

2,6-Diacetoxy- α , α -dibromoacetophenone.—Four grams of 2,6-diacetoxyacetophenone was dissolved in 50 cc. of glacial acetic acid and 5.6 g. of bromine dissolve in 25 cc. of glacial acetic acid was added dropwise with stirring. The addition took one hour and sometimes heating was required to initiate the reaction which then continued to completion at room temperature. The reaction mixture was then poured into ice water with stirring and the crude brominated compound separated in greenish crystals. These were filtered and twice recrystallized from isopropyl alcohol to give 5.3 g. of white crystals which melted at 113° (corr.).

Anal. Calcd. for $C_{12}H_{10}O_6Br_2$: C, 36.54; H, 2.53; Br, 40.50. Found: C, 36.79; H, 2.66; Br, 39.82.

Both of the above halogen compounds gave an active halogen test by first heating with alcoholic sodium ethoxide solution, then testing the resulting solution after acidification with silver nitrate.

2,6-Dihydroxy- α -bromoacetophenone.—A mixture of 3 g. of 2,6-diacetoxy- α -bromoacetophenone, 80 cc. of 60% ethanol, 20 cc. of hydrobromic acid (40%) and 1 mg. of sodium hydrosulfite was refluxed for one hour. The solvent was then distilled at 30° and 30 mm. pressure to leave yellow platelets which were recrystallized twice from benzene to give a yield of 1.6 g. It melted at 143° (corr.). This compound gave a green ferric chloride test.

Anal. Calcd. for $C_8H_7O_3Br$: C, 41.55; H, 3.03. Found: C, 41.84; H, 2.99.

4-Hydroxycoumaran-3-one.—A solution of 1 g. of 2,6-dihydroxy- α -bromoacetophenone, 1 g. of sodium acetate trihydrate, 1 mg. of sodium hydrosulfite and 50 cc. of ethanol was refluxed for one hour. Twenty cubic centimeters of water was added and 30 cc. of ethanol was distilled from the reaction mixture. The resulting solution

was allowed to cool and placed in a refrigerator overnight. Brown crystals separated and were filtered and recrystallized twice from high boiling petroleum ether to give 0.4 g. of brown granular crystals. This compound began subliming at 85° and finally melted at 120° (corr.). It gave a violet ferric chloride test for phenols.

Anal. Calcd. for $C_8H_6O_3$: C, 64.00; H, 4.00. Found: C, 64.21; H, 4.17.

In this last reaction a few milligrams of sodium hydrosulfite was added to the reaction mixture to minimize oxidation of the rather unstable 2,6-dihydroxy- α -bromoacetophenone.

3,4-Dibenzoxybenzofuran.—A solution of 0.5 g. of 4-hydroxycoumaran-3-one, 1 g. of benzoyl chloride, 1 g. of sodium carbonate, 10 cc. of water and 15 cc. of acetone was warmed gently for thirty minutes, then poured into ice water. The benzoylated compound separated and was filtered. It was recrystallized from ethyl acetate to give 1.0 g. of colorless needles; m. p. 183° (corr.).

Anal. Calcd. for $C_{16}H_{10}O_4$: C, 73.74; H, 3.91. Found: C, 73.47; H, 4.03.

Summary

4-Hydroxycoumaran-3-one has been synthesized by the following sequence: 2,6-dihydroxyacetophenone \rightarrow 2,6-diacetoxyacetophenone \rightarrow 2,6-diacetoxy- α -bromoacetophenone \rightarrow 2,6-dihydroxy- α -bromoacetophenone \rightarrow 4-hydroxycoumaran-3-one. The low melting point and tendency to sublime exhibited by this compound indicate that the hydroxyl group is probably chelated with the carbonyl group.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Electrical Properties of Solids. IV.* The Influence of Thermal History on Polyvinyl Chloride Plastics

BY RAYMOND M. FUOSS

I. **Introduction.**—Plastics containing polyvinyl chloride have two characteristics which sharply differentiate them from most of the systems ordinarily studied by physico-chemical methods: the electrical properties of a given sample depend on the method of preparing the sample¹ and, after preparation, the properties of a given sample change with time. Obviously the influence of the corresponding variables must be eliminated before any correlation between properties and chemical composition and structure is attempted. The most important item in the preparation of the sample is the thermal history;

two samples of the same composition with identical thermal histories will give results which check as precisely as might be desired (assuming that trivial variables, such as those due to surface effects and humidity, are eliminated).²

The changes with time are of at least two kinds: (1) a slow decrease of dielectric constant, amounting to several per cent., while the density remains constant and (2) a slow increase of d. c. conductance, which in turn induces an increase in dielectric constant and a. c. absorption. These two effects combine to produce a minimum in the dielectric constant-time curve.

It is the purpose of this paper to present and

(* Paper III, THIS JOURNAL, 60, 456 (1938).

(1) Fuoss, *Trans. Electrochem. Soc.*, 74, 91 (1938).

(2) Fuoss, THIS JOURNAL, 59, 1703 (1937).

discuss some experimental results of a study of the properties outlined above. Not enough data are yet available to give a complete description of the plastic solid, because so very much more remains to be done. Enough has been accomplished, however, to show several promising lines of attack on the general problem, and it is believed that the results are sufficiently interesting and suggestive to be made available to other workers in this field.

II. Experimental Methods.—All measurements were made on disks of plastic 10 cm. in diameter and 6 mm. in thickness. All samples were surfaced in some way to eliminate series capacity due to air films between the sample and electrodes. Diluted aquadag, powdered graphite, or tin foil, the latter rubbed on with a minute amount of petrolatum, all gave satisfactory results; depending on the composition and flexibility of the sample, one or another method was preferred. (It might be well to point out that *tin* must be used in the foil method: all other available foils were too hard to give adequate contact.)

The cell¹ and bridges¹⁻³ used in the measurements have been described previously.

In general, the samples were prepared by cold mixing a weighed amount of polyvinyl chloride and plasticizer. (The polyvinyl chloride was from the same lot as that used in preparing samples for the two previous papers of this series.^{3,4}) The mixture was then worked on a rubber mill under controlled and recorded conditions (time and temperature of milling, thickness of sheet, speed of rolls and size of batch) Disks about 0.5 mm. thick and 9.84 cm. in diameter were stamped from the final mill sheet. These disks will shrink much more parallel to the milling direction (as much as 40%) on heating to 150° than perpendicular to this direction, but heating above 100° under pressure will gradually destroy this elastic memory. In order to obtain samples for electrical measurements which

would remain circular, 15-20 disks from the mill sheet were stacked with mill directions crossed on consecutive sheets and compressed to a single disk in a hot closed mold under hydraulic pressure. Time and temperature of pressing were always recorded. After pressing, the sample was weighed, surfaced, placed in the cell and allowed to come to temperature equilibrium in an oil thermostat held at $40.00 \pm 0.01^\circ$.

Electrical measurements were then made. Thickness of cell plus sample was determined before and after the electrical measurements, and also during them, if the run lasted more than an hour. (As previously pointed out,¹ the dimensions change with time, and since the thickness enters the calculation of dielectric constant and conductance explicitly, it must be determined accurately.)

III. Results and Discussion.—It has been shown¹ that the d. c. conductance of plastics containing polyvinyl chloride plasticized with tricresyl phosphate increases on exposure to heat. The preparation of the sample involves two heat treatments, milling and pressing. The relation between d. c. conductance, which is a measure of the hydrogen chloride produced by pyrolysis, and the time and temperature of heating, is given by the equation

$$\kappa_0 = A \int_0^t \exp. [-B/T(t)] dt \quad (1)$$

where A depends on the composition of the plastic and on the temperature at which the electrical measurement is made.

In order to find a correlation between conductance and the actual amount of hydrogen chloride present, a series of samples was made up, with various amounts of lead abietate dissolved in the plasticizer. These samples were then heated for different times at different temperatures. A typical result is shown in Fig. 1, which is for a set of samples containing 0.5% lead abietate in the tricresyl phosphate. The composition was 60% polyvinyl chloride by weight. After milling fifteen times at 105°, which was sufficient to plasticize the polymer, the samples were pressed at 145° for times ranging from four to twelve minutes. As will be seen in the figure, the d. c. conductance, measured at 40°, was low (0.08×10^{-10}) and independent of heating time up to six minutes; beyond this time, however, the conductance increased rapidly with further heating. The break in the curve clearly corresponds to the time required for the lead present initially as abietate to be converted into chloride. After the lead is consumed, the conductance rises parallel to the conductance-time curve for the blanks (similar sample containing no dissolved lead).

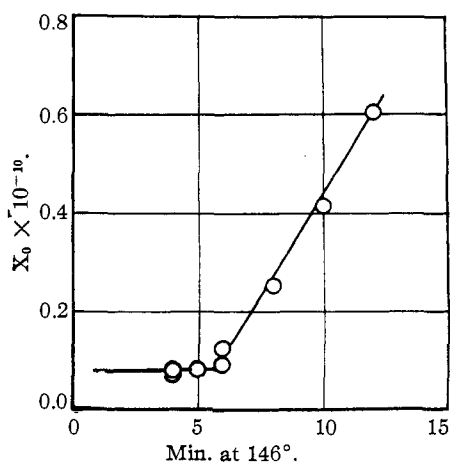


Fig. 1.—Determination of critical time by conductance method.

(3) Fuoss, *THIS JOURNAL*, **60**, 451 (1938).

(4) Fuoss, *ibid.*, **60**, 456 (1938).

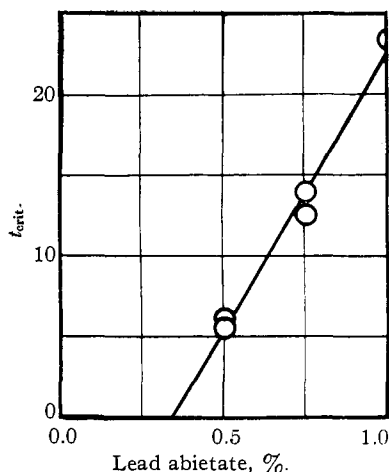


Fig. 2.—Dependence of critical time on lead content.

Figure 2 is a summary of data referring to samples heated at 145° , containing various percentages of lead abietate. The ordinate is the time required to consume the lead added. Since the line does not go through the origin, we conclude that the components of the plastic contained some material which reacts with lead abietate before the pressing. The intercept at zero time in Fig. 2 corresponds to 0.35% of lead abietate; 100 parts per million of hydrogen chloride originally in the polyvinyl chloride would use up this quantity of lead. An aqueous extract of the polyvinyl chloride gave a turbidity with silver nitrate solution, which indicated this order of magnitude of extractable chloride. After allowing for the lead consumed initially, 1.00 g. of lead abietate per 100 g. of plasticizer corresponds to 60 mg. of hydrogen chloride per 100 g. of polyvinyl chloride in the 40:60 plastic.

The dependence of lead consumption on temperature of heating is shown in Fig. 3, where data covering the range 130 – 160° are presented. The times were obtained as the breaks in the conductance–heating time curves; these samples contained 0.7% lead abietate in the tricresyl phosphate. Assuming that the amount of lead chloride formed is measured by the time to the break in the heating curve, the slope of the line in Fig. 3 gives 33 kcal. as the energy associated with the reaction between the products of pyrolysis and the lead abietate in the plastic. This value is practically the same as that found by Dr. M. M. Sprung⁵ for the pyrolysis of dry polyvinyl chloride in a stream of nitrogen. The rate of evolution of

(5) Unpublished work done in this Laboratory.

hydrogen chloride at various temperatures was plotted against reciprocal of absolute temperature; a straight line was obtained, whose slope gave 35 kcal. In a typical experiment, 47 mg. of hydrogen chloride was obtained per 100 g. of polyvinyl chloride in fifteen minutes at 150° . This is about twice as much as was found by the lead abietate (21 mg. hydrogen chloride per 100 g. polyvinyl chloride in twelve minutes at 146°) method in the plastic, and suggests that several reactions, competing for hydrogen chloride, are taking place in the presence of tricresyl phosphate containing lead abietate.

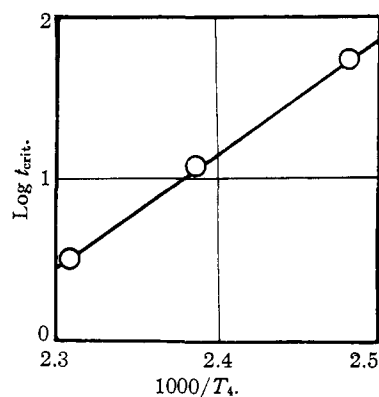


Fig. 3.—Temperature coefficient of pyrolysis.

There is other experimental evidence that the chain of reactions in the plastic is not simple pyrolysis of polyvinyl chloride to give hydrogen chloride, followed by metathesis between hydrogen chloride and lead abietate. If samples are made up containing 60 parts polyvinyl chloride and 40 parts of another plasticizer, such as dibenzyl sebacate, dibutyl phthalate, diphenyl ether, amyl naphthalene and so on, their d. c. conductance is always much higher (regardless of the intrinsic conductance of the plasticizer) for a given thermal history than that of samples made with tricresyl phosphate. This suggests the possible explanation that the hydrogen chloride set free by pyrolysis of the polymer reacts with the tricresyl phosphate, forming phosphorus oxychloride as the ultimate end-product of reaction by the reverse of the usual synthesis of tricresyl phosphate. Then the products of this reaction in turn react with the lead abietate. This assumption was checked by adding 10% octyl borate to a sample made up with dibenzyl sebacate: the resulting sample gave a conductance as low as that obtained with tricresyl phosphate, and octyl borate is a compound

which one would expect to react with hydrogen chloride to give non-electrolytic products.

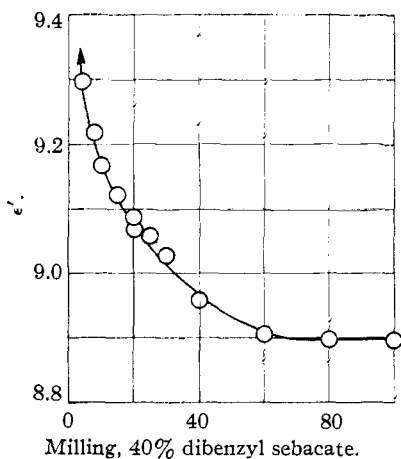


Fig. 4.—Dependence of dielectric constant on milling for polyvinyl chloride-dibenzyl sebacate.

It should be mentioned that the milling was kept to the minimum for thorough mixing in the above set of samples where press time and temperature were under investigation. Separate experiments showed that the d. c. conductance produced by the milling alone was 0.02×10^{-10} , or about 25% of the lowest and 2% of the highest d. c. conductance involved. The minimum value of 0.08×10^{-10} at 40° is due to the presence of electrolyte which will not react with lead abietate; the latter is an extremely weak electrolyte.^{6,7}

For plastics made with tricresyl phosphate as plasticizer, the primary effect on electrical properties of milling is an increase of d. c. conductance due to pyrolysis. This is not in general true, however; for example, with dibenzyl sebacate as plasticizer, the dielectric constant decreases with increased number of millings, and becomes constant after about fifty times through the mill at 105° as is shown in Fig. 4. Apparently different plasticizers require different amounts of milling to reach homogeneity. With tricresyl phosphate, the dielectric constant was independent of the number of times the mixture was milled; in fact, samples made by hot pressing an unmilled mixture of polyvinyl chloride and tricresyl phosphate, which had been thoroughly

rubbed together cold in a mortar, gave the same dielectric constant as milled material, if allowance for differences in d. c. conductance were made.

The density was the same for the various samples of Fig. 4, and the dielectric constant decreased with increased milling; hence the action of the mill in the plasticization process is more than mere mixing for the case of dibenzyl sebacate. The rate at which the dielectric constant-milling curve reaches its asymptote at a fixed milling temperature might be used as a measure of plasticizing power of a given liquid. On this basis, tricresyl phosphate is a more effective plasticizer than dibenzyl sebacate.

Practically all of the plastics studied so far show a small but systematic change of dielectric constant with time. An example is shown in Fig. 5 for 60 and 1000 cycle measurements at 40° on a sample containing 40% tricresyl phosphate and 60% polyvinyl chloride. If the logarithm of the difference between the dielectric constant at time t and its asymptotic value is plotted against the square root of the age of the sample, reckoned from the time it was cooled in the disk mold, a straight line is obtained. The slope depends upon frequency.

A similar relation between logarithm of relaxation and time elapsed after elastic strain has been observed by Dr. W. I. Patnode of this Laboratory in a study of the mechanical properties of plastics. When the samples considered here are

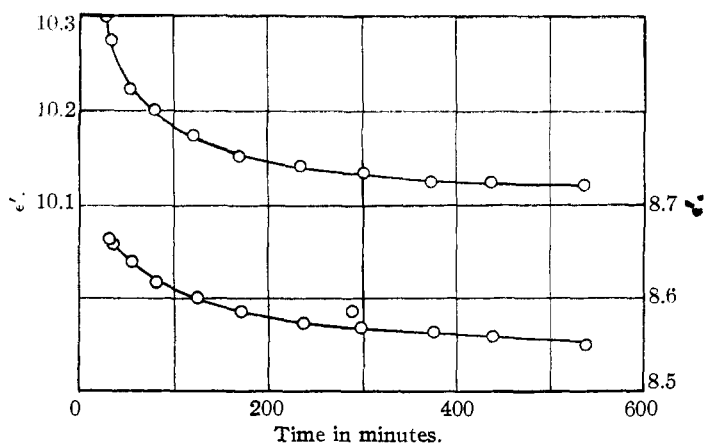


Fig. 5.—Aging curves at 60 (top) and 1000 (bottom) cycles.

taken from the disk mold, there is an immediate shrink of about 1% in diameter, together with an increase in thickness. These changes continue for days, but occur in such a way that the density, within an experimental error of 0.1%, is con-

(6) Deitz and Fuoss, *THIS JOURNAL*, **60**, 2394 (1938).

(7) Elliott and Fuoss, *ibid.*, **61**, 294 (1939).

served. The change in dielectric constant is therefore due to an internal rearrangement of some sort. Polyvinyl chloride molecules are chains of enormous length, held together in the chain direction by C-C bonds. When a sample is pressed, local strains are set up, as shown by the colored patterns which appear in polarized light. If the sample has a fairly high viscosity (less than 70% plasticizer), these strains can relax only slowly, because freedom of orientation comparable to that in liquids is made impossible by the chain structure. Relative motion of whole molecules is impossible in general, but segments of chains can slip past one another, given sufficient energy, so that there exists in the plastic the analog of liquid viscosity, but one dimension of freedom of motion is lost. Adjacent parts of the same or different molecules in a given configuration may have a position of lower potential energy available, but can reach it only when a positive fluctuation in kinetic energy gives them sufficient energy to get over the potential barrier between the metastable and the stable positions. Obviously at the start of the relaxation process, there will be many strained regions which can easily rearrange, irreversibly, of course; therefore the initial change in dielectric constant, which is a measure of internal orientation, is rapid. But as more and more energy is required to rearrange the remaining strained regions, the number of probable transitions per unit time must necessarily decrease, and the system asymptotically approaches a state in which all molecules occupy stable mutual positions. Similar arguments based on increase of entropy have been advanced to explain the relaxation of stress in stretched rubber and like compounds.⁸

After several days, the dielectric constant of a polyvinyl chloride plastic slowly starts to increase again. This change is quite different from the initial decrease, and can be correlated with the simultaneous increase in d. c. conductance. The production of hydrogen chloride which occurs in the pressing continues at room temperature (although at a very much reduced rate), and as hydrogen chloride concentration increases, the dielectric constant increases with it. Simultaneously, the pure a. c. absorption, as measured by the loss factor, ϵ'' , increases.

The loss factor is defined for our present work by the equation

$$\epsilon'' = 18 \times 10^{11}(\kappa - \kappa_0)/f \quad (2)$$

(8) Meyer, *Chemistry & Industry*, 67, 439 (1938).

where κ is the specific conductance at frequency f and κ_0 is the d. c. conductance measured on a d. c. bridge.

Equation (2) tacitly implies that the electrolytic conductance is independent of frequency and that its value is determined by d. c. measurement; obviously any variation of electrolytic conductance with frequency would induce a spurious change in apparent a. c. loss factor as defined above. This assumption may require later scrutiny; certainly in the range of high frequencies, it is known that electrolytic conductance is a function of frequency due to relaxation effects.

The correlation between a. c. and d. c. properties is shown in Figs. 6 and 7, where ϵ' and ϵ'' are plotted against the *square root* of d. c. conductance. (It was found empirically that the data approximate linearity with this choice of coördinates; we are at present unable to say whether this form is significant or coincidental.) The important fact shown by Figs. 6 and 7 is that the a. c. properties can be correlated directly with the d. c. conductance; since the latter is determined by the thermal history; we have in the d. c. conductance a variable which summarizes the thermal history as far as electrical properties are concerned.

The samples whose constants are shown in Figs. 6 and 7 were all 40% tricresyl phosphate-60% polyvinyl chloride. Different thermal histories were obtained by varying time and temperature of milling and pressing. It will be noted that data, self-consistent within a few tenths per cent. in dielectric constant, were obtained. In order to eliminate the effect of aging, all data for Figs. 6 and 7 were interpolated to two hours after preparation, from a series of measurements made on each sample. The rate of change of ϵ' and ϵ'' with electrolytic conductance decreases with increasing frequency; details of this behavior will be presented in a later paper.

The data of Figs. 6 and 7 show that we may write

$$\epsilon' = \epsilon'_0 + A\sqrt{\kappa_0} \quad (3)$$

$$\epsilon'' = \epsilon''_0 + B\sqrt{\kappa_0} \quad (4)$$

where ϵ'_0 and ϵ''_0 are the a. c. constants referring to the hypothetical electrolyte-free plastic. The terms in $\sqrt{\kappa_0}$ represent the contributions to a. c. mechanism due to the presence of electrolyte. It is planned to study this question further by using known concentrations of known electrolytes in plastics of various compositions. Incidentally,

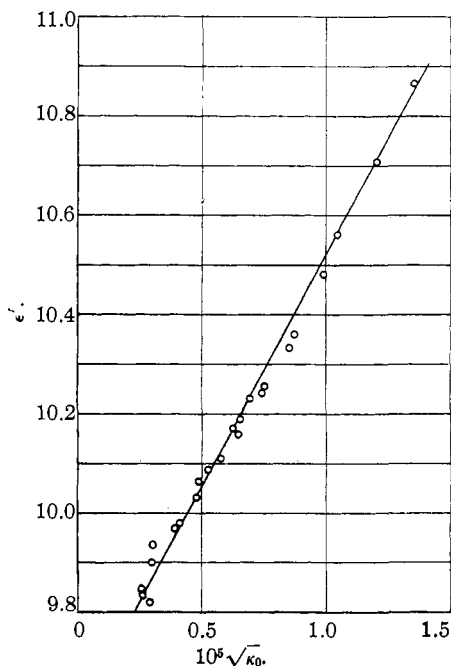


Fig. 6.—Dependence of 60 cycle dielectric constant on d. c. conductance.

this will permit a study of electrolytic conductance in the range of very high viscosities ($\eta \sim 10^6$ poises).

Summary

1. The electrical properties of polyvinyl chloride plastics depend on thermal history. Increased time and temperature of heating give increased d. c. conductance.

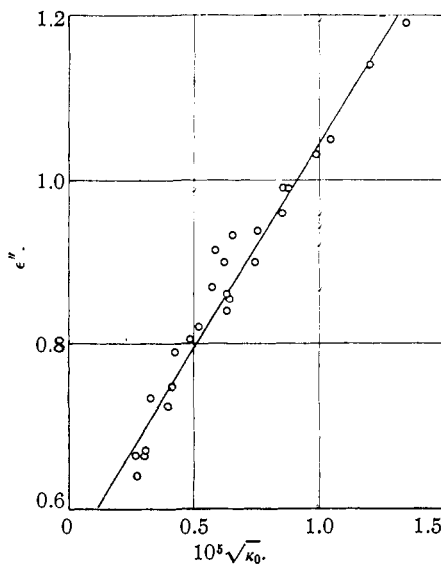


Fig. 7.—Dependence of 60 cycle loss factor on d. c. conductance.

2. The amount of pyrolysis can be followed by adding a soluble lead compound such as lead abietate to the plasticizer and determining the conductance for various heating times and temperatures.

3. The dielectric constant changes with time in a way which suggests a relaxation mechanism.

4. There is a one to one correlation between d. c. conductance, dielectric constant and loss factor.

SCHENECTADY, N. Y.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

Electrical Properties of Solids. V. Their Variation at 40° with Frequency and Composition in the System Polyvinyl Chloride-Tricresyl Phosphate

BY RAYMOND M. FUOSS

I. Introduction

Polyvinyl chloride as ordinarily obtained is an amorphous white powder, which can be converted under hydraulic pressure at 120° into a transparent brittle solid. By the addition of various liquids, such as tricresyl phosphate, it can be softened or "plasticized," to give solids ranging from glass-like to jelly-like substances, going through a tough rubber-like form at about 35–45% plasticizer. Dilute solutions of the polymer in plasticizers are very viscous liquids. The two-phase system polymer-plasticizer thus permits a

study of electrical properties over an enormous range of macroscopic viscosity. By varying the chemical nature of the two components, or by adding a third, a wide range of conductance and dielectric constant can then be investigated.

In previous papers in this series, experimental methods¹ for obtaining electrical data of reasonable precision on solids have been described, and a preliminary account of some of the properties of the system polyvinyl chloride-tricresyl phosphate

(1) (a) FUOSS, THIS JOURNAL, **59**, 1703 (1937); (b) **60**, 451 (1938); (c) **60**, 456 (1938); (d) **61**, 2329 (1939).