

MAXWELL-WAGNER LOSS AND ABSORPTION CURRENTS IN DIELECTRICS

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Summary

The dielectric loss factors of a number of heterogeneous mixtures have been measured at frequencies up to 3 Mc/s. The mixtures consisted of a non-polar base material and small percentages of a slightly conducting solid or liquid "impurity".

Two types of dispersion of the solid impurity were studied, one using discrete spheres and the other using a fine powder covering the surfaces of large grains of the base material. For the discrete spheres, good agreement with Wagner's theory was obtained. The results for the powdered solid impurity and the liquid impurity show that such mixtures can give rise to dielectric loss factors that increase slowly with decreasing frequency over a wide frequency range, and finally merge with the loss due to D.C. conductivity. The mixtures also gave rise to anomalous charging currents when direct current was applied. These currents were measured, and their relation to the A.C. loss factors indicated.

The behaviour of the mixtures under different D.C. and A.C. potential gradients was also studied. It was found that the steady-state D.C. conductivity increased with increasing potential gradient, but that the A.C. loss factor at a particular frequency did not change. An explanation is suggested for this behaviour.

The results are compared with the published data for practical dielectrics, and support the view that, at least for non-polar dielectrics, the small loss factors and D.C. charging currents frequently observed may be due to conducting impurities present as a separate phase.

I. INTRODUCTION

Several materials of practical importance have loss factors that are small at radio and audio frequencies but increase considerably with decreasing frequency below this range. The mechanism responsible for this loss is not clearly understood. Since loss of this type is found in materials of very different natures, it is probable that a number of mechanisms are involved. In some cases (e.g. glass, and perhaps some polar materials) it is likely that the loss is an inherent property of the material; but in other cases, and especially with non-polar materials, it is usually thought that the loss is due to impurities. However, very little is known about the nature, quantity, or distribution of impurities that would lead to dielectric loss of the observed type, and few investigations have been made on systems of known composition and structure.

The present paper gives the results of an experimental investigation of certain non-polar materials to which have been added small quantities of slightly conducting "impurities". In all cases the added impurity formed a separate

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phase, so that the systems studied were heterogeneous mixtures. Dielectric loss due to slightly conducting impurities present as a separate phase in a material is now referred to as "Maxwell-Wagner loss", since it was first investigated theoretically by Maxwell (1892) and Wagner (1914). A brief summary of the theoretical properties of Maxwell-Wagner systems will simplify the discussion of the experimental results.

For the simple case of spherical particles (conductivity σ_2 ohm⁻¹ cm⁻¹, relative permittivity ϵ'_2) distributed at random in a base material of relative permittivity ϵ'_1 , Wagner (1914) showed that the loss factor* of the mixture is given by

$$\epsilon'' = \frac{9q(\epsilon'_1)^2}{2\epsilon'_1 + \epsilon'_2} \cdot \frac{f/f_{max}}{1 + (f/f_{max})^2}, \dots\dots\dots (1)$$

where

$$f_{max} = 1.8 \times 10^{12} \sigma_2 / (2\epsilon'_1 + \epsilon'_2), \dots\dots\dots (2)$$

q is the volume fraction of conducting material present in the mixture, and f is the frequency in c/s. The equations hold only for values of q so small that interaction between the fields of neighbouring particles can be neglected. Expressions similar to (1) and (2) were obtained by Sillars (1937) for the case of spheroidal particles whose unique axes are parallel to the applied field.

Figure 1 shows the variation of ϵ'' with frequency for spheres and prolate spheroids with two different axis ratios. The curves were calculated from the equations of Wagner and Sillars, using the following constants :

$$\epsilon'_1 = 2.3, \epsilon'_2 = 5.0, \sigma_2 = 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}, q = 0.01.$$

The dashed line in Figure 1 shows the loss factor that would be obtained if the same impurity were in the form of one or more uniform cylinders extending from one electrode to the other. Provided $\epsilon'_2 \gg \epsilon'_1$, as would usually be the case, this line represents an upper limit to the loss factor at any frequency, and for any shape and distribution of the impurity. The equation for the dashed line is

$$\epsilon'' = 1.8 \times 10^{12} \cdot q \sigma_2 / f, \dots\dots\dots (3)$$

or more generally,

$$\epsilon'' = q \cdot \epsilon''_2, \dots\dots\dots (4)$$

where ϵ''_2 is the loss factor of the impurity itself.

The importance of the shape of impurity particles in a Maxwell-Wagner system can be clearly seen from Figure 1, since all curves are for the same amount of a given impurity. Uneven distribution of particles of a given shape may be equally important. When only the nature and amount of impurity are known, the only quantitative estimate of the properties of a mixture that appears

* ϵ' and ϵ'' are respectively the real and imaginary parts of the complex relative permittivity. ϵ'' is related to the conductivity σ and the frequency f by the equation

$$\sigma = 0.55 \epsilon'' f \times 10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1},$$

and to the loss angle δ by the equation

$$\epsilon'' = \epsilon' \tan \delta.$$

possible is the loss factor at frequencies greater than f_{max} (equation (2)). The experimental results given later have been assessed in this way.

The materials used were chosen for experimental convenience, rather than as being typical of materials or impurities of practical importance. The non-polar base materials used were paraffin wax, *n*-docosane (a pure long-chain saturated hydrocarbon, $C_{22}H_{46}$) and polytetrafluoroethylene (P.T.F.E.). The latter was used in the form of the spongy powder supplied for moulding.

Results are given for one solid and one liquid impurity, although a number of other materials were used as impurities during the investigation (Hamon and Meakins 1950). The impurities for which results are reported are *n*-decyl

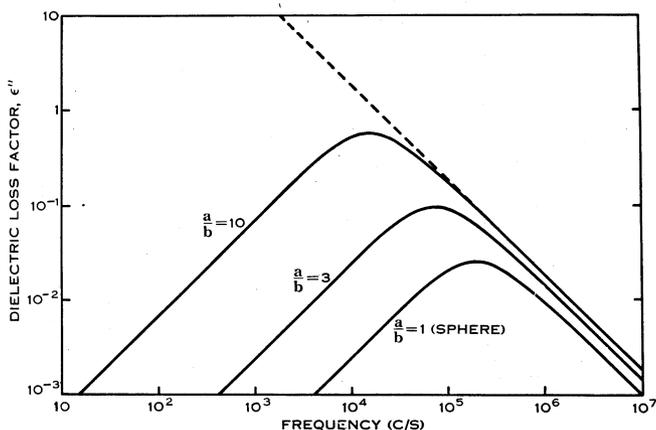


Fig. 1.—Dielectric loss factor as a function of frequency for spherical particles and for prolate spheroids with their long axes parallel to the field, calculated from the equations of Wagner and Sillars. a/b = ratio of axes.

alcohol ($C_{10}H_{21}OH$, m.p. $6.4^\circ C$), and copper phthalocyanine. The conductivities of the samples of these materials used in the present programme were of the order of 10^{-8} and 10^{-6} $\text{ohm}^{-1} \text{cm}^{-1}$ respectively.

The absorption and conduction currents obtained when a D.C. potential was applied to the samples were measured, as well as the more usual A.C. properties. For convenience in correlating the A.C. and D.C. results, the currents measured on direct current have been converted to loss factors at very low frequencies (Hamon 1952) and plotted on the one graph with the directly observed A.C. loss factors.

II. MATERIALS AND PROCEDURE

(a) Materials

The *n*-decyl alcohol was obtained from commercial material by vacuum distillation through an efficient fractionating column. *n*-Docosane from a previous programme was purified by recrystallization before use. The paraffin wax and P.T.F.E. powder were used as received, but selection on the basis of electrical tests was necessary for the wax, as not all samples showed sufficiently

low dielectric loss. The copper phthalocyanine powder was a commercial product and was not purified before use.

For each of the three solids used as base material (paraffin wax, *n*-docosane, and P.T.F.E.) the measured loss factor was less than 0.001 at all frequencies from 0.0001 c/s to 100 kc/s.

(b) *Preparation of Samples*

The method of mixing depended on the nature of impurity and base, and will be described in Section III. After mixing, the material was in all cases pressed into a flat circular disk by a hydraulic press.

The compositions are expressed as percentages by volume.

(c) *Electrical Measurements*

The disks were measured between mercury electrodes of the type described by the Electrical Research Association (1933). On several occasions the results obtained with these electrodes were checked against those obtained with aluminium foil electrodes, which were pressed onto the sample when in the mould. No significant differences were found, either on direct or alternating current. The measuring techniques used are given in earlier publications (see, e.g. Dryden and Welsh 1951; Hamon 1952).

All measurements were carried out in shielded enclosures at a temperature of 20 °C. It was estimated that the loss factor values deduced from bridge measurements were not in error by more than ± 5 per cent. or ± 0.001 , whichever was greater, but the values deduced from D.C. measurements might have been in error by ± 10 per cent. The measurements of D.C. conductivity at different potential gradients, reported in Section III (e), were made in a bridge circuit so that more accurate relative values could be obtained.

The conductivity of the *n*-decyl alcohol was measured in a conductivity cell with bright platinum electrodes. The cell was calibrated with 0.01N and 0.001N potassium chloride solutions.

Double logarithmic coordinates have been used for the graphs of loss factors as functions of frequency. With these coordinates, steady-state D.C. conduction corresponds to a straight line with a slope of -45° at the low frequency end of the curve. To save space, experimental points in this region corresponding to loss factors greater than 100 have not been shown on the curves.

III. RESULTS AND DISCUSSION

(a) *Discrete, Solid Particles of Impurity*

It was thought worth while, as a basis for work on more complicated mixtures, to prepare a mixture containing discrete spherical particles of impurity, and to compare the measured values of loss factor with those calculated from equations (1) and (2). Sillars (1937) prepared such a mixture by dispersing water in paraffin wax, but numerical agreement between observed and calculated results was not good.

The material used as impurity in the present work was copper phthalocyanine. The powder was pressed into a disk and its relative permittivity and

loss factor measured at different frequencies (Fig. 2). The disk, which was hard and brittle, was crushed and the resulting particles sieved to obtain a fairly uniform size. The particles were then ground to approximately spherical shape by a compressed air device (Bond 1951). After further sieving to remove dust formed by the grinding, the particles were mixed with paraffin wax, the volume concentration being 0.62 per cent.

Figure 3 shows the loss factor measured on a disk sample pressed from the above mixture, together with the values calculated from equations (1) and (2). Since neither σ_2 nor ϵ_2' was sufficiently independent of frequency, it was necessary

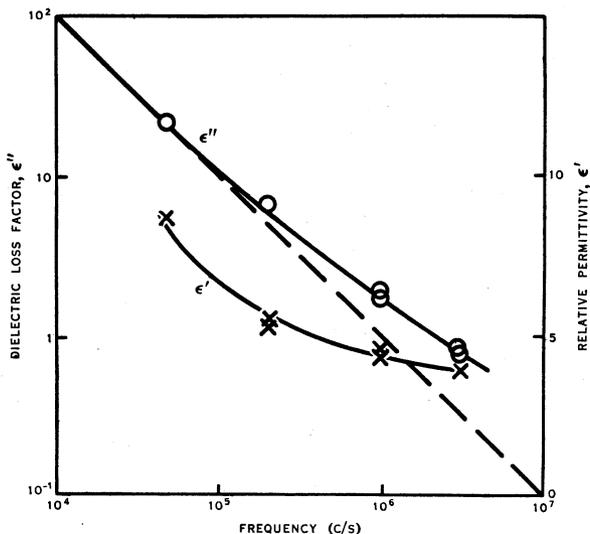


Fig. 2.—Dielectric loss factor and relative permittivity, as functions of frequency, for copper phthalocyanine.

to use different values at each frequency at which a calculated value of the loss factor of the mixture was required. The values were obtained from Figure 2, using the relation

$$\sigma = 0.55 \epsilon'' f \times 10^{-12} \dots \dots \dots (5)$$

The measured value of ϵ_1' , the relative permittivity of the wax, was 2.30. The curve calculated in this way is shown by the dashed line in Figure 3, and is slightly broader than the curves in Figure 1. The agreement between the observed and calculated values is satisfactory except at frequencies below about 5×10^4 c/s, where the observed values are appreciably greater than the calculated ones. This discrepancy may be due to slight lack of uniformity in the properties of the pressed disk, or to the fact that the particles were not exactly spherical. A photograph of part of the disk is reproduced in Plate 1, Figure 1.

Similar experiments were carried out using particles that had not been ground. The shape, height, and position of the loss factor curve were not altered appreciably by using particles of irregular shape. These tests also showed that

the loss factor is approximately linear with concentration, at least up to concentrations of about 3 per cent. This is to be expected, as it is unlikely that interaction between the electric fields of neighbouring particles will be significant at such low concentrations.

(b) *Finely Powdered Impurity at the Boundaries of Large Grains*

A model that should more nearly approximate to some practical materials can be made by covering large grains of the base material with an impurity in the form of a fine powder. A mixture of this kind can be expected to show a steady-state D.C. conductivity if the covering of each grain is sufficiently complete to produce conducting paths that are continuous from one electrode to the other.

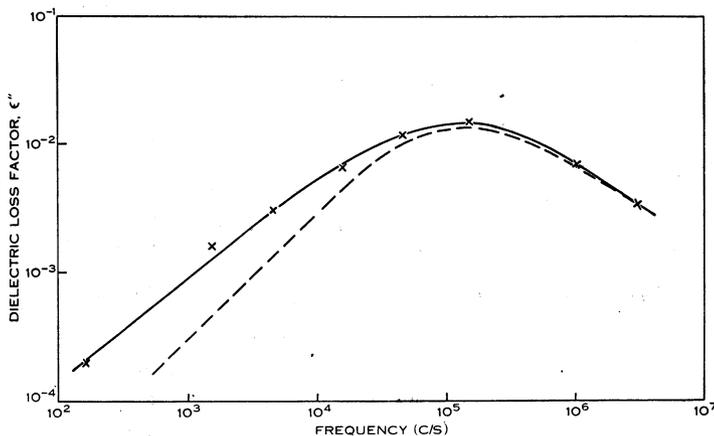


Fig. 3.—Dielectric loss factor as a function of frequency for discrete spherical particles of copper phthalocyanine embedded in paraffin wax. Solid curve, experimental; dashed curve, calculated from Wagner's equation.

For a given concentration, the D.C. conductivity should depend on the ratio between the diameters of the particles of base material and impurity, being greater for large ratios. In general, only a small fraction of the impurity will be favourably placed for D.C. conduction and the greater part of the impurity will only be able to contribute to energy loss in an A.C. field.

Figure 4 shows loss factor-frequency curves for three mixtures of copper phthalocyanine powder and paraffin wax. In preparing these samples the wax was crushed and sieved to get particles whose sizes were between about 0.05 and 0.15 cm. These particles were mixed with copper phthalocyanine powder (particle size about 10⁻⁴ cm) by shaking. The mixtures were pressed in the usual way. A photomicrograph of a thin section of the 0.62 per cent. sample is shown in Plate 1, Figure 2. The concentration of impurity at grain boundaries can be seen clearly.

The results shown in Figure 4 are of the general shape to be expected from the above considerations. The two higher concentrations, 0.62 and 1.9 per cent., show steady-state D.C. conductivity at frequencies below 1 c/s and 0.001 c/s

respectively, while in the 0.19 per cent. sample the concentration is too low for D.C. conductivity. At frequencies higher than f_{max} (1.4×10^5 c/s, see Fig. 3) all three curves approach the limit curves discussed in Section I, which in this case are respectively 1.9, 0.62, and 0.19 per cent. of the loss factor curve for the copper phthalocyanine in bulk (Fig. 2). Except in this high frequency region, the loss factor is no longer linear with concentration, as was the case with discrete particles.

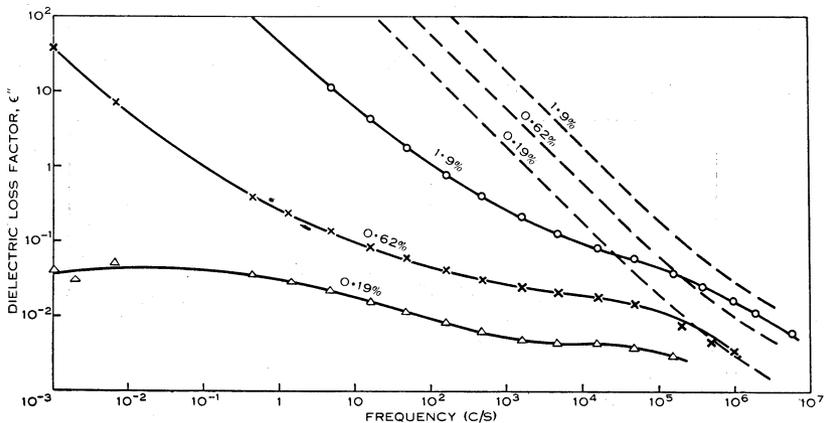


Fig. 4.—Dielectric loss factor as a function of frequency for three percentages of copper phthalocyanine powder mixed with paraffin wax. The dashed curves give the theoretical upper limit to the loss factor.

(c) Liquid Impurities

Results similar to those in Figure 4 were obtained when liquid long-chain alcohols were mixed with either paraffin wax, docosane, or P.T.F.E. powder.

Figure 5 shows the results for *n*-decyl alcohol mixed with P.T.F.E. powder at three concentrations. To ensure uniform distribution of the alcohol, it was dissolved in pure dry light petroleum before being added to P.T.F.E. The light petroleum was then evaporated off until the weight was constant.

Since the alcohol is colourless, the nature of its distribution in these disks is not as well known as in the case of the copper phthalocyanine-wax mixtures. It appears certain, however, that the alcohol forms a film on the surfaces of the P.T.F.E. grains, in much the same way as the copper phthalocyanine powder covers the wax grains. The formation of a solid solution, or appreciable penetration of the P.T.F.E. by the alcohol molecules, is not to be expected in view of the inert nature of the P.T.F.E. towards all normal solvents.

The increasing dependence of loss factor on concentration as the frequency decreases is clearly shown in Figure 5. At 1 c/s, for example, the loss factor increases by a factor of about 600 when the concentration increases by a factor of 9, while at 10^4 c/s the corresponding increase in loss factor is only about 30 times. From another point of view, the higher the loss factor at a particular frequency the steeper the curve of loss factor as a function of frequency. A

point of similarity with commercial materials is that an appreciable part of each of the curves of Figure 5 can be approximated by the empirical equation

$$\epsilon'' = \kappa f^{-\alpha},$$

where κ and α are positive constants (see, e.g. Hartshorn and Ward 1935).

For frequencies up to 10^5 c/s, the conductivity and relative permittivity of *n*-decyl alcohol are independent of frequency. The conductivity, however, depends on the degree of purity, and increases appreciably even when stored in a stoppered bottle in a desiccator. The conductivity of the alcohol used for the three samples whose properties are shown in Figure 5 was 9.6×10^{-9} ohm $^{-1}$ cm $^{-1}$,

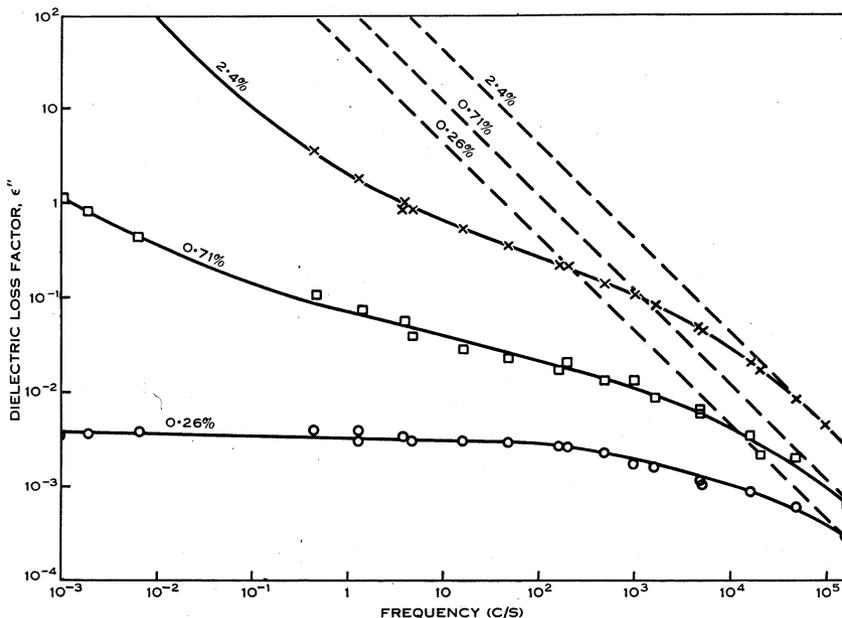


Fig. 5.—Dielectric loss factor as a function of frequency for three concentrations of *n*-decyl alcohol in P.T.F.E. The dashed lines give the expected upper limit to the loss factor.

and the limit curves shown in the figure are based on this value. The value of f_{max} , the frequency at which maximum loss would be expected for discrete spherical particles of decyl alcohol in P.T.F.E., is 1.5×10^3 c/s. It is seen from Figure 5 that the loss factor falls steeply with increasing frequency above f_{max} , and that the limiting values are reached, or even slightly exceeded, at a frequency of 10^5 c/s. This point will be discussed further in relation to the results shown in Figure 6.

To compare different base materials, the results for mixtures of 1 per cent. by volume of decyl alcohol with P.T.F.E., paraffin wax, and docosane are shown in Figure 6. The P.T.F.E. curve was obtained from the results given in Figure 5 by interpolation between the 2.4 and 0.71 per cent. curves, using the formula $\epsilon'' = A\theta^n$, where θ is the concentration and A and n are constants at a particular

frequency. The *n*-docosane and paraffin wax samples were prepared either by mixing the liquid alcohol with the molten base material, allowing the mixture to solidify, then crushing and pressing in a mould, or, more simply, by grinding the alcohol and base material with a mortar and pestle at room temperature and then pressing. The two techniques gave essentially the same result. Samples were reproducible to within about ± 20 per cent. in loss factor, as can be seen from the paraffin wax curve which has been drawn through points obtained from three different samples. Some mutual solution of alcohol and base is to be expected in the case of paraffin wax and docosane, but the fact that the loss factor curves are sensibly independent of the method of mixing, and are of the same general shape as the P.T.F.E. curves, shows that the extent of this mutual solution is probably small.

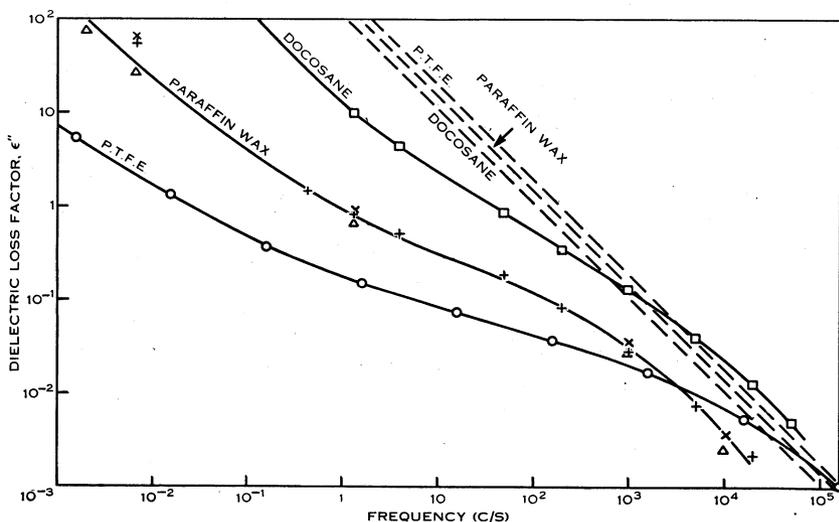


Fig. 6.—Dielectric loss factor as a function of frequency for 1 per cent. mixtures of *n*-decyl alcohol with three different base materials. The dashed curves give the theoretical upper limit to the loss factor.

Separate limit lines have been shown in Figure 6 for each sample, since the conductivity of the alcohol was slightly different in each case.

The loss in the *n*-docosane sample is appreciably higher at all frequencies than that in either the wax or P.T.F.E. samples, and is over twice as great as the expected upper limit at high frequencies. This suggests that the conductivity of the decyl alcohol in the mixture is greater than the bulk value. This could be due to orientation of the alcohol molecules as a result of adsorption on the docosane.

A similar effect is present to a smaller extent in the P.T.F.E. samples, since the difference in relative permittivities of the alcohol and P.T.F.E. (8 and 1.9 respectively) should prevent the loss factor becoming equal to the upper limit at any frequency.

The low value of loss factor at low frequencies in the P.T.F.E. sample is considered to be due to the large surface area of the P.T.F.E. powder. Although the grains of the powder were fairly large, each grain had a spongy texture.

It is interesting to note that loss factor curves similar to those shown in this and the preceding section have been obtained with a number of freshly ground crystalline materials (Dryden and Meakins 1953). In these systems the dielectric loss is thought to be due to conducting layers of water or aqueous solution on the freshly exposed surfaces of the crystals. Many commercial insulating materials also give dielectric absorption of this type (see, e.g. Massachusetts Institute of Technology 1948).

(d) *Anomalous Charging Currents*

The anomalous D.C. charging currents, from which the loss factors below 0.1 c/s were calculated, have not been considered separately in this section. In general, these currents varied with time according to the empirical law $i \propto t^{-n}$, where n is a constant for a particular sample. This empirical law has been found to hold for a large number of insulating materials.

Special mechanisms, such as the formation of space charges, and contact imperfections, have been suggested in the past to account for the anomalous currents. At least in the present cases, however, it appears simpler to assume that the anomalous currents are only another result of the heterogeneity that causes loss in A.C. fields.

(e) *The Effect of Potential Gradient*

It is well known (see, e.g. Hartshorn and Rushton 1934, 1938) that the steady-state D.C. conductivity of many commercial insulating materials increases with the applied potential gradient even at low values of the gradient, while the effective A.C. conductivity is usually independent of potential gradient, at least up to about half the breakdown value. Reversible absorption currents are usually proportional to the applied potential so that the effective "absorption conductivity" is independent of applied voltage.

On testing a number of mixture samples at different applied voltages, the same behaviour was observed. Figure 7 shows the variation of D.C. conductivity with applied potential gradient for one sample with liquid impurity (n -decyl alcohol) and one with solid impurity (copper phthalocyanine powder). In both cases the conductivity increases with the potential gradient. It was observed that the fractional increase in conductivity, for a given field change was smaller the greater the concentration of impurity. This is to be expected, since the conductivity of the impurity in bulk (n -decyl alcohol or copper phthalocyanine) does not depend on the applied potential gradient.

Figure 7 shows that the conductivity of the sample containing decyl alcohol can be represented by the empirical equation

$$\sigma = \sigma_0 (1 + mx),$$

where σ_0 and m are constants, and x is the potential gradient in the material. This relation is of the same form as that found for cellulose acetate and varnished cloth by Hartshorn and Rushton (1934, 1938).

Hartshorn and Rushton (1938) discussed a number of mechanisms for the dependence of D.C. conductivity on potential gradient, such as electrophoresis, movement of liquid in capillaries, and ionization by collision. None of these mechanisms seems appropriate for the mixture of paraffin wax and copper phthalocyanine (Fig. 7). A simpler mechanism is suggested in this case, namely, that the field dependence is due to the "breakdown" of small gaps in otherwise continuous paths of impurity. The nature of the breakdown process cannot be specified in detail, but the fact that the conductivity-potential gradient curve is reversible within the limits of measurement implies that no permanent physical or chemical change takes place when the gaps become conducting.

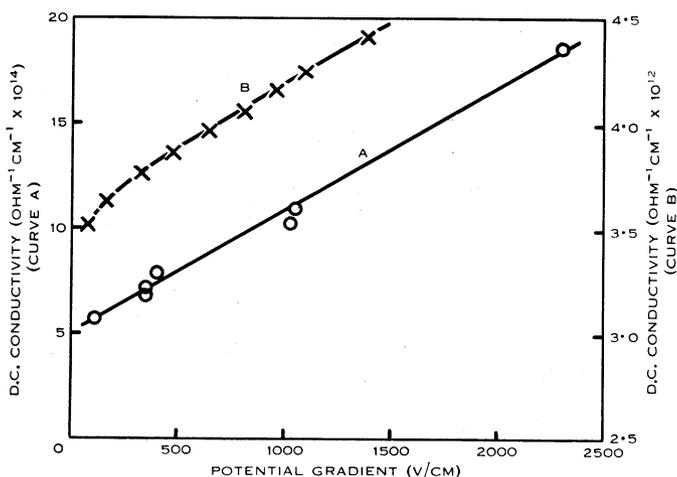


Fig. 7.—D.C. conductivity as a function of potential gradient for 1 per cent. *n*-decyl alcohol in paraffin wax (curve A) and for 1.9 per cent. copper phthalocyanine powder in paraffin wax (curve B).

Measurements of D.C. conductivity as a function of potential gradient were also made on a number of chemically pure organic materials. Some dependence was found, but it was generally less marked than in the mixtures discussed above. The observed field dependence in organic materials may be due to the presence of traces of moisture, or of different crystal modifications (Hamon and Meakins 1952).

IV. CONCLUSION

The loss factor-frequency curves in Figures 4, 5, and 6 show that a loss factor that increases slowly with decreasing frequency over a wide frequency range can be due to an impurity dispersed as a separate phase at the boundaries of grains of an otherwise loss-free material. The results obtained indicate something of the complicated relation between the properties and amount of impurity, its dispersion, and the electrical effects it produces. Although non-polar base materials were used, there is evidence that the *n*-decyl alcohol is in some cases adsorbed onto the base material, and that its electrical properties are altered by this process. In materials of practical importance, particularly

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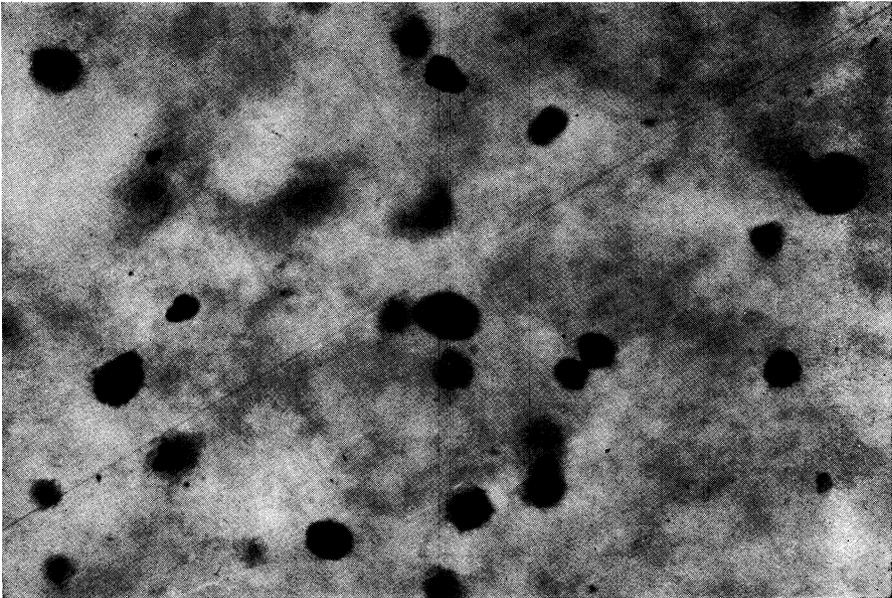


Fig. 1.—Photomicrograph of a section of a sample containing discrete spherical particles.
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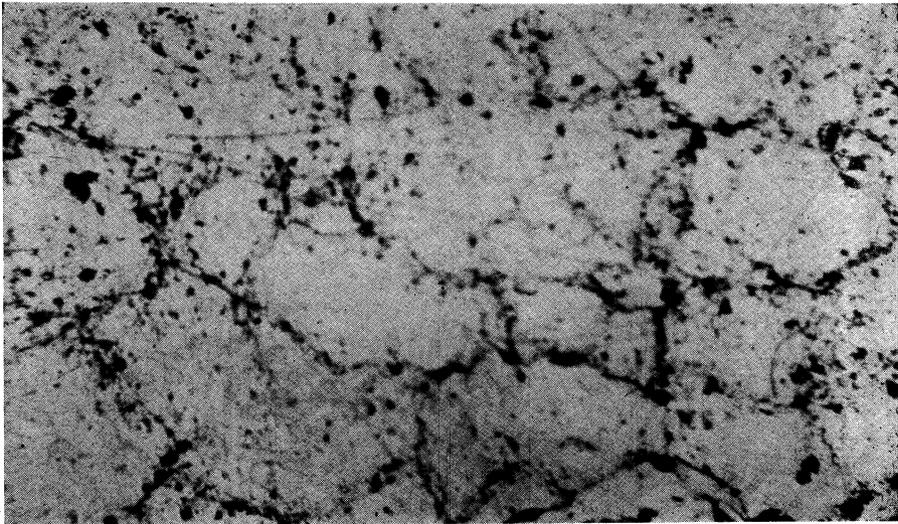


Fig. 2.—Photomicrograph of a section of a sample containing 0.62 per cent. copper phthalocyanine powder in paraffin wax, showing concentration of the powder at grain boundaries.

with polar materials exposed to atmospheric moisture, it is probable that adsorption plays an even more important part. In such cases one can no longer use the idea of a simple mixture of components, each retaining its bulk electrical properties.

V. ACKNOWLEDGMENTS

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