

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 $15-3 \times 10^6$ 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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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

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

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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

$$1/\kappa = \rho = r e^{\beta/T} \quad (1)$$

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

$$V_B^2 = 8\alpha\rho_0 T_0^2/\beta \quad (2)$$

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-

(1) FUOSS, THIS JOURNAL, 60, 451 (1938).

ples were pressed for twenty minutes at 150°. To the sheets were applied circular C-film contacts as described in the preceding paper. (The sheets were made larger than the metallic electrodes in order to prevent arc-over or tracking across the edges.) The measurements were made by placing the samples between hollow electrodes² through which flowed a rapidly circulating stream of thermostated oil. Measurements of the conductance were first made at low voltage (20–200 volts, 60 cycles) and then at high voltages. After a steady state had been reached at the high voltage, the low voltage determination was repeated, to make sure that no permanent change had occurred, and then another higher voltage reading was made. This procedure was repeated until a voltage was reached which reduced the resistance to about 50% of the low voltage value.

III. Thermal Properties.—The *specific heat* of the material was determined by the method of mixtures: chips of the plastic from a Dewar were dropped into hot water in a second Dewar, and the change in temperature measured. (Data: initial temp. plastic 28.1°, wt. plastic 184 g.; wt. water, 500 g.; initial temp. water, 63.86°; final temp. water plus plastic, 59.10°.) The specific heat obtained was 0.417 cal./g.

The *thermal conductivity* α , was measured by putting a sample at room temperature between the electrodes at some higher temperature, and recording the time-temperature curve of the midpoint of the sample as determined by a thermocouple placed in the mid-plane. If T_i is the initial temperature, and T_0 is the surface temperature, it can easily be shown that the center temperature T at time t is given by

$$\frac{T_0 - T}{T_0 - T_i} = \frac{4}{\pi} \left(e^{-k^2 t} - \frac{1}{3} e^{-9k^2 t} + \frac{1}{5} e^{-25k^2 t} + \dots \right) \quad (3)$$

where

$$k = \pi^2 \alpha / d^2 \delta \sigma \quad (4)$$

In (4), d is the thickness of the sample, δ its density (here 1.30) and σ the specific heat. An analysis of the $T - t$ curves gives k and thence α . As the average of determinations made with several thicknesses at values of T_0 ranging from 50 to 100°, the heat conductance was found to be $1.42 \pm 0.07 \times 10^{-3}$ joules/cm. per degree gradient.

IV. Voltage Curves.—Measurements were made at 60 cycles on a number of samples of different thicknesses, at surface temperatures from 40 to 100°. In order to save space, detailed re-

sults for the thickest sample (1.24 cm.) only will be given. In Table I, ρ is the specific resistance at voltage V (root mean square).

TABLE I

$V \times 10^{-3}$	$\rho \times 10^{-3}$	$V \times 10^{-3}$	$\rho \times 10^{-3}$
$t = 40.7^\circ$		$t = 70.5^\circ$	
0.50	37.01	0.20	1.786
2.08	36.64	2.06	1.629
3.11	36.18	3.00	1.424
4.08	35.63	4.06	1.005
5.08	34.95	4.62	0.706
6.55	33.69	$t = 80.5^\circ$	
$t = 50.7^\circ$		0.20	0.795
		1.02	.757
0.10	14.91	1.85	.662
1.02	14.86	2.50	.548
2.04	14.65	3.03	.399
3.02	14.24	$t = 90.8^\circ$	
4.10	13.71	0.10	0.383
5.10	12.90	0.99	.347
6.12	12.06	1.53	.296
$t = 60.0^\circ$		2.07	.229
		2.50	.149
0.30	4.742	$t = 100.6^\circ$	
2.12	4.538	0.10	0.2068
3.02	4.325	1.02	.1716
4.03	3.911	1.52	.1232
5.17	3.319		

A typical voltage curve is shown in Fig. 1, where ρ is plotted against V^2 (1.24-cm. sample at

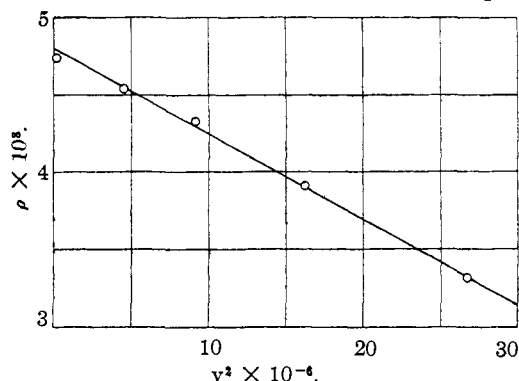


Fig. 1.—Resistance voltage curve at 60°.

60°). It will be seen that the curve is, within the experimental error, linear; extrapolation to zero resistance gives 9500 as the runaway voltage. As a matter of fact, the theoretical analysis, to be presented later, shows that the $\rho - V^2$ curves are approximately linear up to voltages where the resistance has dropped to about half its initial value; beyond this point, the curve becomes concave down, so that the limiting voltage appears at somewhat lower values than are obtained from the straight line extrapolation.

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

This extrapolated value

$$E = [\rho_0 / (\partial\rho / \partial V^2)_{V=0}]^{1/2} \quad (5)$$

furnishes, however, a convenient empirical number for comparing different samples. In Fig. 2,

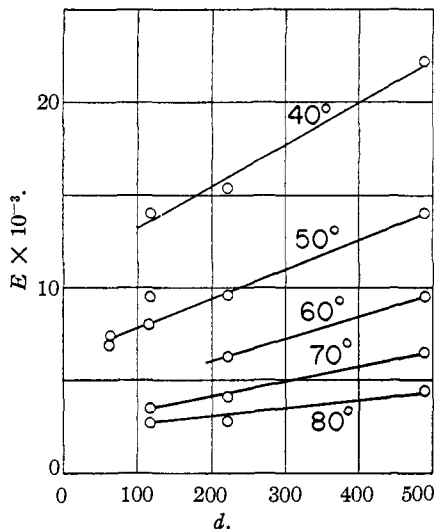


Fig. 2.—Extrapolated breakdown voltage as a function of thickness and temperature.

results on samples of different thicknesses and temperatures are compared, by plotting E against thickness in mils (one mil = 0.00254 cm.). It will be noted that E increases by about 50% for a ten to one change of thickness at all temperatures; in other words, the resistance decreases faster with increasing voltage for the thinner samples. This difference has two causes: first, the copper electrodes have a finite thickness and therefore the surface in contact with the sample is at a higher temperature than the oil temperature T_0 , and, second, the thin air film between the C-film electrodes and the copper electrodes decreases heat conduction across the interface. Both of these effects tend to increase the average temperature (decrease the resistance) of the sample, and relatively more, the thinner the sample. If (thermal) surface effects were completely eliminated, the value of $(\partial\rho / \partial V^2)_{V=0}$ would be independent of thickness, because the fundamental phenomenon is a pure volume effect.

V. Theory.—If we measure distances x from the center of the sample, the temperature (T) and potential (φ) distribution for a steady state are given by the solution of the differential equations

$$\frac{\partial}{\partial x} \left(\alpha \frac{\partial T}{\partial x} \right) + \kappa(x) \left(\frac{\partial \varphi}{\partial x} \right)^2 = 0 \quad (6)$$

$$\frac{\partial}{\partial x} \left(\kappa \frac{\partial \varphi}{\partial x} \right) = 0 \quad (7)$$

subject to the boundary conditions

$$T = T_0 \text{ at } x = \pm d/2 \quad (8)$$

$$\varphi = \pm V/2 \text{ at } x = \pm d/2 \quad (9)$$

These equations have been treated by Fock³ who calculated the runaway voltage (that corresponding to $\rho = 0$) for several types of conductors.

The treatment given below differs somewhat from Fock's, because the boundary conditions are different and because we are interested not only in the maximum value of V for which (6) and (7) have solutions, but in the whole $\rho - V$ curve.

The solution is obtained most conveniently in parametric form in terms of the temperature T_m at the mid-plane. By integrating (6) and (7), subject to (8) and (9), we find

$$V^2 = 8\alpha r \beta [J(u_m) - J(u_0)] \quad (10)$$

where

$$u = T/\beta \quad (11)$$

and

$$-J(x) = x^2 e^{1/x} (1 + 2/x + 3/x^2 + \dots) \quad (12)$$

The approximation $\partial\alpha/\partial T = 0$ has been made. The measured specific resistance ρ is given by

$$\rho = \frac{1}{d} \int_{-\frac{d}{2}}^{+\frac{d}{2}} \rho(x) dx \quad (13)$$

$$= 2r \sqrt{J(u_m) - J(u_0)} / \int_{u_0}^{u_m} \frac{d\tau}{\sqrt{J(u_m) - J(\tau)}} \quad (14)$$

By assigning a value to u_0 , we can calculate u_m as a function of V by means of (10); then (14) gives ρ in terms of u_m , and by combining the results we obtain ρ as a function of V .

The runaway voltage V_B corresponds to $T_m = \infty$ and from (10), we obtain

$$V_B^2 = 8\alpha r_0 T_0^2 / \beta \quad (15)$$

on setting $u_m \gg u_0$ and neglecting higher terms in the asymptotic expansion (12).

VI. Comparison of Theory and Experiment.

—If we plot the logarithms of the specific resistance extrapolated to zero voltage on $\rho - V^2$ plots against $1/T$ (data, Table I), we obtain the straight line shown in Fig. 3, which gives the constants of (1) the values $r = 6.08 \times 10^{-6}$, $\beta = 1.068 \times 10^4$. If we set $\beta = Q/R$, we find $Q = 21.25$ kcal.

Having shown that the temperature dependence of the plastic satisfies (1), we may substitute the constants in (10) and (14) and calculate the $\rho - V^2$ curve. If we plot $\rho(V)/\rho(0)$ against $(V/V_B)^2$, it is possible to compare data over a fairly wide temperature range on the same plot. In Fig. 4, we have a comparison of calculated and observed

(3) V. Fock, *Arch. Elektrotech.*, **19**, 71 (1927).

values for the temperature range 40–70°, where the various circles represent data taken from Table I and the solid line is calculated from (10) and (14), using the constants derived from Fig. 3. Since

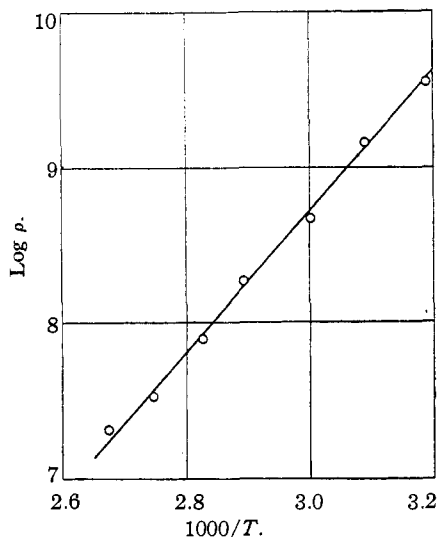


Fig. 3.—Dependence of resistance on temperature.

the agreement is satisfactory, we may conclude that the theory is correct and it may be used to extrapolate into regions where bridge measurements cannot safely be made; in other words, the agreement between theory and experiment shown in Fig. 4 gives us confidence in using (15) to predict runaway, voltage, given the necessary data ($\alpha, \rho_0, T_0, \beta$).

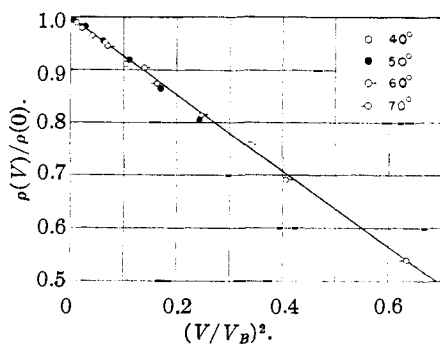


Fig. 4.—Comparison of theory and experiment: solid line, calculated; circles, observed.

The solution of the partial differential equations corresponding to (6) and (7) which contain time as the variable cannot be obtained except by an extremely laborious numerical integration. Some general conclusions, however, can be drawn regarding the resistance–time curves for a fixed voltage. For $V < V_B$, the resistance will drop

rapidly with time at first and approach a constant asymptote. For $V = V_B$, the resistance will become zero at infinite time, provided chemical decomposition does not occur. For $V > V_B$, the resistance–time curve will have an inflection point, beyond which the resistance will tend to zero very rapidly. An example of such a curve is shown in Fig. 5. A sample 1.27 cm. thick was placed in the cell at 70°. The specific resistance was 1.385×10^8 , which gives a value $V_B = 4.13 \text{ KV}$ from (15). A voltage about 12% greater was applied, and the time–resistance curve was followed. After twenty-seven and five-tenths minutes the resistance had dropped to 10% of the initial value and within another minute, thermal failure occurred; the temperature in the mid-plane exceeded the decomposition temperature of the plastic and rapid evolution of hydrogen chloride took

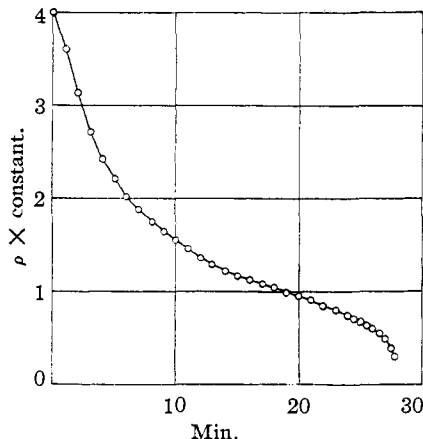


Fig. 5.—Resistance (in arbitrary units) as a function of time.

place. Figure 6 is a photograph of a section cut from the sample through the spot where failure happened. It will be noted that the process is a true volume effect, and the gas bubble appears where it should: symmetrical to the mid-plane. If thermal failure had not occurred, the resistance would have dropped practically to zero (“run-away”).

While the voltage at which thermal failure or runaway occurs is independent of thickness, the time to reach a steady state for $V < V_B$ or to fail for $V \geq V_B$ depends markedly on thickness. The exponent appearing in the solution of the differential equations involving time will be proportional to

$$kt = \alpha t / \sigma \delta d^2 \tag{16}$$

as can be seen by dimensions, so a thin sample will

reach equilibrium or failure much sooner than a thick one. This conclusion has been checked experimentally.

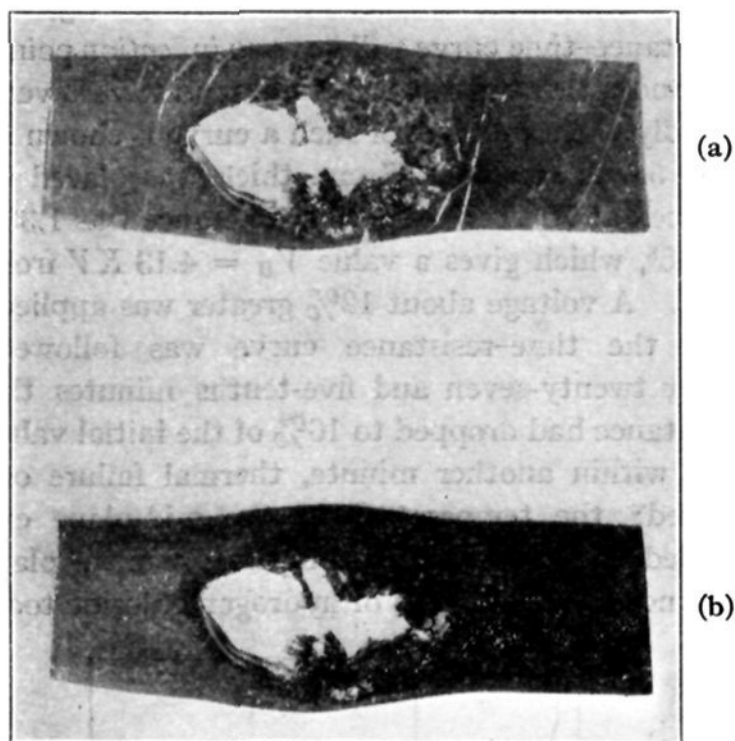


Fig. 6.—Cross section of sample: (a) photographed by reflected light; (b) by transmitted light.

Equation (15) has a very important application, in that it defines runaway voltage in terms of other physical properties of the material. It should be emphasized that (15) applies only to the case where the surfaces of the slab are held at T_0 ; if this condition is not met, failure can occur at lower voltages. (The result also depends on the form of the $\rho_0 - T$ curve.)

We can also use (15) to estimate the initial slopes of the $\rho - V^2$ curves. Since the theoretical $\rho - V^2$ curve is only slightly concave down, it may be approximated as a straight line running from

$\rho = \rho_0$ at $V = 0$ to $\rho = 0$ at $V^2 = V_B^2$, so the slope of the $\rho - V^2$ plots is approximately

$$\lambda = -\beta/8\alpha T_0^2 \approx d\rho/dV^2 \quad (17)$$

which is independent of ρ_0 . This means that the rate of change of resistance with voltage is determined by the thermal conductivity, the temperature and the temperature coefficient by resistance.

Equation (10) also has an obvious application. Most substances become thermally unstable before the mathematical $T_m = \infty$ is reached. We may use (10) to calculate T_m for a given voltage and compare this temperature with the decomposition temperature determined by pyrolysis experiments. For polyvinyl chloride, this temperature is fairly high, so that the $\rho - t$ curve could be followed nearly to electrical runaway, but for other substances, thermal decomposition might occur at voltages less than V_B if the corresponding T_m exceeded the decomposition temperature.

Summary

1. Experimental data on the dependence of conductance on voltage for polyvinyl chloride-tricresyl phosphate are presented.
2. The results are interpreted in terms of a simple theoretical analysis.
3. For a slab of material whose surfaces are kept at a fixed temperature, the maximum voltage at which a steady state is possible is determined explicitly by the specific resistance, and its temperature coefficient, the thermal conductivity and the surface temperature. Electrical failure will occur at voltages exceeding this critical value, and thermal failure may occur at lower voltages.

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