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

Electrical Properties of Solids. II. Preliminary Report on the System Polyvinyl Chloride–Tricresyl Phosphate[1]

BY RAYMOND M. FUOSS

I. Introduction

In the first paper of this series,[2] the magnitude of errors produced by imperfect contact in the measurement of electrical properties of solids was discussed; there it was emphasized that unless surface effects are eliminated, bridge measurements can only give fictitious results. The general methods described in the above paper will now be applied to plastic solids.

The plastic solid presents a rather interesting transition state of matter; mechanically, it appears to possess both the properties of solids (elasticity) and of liquids (viscosity). Electrically, it likewise shows some similarities to both, but also some marked differences from these two states of matter. In this paper will be presented the results of a preliminary investigation of a typical plastic solid composed of polyvinyl chloride and tricresyl phosphate.

II. Apparatus and Materials.—The electrical equipment described in the first paper was modified to permit measurements of materials for which tan δ is greater than unity. The Schering bridge functions best when the current through the unknown is primarily capacitative; when the resistance of the unknown drops (for example, with increasing temperature) to such a value that half or more of the current is in-phase current, the Schering balance becomes very tedious, because it is a sliding balance. In order to measure samples of fairly low resistance, the circuit was changed accordingly to permit rapid conversion of the Schering bridge to a resistance bridge. The two bridge arms R_3 and R_4-C_4 as well as the amplifier were left unchanged. (The maximum value of C_4 is 1000 $m\mu f$; a misprint in the first paper gave it as 1000 $\mu\mu f$.) By means of several switches, the unknown and R_4-C_4 were put in series with the bridge voltage, and the standard condenser S was replaced by a special 100,000 ohm resistance, which, in series with R_3 across the bridge voltage, completed the net work. The amplifier connection was of course, between the point where the unknown was connected to R_4-C_4 on the one side and the point where R_1 joined R_3 on the other. At the same time the high potential and guard electrode terminals were shunted with another 100,000 ohms, which permitted guard balance by means of the former F-resistance, without the necessity of introducing capacity in the guard balance arm. The standard 10^6 ohm resistor was made up of one hundred and twenty manganin wound units connected in series and mounted on an insulated rack 120 cm. long and 80 cm. in diameter. This arrangement permitted adequate dissipation of heat, so that the nominal resistance was unchanged even at 10^4 volts across the bridge (1 kw. load, distributed as 83.3 watts per unit resistor). The coils were wound and mounted to minimize inductance and capacitance; the assembly had a residual equivalent parallel capacitance of 19 $\mu\mu f$, as determined at 60–500 cps. by using "known unknowns."

The a. c. equipment was supplemented by the d. c. bridge shown in Fig. 1. The circuit is similar to that used in the type 544 Megohm Meter, manufactured by the General Radio Company. The high potential electrode of the cell was connected at H, the guard and test electrodes at G and T. The high resistance ratio arms (0.01–1 megohm Shallcross wire-wound resistors) were mounted on a polystyrene panel, along with the selector switches, in order to eliminate surface leakage in the bridge. R_4 was a General Radio 10^4 ohm decade box (steps of 0.1 Ω), so that 10^{12} Ω could be determined to 10%, with precision increasing with decreasing unknown resistance. The bridge midpoints fed a 6J7 d. c. amplifier circuit as shown. Balance was indicated by zero deflection on the microammeter G when the battery switch S was closed.

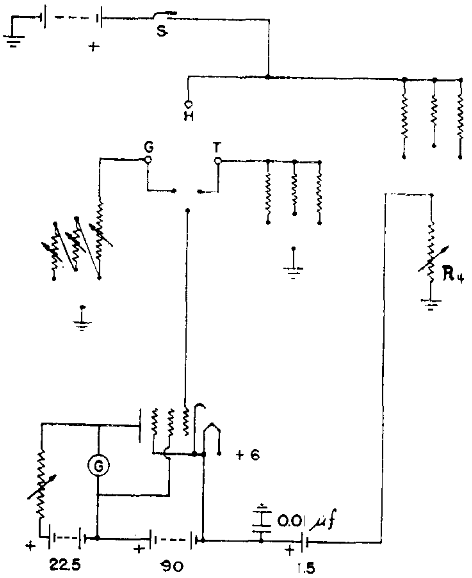

Fig. 1.—D. c. bridge and amplifier.

The cells described in the previous paper were replaced by cells having a wider test-guard spacing in order to permit easier centering of the samples, which had, as will be seen later, the effective electrodes pressed into perfect contact on their surfaces. Also the guard electrode was constructed so that it covered the back of the test elec-

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[1] An abstract of this paper was presented at the Symposium on Insulation at the Rochester meeting of the American Chemical Society, September 9, 1937.

[2] Fuoss, THIS JOURNAL, **59**, 1703 (1937).

trode, thus reducing the (small) stray capacitance previously observed.

The material studied was a plastic made up of 40 parts tricresyl phosphate and 60 parts polyvinyl chloride by weight.

The tricresyl phosphate was the isomer mixture commercially available as "Lindol A" (middle 80% boiling at 270–275° at 10 mm.). It was dried by treatment with fuller's earth which had been heated to 150° for several hours. Its density is given by the formula

$$1/d = 0.8447\ (1 + 0.000859t)$$

and its index of refraction is given by

$$n_D = 1.5649 - 0.0003878t$$

The specific conductance of the dried compound was 10^{-12}; the conductance increased rapidly on exposure to moist air, and approached 10^{-10}, the order of magnitude of the conductance of the crude material.[3]

The polyvinyl chloride (PVCl) was a commercial product. It is at present difficult to characterize the substance, because different lots vary in polymer distribution. The viscosity in nitrobenzene solution was determined[4] in an Ostwald pipet having a flow time of 50 sec. at 20° for nitrobenzene. In Table I are given values of the specific viscosity, $[(t_1/t_2) - 1]$, where t_1 and t_2 are, respectively, the flow times of the solution and of nitrobenzene.

TABLE I

VISCOSITIES OF NITROBENZENE SOLUTIONS OF POLYVINYL CHLORIDE

	Specific Viscosity		
g./kg.	20°	25°	30°
1.0	0.104	0.099	0.100
2.5	.287	.277	.272
4.0	.538	.531	.526

III. Bridge Equations.—Assuming surface effects eliminated by suitable surface contacts (the criterion is, of course, that the volume electrical properties calculated from bridge balance be independent of the thickness of the sample) and assuming edge effects eliminated by a guard ring, the following equations apply to the resistance bridge

$$\epsilon' = \frac{R_3C_4}{R_1C_v}\left(1 + \frac{1.9}{C_4R_4}\right) \qquad (1)$$

$$\kappa = \frac{0.08842 \times 10^{-12}}{C_v}\ \frac{R_3}{R_4R_1}\ (1 - 1.9 \times 10^{-12}\omega^2C_4R_4) \qquad (2)$$

where ϵ' is the dielectric constant, C_v is the equivalent vacuum capacity of the sample, κ is the *total* specific conductance, and ω is $2\ \pi$ times the frequency. The terms in parentheses correct for the 19 $\mu\mu$f in R_1; in these terms, the exponent of ten is chosen so that C_4 is substituted numerically in μf. (The numerical constant in Eq. 2 is $1/4\pi \times 9 \times 10^{11}$).

As a result of the work described below, and also in line with the suggestion of other writers[5] it is convenient to separate the conductance into two terms as follows

$$\kappa = \kappa_0 + 0.08842 \times 10^{-12}\omega\epsilon'' \qquad (3)$$

where ϵ'' is the loss factor due to pure a.c. response and κ_0 is the d.c. conductance. It is obvious that κ reduces to κ_0 at zero frequency in a way determined by the dependence of ϵ'' on frequency. *It should be pointed out that* (3) *above replaces* (9) *of the first paper of this series.* We now represent the unknown as a pure resistance $(1/\kappa_0)$ parallel to a condenser in which ϵ'' measures the a.c. loss and assume that no d.c. (except transients) will flow through this hypothetical condenser. The above separation of a.c. and d.c. mechanisms is essential to a clear understanding of the phenomena studied; if a total loss factor ϵ''_t be defined in terms of the total conductance, as follows

$$\epsilon''_t = \kappa/0.08842 \times 10^{-12}\omega \qquad (4)$$

a quantity is obtained which approaches infinity as frequency approaches zero, which is a trivial mathematical consequence of (3) when κ_0 is not zero.

IV. Experimental Methods.—Samples for electrical measurement were prepared as follows: the tricresyl phosphate (40%) and polyvinyl chloride (60%) were mixed thoroughly at room temperature, and then the mixture was passed 10–15 times through a rubber mill at 100–110°. The milling gives a uniform transparent sheet of plasticized polyvinyl chloride. The mill sheet was then pressed (2500 lb./sq. in.) in a disk mold for various times and temperatures to give disks 4 in. (10.16 cm.) in diameter and thicknesses ranging from 50 to 250 mils. The mold had a connection to the vacuum line, so placed that the plunger closed it when the full hydraulic pressure was on; by this means, air bubbles in the samples were avoided. A thermocouple placed in the side of the mold was connected to a recording potentiometer, so that a complete record of the thermal history of each sample could be made. The conductance of the material is quite sensitive to the thermal history; results of a study of the pyrolysis of polyvinyl chloride will be presented in a later paper.

In the early work, it was found that the observed conductance and dielectric constant de-

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(3) The purification and the determination of the physical constants of the tricresyl phosphate were done by Dr. V. Deitz of this Laboratory, to whom grateful acknowledgment is made.

(4) These data were very kindly determined for us by a coöperating laboratory.

(5) H. H. Race, *Phys. Rev.*, **37**, 430 (1931).

pended on the thickness of the sample. Furthermore, results on a given sample were erratic, and variations as large as 10% appeared on simply removing the sample from the cell and replacing it. Imperfect contact was suspected as the source of the difficulties, and a systematic investigation was made, using many different samples, varying in thickness, composition and thermal history. Measurements were made at temperatures from 30 to 120° at frequencies from 15 to 500 cycles. In order to save space, these data will not be given; the result of the investigation was convincing evidence for the presence of an air film of average thickness of the order of 0.005 mm. The data could be duplicated by equations (24), (25) and (26) of the previous paper, using a constant value of C_a, the series film capacity, for different frequencies for a given sample at a given temperature. There was some variation of C_a from sample to sample, but it remained unchanged in order of magnitude. With increasing temperature, C_a increased, corresponding to a better contact as the sample became less rigid. The independence of C_a on frequency is proof that the primary cause for the apparent variation of electrical properties with thickness was due to imperfect contact; other surface effects, such as polarization or surface resistance, would have given results incompatible with the test equations.

A number of attempts were made to produce a contact which would give volume properties independent of the thickness of the sample measured: these included hot-pressing sheet metal or heavy metal electrodes into the plastic; hot pressing tin, aluminum and lead foil electrodes onto the sample; rubbing foil electrodes onto the pressed sample; and applying gold leaf, metallic paints, aqua-dag, oil-dag or dry graphite. None of these methods was entirely successful: the colloidal graphite suspensions gave the best results, but bending the sample cracked the films. For samples 5 mm. or more thick, the air film error was negligible for the higher frequencies, but for less than 1000 cycles, some surface treatment was necessary. The best method found so far for making contact is as follows: a separate lot of plastic was made up in the proportions 30 g. of carbon black, 30 g. of polyvinyl chloride and 40 g. of tricresyl phosphate. After mixing and milling, it was calendered out to sheets about 5 mils thick. Disks of this carbon-loaded plastic, which had at room temperature a specific conductance of about 10^{-4} mho/cm., were hot-pressed onto the two sides of the test disk, and then a ring 40 mils wide was cut through one C-film by means of a special compass cutter in order to give a test area and a guard area. The electrodes were thus part of the sample; while the resistance of the C-film is high compared to that of metals, it is still very low compared to that of the unknown. Samples prepared in this way gave volume properties which were independent of thickness, the latter varying from 50 to 250 mils. This procedure is recommended for low frequency work on plastic materials; for high frequencies, the series resistance of the C-films becomes a source of error, and then the metallic foil electrode or pressure contact is preferable. It is, of course, obvious that the cell constant is determined by the diameter of the ring cut in the C-film and the thickness of the sample, rather than by the diameter of the (smaller) metallic electrode in contact with it, which leads to the bridge.

V. Conductance and Dielectric Constant as Functions of Frequency and Temperature.—A number of samples have been studied but lack of space prevents a detailed presentation of all the data available. Instead, data for a single representative sample will be tabulated and discussed. The sample (No. 250) contained 40% tricresyl phosphate and 60% polyvinyl chloride by weight (density at room temperature, 1.30). It received two ten-minute pressings at 150°, the first to form the sample into a disk 10.16 cm. in diameter and 5.94 mm. thick, and the second to apply the C-film electrodes.

The results are given in the following tables, where ω is 2π times the frequency f, ϵ' is the dielectric constant and κ is the total specific conductance. In Table II are given the data for 30°, where a comparison of measurements on the Schering and the resistance bridges was possible.

The results given in Table II are shown in Figs. 2, 3 and 4. It will be noted that the agreement between Schering and resistance bridge measurements is satisfactory. Many other comparisons have been made, and in all cases agreement was found within the sensitivity of the bridge balance. It might be mentioned that the sensitivity of the Schering bridge decreases rapidly when $\tan \delta$ exceeds unity, while that of the resistance bridge decreases for $\tan \delta$ less than unity.

Three important empirical facts are contained in the data of Table II: (1) the κ–ω curve is

TABLE II

CONDUCTANCE AND DIELECTRIC CONSTANT, t = 30°

ω	κ	ϵ'
	Schering Bridge	
131.4	1.450×10^{-10}	11.20
167.7	1.492	11.00
206.6	1.571	10.69
276.6	1.675	10.34
377.0	1.806	9.99
476.2	1.985	9.66
	Resistance Bridge	
79.6	1.337	11.87
133.2	1.427	11.25
166.8	1.482	10.96
203.1	1.542	10.70
269.7	1.648	10.33
371.6	1.797	9.95
377.0	1.810	9.94
448.5	1.910	9.72
1067	2.759	8.78
1384	3.162	8.52
1872	3.862	8.19
2356	4.415	8.00
2910	5.115	7.80

κ(D. C.) = 1.225×10^{-10}

linear; (2) the a.c. conductance extrapolates to the d.c. conductance on a κ–ω plot and (3) the dielectric constant decreases slowly with increasing frequency, satisfying the following *interpolation* formula

$$\epsilon' = \alpha - \beta \log \omega \qquad (1)$$

over the frequency range investigated. These facts permit a compact presentation of the remaining data for this sample which is given in Table III.

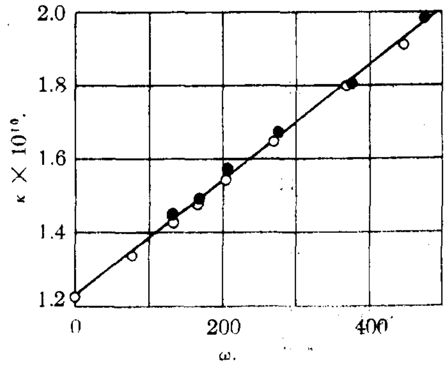

Fig. 2.—Conductance–frequency curve at 30°: open circles, resistance bridge; solid circles, Schering bridge.

TABLE III

t, °C.	$\kappa_0 \times 10^9$	ϵ''	α	β
30	0.123	1.73	17.3	2.83
40	0.556	1.68	18.0	2.44
50	2.01	1.52	17.3	1.80
60	5.82	1.20	15.7	1.12
70	14.25	0.80	14.9	0.90

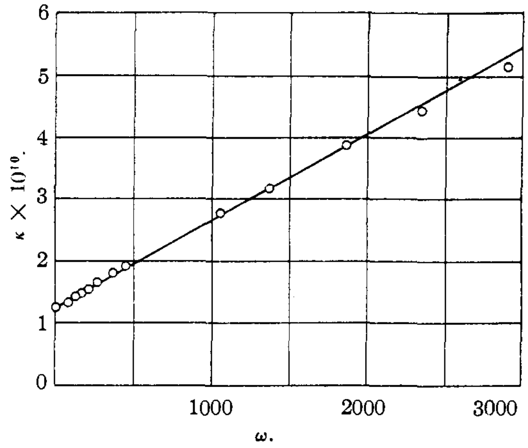

Fig. 3.—Conductance–frequency curve at 30°.

The d. c. conductance κ_0 is identical, within the experimental error, with the a. c. conductance extrapolated linearly to zero frequency. It behaves like an electrolytic conductance, and is due to the residual conductance of the plasticizer plus that due to the hydrogen chloride produced by pyrolysis of the polyvinyl chloride during the preparation of the sample. Other factors also may contribute to κ_0; this question is still under investigation. If log κ_0 is plotted against $1/T$, a straight line is obtained, from which a "heat of activation" of 24.6 kcal. is obtained.

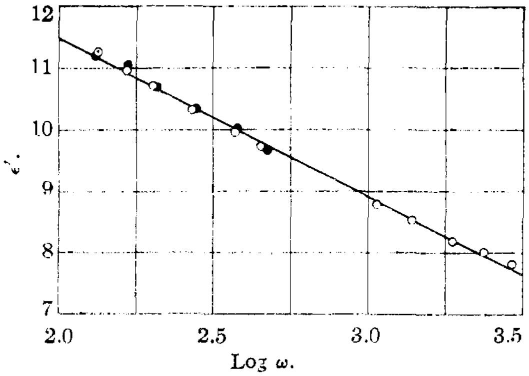

Fig. 4.—Dependence of dielectric constant on frequency at 30°.

Several runs were made at higher frequencies on a parallel resistance bridge by Mr. S. I. Reynolds of this Laboratory. The results are given in Table IV.

Reference to equation (3) shows that ϵ'', the a. c. loss factor, is proportional to the slope on a κ–ω plot; consequently, if the κ–ω plot is linear,

TABLE IV

	t = 50°		t = 70°	
$f \times 10^{-3}$	ϵ'	κ	ϵ'	κ
0.5	12.0	2.7×10^{-9}	13.1	1.41×10^{-8}
1.0	11.1	3.1	12.4	1.46
2	10.7	3.4	11.7	1.52
4	...	...	11.1	1.67
6	9.7	6.95	...	...
10	8.9	7.66	10.4	2.10
100	7.1	78.7	8.83	8.15
500	...	...	7.62	41.3
600	5.6	362	...	...
1000	5.2	532	6.83	82.3
2000	4.8	900	...	...
3000	...	...	5.55	208

ϵ'' is a constant. Figures 2 and 3 show that this is true over the low frequency range; Fig. 5 is the corresponding curve for the 50 and 70° high frequency data. In the latter figure, log $(\kappa - \kappa_0)$ is plotted against log f; the logarithmic scale is necessary on account of the wide range of the variables. The circles are the observed points, and the solid line is drawn at 45° to the axis. If ϵ'' were a true constant, the log-log points would, of course, lie on this line. It will be seen that there is a slight deviation.

Furthermore, the fact that the low frequency curves extrapolate into the d. c. conductances shows that the approximate constancy of ϵ'' will persist to much lower frequencies than the present lower limit of our actual a.c. measurements (about 15 cycles).

The quantity ϵ'' is a measure of the energy absorption per cycle due to pure a. c. response, and for the case of polar liquids is a maximum at a definite frequency characterized by a time of relaxation[6] which can be expressed in terms of viscosity, temperature and molecular size. The suggestion has been made that solid dielectrics might have several components with different times of relaxation[7,8] so that the superposition of their absorption maxima would give a broader resultant absorption than corresponds to a single responsive component. Obviously the wider the maximum, the wider a distribution of relaxation times will be required. In the case of the polyvinyl chloride plastics, ϵ'' is practically constant at order of magnitude unity over a very wide range of frequencies, which might be interpreted to mean practically uniform distribution of oscillators with times of relaxation ranging at least from the order of seconds to microseconds.

One difficulty with this picture physically is the width of the distribution; it is, of course, possible that the molecular weight distribution of the polyvinyl chloride is very broad, and another factor which would further broaden the distribution of relaxation times is the possibility that the macro-molecules do not necessarily follow the field as units, but can oscillate in segments. The other difficulty is the low frequency behavior. For any mechanism based on dipole response, ϵ'' must vanish for zero frequency, which means that the κ–ω curves must approach κ_0, the electrolytic conductance, with zero slope. Experimentally, the curves were linear down to 15 cycles, with no evidence for curvature, and since the 15–500 cycle segment of the curve extrapolates to the d. c. conductance within the experimental error, the frequency at which ϵ'' could begin to tend to zero must be very small: so small that the corresponding time of relaxation becomes so large that physical interpretation in terms of dipole mechanisms again becomes doubtful.

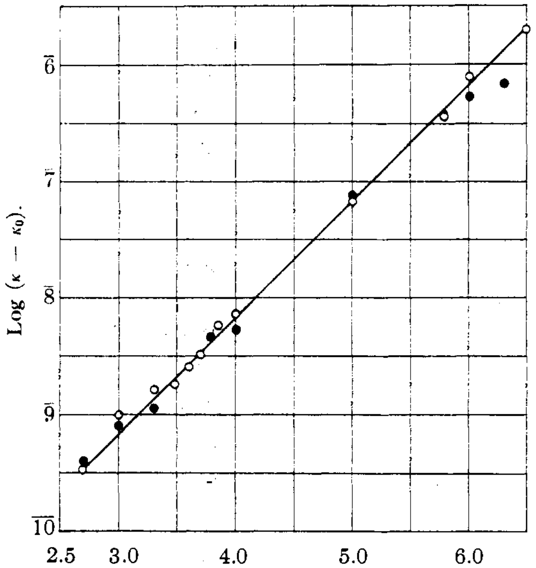

Fig. 5.—Conductance-frequency curve: open circles, 70°; solid circles, 50°.

Two other mechanisms have been suggested to account for a. c. absorption: Drude's quasi-elastically bound ions and the Maxwell-Wagner polyphase dielectric. The fact that there is no correlation between the electrolytic conductance and the a. c. loss factor seems to exclude the Drude mechanism. The Maxwell–Wagner mech-

(6) Debye, *Physik. Z.*, **36**, 100 (1935); **36**, 193 (1935); Debye and Ramm, *Ann. Physik*, **28**, 28 (1937).

(7) K. W. Wagner, *ibid.*, **40**, 817 (1913).

(8) W. A. Yager, *Physics*, **7**, 434 (1936).

anism requires that the plastic be at least two phase, and the observed width of the absorption region requires a wide distribution of conductance and dielectric constants for these phases. Again, the interpretation is possible but not convincing. It will be necessary to study a wider variety of systems before substantial progress can be made in the interpretation of the properties of plastic solids in terms of molecular parameters. At the present time, none of the proposed mechanisms appears to give a satisfactory explanation.

Summary

1. The conductance of polyvinyl chloride, plasticized with 40% tricresyl phosphate, is made up of two parts, an electrolytic conductance and a pure a. c. response which is practically independent of frequency over the range 15–3 × 10^6 cycles.

2. The electrolytic conductance varies exponentially with reciprocal temperature.

3. The a. c. loss factor changes only slowly with temperature.

4. The dielectric constant is approximately a linear function of the logarithm of the frequency over a fairly wide frequency range, and increases with increasing temperature above 60 cycles.

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Electrical Properties of Solids. III. Thermal Breakdown of Plasticized Polyvinyl Chloride

BY RAYMOND M. FUOSS

I. Introduction

Polyvinyl chloride, plasticized with tricresyl phosphate, passes current in phase with voltage by two mechanisms,[1] by electrolytic conductance (a d. c. mechanism) and by a. c. absorption. The former (frequency independent) component increases exponentially with temperature, while the latter, although increasing proportionally to the frequency, is not very sensitive to temperature. At low frequencies and high temperatures the a. c. contribution is negligible and the conductance of the plastic satisfies the very simple law

$$1/\kappa = \rho = re^{\beta/T} \qquad (1)$$

where κ is specific conductivity, ρ is specific resistance and r and β are constants.

If a slab of conducting material is subjected to a voltage gradient perpendicular to the surfaces and the surfaces are maintained at a fixed temperature, then the material will be heated by the current flowing. Since the surfaces are held at constant temperature, the center will be at a higher temperature due to the energy dissipated by the current, and if the conductance has a positive temperature coefficient, the net resistance of the sample will be less the higher the applied voltage. If the voltage is too high, it will be impossible to reach a steady state, and the resistance will tend toward zero, producing a steadily higher mid-plane temperature. Now polyvinyl chloride liberates hydrogen chloride by pyrolysis at elevated temperatures (150° and higher); if the temperature is sufficiently high, bubbles appear because the gas is produced faster than it can be absorbed or diffuse out. As a consequence of this property and of the simple form of the conductance–temperature relationship, the system polyvinyl chloride–tricresyl phosphate is especially suited for a study of thermal breakdown.

In this paper will be presented the results of a theoretical and experimental study of the thermal breakdown of polyvinyl chloride plasticized with tricresyl phosphate. It will be shown that the resistance decreases approximately as a linear function of the square of the applied voltage, with a theoretically predictable slope, and that the maximum voltage V_B at which a steady state is possible, *subject to the condition of constant surface temperature* T_0, is given by

$$V_B^2 = 8\alpha\rho_0T_0^2/\beta \qquad (2)$$

where α is the thermal conductivity, ρ_0 is the specific resistivity at T_0 and β measures the rate of change of ρ with T as given by (1).

II. Methods and Materials.—The samples studied were sheets 8 in. (20.32 cm.) square and 0.0625 to 0.5 in. (1.6 to 12.7 mm.) thick. The composition was 40 parts tricresyl phosphate and 60 parts polyvinyl chloride by weight; the sam-

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