

R. E. McCurry
R. M. Schaffert

Space-Charge-Limited Currents in Resin Films

Knowledge of the electrical characteristics of thin resin films is important in such applications as protecting photoconductive surfaces. Since these resins are essentially insulators, the charge-decay technique offers a simple method of determining their current-voltage characteristics. The rate of decay of the surface charge on an insulating film, coated on a metal base, will depend upon the current through the film, since surface conduction is negligible.¹

Space-charge-limited currents in insulating solids have been considered by Mott and Gurney² and by Rose.³

Analysis of data obtained from experiments on resin films showed that, in most cases, currents through the resin films followed a square-law dependence on voltage.

The current density during discharge through the film is given by

$$J = -C \frac{dV}{dt}, \quad (1)$$

where C is the film capacitance in farads per cm², V is the voltage across the film in volts, and t is the time in seconds.

For a trap-free insulator, Rose has shown that the space-charge-limited current is given by

$$J = 10^{-13} \left(V^2 \mu \frac{k}{L^3} \right) \text{ amps per cm}^2, \quad (2)$$

where μ is the mobility in cm²/volt-sec, k is the dielectric constant, and L is the film thickness in cm.

Equating (1) and (2),

$$-C \frac{dV}{dt} = 10^{-13} \mu k \frac{V^2}{L^3}, \quad (3)$$

and since

$$C = 10^{-13} \frac{k}{L},$$

$$-\frac{dV}{V^2} = \frac{\mu}{L^2} dt. \quad (4)$$

Integrating,

$$\frac{1}{V} = \frac{\mu t}{L^2} + \frac{1}{V_0}, \quad (5)$$

or

$$\mu = \left(\frac{1}{V} - \frac{1}{V_0} \right) \frac{L^2}{t}. \quad (6)$$

If plots of $1/V$ vs t (Eq. 5) are linear, the current during charge decay follows the square law. Mobility of charge carriers through the film can be computed from Eq. 6.

For an insulator with shallow traps, Rose obtains the formula

$$J = 10^{-13} \left[V^2 (\mu_0 \theta) \frac{k}{L^3} \right], \quad (7)$$

where μ_0 is the drift mobility of free carriers, and θ = the fraction of free carriers in the total space-charge.

Equation 2 will be the same as Eq. 7 if μ is replaced with the quantity $\mu_0 \theta$, which may be regarded as the effective mobility with trapping.

Experimental results

The following resin samples⁴ were used in this study: (1) Cellulose acetate, FM-1; (2) Formvar (polyvinyl formal), Type S; (3) SR-53 and SR-82 (silicone resins); (4) Styron (polystyrene); and (5) Zytel 61 (alcohol-soluble polyamide).

Films, in the thickness range from 6 to 52 microns, were formed from resin solutions on aluminum substrates by a dipping technique. The films were then air dried. When thoroughly dry, film thickness and potential decay were measured.

A diagram of the charge decay apparatus is shown in Fig. 1. First, the films were charged by a screen-controlled corona discharge to a uniform surface potential in the range from 100 to 800 volts. Then the charged film was moved beneath the recording electrometer which provided a record of potential as a function of time (Fig. 2).

Figures 3, 4, and 5 are plots of data taken at 24 percent relative humidity and 78°F on the sample films. These curves show that, at low relative humidity, $1/V$ vs t is linear for these materials.

At high relative humidity, moisture absorption becomes important; consequently the various materials behave differently. Figure 6 shows that the major portion of the $1/V$ vs t curves is linear for polystyrene and silicone resin films at 68 percent relative humidity and 78°F. The 38-micron Formvar film, however, produced the nonlinear curves (1 and 2) of Fig. 7, whereas the 24-micron film curves (3 and 4) are linear. Figure 8 shows that Zytel 61 and cellulose acetate films give nonlinear curves at 45 percent relative humidity (at 68 percent relative humidity, the charge decay was too rapid to be detected with the apparatus).

Table 1 lists charge mobility, computed using Eq. 6, for positive and negative surface charge on the resin films at 24 percent and 68 percent relative humidity. Charge mobility in the polystyrene film increases by approximately a factor of 2; in the silicone resin films, by one order of magnitude; and in the Formvar films, by as much as 3 orders of magnitude with a relative humidity change from 24 to 68 percent.

The conductivity, σ , can be computed from charge mobility, dielectric constant, and thickness. From Ohm's law,

$$\sigma = J \frac{L}{V} \quad (8)$$

Combining Eq. 8 and Eq. 2,

$$\sigma \approx 10^{-13} k \mu \frac{V}{L^2} \quad (9)$$

Conductivity can also be computed directly from the charge-decay data, using the equation,

$$\sigma \approx k \left(\frac{\Delta \ln V}{\Delta t} \right) 10^{-13} \quad (10)$$

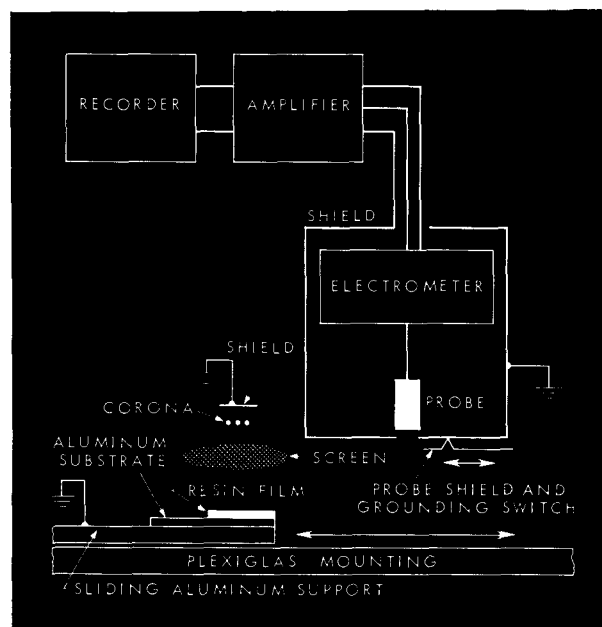
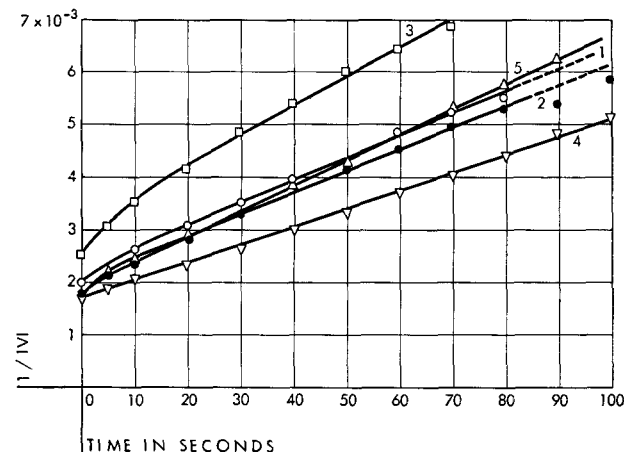
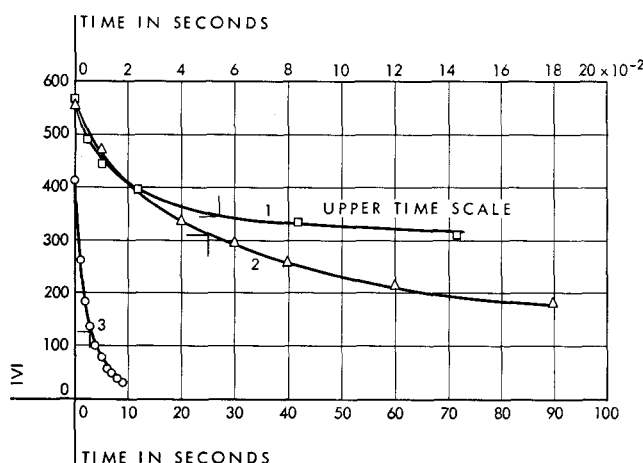


Figure 1 Charge decay apparatus.

Figure 2 Typical charge decay curves for resin films. (Temperature, 78°F. Relative humidity: Curves 1 and 3, 68%; Curve 2, 24%.)

Curve	Resin	Surface Charge	Film Thickness (microns)
1	SR-53	Negative	7×10^{-4}
2	Cellulose Acetate	Positive	6×10^{-4}
3	Formvar	Positive	38×10^{-4}

Figure 3 Reciprocal voltage vs time during charge decay of resin films. (Relative humidity, 24%.)

Curve	Resin	Surface Charge	Film Thickness (microns)
1	Cellulose Acetate	Positive	8
2	Cellulose Acetate	Positive	6
3	Cellulose Acetate	Negative	6
4	Zytel 61	Positive	12
5	Zytel 61	Negative	12

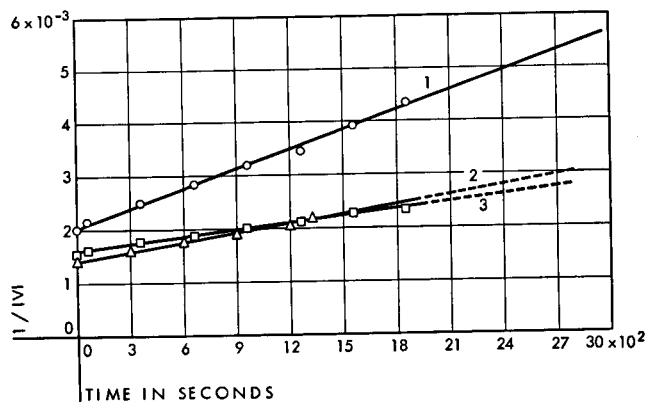


Figure 4 Reciprocal voltage vs time during charge decay of Formvar films. (Relative humidity, 24 %.)

Curve	Surface Charge	Film Thickness (microns)
1	Positive	38
2	Positive	24
3	Negative	24

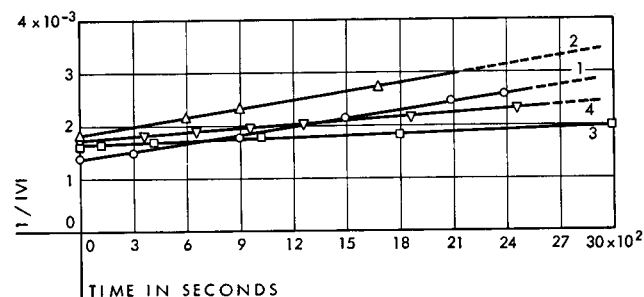


Figure 5 Reciprocal voltage vs time during charge decay of resin films. (Relative humidity, 24 %.)

Curve	Resin	Surface Charge	Film Thickness (microns)
1	Polystyrene	Positive	52
2	Polystyrene	Negative	52
3	SR-53	Positive	7
4	SR-82	Positive	16

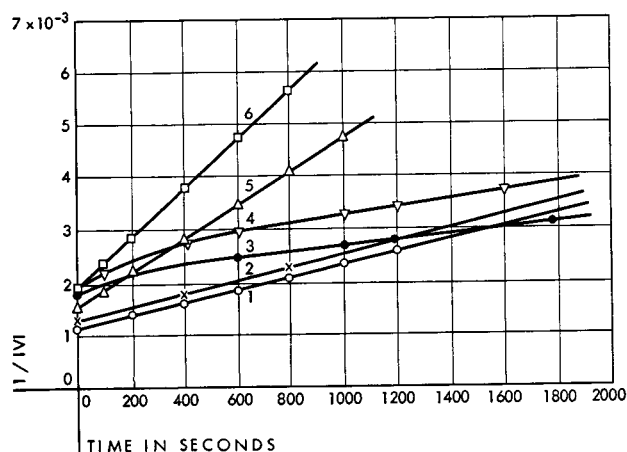


Figure 6 Reciprocal voltage vs time during charge decay of resin films. (Relative humidity, 68 %.)

Curve	Resin	Surface Charge	Film Thickness (microns)
1	Polystyrene	Positive	52
2	Polystyrene	Negative	52
3	SR-53	Positive	7
4	SR-53	Negative	7
5	SR-82	Positive	16
6	SR-82	Negative	16

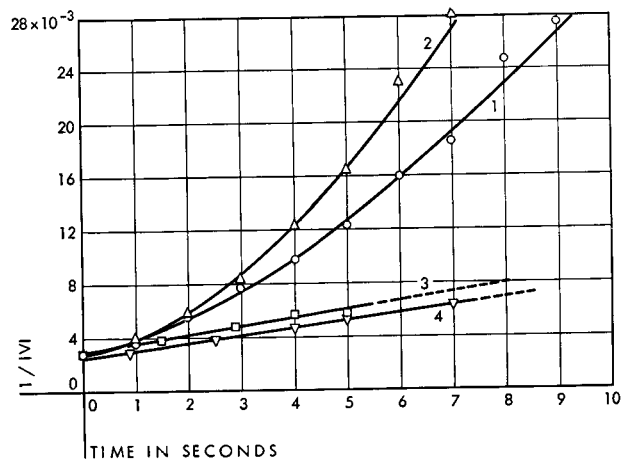


Figure 7 Reciprocal voltage vs time during charge decay of Formvar films. (Relative humidity, 68 %.)

Curve	Surface Charge	Film Thickness (microns)
1	Positive	38
2	Negative	38
3	Positive	24
4	Negative	24

Table 1 Charge mobility in resin films.

Resin	Thickness in cm	Charge mobility in cm ² /V-sec			
		24% Relative Humidity		68% Relative Humidity	
		Positive Surface Charge	Negative Surface Charge	Positive Surface Charge	Negative Surface Charge
Cell. acetate	6 × 10 ⁻⁴	1.2 × 10 ⁻¹¹	1.7 × 10 ⁻¹¹	—	—
Cell. acetate	8 × 10 ⁻⁴	2.7 × 10 ⁻¹¹	2.2 × 10 ⁻¹¹	—	—
Formvar	24 × 10 ⁻⁴	3.3 × 10 ⁻¹²	2.5 × 10 ⁻¹²	4.1 × 10 ⁻⁹	3.4 × 10 ⁻⁹
Formvar	38 × 10 ⁻⁴	1.8 × 10 ⁻¹¹	1.5 × 10 ⁻¹¹	—	—
Polystyrene	52 × 10 ⁻⁴	1.4 × 10 ⁻¹¹	1.5 × 10 ⁻¹¹	3.3 × 10 ⁻¹¹	3.3 × 10 ⁻¹¹
SR-53	7 × 10 ⁻⁴	5.6 × 10 ⁻¹⁴	4.7 × 10 ⁻¹⁴	2.9 × 10 ⁻¹³	4.0 × 10 ⁻¹³
SR-82	16 × 10 ⁻⁴	6.6 × 10 ⁻¹³	8.5 × 10 ⁻¹³	8.4 × 10 ⁻¹²	1.2 × 10 ⁻¹¹
Zytel 61	12 × 10 ⁻⁴	5.0 × 10 ⁻¹¹	7.0 × 10 ⁻¹¹	—	—

Table 2 Charge density and conductivity in resin films.

Resin	Thickness in cm	Dielectric Constant	Electric Field (V/cm)	Charge Carrier Density†	Conductivity in ohm ⁻¹ - cm ⁻¹			
					24% Relative Humidity		68% Relative Humidity	
					Positive Surface Charge	Negative Surface Charge	Positive Surface Charge	Negative Surface Charge
Cell. Acetate	6 × 10 ⁻⁴	5.2	5 × 10 ⁴ 1 × 10 ⁵	2.7 × 10 ¹⁴ 5.5 × 10 ¹⁴	5.0 × 10 ⁻¹⁶ 1.0 × 10 ⁻¹⁵	7.4 × 10 ⁻¹⁶ 1.5 × 10 ⁻¹⁵	—	—
Cell. Acetate	8 × 10 ⁻⁴	5.2	5 × 10 ⁴ 1 × 10 ⁵	2.0 × 10 ¹⁴ 4.1 × 10 ¹⁴	9.0 × 10 ⁻¹⁶ 1.8 × 10 ⁻¹⁵	7.2 × 10 ⁻¹⁶ 1.4 × 10 ⁻¹⁵	—	—
Formvar	24 × 10 ⁻⁴	3.4	5 × 10 ⁴ 1 × 10 ⁵	4.4 × 10 ¹³ 8.9 × 10 ¹³	2.4 × 10 ⁻¹⁷ 4.7 × 10 ⁻¹⁷	1.8 × 10 ⁻¹⁷ 3.5 × 10 ⁻¹⁷	2.9 × 10 ⁻¹⁴ 5.8 × 10 ⁻¹⁴	2.4 × 10 ⁻¹⁴ 4.8 × 10 ⁻¹⁴
Formvar	38 × 10 ⁻⁴	3.4	5 × 10 ⁴ 1 × 10 ⁵	2.8 × 10 ¹³ 5.6 × 10 ¹³	8.0 × 10 ⁻¹⁷ 1.6 × 10 ⁻¹⁶	6.5 × 10 ⁻¹⁷ 1.3 × 10 ⁻¹⁶	9.6 × 10 ⁻¹⁴ 1.7 × 10 ⁻¹³	1.3 × 10 ⁻¹³ 2.0 × 10 ⁻¹³
Polystyrene	52 × 10 ⁻⁴	2.5	5 × 10 ⁴ 1 × 10 ⁵	1.5 × 10 ¹³ 3.0 × 10 ¹³	3.4 × 10 ⁻¹⁷ 6.7 × 10 ⁻¹⁷	3.6 × 10 ⁻¹⁷ 7.2 × 10 ⁻¹⁷	8.0 × 10 ⁻¹⁷ 1.6 × 10 ⁻¹⁶	8.0 × 10 ⁻¹⁷ 1.6 × 10 ⁻¹⁶
SR-53	7 × 10 ⁻⁴	3.4	5 × 10 ⁴ 1 × 10 ⁵	1.5 × 10 ¹⁴ 3.1 × 10 ¹⁴	1.4 × 10 ⁻¹⁸ 2.7 × 10 ⁻¹⁸	1.1 × 10 ⁻¹⁸ 2.3 × 10 ⁻¹⁸	7.0 × 10 ⁻¹⁸ 1.4 × 10 ⁻¹⁷	1.0 × 10 ⁻¹⁷ 1.9 × 10 ⁻¹⁷
SR-82	16 × 10 ⁻⁴	3.4*	5 × 10 ⁴ 1 × 10 ⁵	6.6 × 10 ¹³ 1.3 × 10 ¹⁴	7.0 × 10 ⁻¹⁸ 1.4 × 10 ⁻¹⁷	9.0 × 10 ⁻¹⁸ 1.8 × 10 ⁻¹⁷	9.0 × 10 ⁻¹⁷ 1.8 × 10 ⁻¹⁶	1.3 × 10 ⁻¹⁶ 2.6 × 10 ⁻¹⁶
Zytel 61	12 × 10 ⁻⁴	3.7	5 × 10 ⁴ 1 × 10 ⁵	9.6 × 10 ¹³ 1.9 × 10 ¹⁴	7.7 × 10 ⁻¹⁶ 1.5 × 10 ⁻¹⁵	1.1 × 10 ⁻¹⁵ 2.2 × 10 ⁻¹⁵	—	—

*Dielectric constant of SR-82 film assumed to be the same as that of SR-53 films.

†Number of electronic charges per cm³.

The charge carrier density, N , is given by

$$N = \frac{\sigma}{\epsilon \mu}, \quad (11)$$

where ϵ is the electronic unit of charge (coulombs).

Combining Eq. 11 with Eq. 9,

$$N = 10^{-13} \frac{kV}{\epsilon L^2}. \quad (12)$$

Thus, for dielectric films in which the space-charge square law holds, the charge carrier density is a function only of dielectric constant, field strength and film thickness.

Equations 12 and 9 were used to compute the values for charge carrier density and conductivity for films where the space-charge square law was applicable. Where this law did not hold, Eq. 10 was used to compute conductivity. These data are listed in Table 2 for two different field strengths.

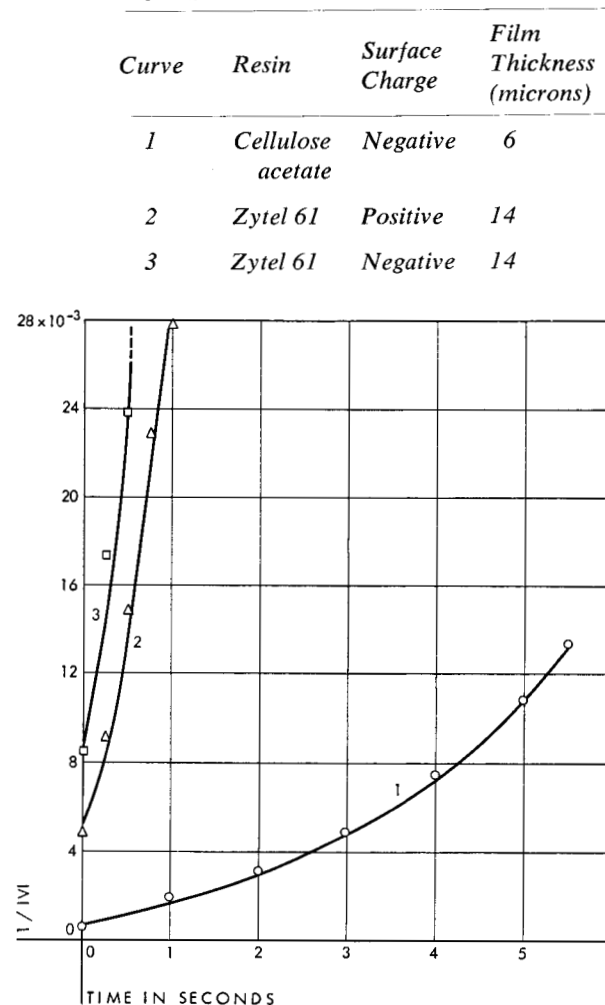
Discussion

The current during discharge through the resin films approaches equilibrium values only when the discharge is very slow, as in Figs. 3 through 5. If the discharge is rapid, the current is more in the nature of a transient discharge and never approaches an equilibrium condition. This may account for the nonlinear relationships in Figs. 7 and 8. Note also that some of the curves in Figs. 3 and 6 show an initial nonlinearity which, in accordance with the previous arguments, can be attributed to an initial rapid decay preceding space-charge build-up.

The two Formvar samples exhibit considerable difference in behavior at high relative humidity (Fig. 7). The thicker sample did not follow the space-charge square-law under these conditions. In general the computed values for conductivity and mobility are greater for the thicker films of both Formvar and cellulose acetate. This suggests a possibility that these properties are dependent on film thickness. However, the limited data obtained in these experiments do not warrant conclusions on this point.

The charge-decay data do not indicate whether the charge carriers are negative or positive or whether the conductivity is ionic or electronic. The extremely low values for mobility, in the light of the square-law space-charge relationship, indicates either electronic conduction with a high density of shallow traps or ionic conduction through a highly viscous medium. If the carriers are electronic charges, the increase in conductivity at high relative humidity might be explained as an increased rate of charge injection due to water adsorption at the surface of the film. However, this would not account for the increased mobility. The increase in mobility with relative humidity would seem to favor ionic conductivity on the theory that water absorbed in the films would provide easier paths for the free ions, whereas it is difficult to visualize increased electronic mobility as a result of water molecules in the film.

Figure 8 Reciprocal voltage vs time during charge decay of resin films. (Relative humidity, 45 %.)



The authors gratefully acknowledge the contributions of J. A. Underhill in the development of experimental procedures, and the assistance of E. R. York, in the preparation of resin films.

References and footnotes

1. The films covered a large area (about 15 in²) and were uniformly charged. The charge decay was measured over a small area (about 0.25 in²) near the center of the sample. The potential gradient through the film and normal to the surface is very large ($\sim 10^5$ V/cm.), whereas the gradient in the plane of the surface is small ($\sim 10^2$ V/cm.).
2. N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals*, Oxford University Press, 1946 ed., p. 172.
3. A. Rose, "Space-Charge-Limited Currents in Solids," *Phys. Rev.*, **97**, 1538 (1955).
4. The samples listed were manufactured by: (1) Hercules Powder Company; (2) Shawinigan Resins Corporation; (3) General Electric Company; (4) Dow Chemical Company; and (5) E. I. DuPont de Nemours & Company. (Formvar, Styron, and Zytel are trademarks of the manufacturer.)

Received January 12, 1960