Dielectric Investigation on Coals. II. Mixture of Coal Powder and Paraffin Wax.

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Introduction

Attempts have been described in a previous report[1] to prepare coal disks for examination from a coal block. Difficulties in the preparation of disks suitable for dielectric measurements are generally so great that this method can hardly be considered as practical or as convenient. In the experiments described in the present article a new method using powdered coal was employed. The coal specimen is reduced to powder form, mixed with melted paraffin wax and cooled in a suitable mould. Test pieces prepared thus from the solidified materials contain usually 56 volume percent of coal. From the dielectric properties of these mixtures the dielectric constants and loss factors of the component coals are to be calculated by using a proper equation for mixtures.

Experimental

Six specimens of Japanese bituminous coal were examined. Five were chosen among those* studied in a previous paper: I Moziri No. 4, carbon, 85.25%; II Moziri No. 3, carbon, 81.71%; III Moziri No. 9, carbon, 82.98%; IIIa Moziri No.11, carbon, 82.07%; and Vc Mitui-Bibai No. 1-3, carbon, 80.62%. The remaining one is: B Mayazi North-No. 1, for which the proximate analysis is: moisture, 1.01; ash, 8.43; volatile matter, 41.04 and fixed carbon, 49.52 %. Ultimate analysis for B is: ash, 2.47; C, 85.24; H, 5.86; O, 7.06; N, 1.67 and S, 0.16%. Paraffin wax used for preparing mixtures has the following properties at room temperature: dielectric constant, 2.46; loss factor, 0.0000 and specific gravity, 0.904.

Vitrain of coal specimen was pulverized in an agate mortar to a particle size below 100 meshes. The coal powder was dried in a desiccator at 105°C under 10^{-2} mmHg for 4-5 days. Then 15 g. of powder which had been thus thoroughly dried was poured into about 10 g. of melted paraffin wax, well mixed and solidified in a mould. A test piece of diameter ca. 40 mm and thickness ca. 5 mm was prepared from the solidified materials. Care was taken to secure uniform distribution of coal particles in the mixture.

The volume fraction of each mixture was controlled to have a constant value 0.56. Deviation from this standard was checked by collating the amounts of ash contained in the mixture and in the original coal specimen. Further examination was made of the range of errors in the final dielectric constant of coal which should arise from inaccuracies of the volume fraction taken (Fig. 1). Curve (b) represents the relation of Böttcher* between the dielectric constant of coal and that of mixture

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

* Chemical analyses of these samples were given in Ref. 1).

* See later reference.—Ref. 5).

Table I

Dielectric constant (ε') and loss factor (ε'') of coal-powder paraffin-wax mixture
(coal powder 56 vol%)

Sample No.		300c	1kc	3kc	10kc	100kc	300kc	1Mc	3Mc	10Mc	20Mc	50Mc
I	ε'	3.48	3.46	3.42	3.40	3.32	3.30	3.28	3.26	3.26	3.26	3.27
	ε''	0.0570	0.0492	0.0396	0.0365	0.0266	0.0287	0.0301	0.0259	0.0220	0.0213	0.0136
II	ε'	—	3.59	3.57	3.52	3.30	3.24	3.22	3.20	3.18	3.22	3.17
	ε''		0.0895	0.0805	0.0704	0.0270	0.0205	0.0183	0.0150	0.0147	0.0109	0.0159
III	ε'	3.40	3.38	3.34	3.32	3.26	3.22	3.21	3.21	3.19	3.18	3.18
	ε''	0.0295	0.0294	0.0268	0.0252	0.0212	0.0180	0.0185	0.0152	0.0129	0.0126	0.0114
IIIa	ε'	—	3.38	3.36	3.33	3.30	3.28	3.27	3.25	3.23	3.18	—
	ε''		0.0352	0.0295	0.0267	0.0222	0.0223	0.0206	0.0195	0.0186	0.00868	
Vc	ε'	3.61	3.57	—	3.51	3.46	—	3.42	—	3.37	—	—
	ε''	0.0600	0.0344		0.0327	0.0230		0.0247		0.0211		
B	ε'	3.34	3.33	—	3.32	3.28	—	3.26	—	3.24	—	—
	ε''	0.0390	0.0304		0.0256	0.0135		0.0139		0.0112		

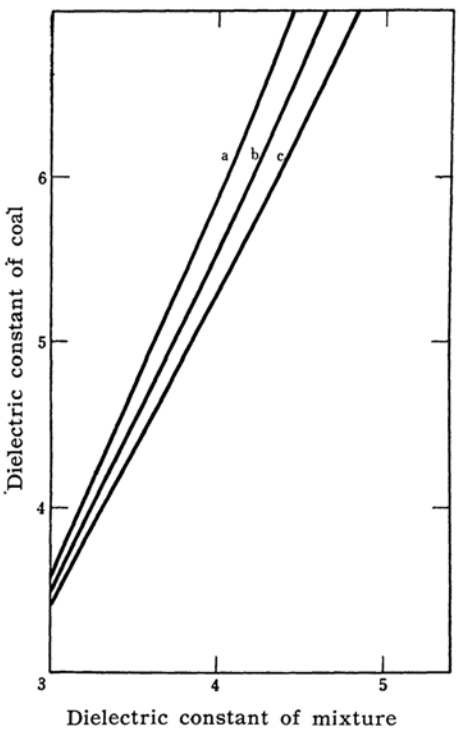

Fig. 1. The relation between the dielectric constant of coal itself and that of the powdered mixture as given by Bottcher equation. Volume fraction of coal in the mixture: curve a, 0.52; curve b, 0.56 and curve c, 0.60.

which has 56 vol% coal. If the volume percentages happen to become 52% or 60%—possibly they correspond to the maximum deviations—the relation between $\varepsilon'_{\text{coal}}$ and $\varepsilon'_{\text{mixture}}$ will be represented by either curve (a) or (c). A glance at these curves will show that possible maximum error in $\varepsilon'_{\text{coal}}$ amounts to several percent, viz., below $\pm 6\%$ for $\varepsilon'_{\text{coal}}<5$; below $\pm 6.4\%$ for $\varepsilon'_{\text{coal}}<6$.

Three methods of dielectric measurement were used in the frequency range covered. Measurements at frequencies from 300 c/s to 10 kc/s were carried out by means of an impedance bridge. Between 100 kc/s and 50 Mc/s a Q meter was used. A standing-wave method[2] of measuring dielectric properties was used at frequency of 4000 Mc/s.

The accuracy of measurement is considered, in general, to be $\pm$ 3 percent for ε'; but to be $\pm$ 15 percent at the microwave frequency. For ε'' the accuracy is much less, but the order of the values is reliable.

The results of measurements are collected in Tables I and II. They refer to paraffin-wax mixtures, having 56 vol% coal (Table I) and 50 vol% coal (Table II), respectively. All the measurements were carried out at room temperature.

Table II

Dielectric constants of 50 vol% mixtures of Mayazi coal B of various degrees of drying

condition	100 kc	300 kc	1Mc	3Mc	10 Mc	4000 Mc
vac. dry (v.d)	3.17	—	3.14	—	3.11	2.8
air dry (a.d)	3.36	—	3.34	—	3.30	2.8
wet (v.d-w)	3.75	3.64	3.54	3.51	3.30	3.0
wet (a.d-w)	4.62	4.44	4.31	4.18	4.03	2.7
paraffin*	2.43	—	2.40	—	2.37	2.32

* Paraffin wax employed in this measurement contained some impurities.

Discussion

There are available many equations[3,4] concerning the dielectric constants of non-homogeneous mixtures. Suppose that coal particles be nearly spherical in shape and that they be insulated by the medium

2) W. Jackson, *Trans. Faraday Soc.*, **42A**, 91 (1946).
3) W. F. Brown, *J. Chem. Phys.*, **23**, 1514 (1955); R. S. Smith, *J. Appl. Phys.*, **27**, 824 (1956).
4) M. Kubo and S. Nakamura, This Bulletin, **26**, 318 (1953); K. Higasi, *Monogr. Res. Inst. Appl. Elec.*, Hokkaido Univ., **5**, 9 (1955).

TABLE III

DIELECTRIC CONSTANTS OF COALS ESTIMATED BY USING THE FORMULAE OF BÖTTCHER (Bo) AND BRUGGEMAN (Br)

		300c	1kc	3kc	10kc	100kc	300kc	1Mc	10Mc	50Mc
I	Bo	4.45 (0.98)	4.41 (0.97)	4.33 (0.95)	4.29 (0.95)	4.12 (0.92)	4.08 (0.90)	4.04 (0.90)	4.00 (0.91)	4.02 (0.89)
	Br	4.49 (0.99)	4.44 (0.98)	4.35 (0.96)	4.32 (0.96)	4.14 (0.92)	4.10 (0.91)	4.05 (0.91)	4.00 (0.91)	4.02 (0.89)
II	Bo	—	4.68 (1.07)	4.64 (1.08)	4.53 (1.09)	4.08 (0.98)	3.96 (1.00)	3.92 (1.00)	3.84 (1.01)	3.81 (1.00)
	Br	—	4.71 (1.08)	4.68 (1.09)	4.56 (1.10)	4.10 (0.99)	3.97 (1.00)	3.94 (1.01)	3.84 (1.01)	3.82 (1.01)
III	Bo	4.29 (1.07)	4.25 (1.06)	4.17 (1.05)	4.12 (1.04)	4.00 (1.02)	3.92 (1.01)	3.90 (1.01)	3.86 (1.00)	3.84 (1.00)
	Br	4.32 (1.08)	4.27 (1.07)	4.18 (1.05)	4.14 (1.05)	4.00 (1.02)	3.94 (1.02)	3.91 (1.01)	3.86 (1.00)	3.84 (1.00)
IIIa	Bo	—	4.25 (1.01)	4.21 (1.02)	4.14 (1.01)	4.08 (1.02)	4.04 (1.04)	4.02 (1.04)	3.94 (1.04)	—
	Br	—	4.27 (1.02)	4.22 (1.02)	4.14 (1.01)	4.10 (1.03)	4.05 (1.04)	4.02 (1.04)	3.95 (1.05)	—
Vc	Bo	4.73 (1.00)	4.64 (0.99)	—	4.51 (1.01)	—	—	—	—	—
	Br	4.77 (1.01)	4.68 (1.00)	—	4.54 (1.01)	—	—	—	—	—

of paraffin wax. The following equation of Böttcher[5] is claimed to have general applicability to such a dispersed system

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

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 particle in the mixture.

Bruggeman's equation[6] which has been successfully applied to the analysis of rubber-carbon black mixtures[7] has the following form:

$$\frac{\varepsilon'_2-\varepsilon'}{\varepsilon'_2-\varepsilon'_1}=(1-v_2)\sqrt[3]{\frac{\varepsilon'}{\varepsilon'_1}} \qquad (2)$$

From the values of dielectric constants of mixtures recorded in Table I, the dielectric constants of the coals were calculated by using both Eqs. (1) and (2). The results of the calculation are shown in Table III in which Bo and Br denote Böttcher and Bruggeman, respectively. As the dielectric constants of these coal specimens are known by the direct determination on coal disks[1], a comparison between the estimated and actual values will be of interest. The ratio of $\varepsilon'_{estimated}/\varepsilon'_{actual}$ was taken for each sample and for each of the two equations—(See the values in parentheses in Table III). The general agreement may be regarded as satisfactory for most practical purposes.

In the above consideration it is assumed that the coal particles are insulated from each other by the paraffin-wax medium. On the contrary, coal particles are very densely packed in the mixture, so that in some places they must be touching each other. That is, some of them are supposed to be in good contact producing chains or larger aggregates. Considering this situation, two extreme cases will be examined for the sake of illustration. Suppose that neither coal particles nor paraffin wax are mixed but exist in a state of parallel layers. Let it be supposed in one case that the layers are parallel to the electric field; there will be the relation:

$$\varepsilon'=(1-v_2)\varepsilon'_1+v_2\varepsilon'_2 \qquad (3)$$

and in the other case that they are all perpendicular to the field; there will be the relation:

$$\frac{1}{\varepsilon'}=\frac{1-v_2}{\varepsilon'_1}+\frac{v_2}{\varepsilon'_2} \qquad (4)$$

In order to make clear the relations existing among these equations of entirely different appearance, viz., Eqs. (1), (2), (3) and (4), an inspection of Fig. 2 will be useful in which on the basis of these equations ε'_2 is plotted against ε' using the same assumptions: $v_2=0.56$ and $\varepsilon'_1=2.46$. It is to be noted that curves 4 and 5 which represent Bruggeman and Böttcher equations, respectively, lie in the middle

5) C. J. F. Böttcher, *Rec. trav. chim.*, **64**, 47 (1945); C. J. F. Böttcher, "The Theory of Electric Polarisation," Elsevier, Amsterdam (1952), p. 417.

* Hereafter ε' and ε'_2 will be used instead of $\varepsilon'_{mixture}$ and ε'_{coal}, respectively.

6) D. A. G. Bruggeman, *Ann. Phys.*, **24**, 636 (1935).

7) B. Gross and R. M. Fuoss, *J Phys. Chem.*, **60**, 474 (1956). See references cited there.

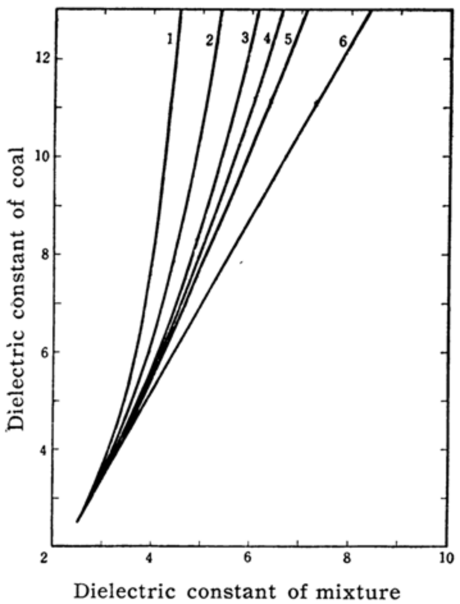

Fig. 2. Relations between the dielectric constant of coal itself and that of the powdered mixture with 56 vol % coal. Curve 1, given by Eq. (4) for a series arrangement; curve 2, Clausius-Mosotti relation; curve 3, Eq. (6) of Lewin; curve 4, Eq. (2) of Bruggeman; curve 5, Eq. (1) of Bottcher; and curve 6, Eq. (3) for a parallel arrangement.

part of the region outlined by curves 1 and 6 which are given by Eqs. (4) and (3).

As the mixture in the present study is not to be considered as a homogeneous phase, the use of the Clausius-Mosotti equation to which Groenewege et al.[8] referred, will be absurd. But as is seen by curve 2 in Fig. 2 this equation does represent some average state between those defined by Eqs. (4) and (1) or Eqs. (4) and (2).

Next, let the case be examined when the coal component has a different volume fraction from 0.56. In Table IV the case of 50 vol % coal is studied. Estimated

TABLE IV

ESTIMATED DIELECTRIC CONSTANTS FOR MAYAZI COAL (vac. dry)

		100kc	1Mc	10Mc	4000Mc
Bo	56%	4.04	4.00	3.96	——
	50%	4.05	4.02	3.99	3.34
Br	56%	4.05	4.00	3.97	——
	50%	4.08	4.04	4.00	3.35

8) M. P. Groenewege, J. Schuyer and D. W. van Krevelen, *Fuel*, **34**, 339 (1955).

values from 50 % are in good agreement with those from 56 %. Consequently, it may be concluded that the use of Eqs. (1) and (2) is justified so far.

It is to be noted that the above equations are related only to the dielectric constant and not to the loss factor. A more general equation including the latter has recently been provided by Lewin[9] for the case of perfectly spherical particles* in insulating medium. For the complex dielectric constants as defined by $\varepsilon^*=\varepsilon'-j\varepsilon''$, $\varepsilon_1^*=\varepsilon_1'-j\varepsilon_1''$ and $\varepsilon_2^*=\varepsilon_2'-j\varepsilon_2''$, the following equation holds:

$$\varepsilon^*=\varepsilon_1^*\left(1+\frac{3v_2}{\dfrac{\varepsilon_2^*F(\Theta)+2\varepsilon_1^*}{\varepsilon_2^*F(\Theta)-\varepsilon_1^*}-v_2}\right), \qquad (6)$$

where

$$F(\Theta)=\frac{2(\tan\Theta-\Theta)}{(\Theta^2-1)\tan\Theta+\Theta},$$

and

$$\Theta=\frac{2\pi a}{\chi}\sqrt{\varepsilon_2^*}$$

in which a is the radius of the coal particle and λ is the wave length of the electric wave used in the dielectric measurement. The application of Eq. (6) to the present problem was made first for the case when there is no loss factor (see curve 3 in Fig. 2). Then calculation was repeated for the cases when the mixtures have appreciable loss factors. It was ascertained by these calculations that even when ε'' amounts to a considerable magnitude 0.1**, the dielectric constant can be safely estimated within experimental error with the payment of little attention to the presence of the loss factor.

Böttcher and Bruggeman equations have been originally derived only for real dielectric constants, but they may be transformed into more general equations including the imaginary part when a complex dielectric constant is used instead of the real one. It can be proved by numerical calculations using the general equation of Böttcher thus obtained that the existence of appreciable loss factors does not vitiate the results of the estimation shown in Table III.

9) L. Lewin, *J. Inst. Elec. Engrs.*, **94**, 65 (1947); E. Meyer, H. J. Schmidt und H. Severin, *Z. angew. Phys.*, **8**, 257 (1956).

* A comparison of the theoretical curve 3 (Fig. 2) for perfectly spherical particles with the experimental data will suggest that the formation of chains does occur in the mixture.

** The maximum value of ε'' observed in the present study is 0.0895 at 1 kc/s obtained for the coal sample II.

Lastly the results shown in Table II will be again considered. It will be seen that an air-dry sample—coal powder was dried in air for 4–6 days at 105°C—has a slightly higher dielectric contant than that of the vacuum dried sample. This may indicate that some polar substances are produced upon oxidation*. Further, water absorption by dried samples (air-dry as well vac-dry samples) greatly increases the dielectric constant.

It should be noted that all the samples come to have the same dielectric constant of about 2.8 at the frequency of 4000 Mc/s. This fact suggests that all the dipoles in the coal—irrespective of whether they originally belong to the coal, or are produced on oxidation, or are of the water molecules adsorbed by the coal—are completely blocked from rotation**. Further this view is substantiated by the fact that the dielectric constant 3.35 for coal at this frequency of 4000 Mc/s can be regarded as the optical dielectric constant (See Table IV). In fact this magnitude is just equal to the square of the refractive index[10] of the coal having the same carbon content.

* See, in this connection, W. N. Adams and G. J. Pitt, *Fuel*, **34**. 383 (1955).

** The condition of non-rotation of dipoles is not satisfied in the liquid state until the frequency become higher than 30,000 Mc/s (at room temperature). The corresponding frequency in the solid state is expected to be low, since the viscosity or the hindering potential of rotation should be much higher than in the liquid state (C. P. Smyth, "Dielectric Structure and Behavior," (1955)).

10) D. W. van Krevelen, *Brennstoff-Chem.*, **34**, 167 (1953).

Summary

A new method using powdered coal and paraffin wax was proposed for measuring the dielectric constant of coal concerned. In order to check the validity of this method, experiments were conducted on five coal specimens for which direct determination of dielectric constant had been made by the writers. Special attention was paid to the choice of a mixture formula and also to the influence of the electric conductivity upon the dielectric constant. It was concluded then that the present method could reproduce the dielectric constant of the coal with the fair precision of ± 10 %.

The microwave measurement on one specimen reveals that all the dipoles in coal are completely inhibited from rotation at this frequency.

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