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Determination of Dielectric Behavior at Low Frequencies from Measurements of Anomalous Charging and Discharging Currents

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The relation between anomalous charging or discharging currents and ac dielectric behavior of a material is discussed together with the use of the Hamon approximation for calculating the loss factor from these currents.

The validity of the assumption used in deriving the Hamon approximation is discussed with reference to the behavior of a material with a Cole–Cole distribution of relaxation times. An analytical derivation of the Hamon approximation which has appeared in the literature is described together with a discussion of the limits of its validity. A description of the experimental methods which have been used to measure these anomalous currents (dc transient technique) is given, and experimental data in the literature showing the continuity of the loci of relaxation processes and values of loss factor from the audio frequency region into the very low-frequency region (e.g., 10^{-4} to 10^{-2} cps) is discussed.

Solids often have long relaxation times at ordinary temperatures and are then suitable for examination with the dc transient technique. Moreover, the components of loss due to relaxation and conduction may be separately determined using this technique, and this is an essential prerequisite to an understanding of the different mechanisms involved. When peaks in loss factor are obtained, all the usual dielectric information may be obtained—including distribution of relaxation times, activation energy and entropy for dipole orientation, and dipole-moment values for the structural units involved.

INTRODUCTION

The dielectric behavior of an insulator is of direct technological importance, and the interpretation of the dielectric behavior of a material in terms of its molecular structure is an essential scientific objective.

Dielectric measurements may be made over a very wide range of frequency, from the microwave region, through the radio- and audio-frequency regions, down to very low frequencies which are obtained by analysis of the transient displacement (or anomalous charging and discharging or absorption) currents which flow after the application and removal of a step voltage. The latter type of measurements receive special attention in this article.

Until fairly recently the lowest frequency obtainable with conventional bridges had been about 10 cps using a Schering bridge, although special bridges supplied with a motor driven potentiometer have been used down to about 0.1 cps (e.g., Ref. 1). New types of bridges have been developed for use at lower frequencies by Mole and Smith,[2] Nakajima and Kondo,[3] and Schieber.[4] The Schieber bridge covers the range from about 0.008 cps to 200 cps with a range of conductance from 10^{-9} to 10^{-15} mho and capacitance up to 100 pF and has been successfully used for example by Williams[5] for measuring dielectric properties. However, still lower frequencies may be obtained by measuring the transient charge or the transient charging and discharging currents which flow after the application or removal of a step voltage. The technique also has other advantages, as are later described. A very interesting method of measuring the equivalent of the transient charge following application of a step voltage was described by Cole *et al.*[6] some time ago. In the method the transient current following application of a linearly rising voltage was actually measured. However, dielectric information is obtained more easily from the measurement of the transient currents following a step voltage change.

The relation between these transient currents and the ac dielectric behavior has been known for a long time. The ac dielectric behavior is defined by the complex dielectric constant[7,8] $\epsilon=\epsilon'-j\epsilon''$, where ϵ' is the dielectric constant and ϵ'' the loss factor. When an alternating voltage V is applied to a capacitor with a dielectric filling the space between the plates, the resultant alternating current I is given by

$$I=I_L+I_C, \tag{1}$$

as shown in Fig. 1.

When the polarization of the material cannot keep in phase with the applied field, the current has a component in phase with the applied voltage or field which causes dissipation of energy as heat. I_L will also contain a component due to dc conductivity.

The total current I may be written as

$$I=j\omega(\epsilon'-j\epsilon'')C_aV. \tag{2}$$

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[1] B. V. Hamon, Proc. Inst. Elec. Engrs. (London) **99**, 115 (1952).

[2] G. Mole and D. C. G. Smith, "Precision Electrical Measurements," Paper 15, London HMSO, 1955.

[3] T. Nakajima and K. Kondo, Bull. Electrotech. Lab. (Tokyo) **20**, 641 (1956).

[4] D. J. Schieber, J. Res. Natl. Bur. Std. **65C**, 23 (1961).

[5] G. Williams, *Molecular Relaxation Processes* (Academic Press Inc., New York, 1966), p. 21.

[6] D. W. Davidson, R. P. Auty, and R. H. Cole, Rev. Sci. Instr. **22**, 678 (1951).

[7] A. R. Von Hippel, *Dielectrics and Waves* (John Wiley & Sons, Inc., New York, 1954), p. 4.

[8] H. Frohlich, *Theory of Dielectrics* (Oxford University Press, London, 1949).

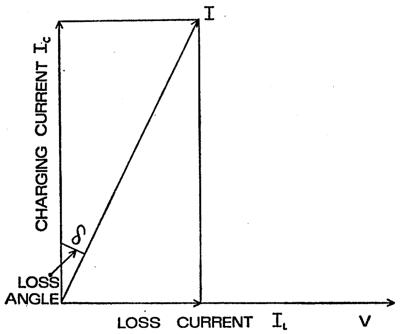

FIG. 1. Vector diagram for a capacitor with a dielectric filling the space between the plates.

C_a is the value of the capacitance with air or a vacuum between the plates.

When a step voltage is applied to the same material, the direct current which flows behaves as shown in Fig. 2. If $i(t)$ represents the (reversible part of the) anomalous charging current or the discharging current at a time t after the application or removal of the steady voltage V, then $i(t)$ (or the current response $\phi(t)$ per unit voltage) and the complex dielectric constant are related by the equations[8,9]

$$\epsilon'(\omega)=\left[C_a^{-1}\int_0^\infty \phi(t)\cos\omega t dt\right]+\frac{C_0}{C_a}, \tag{3}$$

$$\epsilon''(\omega)=\left[C_a^{-1}\int_0^\infty \phi(t)\sin\omega t dt\right]+\frac{G}{\omega C_a}, \tag{4}$$

where C_0 is the capacitance at very high frequencies, G is the steady-state dc conductance, and ω is the angular frequency. The first terms on the right-hand side of these equations represent the contributions to the dielectric constant and loss of the relaxation process in the material. The second term on the right-hand side of Eq. (3) gives the contribution to the dielectric constant of the virtually instantaneous electronic and atomic polarizations, while that on the right-hand side of Eq. (4) gives the contribution to the loss of the dc conductivity of the material. $\phi(t)$ is known as the relaxation function of the material. Various calculations of the loss factor ϵ'' using Eq. (4) have been made in the past by expressing the current as an approximate function of time. Hamon[1] gives various references. However, the methods were tedious and not suitable for a rapid evaluation of ϵ''. Equations (3) and (4) are quite general, apart from the assumption of superposition, which is discussed below. (The superposition principle holds good for many materials.) These relations are derived by considering that the sinusoidal voltage applied to a material may be split up into a series of minute steps. The resultant alternating current is then given by the integral involving the current response to a step voltage. However, an important assumption is that the superposition principle is valid. This states that each step change in voltage produces the same current as if it alone were acting. The total current at any time is then the algebraic sum of the currents appropriate to all the step changes. It is also assumed that the currents are proportional to the applied voltages.

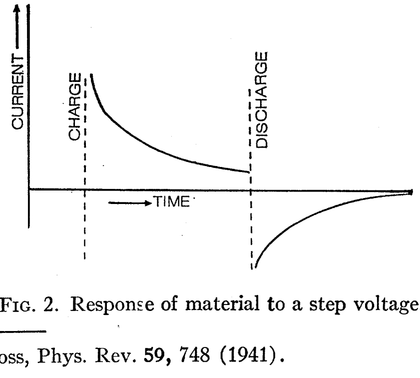

FIG. 2. Response of material to a step voltage.

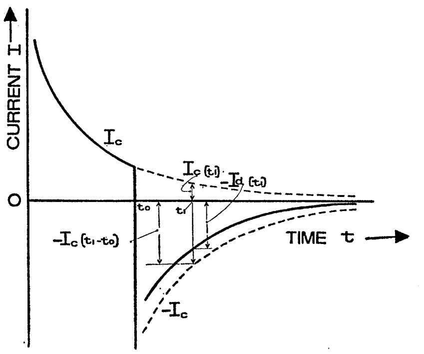

FIG. 3. Behavior of the charging and discharging currents, illustrating the law of superposition (schematic).

Thus in Fig. 3 a step voltage is applied at $t=0$ to a capacitor with a dielectric between the plates. After the initial surge a relatively small anomalous charging current I_c (not including the steady state current) is produced. This may decay over a period of months. If the capacitor plates are short circuited after a time t_0, an opposite discharging current $-I_d$ (of magnitude I_d) is produced. This decays according to the same law. The discharging current $-I_d$ may be represented at any time $t_1>t_0$ in terms of the current $-I_c$ starting at $t=t_0$ and the positive charging current $+I_c$ extrapolated to $t=t_1$. According to the law of superposition,

$$-I_d(t_1)=-I_c(t_1-t_0)+I_c(t_1). \tag{5}$$

Obviously I_d is less than its correct value because steady-state conditions had not been obtained on the charge.

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[9] B. Gross, Phys. Rev. 59, 748 (1941).

HAMON APPROXIMATION

In the past it has been found that over a range of time the relaxation function $\phi(t)$ for many materials at a fixed temperature obeys the relation

$$\phi(t)=AC_a t^{-m}, \tag{6}$$

where A and m are constants for a given material.

Using this expression for $\phi(t)$ in Eqs. (3) and (4) gives

$$\epsilon'(\omega)=\{\omega^{m-1}A\Gamma(1-m)\cos[(1-m)\pi/2]\}+(C_0/C_a) \qquad 0<m<1, \tag{7}$$

and

$$\epsilon''(\omega)=[\omega^{m-1}A\Gamma(1-m)\cos(m\pi/2)]+(G/\omega C_a) \qquad 0<m<2. \tag{8}$$

Over the ranges given for m the integrals converge. These relations have been known for some time but it was left to Hamon[1] to show that the expression for ϵ'' could be reduced to a simple approximation.

Thus ϵ'' may be expressed in terms of the relaxation function $\phi(t_1)$ at a perpendicular time t_1 as

$$\epsilon''=[\phi(t_1)/\omega C_a]+(G/\omega C_a), \tag{9}$$

provided that ω and t_1 are related by the equation

$$\omega t_1=[\Gamma(1-m)\cos(m\pi/2)]^{-1/m}. \tag{10}$$

The expression on the right-hand side of Eq. (10) is almost independent of m in the range $0.3<m<1.2$ having the mean value 0.63 and so Eq. (9) may be written as

$$\epsilon''\simeq[i(t)/\omega C_a V]+(G/\omega C_a) \tag{11}$$

where

$$t=0.63/\omega=0.1/f. \tag{12}$$

Equation (11) is accurate to $\pm 3\%$ for $0.3<m<1.2$.

Hamon also shows that, even when $\phi(t)$ departs considerably from the form in Eq. (6), the approximation in Eq. (11) is still reasonably accurate. (The use of the approximation for values of m outside the above limits has been discussed by Nakajima.[10]) However, the assumption in Eq. (6) cannot hold from $t=0$ to ∞, as is now shown.

ANALYTICAL DERIVATION OF THE HAMON APPROXIMATION

The behavior of the transient displacement current $i(t)$ as a function of time for a material obeying a Cole–Cole[11] distribution has been evaluated by the same workers.[12] For a Cole–Cole distribution

$$\epsilon=\epsilon'-j\epsilon''=\epsilon_\infty+\{(\epsilon_0-\epsilon_\infty)/[1+(j\omega\tau_0)^n]\}, \tag{13}$$

where the high-frequency dielectric constant $\epsilon_\infty=C_0/C_a$, ϵ_0 is the static dielectric constant, τ_0 is the most probable relaxation time, and $n=1-\alpha$ where α is the factor determining the width of the distribution. Both n and α vary between 0 and 1. For small n the distribution is broad, and for n near unity the distribution is narrow.

The reversible transient current $\phi(t)$ flowing at a time t after the application or removal of a unit step voltage is given by the inverse Fourier transform of the single equation representing Eqs. (3) and (4) as

$$\phi(t)=\pi^{-1}\int_0^\infty \epsilon_R(j\omega)\exp(j\omega t)\,d\omega \tag{14}$$

if C_a is equal to unity. (ϵ_R is the contribution to the complex dielectric constant of the relaxation mechanism.)

Using the expression for ϵ in Eq. (13), Cole and Cole[12] evaluated the integral in Eq. (14) as a series using the Heaviside operator.

This gave

$$\phi(t)=\left(\frac{\epsilon_0-\epsilon_\infty}{\tau_0}\right)n\left(\frac{t}{\tau_0}\right)^{-(1-n)}\sum_{r=1}^{\infty}\frac{(-1)^{r-1}r}{\Gamma(1+rn)}\left(\frac{t}{\tau_0}\right)^{(r-1)n} \tag{15}$$

or

$$\phi(t)=\left(\frac{\epsilon_0-\epsilon_\infty}{\tau_0}\right)n\left(\frac{t}{\tau_0}\right)^{-(1+n)}\sum_{r=1}^{\infty}\frac{(-1)^{r-1}r}{\Gamma(1-rn)}\left(\frac{t}{\tau_0}\right)^{-(r-1)n}. \tag{16}$$

For $t\ll\tau_0$ Eq. (15) gives

$$\phi(t)=[(\epsilon_0-\epsilon_\infty)/\tau_0][1/\Gamma(n)](t/\tau_0)^{-(1-n)}, \tag{17}$$

and for $t\gg\tau_0$ Eq. (16) gives

$$\phi(t)=[(\epsilon_0-\epsilon_\infty)/\tau_0][n/\Gamma(1-n)](t/\tau_0)^{-(1+n)}. \tag{18}$$

Thus, for a given material with a given width of distribution at a particular temperature, the double log plot of reversible current against time has a slope of $-(1-n)$ or $-\alpha$ at times very short compared with τ_0, and $-(1+n)$ or $-(2-\alpha)$ at times very long compared with τ_0. At times in the vicinity of τ_0 the plots "bend over" and the numerical value of the slope passes through unity. This is the dispersion region in which a peak in ϵ'' will be found. The behavior of the

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[10] T. Nakajima, Bull. Electrotech. Lab. (Tokyo) **24**, 755 (1960).

[11] K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).

[12] K. S. Cole and R. H. Cole, J. Chem. Phys. **10**, 98 (1942).

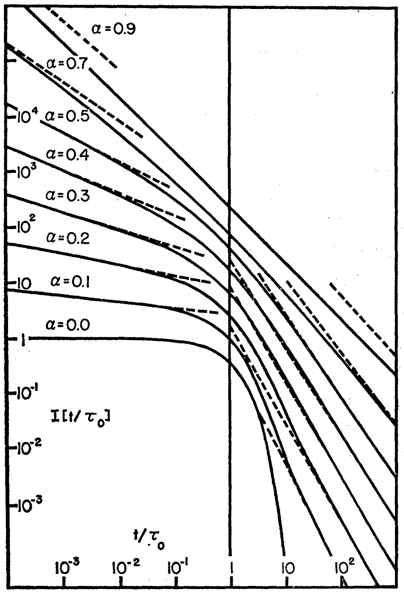

FIG. 4. "Calculated transient currents as a function of time. The curve for increasing values of the parameter α have been successively displaced vertically upward by half-decade intervals for greater clarity," Fig. 1 of Ref. 12.

double log plots is shown[12] in Fig. 4. For narrow distributions the curves bend more sharply than those for broader distributions. Many materials obey a Cole–Cole distribution accurately or approximately, and it is obvious that the assumption of reversible current proportional to t^{-m} cannot hold for any material over the time range from 0 to ∞. This raises a certain difficulty in accepting the Hamon approximation. However, this problem has been solved by Williams.[13]

At low frequencies where $\omega\tau_0 \ll 1$, the loss factor for a Cole–Cole distribution is given by

$$\epsilon''(\omega) = (\epsilon_0 - \epsilon_\infty)(\omega\tau_0)^n \sin(n\pi/2), \tag{19}$$

and at high frequencies where $\omega\tau_0 \gg 1$

$$\epsilon''(\omega) = (\epsilon_0 - \epsilon_\infty)(\omega\tau_0)^{-n} \sin(n\pi/2). \tag{20}$$

By combining short times and high frequencies [Eqs. (17) and (20)], we get

$$\epsilon''(\omega) = \left[\frac{\Gamma(n)\sin(n\pi/2)}{(\omega t)^{-(1-n)}}\right]\frac{\phi(t)}{\omega}. \tag{21}$$

Similarly, by combining long times and low frequencies [Eqs. (18) and (19)], we get

$$\epsilon''(\omega) = \left[\frac{\Gamma(1-n)\sin(n\pi/2)}{n}\right]\frac{1}{(\omega t)^{-(1+n)}}\frac{\phi(t)}{\omega}. \tag{22}$$

With C_a and V both equal to unity, the Hamon approximation, for the relaxation component only, from Eq. (11) is $\epsilon'' = i(t)/\omega$ and may now be obtained by choosing ωt combinations. For Eq. (21)

$$\omega t = [\Gamma(n)\sin(n\pi/2)]^{-1/(1-n)} = X_1, \tag{23}$$

and for Eq. (22)

$$\omega t = \left[\frac{\Gamma(1-n)\sin(n\pi/2)}{n}\right]^{-1/(1+n)} = X_2. \tag{24}$$

The values of X_1 and X_2 were evaluated by Williams for a range of n values as shown in Table I.

X_1 is equal to 0.62 ± 0.03 for n between 0 and 1, but X_2 is equal to 0.61 ± 0.02 for values of n up to 0.3 only. Thus for times much shorter than τ_0 the Hamon approximation, as given by Eqs. (11) and (12), is obtained for all n values, but for times much longer than τ_0, it is valid for n values up to 0.3 only. This corresponds with numerical values of the long time slopes of the double log plots of current against time not exceeding 1.3, and obviously correlates with the limits of m in the original Hamon assumption [Eq. (6)].

Thus the very short time and high-frequency (and very long time and low-frequency) behavior of a material with a Cole–Cole distribution of relaxation times does conform with the Hamon approximation. However, the most important region is the actual dispersion region where $\omega\tau_0 \simeq 1$ and $t \simeq \tau_0$. Then the previous theory does not apply. In particular, the higher terms in the $\phi(t)$ expansion and the full expression for $\epsilon''(\omega)$ must be used.

This was done by Williams using values of $\phi(t)$ at various (t/τ_0) and n values, which had been tabulated by Cole and Cole,[12] by evaluation of the series [Eqs. (15) and (16)] and putting $(\epsilon_0 - \epsilon_\infty)/\tau_0$ equal to unity. The various (t/τ_0) values corresponded to the equivalent frequencies ($\omega = X_1/t$ and $\omega = X_2/t$), and the correct ϵ'' values at these frequencies were calculated

TABLE I. Variation of X_1 and X_2 with n.

n	X_1	X_2
0.1	0.643	0.628
0.2	0.646	0.614
0.3	0.646	0.595
0.4	0.643	0.570
0.5	0.637	0.542
0.6	0.627	0.503
0.7	0.618	0.455
0.8	0.612	0.384
0.9	0.587	0.292

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[13] G. Williams, Trans. Faraday Soc. 58, 1041 (1962).

using the full Cole–Cole expression

$$\epsilon''(\omega)=\frac{(\epsilon_0-\epsilon_\infty)(\omega\tau_0)^n\sin(n\pi/2)}{1+2(\omega\tau_0)^n\cos(n\pi/2)+(\omega\tau_0)^{2n}}. \tag{25}$$

This gave $\epsilon''(\omega)$ as the product of a number and $(\epsilon_0-\epsilon_\infty)$.

Values of loss factor were also calculated using the values of $\phi(t)$ tabulated by Cole and Cole according to the Hamon approximation $\epsilon''(\omega)=i(t)/\omega$ using the appropriate X_1 and X_2 values. These were also obtained as the product of a number and τ_0. Williams tabulated values of the ratio (ϵ'' Hamon/ϵ'' Cole–Cole) for values of t/τ_0, from 1×10^{-4} through unity to 5×10^2 and values of n, from 0.1 to 1. ψ_1 was the ratio using the appropriate value of X_1 relating to the short time, high-frequency side of a peak in ϵ'', where $t<\tau_0$ and ψ_2 was the value calculated using the appropriate value of X_2 relating to the long time, low-frequency side of a peak in ϵ'' where $t>\tau_0$. The ψ_1 values were usually close to unity for all values of t up to τ_0, particularly for broad distributions. This means that where the numerical value of the tangential slope of the double log plots of $i(t)$ against t is less than or equal to unity (for $t\leq\tau_0$), the Hamon approximation [Eqs. (11) and (12)] may be used. However, for the low-frequency side of a peak in loss factor where $t>\tau_0$, the position is more complicated. For values of n larger than 0.3 the X_2 value deviates significantly from 0.63, and this suggests that the use of $\omega t=0.63$ is no longer valid and that the Hamon approximation is not directly useful. However, the ψ_2 values for n values of 0.1 and 0.3 were close to unity and when the numerical value of the ultimate slope of the double log plot of $i(t)$ against t is equal to or less than 1.3, the Hamon approximation may be used for times $t>\tau_0$ to give ϵ'' values on the low-frequency side of the peak. On the other hand, when the numerical value of the ultimate slope exceeds 1.3, the Hamon approximation becomes inaccurate to an extent depending on how much the ultimate slope exceeds 1.3. However, the results of Williams, using X_1 values for $t>\tau_0$, suggest that the original Hamon equations may be used to give reasonably accurate ϵ'' values on the low-frequency side of a peak down to 0.05 to 0.01 ω_m (ω_m is the angular frequency giving maximum loss factor), provided that the distribution is not too narrow. This point is discussed in more detail later on. Thus Williams has given an essential confirmation of the Hamon approximation in terms of the ac properties of a material.

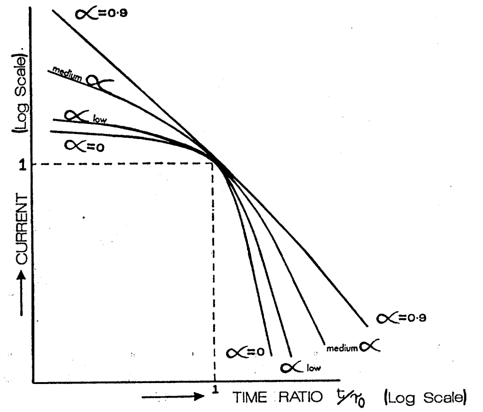

FIG. 5. Curves of current against time for a range of α values (schematic).

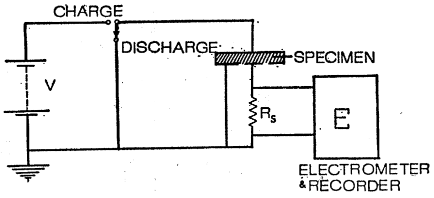

FIG. 6. Simplified circuit diagram for measuring anomalous charging and discharging currents.

Hamon[1] points out that there does not seem to be a corresponding simple procedure for deriving the dielectric constant ϵ' as a function of frequency. Since the components of the dielectric constant and the loss factor due to relaxation are interrelated, little more information would be obtained by plotting ϵ' as a function of frequency. However, the dielectric constant increment $(\epsilon_0-\epsilon_\infty)$ may be obtained by curve fitting, as suggested by Field.[14] The log current–log time curve of a dielectric is matched to a family of curves for Cole–Cole distributions of a range of widths by raising the latter so that they all pass through the point "1, 1", as illustrated schematically in Fig. 5. A subsidiary curve gives the factor K as a function of the Cole–Cole parameter α by which all the currents must be multiplied to return them to their original values. The curve for the material is matched to give the best value of α. If I is the current and τ_0 the most probable relaxation time corresponding to the 1, 1 point where the curves have a slope of -1, then the dielectric constant increment $(\epsilon_0-\epsilon_\infty)$ is given by

$$\epsilon_0-\epsilon_\infty=I\tau_0/KVC_a, \tag{26}$$

where V is the applied steady voltage and C_a is the capacitance with a vacuum replacing the material.

The curve fitting is carried out on the reversible part of the charging current or the discharging current.

An interesting method of obtaining the dielectric constant has been described by Reddish.[15]

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[14] R. F. Field, *Dielectric Materials and Applications* (M.I.T. Press, Cambridge, Mass., 1954), p. 52.

[15] W. Reddish, J. Polymer Sci. Pt. C, **14**, 123 (1966).

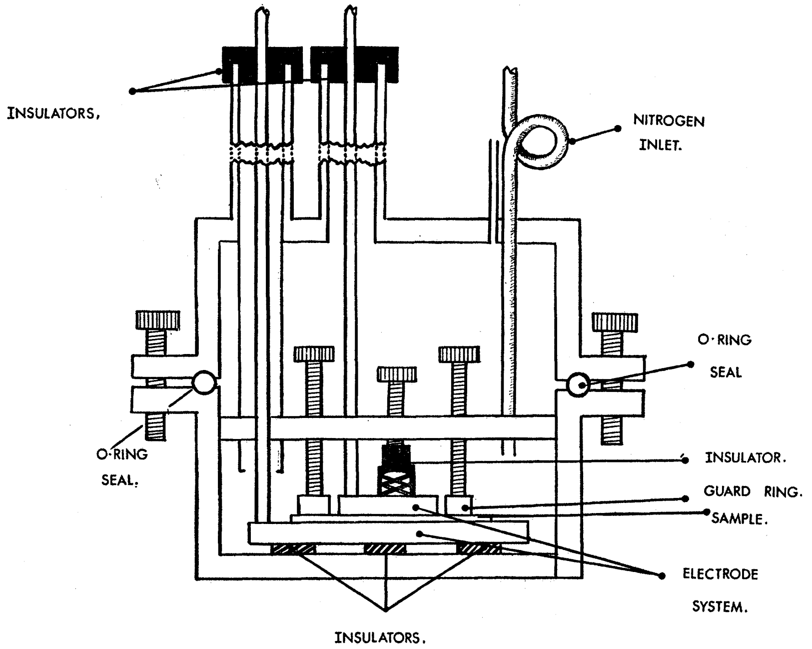


Fig. 7. Three-terminal screened electrode assembly.

EXPERIMENTAL METHODS

The principle of the method for measuring the transient currents is illustrated in the simple circuit in Fig. 6. More detailed circuits have been given by Field.[14] The current flowing through R_s is amplified by a dc amplifier (e.g., as in an electrometer) and recorded with a suitable recorder. To ensure that the full polarizing voltage appears across the specimen, the value of R_s should be considerably less than the instantaneous effective resistance of the sample. With a good electrometer this is usually possible. If it is not possible, a compensating device should be included to supply a voltage equal but opposite to that across R_s. Some types of commercially available electrometers do in fact include a feedback arrangement which performs this function. Feedback may also be used to reduce the time constant of the electrometer by reducing the effective input capacitance. (This reduction may apply also to the capacitance of the cable connecting the electrometer to the electrode assembly.) S is a switch allowing the application or removal of the step voltage.

During the actual operation of this switch R_s should be short circuited to protect the amplifier or electrometer against large transient currents. Screened cable should be used along the circuit path carrying the transient currents which must be measured. A "noise-free" cable carrying graphite on the polyethylene under the screening braid should be used to connect from the guarded plate of the electrode assembly containing the specimen to the input of the dc amplifier or electrometer. Batteries should be used to supply the polarizing voltage to prevent an ac voltage from appearing in the circuit path containing the specimen. The three-terminal electrode assembly with guard ring should be used in a screened container with chimneys surrounding the outgoing leads so that it may be immersed in a liquid bath at a carefully controlled temperature (±0.1°C). A suitable arrangement is shown in Fig. 7. Air and water vapor, etc., may be removed by a flow of dry nitrogen to prevent degradation or the formation of ice in the system (depending on the temperature used).

The time constant CR_s, where C is the effective capacitance in parallel with R_s, should be kept down to the order of a second or less to ensure that the transient

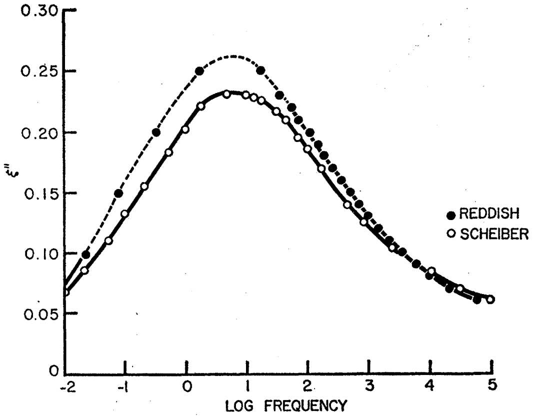
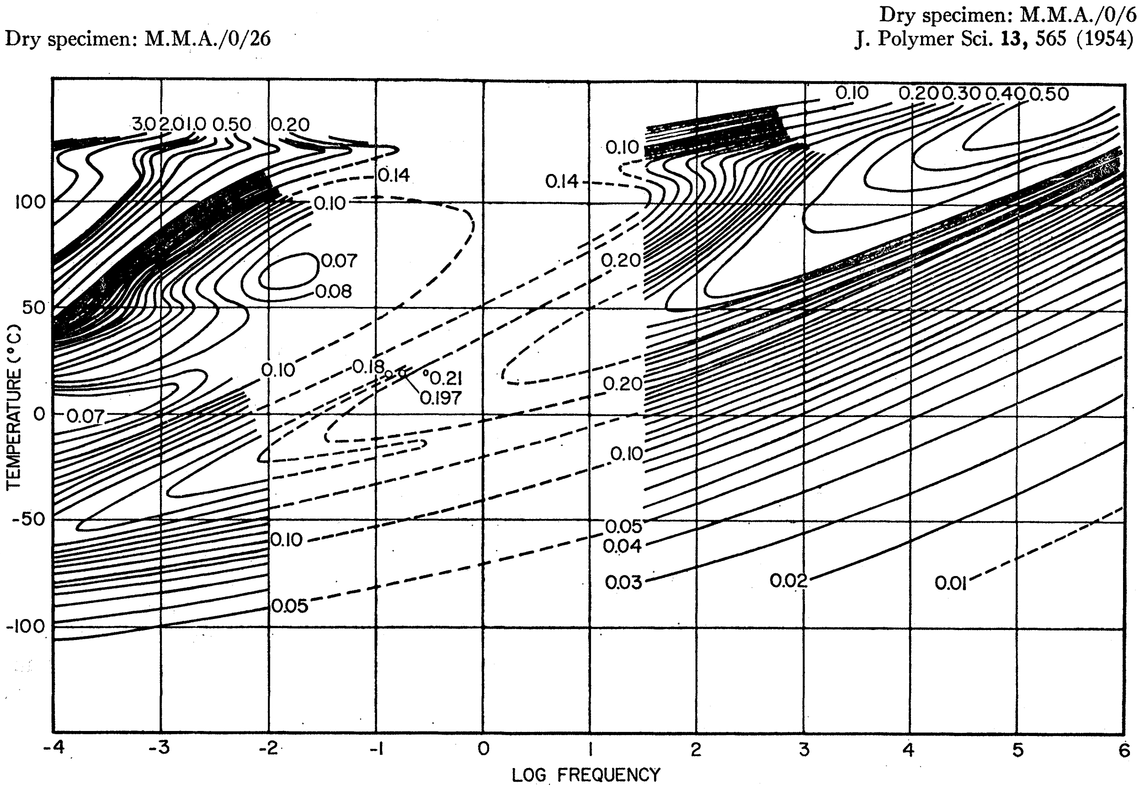


Fig. 8. $\epsilon''v \log f$ at room temperature for P.M.M.A. (Reddish, Schieber)," Fig. 4 of Ref. 17.


Dry specimen: M.M.A./0/26

Dry specimen: M.M.A./0/6
J. Polymer Sci. **13,** 565 (1954)

FIG. 9. "Contour map of dielectric losses of poly (methyl methacrylate) (P.M.M.A.)," Fig. 3 of Ref. 17.

currents are faithfully followed and recorded. The reduction of the input capacitance or of the effective values of R_s produced by the feedback of the amplifier is helpful in this respect. The actual capacitance of the resistance itself should also be kept small.

The usual time range employed for measuring the discharging current is 10–1000 sec corresponding to a frequency range (Hamon approximation) of 10^{-4} cps to 10^{-2} cps.

The polarizing voltage should be left on for a sufficiently long time to ensure that the discharge curve is the mirror image of the charging curve (after subtraction of the steady-state current). This does not mean that it must be kept on until steady conditions have been reached but only until the reversible part of the charging current has decayed to a sufficiently small value. Suppose that the material has a Cole–Cole distribution and that the temperature is adjusted so that a peak occurs in loss factor ϵ'' at a frequency f_m of (say) 5×10^{-4} cps. This corresponds to a τ_0 value $(=1/\omega_m)\simeq5\frac{1}{2}$ min. If the polarizing voltage is applied for about three hours, this is approximately $30\tau_0$. Reference to Fig. 4 shows that the slope of the corresponding double log plot must have been near -1 for an appreciable part of the charge. If current measurements started at 10 sec, they will have lasted for 3 decades up to 3 h, and therefore the current after 3 h should have decayed to less than 1% of its initial value. When the voltage is now removed, according to the superposition principle the observed discharging current is the algebraic sum of the true discharging current and the residual reversible charging current. Thus the observed discharging current will be slightly less than its true value but should be accurate to better than 1% initially, although the percent error will increase as times goes on. On this basis a 3-h charge should be sufficient for temperatures giving peaks in loss factor around 10^{-4} cps and higher, i.e., for nearly all important practical purposes. The steady state dc current may be obtained by subtracting the discharging current at a time t from the charging current at the corresponding time.

The discharging currents may be measured for periods of longer than 1000 sec to give loss-factor values at frequencies lower than 10^{-4} cps, but here the polarizing voltage should be applied for longer than 3 h. The discharging currents may also be measured at times shorter than 10 sec to give loss-factor values at frequencies higher than 10^{-2} cps. Thus Reddish and Buckingham[16] have measured the currents at times

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[16] W. Reddish and K. A. Buckingham (private communication).

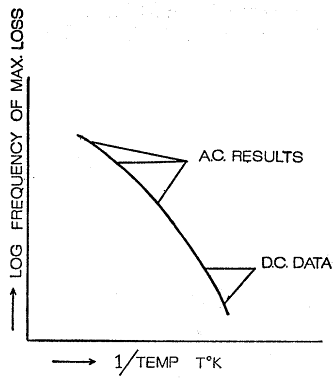

FIG. 10. Variation of frequency of maximum loss with temperature, showing the continuity of the locus of the relaxation process (schematic).

down to milliseconds after the application or removal of the voltage to give the loss factor at frequencies approaching·10 cps. Thus here the frequency range may overlap with that of a Schering bridge. However, it must be remembered that measurements at shorter times necessitate a shorter time constant CR_s because the currents are changing more rapidly.

The value of the measurement of these transient currents is not limited to obtaining loss-factor values at low frequencies. This type of measurement gives a clear way of separating the loss due to relaxation from the loss due to dc conductivity. The charging currents are superposed relaxation conductivity and dc conductivity components, while the discharging currents are relaxation conductivity only. Thus a clear separation is achieved and the loss factor due to relaxation only is obtained by transforming the discharging current. The steady-state current gives the loss due to dc conductivity. Bridge and other ac methods yield the total loss without separation of the components.

As mentioned earlier the use of the Hamon approximation when the numerical value of the slope of the double log plot of transient displacement current against time exceeds 1.3 at long times would appear to be invalid. This corresponds to materials with Cole–Cole distributions of relaxation times with n greater than 0.3, i.e., narrower distributions than that for an n value of 0.3. However, the method (used by Williams[13]) of comparing the ϵ'' value obtained from the approximation with that obtained from the full Cole–Cole expression may be used to test any approximation for ϵ''. Thus, although the X_2 values derived by Williams deviated appreciably from 0.63 for n value greater than 0.3, this does not exclude the possibility of using the original Hamon approximation [Eqs. (11) and (12)]. An inspection of ψ_1 values calculated by Williams[13] using X_1 values for times $t > \tau_0$ and n values>0.3 shows that, for n equal to 0.5 anyway, the original Hamon approximation may be used with reasonable accuracy for times from τ_0 up to $10\tau_0$, or more. For a Cole–Cole distribution the angular frequency ω_m giving maximum loss factor ϵ_m'' is given by $\omega_m = 1/\tau_0$, and so these times correspond to ω values down to $0.063\omega_m$ or lower. However, for measurements in the frequency range 10^{-4} to 10^{-2} cps, where a loss peak occurs in his range, frequencies down to $0.06\omega_m$ would probably cover as low a frequency as is required.

APPLICATIONS OF THE dc TRANSIENT TECHNIQUE

Examples of the use of the dc transient technique and the Hamon approximation are to be found with various materials. Thus Hamon[1] shows results for docosyl alcohol, paraffin wax, and mica obtained using (a) bridges covering the frequency range 5–10^5 cps, (b) a bridge supplied with a sinusoidal potential difference from a motor driven potentiometer covering the frequency range 0.16–4 cps, and (c) dc measurements covering the time range 15–200 sec and frequency range 0.0005–0.007 cps, and sometimes higher frequencies up to about 1 cps. In the latter measurements the loss factor values calculated using the Hamon approximation agreed well with the bridge readings where the frequency ranges overlapped, and the low-frequency plot of ϵ'' against log frequency proved to be a smooth continuation of the plots obtained at higher frequencies from the bridge readings. Other examples exist with polymers and a few are mentioned here. Thus Reddish[17] shows that loss factor values for polymethyl methacrylate obtained using the Hamon approximation from dc step response measurements agreed fairly well with values obtained from the readings of the very low-frequency bridge described by Schieber[4] (Fig. 8). Contour maps for the same material showed the continuity of the contour lines for ac and dc results[17] (Fig. 9). (Figures 8 and 9 are reproduced from Ref. 17 by permission of the International Union of Pure and Applied Chemistry and Butterworths Scientific Publications.) Similarly, contour maps obtained by Reddish[18] for polyvinyl chloride showed that the locus of the principal relaxation process, which shows up as loss peaks in the audio frequency region, extended continuously into the very low-frequency region associated with the time scale of dc step-response data. The dc transient technique has also been used by Williams[19,20] to study poloxymethylene and polyacetaldehyde. With both polymers loss peaks in, or corresponding to, the low-frequency and audio-frequency ranges were obtained, and plots of log of frequency of maximum loss (f_m) for relaxation only against reciprocal absolute temperature (or log frequency against reciprocal of absolute temperature of maximum loss) gave smooth curves similar to that shown schematically in Fig. 10

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[17] W. Reddish, Pure Appl. Chem. **5**, 723 (1962).

[18] W. Reddish, Soc. Chem. Ind. (London), Monograph **5**, 138 (1959).

[19] G. Williams, Polymer **4**, 27 (1963).

[20] G. Williams, Trans. Faraday Soc. **59**, 1397 (1963).

with an activation energy increasing rapidly at lower temperatures.

Thus the locus of the relaxation process observable in the audio-frequency region extends continuously into the low-frequency region associated with the dc transient technique. This dc transient technique is being used by the writer in a study of the low-frequency dielectric behavior of polyamides.

In conclusion, the Hamon approximation gives a simple method of measuring the loss factor ϵ'' from the transient currents which flow after the application or removal of a step voltage. The convenient range of frequency obtained is low, in the region of 10^{-4}–10^{-2} cps, but higher frequencies may be obtained by making measurements at shorter times. This technique is a clear way of separating the components of loss due to relaxation from that due to dc conductivity. The self-consistency of results from dc step-response data with those obtained in the audio-frequency region has been established. The Hamon approximation is applicable at all times shorter than the most probable relaxation time τ_0 and at times longer than τ_0, except when the numerical value of the slope of the double log plot of transient current against time exceeds 1.3 at long times. When this limit is exceeded, special consideration is required, as illustrated in the section about experimental methods.

Solids often have long relaxation times at ordinary temperatures, and these are then suitable for examination with the dc transient techniques. In particular, polymers have relaxation times in a suitable range in the region of the glass transition. Moreover, conduction and relaxation phenomena can be separated, and this is an essential prerequisite to an understanding of the different mechanisms involved. Finally, once a loss peak is obtained when the loss factor ϵ'' is plotted against (log) frequency in the low-frequency range, all the usual dielectric information can be obtained. Thus the dielectric constant increment $(\epsilon_0-\epsilon_\infty)$ can be obtained from[8]

$$\epsilon_0-\epsilon_\infty=\frac{2}{\pi}\int_{-\infty}^{\infty}\epsilon'' d(\ln\omega), \qquad (27)$$

which holds for any distribution of relaxation times. This can be related to the structure of the dielectric from, for example, the Kirkwood formula as derived by Frohlich[8]:

$$\epsilon_0-\epsilon_\infty=\left(\frac{3\epsilon_0}{2\epsilon_0+\epsilon_\infty}\right)\left(\frac{\epsilon_\infty+2}{3}\right)^2\left(\frac{4\pi N\mu^2 g}{3kT}\right), \qquad (28)$$

where μ is the dipole moment, N is the number of dipoles per unit volume, k is Boltzmann's constant, and T is the absolute temperature. g is the correlation factor allowing for the orientation of neighboring dipoles.

The shape of the plot of ϵ'' against log frequency may be used to evaluate the distribution of relaxation times; the variation of frequency of maximum loss f_m with temperature gives the experimental activation energy Q, i.e., the energy barrier opposing dipole orientation [assuming $f_m=\text{const}\times\exp(-Q/RT)$]. The entropy of activation may also be obtained.