

## The Polymerization of Styrene and Some Concepts of the Electrical Properties of Plastics \*

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WHILST polystyrene is probably the oldest known synthetic resin, having been discovered by E. Simon<sup>1</sup> as far back as 1839, its wide-spread use in industry is of relatively short duration. It was not until the middle 1930's that any considerable attention was given to this plastic, since it was only at this time that successful methods of synthesizing the hydrocarbon cheaply and in quantity were achieved.

The very serious situation arising from the cutting-off of sources of crude rubber, due to the Japanese conquest of Malaya, etc., has necessitated the development of synthetic rubber-like materials. The most favored material is Buna S, known in this country as GR-S, a copolymer of styrene and butadiene. The rubber programme calls for a large amount of this copolymer, and it is estimated that before long styrene will be one of the largest manufactures of any synthetic organic chemical in the world.

The extremely rapid expansion in the manufacture and utilization of styrene will shortly make available large amounts of the material for use in a diverse number of applications, and as more and more knowledge is gained in controlling the polymerization and a better understanding of the desirable properties of this plastic is achieved, further extensions of its applicability to industrial use will be made. This expansion, moreover, has necessitated and will continue to demand, a large amount of investigation into the methods of preparation and polymerization of the monomer with a consequent rapid increase in our theoretical understanding of the processes involved.

When the literature is studied, it is found that a considerable volume of data has been published on this hydrocarbon, especially on those aspects dealing with its conversion from a low-boiling,

highly refractive, limpid liquid monomer to a hard, glassy plastic polymer, but much of this data is invalidated by the impurity of the material employed, or a failure to observe the necessary scrupulous attention to detail required for accurate results. As a consequence, much confusion exists in the literature, and it will be necessary to amass carefully prepared data, thoroughly cross-checked, to enable us to obtain the necessary insight into the polymerization process necessary for a complete control of the reaction.

Much of the work discussed, and some of which has been published,<sup>2</sup> in particular that dealing with inhibitors, retarders and accelerators, is the result of research carried out in the laboratories of the Standard Telephones and Cables, Ltd., London, England, a manufacturing associate of the International Telephone and Telegraph Corporation.

In this paper, it is proposed to deal very briefly with the polymerization processes, paying particular attention to the effect of added substances, and, since one of the important properties of polystyrene is its outstanding electrical characteristics, to give a short summary of the dielectric properties of materials, particularly in the radio frequency range.

### *Polymerization of Pure Styrene by Heat*

Before proceeding with a discussion of the polymerization processes, let us look at a typical example of the results obtained by polymerizing pure styrene at an elevated temperature.

Fig. 1 gives the percentage polymerization against time of a carefully purified sample of monomeric styrene polymerized at 61° Centigrade. It will be seen that the curve falls very broadly into three distinct portions: (1) an initial period during which the polymerization starts slowly and then increases in velocity, (2) a period in which the velocity reaches a maximum and

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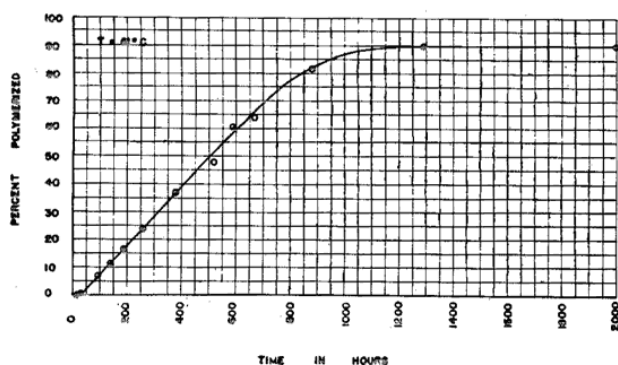


Fig. 1—Polymerization of Pure Styrene at 61° C.

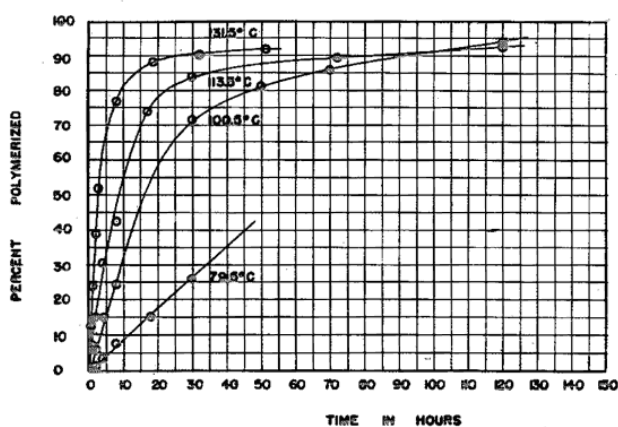


Fig. 2—Effect of Temperature on Polymerization Rate of Styrene.

remains constant, (3) a period in which the rate falls off and approaches asymptotically a final polymerization degree of somewhere near 100%.

The circles on the curve are the actual experimental figures obtained, and are the result of several individual determinations. It will be seen that a smooth curve can be drawn through the experimental data obtained.

Fig. 2 gives similar curves obtained by Schulz and Husemann<sup>3</sup> for different temperatures, showing the increase in reaction rate with increasing temperature of polymerization.

#### Molecular Weight Dependence on Temperature of Polymerization

Fig. 3 shows the effect on the average molecular weight of the temperature at which the polymerization takes place. The higher the temperature, the lower the molecular weight. It must be remembered, however, that the molecular weights used in this graph were determined

viscosimetrically, and we have strong reason to believe that the values obtained in this way are not accurate.

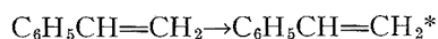
It is now generally conceded that the polymerization of styrene is a chain process, and that three main stages are involved:

- 1—chain initiation
- 2—chain propagation
- 3—chain termination

#### Chain Initiation

Stobbe and Posnjak,<sup>4</sup> in 1909, were probably the first to recognize the chain nature of the reaction. They came to the conclusion, after very careful investigation, that "nuclei of polymerization are formed in styrene, and that these accelerate the polymerization in a remarkable way."

It is probable that chain initiation consists of an activation of the ethylenic double bond in the styrene molecule, giving rise to an energy-rich, "hot" or excited molecule:



Either the double bond is made especially ca-

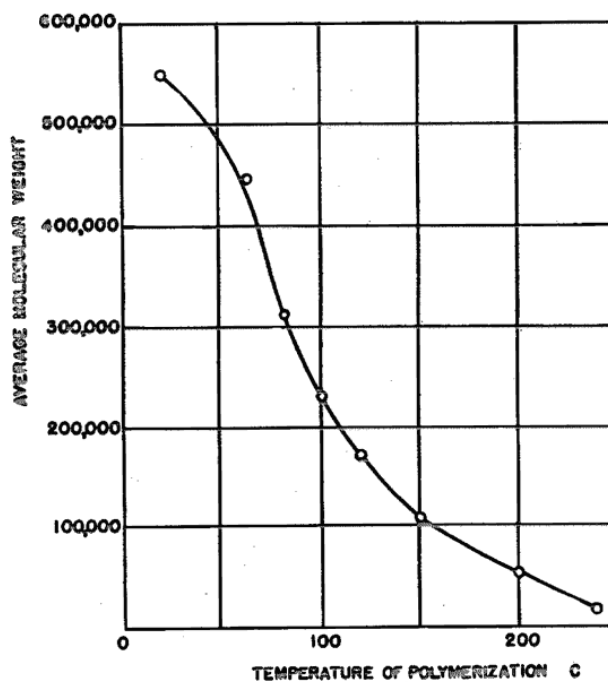


Fig. 3—Molecular Weight Dependence on Temperature for the Polymerization of Styrene.



oxygen was a more active catalyst for the polymerization of styrene at 80° Centigrade than, say, benzoyl peroxide.

Houtz and Adkins<sup>8</sup> in this country, however, working with ozonides and in particular with diisobutylene ozonide, disputed these interpretations and showed that at 25° Centigrade diisobutylene ozonide was a much more potent accelerator of the polymerization than was benzoyl peroxide, and that the decomposition of the ozonide gave rise to no oxygen. They concluded "presumably the catalysts form a molecular complex with the styrene, which is more labile toward polymerization than is styrene alone."

Since there are several points of interest in this controversy, we have investigated these particular reactions a little more fully. Fig. 4 shows polymerization curves obtained at 25° Centigrade for benzoyl peroxide and diisobutylene ozonide.

Curve "A" is that for approximately .54% benzoyl peroxide, whilst Curve "B" is that for .65% diisobutylene ozonide. It will be seen, therefore, that Houtz and Adkins assertion that diisobutylene ozonide is a better catalyst for the polymerization at 25° Centigrade, than benzoyl peroxide, is justified. Curve "C" is obtained with 4.98% of diisobutylene ozonide and it will be seen that the material is substantially polymerized at 25° Centigrade in 230 hours.

A curve for the polymerization of pure styrene at this temperature would not be capable of plotting on this particular graph owing to the slowness of the reaction. Another interesting point to note is that the curves start directly

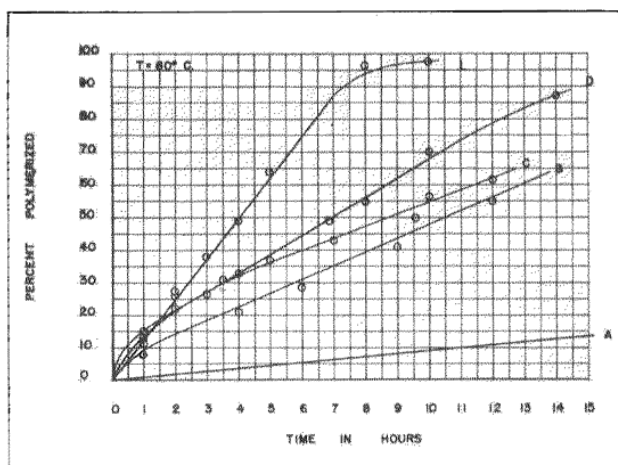


Fig. 5—Polymerization of Styrene with Accelerators at 80° C.

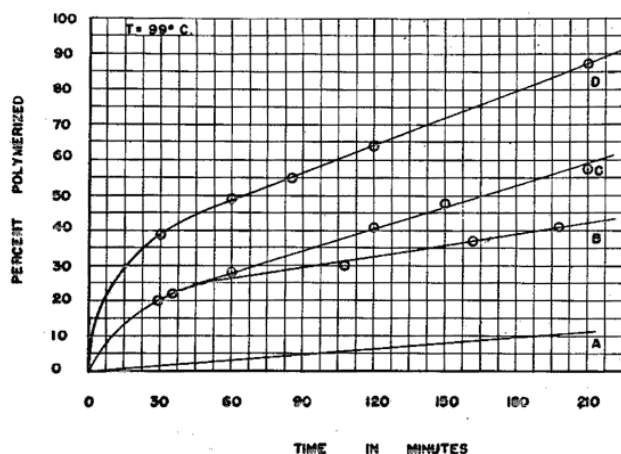


Fig. 6—Polymerization of Styrene with Accelerators at 99° C.

from the point of origin and show no trace of an induction period.

Fig. 5 gives the rate of polymerization of styrene with various accelerators at 80° Centigrade. In this case, two new ozonides have been included, namely, amylene ozonide and diamylene ozonide.

Curve "A" represents the polymerization of pure styrene at this temperature. Curve "B" represents that obtained using .5% amylene ozonide; curve "C," .65% diisobutylene ozonide; curve "D," .46% diamylene ozonide; and curve "E," .54% benzoyl peroxide.

There are several very interesting features to be observed in these curves. The curves for pure styrene and for benzoyl peroxide show a straight-line nature passing through the origin, whilst the curves for the ozonides show a very sharp rise in the polymerization rate at the commencement, followed by a dropping-off to a constant lower rate of polymerization. As the molecular weight of the hydrocarbon portion of the ozonide increases, the effect on the polymerization rate becomes greater.

Fig. 6 gives the curves obtained with various accelerators at 99° Centigrade. Curve "A" is that obtained for pure styrene; curve "B," for .45% diamylene ozonide; curve "C," for .65% diisobutylene ozonide; and curve "D," for .55% benzoyl peroxide.

It should be noticed that all the curves for accelerated samples show an initial rapid increase in the rate of polymerization followed by a falling-off to a steady lower rate.

From the three sets of curves shown in Figs. 4, 5, and 6, it will be seen that the relative effi-

ciency of an accelerator can only be judged when the temperature conditions are stated. Thus, diisobutylene ozonide is a better accelerator than benzoyl peroxide at 25° Centigrade, whilst at temperatures above 80° Centigrade benzoyl peroxide is the better catalyst.

In this case, therefore, both pairs of contributors, Houtz and Adkins, and Staudinger and Lautenschlager, were right and both were wrong, depending solely on the point of the temperature scale considered. The change in slope of the curve at higher temperatures is probably due to the thermal destruction of the accelerator, the decomposition giving rise to substances that act as chain breakers.

This thermo destruction has been noted in particular (McClure, Robertson, and Cuthbertson)<sup>9</sup> with benzoyl peroxide in benzene solution, and it has been shown that decomposition is particularly rapid at temperatures above 80° Centigrade. At low temperatures there is a slow decomposition to benzoyl radicals, and it is probably these benzoyl radicals that initiate the chain.

As of interest, Fig. 7 shows the effect of storing diisobutylene ozonide at 0° Centigrade.

It is well known that the ozonides of the lower alkenes are unstable at elevated temperatures, and it was, therefore, desired to know how feasible it was to store such a material before it would lose its value as a catalyst. The black solid circles show the results obtained on polymerizing styrene with catalyst at 80° Centigrade after keeping the diisobutylene ozonide for 19 days at 0° Centigrade, whilst the white circles

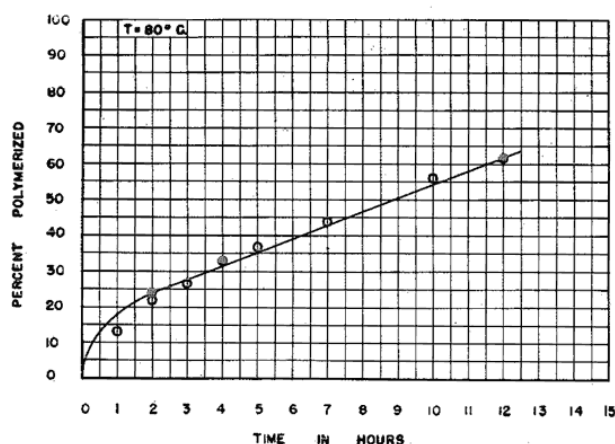


Fig. 7—Effect of Storing Di-isobutylene Ozonide on the Subsequent Polymerization Rate of Styrene.

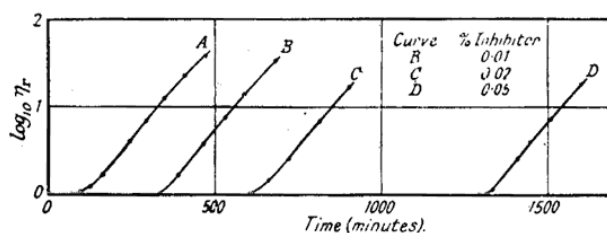


Fig. 8—Polymerization of Styrene in the Presence of Benzoquinone at 90° C.

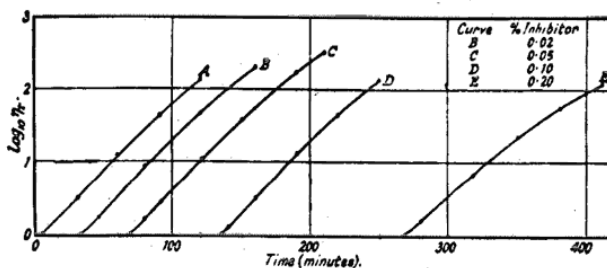


Fig. 9—Polymerization of Styrene in the Presence of Benzoquinone at 120° C.

were obtained with the same concentration of catalyst freshly prepared for the experiment. It will thus be seen that it is possible to prepare ozonides and store them for quite long periods under suitable conditions without decomposition.

Thus far only materials affecting the polymerization rate in a positive direction have been considered. It is now interesting to consider the so-called inhibitors and retarders.

It is a well-known experimental fact that the addition of hydroquinone or other phenolic bodies to monomeric styrene enables this material to be kept much longer without polymerization than in their absence. We shall consider at this stage as inhibitors only those substances which affect the initiation of chains, leaving to a little later the discussion of retarders, whose effect we believe to be the breaking of the chains once they have started.

A considerable amount of work on retarders was carried out by S. G. Foord of S. T. & C. Labs., who was able as a result of his investigations to calculate the actual amount of stabilization that could be achieved at any particular temperature with the quantity of added material.

He was furthermore able to get a qualitative idea of the effectiveness of various groupings on the stabilization. Quinoid compounds in general are very strong inhibitors without any material retarding action in small concentrations. Exceptions to this rule are anthraquinone, which

has been found to be ineffective, and acenaphthene quinone which has only a weak inhibiting action. Phenolic hydroxy groups are comparatively weak stabilizers, phenol itself being ineffective and cresol only a feeble stabilizer; the effectiveness increases with the number of hydroxy groups, but depends on their position in the molecule. It is probable that a substance like hydroquinone acts by reacting with oxygen present to give quinone, which then acts as the inhibitor.

Amino groups are inhibitors and are most effective when attached to a benzene nucleus, particularly in the presence of another active group.

Beta naphthylamine is a more effective inhibitor than alpha naphthylamine. Those nitroso compounds examined, for example  $\alpha$ -nitrosodimethyl aniline and  $\alpha$ -nitroso- $\beta$ -naphthol, show a very strong inhibiting action. The case of benzoquinone has received the most attention.

Fig. 8 shows the effect of different concentrations of benzoquinone on the polymerization of styrene at 90° Centigrade. It will be seen that the slope of the curves, once polymerization has started, is the same in the presence of benzoquinone as in its absence, but that the time for the commencement of the polymerization depends on the concentration of the inhibitor.

Fig. 9 shows similar curves at 120° Centigrade. In this case, it will be seen that large quantities of benzoquinone show a slight retarding effect on the subsequent polymerization rate.

Fig. 10 gives the results for phenanthraquinone at 120° and here again a slight retarding action is observed with increasing concentration of the phenanthraquinone.

As a result of this work, the curves shown in Fig. 11 were obtained for the length of the induction period at 120° Centigrade against the

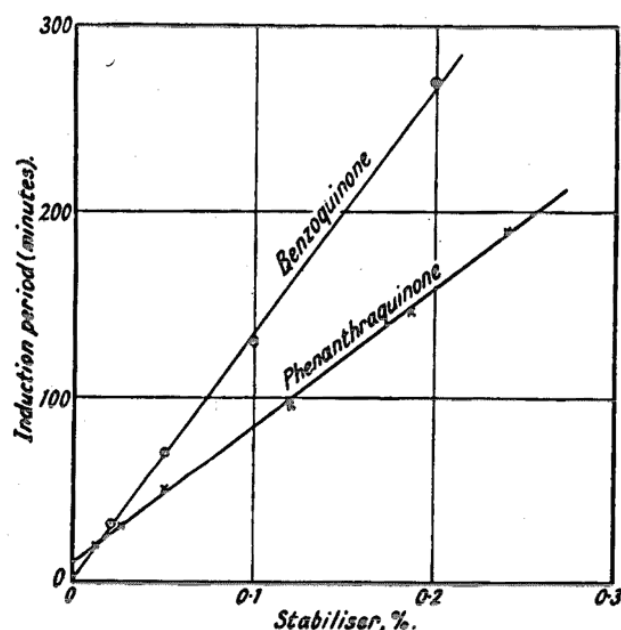
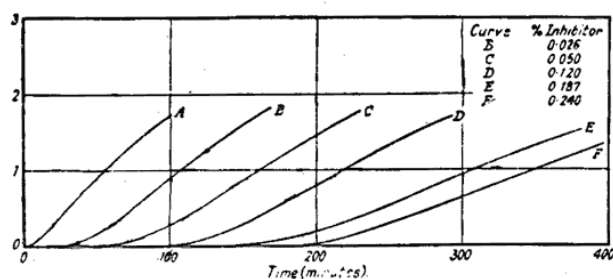


Fig. 11—Effect of Concentration of Stabilizer on the Induction Period for the Polymerization of Styrene.

concentration of the stabilizer for cases of benzoquinone and phenanthraquinone.

From these curves, calculations can be made for the length of time at 120° Centigrade it will be necessary to heat the styrene containing a known amount of stabilizer before polymerization starts. Thus, if the monomer contains 0.1% of benzoquinone, it will have to be heated for 2 hours and 10 minutes before polymerization starts.

It will be seen that benzoquinone is a more effective inhibitor than is phenanthraquinone. An interesting experimentally observed point is that the yellow color of the solution of quinone in styrene gradually lessens as the heating is continued, and the commencement of the polymerization occurs almost at the disappearance of the yellow color.

### Chain Propagation

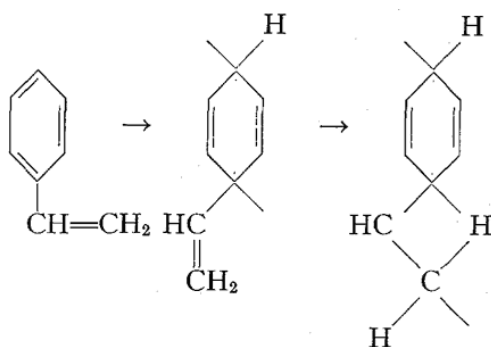
Chain propagation consists of a great many reactions occurring in rapid succession. An activated molecule can collide with an unactivated molecule, giving rise to an addition product still possessing the same form as existed in the primary step.

The heat of activation of chain propagation is relatively small, and is estimated at about 8,000 calories per mole. This energy is provided by the

Fig. 10—Polymerization of Styrene in the Presence of Phenanthraquinone at 120° C.

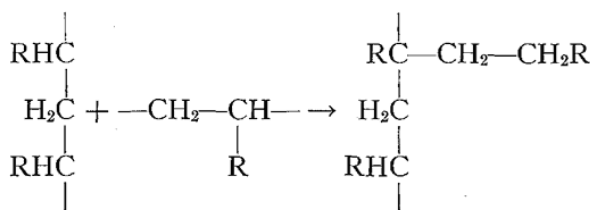


Schulz<sup>11</sup> has assumed a quinonoid structure for the activated monomer, or growing chain,



which, however, has not found much favor principally because of the absence of any color formed during the reaction that might be expected with such a structure.

Flory<sup>12</sup> has yet another mechanism, which involves the wandering of a hydrogen atom from one growing chain to another growing chain.



So far, only polymerization in the monomer has been considered. In the presence of diluents, the results are rather complicated, depending on the nature of the diluent used. Thus, the presence of ethyl benzene serves to slow down the polymerization and to give polymers of lower molecular weight. In carbon tetrachloride, or chloroform, however, the subsequent polymer is found to contain chlorine, indicating that the chlorinated material enters into the growing chain.

Apart from the chain mechanism, leading to high molecular weight materials, it is also possible to get a step-by-step addition reaction giving rise to dimers, trimers, and other lower polymers. Examples of materials causing this reaction are sulphuric acid, acetic acid and activated earths such as flordin.

A great deal more work is necessary in the whole field of polymerization to get a clearer insight into the probable processes. The foregoing account of the polymerization process can only be considered a very rough and by no means exhaustive treatment of the subject matter.

Summarizing very briefly, however, we can

say that the polymerization of styrene is a chain mechanism involving the activation of the double bond by some means or other, followed by a growing of these activated units into the polymer chains by collision with unactivated monomer units. A final chain breaking reaction stops the chains and yields polymer.

It has been seen that various substances affect these processes by stepping up the formation of active centers, breaking the activated centers when formed or by breaking the polymerization chains, once started.

We have not considered the effect of other influences, principally because they have not been studied too comprehensively at the present time. These include pressure, high frequency, radioactive substances, etc.

### Experimental Technique

A study of polymerization calls for the development of a special technique if reproducible results are to be obtained. In our experiments we have used styrene prepared by either of two methods, namely, the commercially prepared material from ethyl benzene, and that prepared by the dehydration of  $\beta$ -phenylethyl alcohol,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$ . The last method of preparation is very convenient as a laboratory method since the alcohol can be purified to a high degree before dehydration, whilst in the dehydration process only water and styrene, together with some unchanged alcohol, are obtained, making final purification of the monomer relatively easy. The purity of the styrene, unfortunately, cannot be very easily determined by the usual methods such as analysis, refractive index, density or electrical properties, since quantities of impurity in the order of 0.001% may markedly affect the polymerization without affecting the physical properties enumerated above. Vacuum fractionation of a purified material, however, when carried out with extreme care, yields reproducible results.

The polymerization is carried out in very thin-walled glass tubes of approximately  $\frac{1}{4}$ " diameter. The tubes are cleaned by the use of hot chromic-nitric acid mixture, followed by thorough washing with distilled water. To remove any traces of adsorbed acid, the tubes are left in an aqueous solution of sulphur dioxide for



several days after which they are again rinsed in distilled water and allowed to stand until required for use. For use, the tubes are dried by washing with redistilled acetone followed by vacuum drying. The tubes hold approximately one to two milli-litres of liquid and, under these conditions, isothermal conditions during the polymerization can be maintained.

The heating is done in the polymerization vessel shown in Fig. 12. Constant temperature is

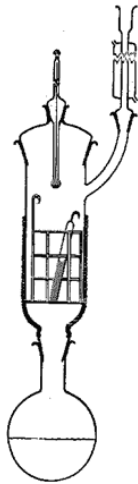


Fig. 12—Apparatus for Polymerization Studies.

attained by boiling a liquid in the flask, the tubes containing the polymerizing material always being in the vapour of the liquid at its boiling point. The liquids used are, chloroform ( $61^{\circ}$  C.), benzene ( $80^{\circ}$  C.), and sec. butyl alcohol ( $99.5^{\circ}$  C.). For  $25^{\circ}$  Centigrade, a constant temperature water bath is employed.

After the requisite time of polymerization, the tubes are removed from the thermostat and rapidly cooled by plunging into ice water. The percentage of polymer present is determined by dissolving a known weight of the sample in propylene oxide, precipitating the polystyrene by the addition of pure methyl alcohol, filtering through a sintered glass crucible and drying to constant weight in a vacuum oven at  $60^{\circ}$  Centigrade. This method of precipitation has been found much superior to the conventional toluene-methyl alcohol precipitation.

#### **Some Observations on the Dielectric Properties of Dielectrics**

Owing to the remarkable increase in the study of dielectric phenomena necessitated by the re-

cent advances in the applications of electronics to industrial operations, and consequent increase in the development of dielectric theory, it is only possible here to touch briefly on some of the more important phases of the development and to discuss them with particular reference to the dielectric constant and the loss factor, two of the most important electrical properties of plastics.

We should first of all ask ourselves, "What is a dielectric?" and "How does it differ from a non-dielectric, or conductor?" It is obvious that some fundamental difference exists between materials like copper and polystyrene; for, apart from their obvious physical difference, their behavior in an electric field is completely different, one being a conductor of electricity whilst the other is not.

A dielectric from a wave-mechanical standpoint may be considered as a material which is so constructed that, at the absolute zero of temperature, the lower bands of allowed energy level are completely full, whilst the higher unoccupied bands are separated from them by a large zone of forbidden energy levels. Conduction in the lower, fully occupied bands is thus impossible because there are no unoccupied energy levels to take care of the energy from the electrons of the applied field, whilst the zone of forbidden energy levels is so wide that it is improbable that an electron from a lower level can acquire enough energy to make the transition to the unoccupied upper band where it could take part in conduction.

More simply, the electrons and other charged particles of a dielectric are only free to be displaced when put in an electric field, but return to their original equilibrium positions when the field is removed.

The dielectric constant, usually symbolized by  $\epsilon'$ , is defined as the ratio of the capacity of a condenser with the dielectric material placed between two plates to the capacity of the same arrangement of plates in a vacuum.

The loss factor, symbolized by  $\epsilon''$ , is equal to the product of the dielectric constant times the cosine of the phase angle between voltage impressed upon, and the alternating current flowing in, the insulation placed between suitable metallic electrodes.

The ratio of  $\epsilon''$  to  $\epsilon'$  is frequently called the dissipation factor, whilst the angle  $\delta$  is defined

by  $\tan \delta = \epsilon''/\epsilon'$  and is called the loss angle. The quantity  $\sin \delta = \cos \theta$  is the power factor, but for small values of  $\epsilon''/\epsilon'$  the power factor, loss angle and dissipation value are for all practical purposes equal.

It will be recalled that Maxwell postulated that the square of the refractive index of a substance measured by visible light was equal to the dielectric constant, but Debye was the first to give some explanation of the fact that the dielectric constants of some substances were higher than those calculated from Maxwell's rule.

We shall use the term "dielectric polarization" to refer to the polarized condition created either by a constant or an alternating current on a dielectric, reserving the term "polarizability" as its quantitative measure.

Polarizability is defined as the electric moment per unit volume induced by an applied field of unit effective intensity. The total polarizability of a material is the sum of the electronic, atomic, dipole, and interfacial polarizabilities, each of which plays an important part in the dielectric properties of the materials and which still require a considerable amount of investigation to determine their exact foundations.

### Electronic Polarizations

The electronic polarizations are due to the displacement of charges within atoms and can be

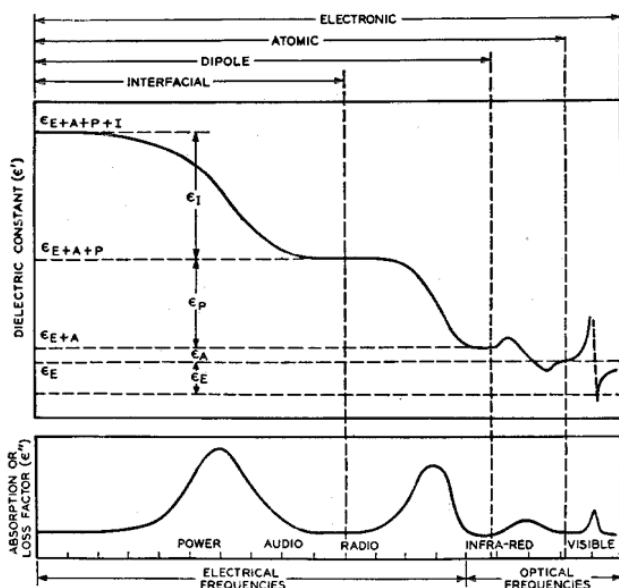


Fig. 13—Effect of Frequency on the Dielectric Constant, and the Loss Factor.

assumed to be proportional to the number of bound electrons in unit volume, and inversely proportional to the forces binding them to the nuclei of the atoms. They can form completely in times generally less than  $10^{-10}$  seconds, and therefore usually contribute a fixed amount to the dielectric constant in the electrical frequency band. But in the optical spectrum they sometimes change rapidly with frequency, giving rise to the well-known absorption bands.

In some materials, for example benzene, the only polarizable elements are electrons, the dielectric constant being the same for all frequencies.

The magnitude of this polarization can be determined very simply by a determination of the refractive index, and the use of two expressions:

$$\epsilon = n^2$$

and

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = P,$$

where  $M$  is the molecular weight and  $d$  is the density.

### Atomic Polarizations

Also to be considered as occurring instantaneously are the atomic polarizations, due to the displacement of ions in an ionic crystal lattice or of atoms in a molecular lattice or molecule. For dielectric materials, however, the atomic polarization is usually negligible.

### Dipole Polarization

The most important type of polarization affecting the electrical properties of plastics and dielectrics in general is that due to the presence of dipoles. Debye has shown that the molecules of all substances, except those where the electric charges are symmetrically located, tend to align themselves in the direction of the applied field. This dipole polarization is superimposed on the electronic and atomic polarizations already discussed. The complete expression deduced by Debye to hold for such polar materials is

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi N\alpha}{3} + \frac{4\pi N}{3} \cdot \frac{\mu^2}{3kT} \cdot \frac{1}{1 + i\omega\tau}$$

where  $\mu$  is the so-called permanent moment of the molecule,  $k$  is Boltzman's constant,  $\tau$  is the

relaxation time and  $\omega$  is  $2\pi$  times the frequency at which the dielectric constant is measured. Debye assumed  $\tau$  as proportional to the internal friction of the material giving the relationship

$$\tau = \frac{\xi}{2kT} = \frac{8\pi\eta\alpha^3}{2kT},$$

where  $\xi$  is the internal friction coefficient,  
 $\eta$  is the coefficient of viscosity,  
 $\alpha$  is the radius of the molecule,  
 and  $T$  is the absolute temperature.

This explanation is obviously only applicable to gases or very dilute solutions of spherical molecules.

### Interfacial Polarizations

So far we have discussed only those polarizations to be expected in a homogeneous material. In heterogeneous materials, however, where the components have different dielectric constants and conductivities, a fourth type of polarization may occur, namely, interfacial polarization.

Since a large number of commercial dielectrics are heterogeneous, it is well to consider the possibility of interfacial polarization. In the case of the dielectric constant of cellulose at low frequencies, for example, there is an interfacial polarization portion due to the presence of water and the dissolved salt. Interfacial polarization is most important at very low frequencies; it may, nevertheless, extend into the higher frequency bands in certain cases.

From the foregoing considerations, it will be obvious that the dielectric constant of a material is not a fixed value, but depends on the frequency and the temperature at which it is measured. With each change in the dielectric constant, we get a period of so-called "anomalous dispersion" where the loss factor becomes a maximum at the point where the rate of change of dielectric constant is greatest.

This will be seen clearly from a consideration of Fig. 13 which gives a diagrammatic representation of the change of dielectric constant and loss factor with frequency. The mid-point of the decreasing dielectric constant curve is often referred to as the relaxation frequency.

Fig. 14 contains some interesting curves for the variation of dielectric behaviour of a chlorinated diphenyl with temperature and frequency.

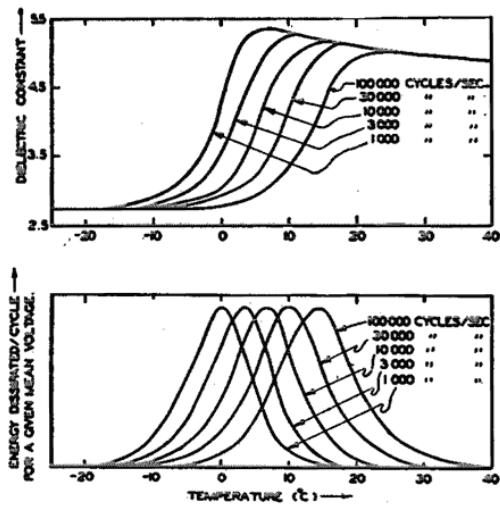


Fig. 14—Temperature Dependence of Dielectric Relaxation Rates for a Chlorinated Diphenyl. (From A. H. White and S. O. Morgan, *J. Frank. Inst.* 216, 635 (1933).)

It shows that the frequency above which the dipolar orientation contribution to the dielectric constant becomes negligible changes very rapidly with the temperature. It also illustrates that in the region of greatest irreversibility, the energy dissipation during each process of polarizing the dielectric is a maximum.

### Circular Arc Method of Expressing Dielectric Phenomena

A very interesting way of expressing dielectric phenomena is given in a recent paper by the Cole brothers,<sup>13</sup> who use the expression:

$$\epsilon^* - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{1 + (i\omega\tau_0)^{1-\alpha}}$$

where  $\epsilon^*$  is the complex dielectric constant (equal to  $\epsilon' - i\epsilon''$ ),  $\epsilon_0$  and  $\epsilon_\infty$  are the static and infinite frequency dielectric constants,  $\omega$  is  $2\pi$  times the frequency, and  $\tau_0$  is the generalized relaxation time.

The parameter  $\alpha$  can assume values between 0 and 1. This expression requires that the locus of the dielectric constant in the complex plane be a circular arc with end points on the axis of the real dielectric constant and the center below the axis.

Some typical results obtained by this method are given in Figs. 15 and 16.

It will be seen that in general the experimental points do lie on such a circular arc. In the case

of slate, however, it will be observed that there is an anomalous portion in the 500 kilocycle region, probably due to interfacial polarizations.

**Eyring Rate Theory and Dielectric Phenomena**

More recently, Kauzmann<sup>14</sup> has pointed out that the Coles' expression has no evident validity in theory, although giving reasonable agreement with experimentally observed results. Kauzmann tackles the problem from the Eyring rate theory, postulating that the dipoles jump from one position to another, and arrives at a possible explanation of the physical nature of the energy losses of dielectrics. He uses the following equations for the dielectric constant and loss factor in terms of the frequency:

$$\epsilon' = \frac{\epsilon_0 - \epsilon_\infty}{1 - x^2} + \epsilon_\infty \quad \text{and} \quad \epsilon'' = \frac{\epsilon_0 - \epsilon_\infty}{1 - x^2} \cdot x,$$

where 
$$x = \frac{2\pi\nu}{k_0 \left( \frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \right)}$$

$k_0$  is the transition probability of the dipoles jumping from one position to another, or the relaxation rate.

For convenience we can write  $dP/dE = -k_0(P - N_0\alpha E)$ ; i.e., the rate of change of polarization in a field  $E$  is given by minus the relaxation rate times the polarization plus the product of the relaxation rate, the number of

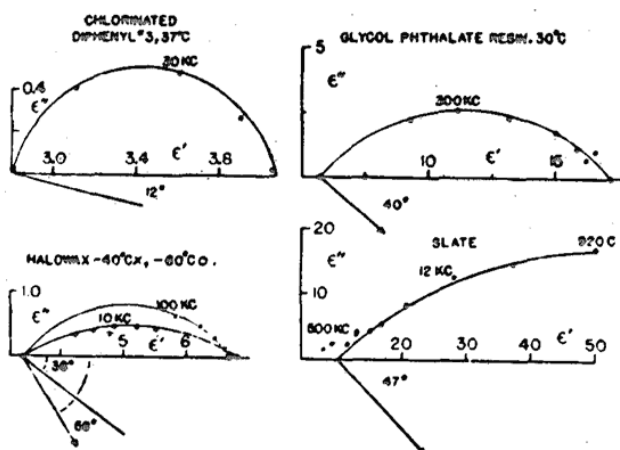


Fig. 16—Complex Dielectric Constants of Solids.

dipoles per unit of volume, the electronic polarization, and the field strength. Suppose  $E$  to be a high frequency field with  $\nu$  much greater than  $k_0$  so that polarization at no time has a chance to build up appreciably. Then  $P$  is approximately equal to 0 and  $dP/dE$  is  $\cong$  to  $k_0 N_0 \alpha E$  and the average power loss is

$$\frac{k_0 N_0 \alpha}{\nu} \langle E^2 \rangle_{av} \text{ per cycle.}$$

This case is similar to a conductor having a specific conductivity of  $k_0 N_0 \alpha$  reciprocal ohms. Physically it arises from the fact that if a dipole be regarded as a positive and a negative ion separated by a fixed distance, we can not detect the fact that the ions are bound to one another unless we use fields which oscillate so slowly that the ions can move a distance greater than that separating them during a single oscillation.

At low frequencies with  $\nu$  much less than  $k_0$ , the physical nature of the loss is less obvious. Here the polarization  $P$  lags slightly behind the field  $E$ . If  $P$  is broken up into two parts, one part in phase with the field, and the other out of phase by  $\pi/2$ , it is readily found that the in-phase part of  $P$  is given by

$$N_0 \alpha E \left( \frac{1 - 4\pi^2 \nu^2}{k_0^2} \right),$$

from which the energy lost as heat per cycle is

$$\frac{4\pi^2 N_0 \alpha \nu}{k_0} \langle E^2 \rangle_{av}.$$

Consequently, if we plot the energy loss per cycle against the frequency, there results a direct

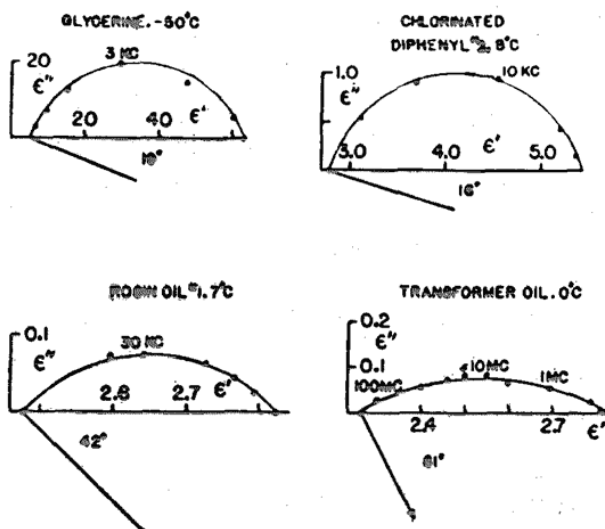


Fig. 15—Complex Dielectric Constants of Liquids.

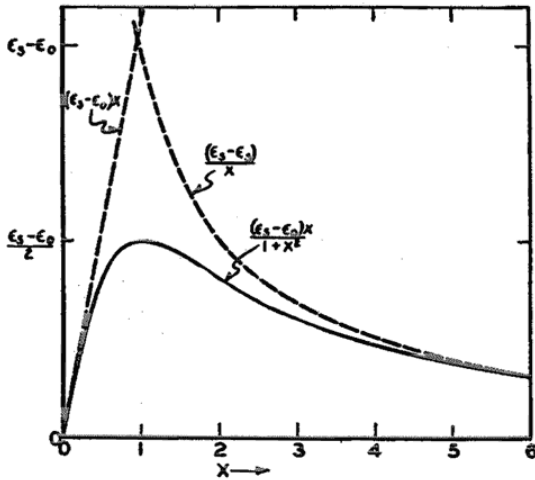


Fig. 17—Linear and Inverse Dependence of the Loss Factor on the Frequency.

proportionality at low frequencies and a hyperbolic relationship at high frequencies with an intermediate maximum. We thus get the curve shown in Fig. 17, and the physical reason for the familiar symmetrical  $\epsilon'$  versus  $\nu$  plot of Fig. 18.

The actual conversion of electrical energy into heat in a dielectric may be attributed to the viscous resistance offered by the medium to dipole rotation.

The above considerations apply very well for dielectrics having dipole moments which are relatively large and, therefore, dielectric constants greater than 2.5 to 3.

**Dielectric Behaviour of Extremely Low Loss Material**

There is a very important group of materials, however, of which polystyrene is one, for which it is not at the present moment easy to find a quantitative explanation for their electrical behaviour. In these dielectrics, the energy losses per cycle are relatively independent of the frequency over wide ranges of frequency. This might perhaps be explained on the theory that, instead of a single relaxation rate, there exists a uniform logarithmic distribution of relaxation rates.

Kauzmann is inclined to discount this explanation. He rather believes that these losses arise from dimensional changes of the dielectric due to electrostriction with constant rubbing over electrode surfaces with which the dielectric is in contact while subject to an oscillating field.

Since in the case of polystyrene we are dealing with a material whose inherent electrical characteristics are excellent, the presence of even minute amounts of polar materials may affect the dielectric constant and power loss.

The necessary technique for measuring quantities of so small a magnitude as are exhibited with polystyrene is relatively new and the accuracy still a little uncertain. It will be necessary to do much more work before the correct answer will be available.

**Importance of Dielectric Loss in Transmission Line Theory**

It may well be asked, what is a practical illustration of the importance of having low dielectric constant and power loss in insulating materials. Consider for example the case of coaxial cable used for the transmission or reception of high frequency.

It is well known that if a source of high frequency power is impressed on one end of a transmission line, the power that comes out of the

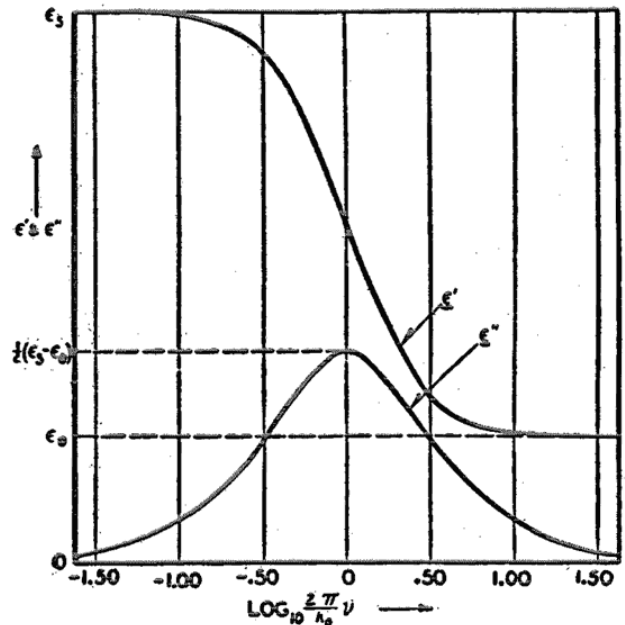


Fig. 18—Frequency Dependence of the Dielectric Constant and Loss Factor.

other end is less, due to the losses in the line. The loss is usually expressed in units known as decibels.\* This loss is composed of that due to

\* Abbreviated db and used to express the difference in power level existing at two points in a network. The number of db =  $10 \log_{10} (P_1/P_2)$ .

the losses in the copper and that due to the losses in the dielectric. For purposes of this discussion, the copper losses need not be considered. The losses due to the dielectric are given by the expression:

$$A_d = 2.78 \times p \times \sqrt{K} \times F \text{ db/100'}$$

where  $p = \text{power factor} = \frac{\epsilon''}{\epsilon'}$ ,

$K = \text{dielectric constant}$ ,

and  $F = \text{frequency in megacycles}$ .

Suppose we have a good dielectric like polystyrene, where  $K = 2.5$  (approx.) and  $p$  is 0.0003. Then at 1 megacycle the losses will be

$$\begin{aligned} A_d &= 2.78 \times 0.0003 \times \sqrt{2.5} \times 1 \text{ db/100'} \\ &= 0.0013 \text{ db/100 ft.} \end{aligned}$$

At 10 megacycles the loss will be 10 times as great, and at 100 megacycles 100 times as great, since neither the power factor nor the dielectric constant of polystyrene change appreciable in this frequency range.

It will thus be seen that increases in the power

factor will have a very marked influence on the losses as the frequency increases.

Should a dielectric be used with a period of anomalous dispersion occurring in the frequency range employed, the losses would vary irregularly over that frequency range—a result even worse than a steady high power loss. It is for this reason that materials like vinylite, koroseal, ethyl cellulose, etc., cannot be used for insulation work at high frequencies.

### Bibliography

1. E. Simon: *Ann.*, **31**, 267 (1839).
2. S. G. Foord: *J.C.S.*, 48 (1940); U.S.P. 2,318,211, 2,318,212, 2,225,471, 2,226,714.  
A. J. Warner & A. A. New: U.S.P. 2,272,996, 2,289,743.
3. Schulz & Husemann: *Z. Phys. Chem.*, **B34**, 187 (1936).
4. Stobbe & Posnjak: *Ann.*, **371**, 259 (1909).
5. Taylor & Vernon: *J.A.C.S.*, **53**, 2527 (1931).
6. Schulz & Wittig: *Naturwissenschaften*, **27**, 387 (1939).
7. Staudinger & Lautenschlager: *Ann.*, **488**, 1 (1931).
8. Houtz & Adkins: *J.A.C.S.*, **53**, 1058 (1931); **55**, 1609 (1933).
9. McClure, Robertson & Cuthbertson: *Can. Jour. Res.*, **20B**, 113 (1942).
10. Gallay: *Kolloid Z.*, **57**, 1 (1931).
11. Schulz & Husemann: *Angew. Chem.*, **50**, 767 (1937); *Z. Phys. Chem.*, **B39**, 266 (1938).
12. Flory: *J.A.C.S.*, **58**, 1871 (1937).
13. Cole: *J. Chem. Physics*, **9**, 341 (1941); **10**, 98 (1942).
14. Kauzmann: *Rev. of Modern Physics*, **14**, 12 (1942).