takeya for his kind interest and also for supplying the coal samples examined in this paper. Cordial thanks are also due to Dr. Y. Ozawa and to Mr. Y. Zyomoto for their friendly help in this work.

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7) K. Kozima, K. Sakasita and T. Yosino, *J. Chem. Soc. Japan* (Pure Chem.) **77**, 1432 (1956)

* These coal specimens were kindly provided by Dr. H. Honda, Resources Research Institute, Kawaguti-City, both to Prof. Kozima and to one of the present writers.

8) H. Inokuchi, This Bulletin, **24**, 222 (1951); **25**, 28 (1952).
9) M. P. Groenewege, J. Schuyer and D. W. van Krevelen, *Fuel*, **34**, 339 (1955).
10) C. P. Smyth, op. cit. p., 191.
11) B. V. Hamon, *Austra. J. Phys.*, **6**, 304 (1953).
12) A. Baba, "Progress in Coal Science," Vol. 2, Hakuasyobo, Tokyo (1956), p. 86.