A Possible Electrode Effect on the Measurement of the Conductivity of Two-Component Xerographic Developers

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Abstract

E. Gutman and G. Hartmann (G-H) have published a study on the electrical conductivity of two component developer materials. The carriers used in conductive developers typically have a metal core surrounded by an oxide layer that, in turn, may be partially covered by a polymer coating. G-H found that either a Schottky model or a Poole-Frenkel model could describe the current through the developer material in the nip of a magnetic brush. Both models have an exponential dependence on the applied electric field or voltage. For low voltages or electric fields, deviations from the exponential voltage dependence were observed as the developer conductivity decreased due to increasing toner concentration. The deviations were reminiscent of contact resistance effects observed with thin film I-V measurements. The analysis of the developer I-V data is consistent with a contact barrier between the electrodes and the developer sample.

Introduction

The electrical conductivity of two-component developers is an important parameter that affects the solid area, line and half-tone development efficiency and background development in xerography. Experiments with insulating developer materials show strong line edge development, associated with electrostatic fringe fields but poor "fill-in" of large uniform solid areas. In contrast, experiments with conductive developer materials show that the fringe field development is suppressed and solid area development is more uniform. These characteristics have been investigated in earlier work.[1-3] Hays[2] has considered the flow of charge through a conductive developer and the dependence on the electric field, magnetic field toner concentration, and developer agitation. Hoshino[4] has investigated the dependence of developer conductivity on the applied electric and magnetic fields. He pointed out that the current through the developer increases more rapidly than linearly with the applied electric field, and he suggested that the oxide layer on the surface of the metal carrier beads limits the current flow. Nash and Bickmore[5] have discussed the aging process for conductive developers. They found that both the carrier conductivity and the coefficient for the dependence of developer conductivity on toner concentration, α, change over time with developer usage. They identified carrier abrasion and toner impaction as the key underlying physical mechanisms for these changes.

This study continues an investigation of the electrical conductivity of two-component developer materials started by Gutman and Hartmann[6] (G-H). Both the previous work and this work use a measurement cell with a development roll that reproduces the electric, magnetic and geometric characteristics of the xerographic development zone. Developer conductivity depends on several externally controllable parameters, such as, the applied voltage, magnetic field, developer roll speed and toner concentration, as well as materials design parameters, such as toner and carrier size, composition and shape.

The geometry of the carrier beads and toner particles in the zone between the measurement electrode and the roller is complicated. The carrier beads typically have a metal core surrounded by an oxide layer, which in turn may be partially covered by an insulating polymer layer. The insulating toner particles break the electrical contacts between the carrier beads. When a voltage is applied between the roller and the measurement electrode, the voltage drop is across the oxide layers and toner particles, because the metallic cores act as electrical short circuits. The toner particles are much more insulating than the oxide layers, so the current will only flow through the metal cores and oxide layers, and the magnitude of the current will be controlled by the oxide layers. Consequently the system can be represented by a simplified geometry of two metal electrodes and an oxide film that simulates the cumulative effect of all the contacting oxide surfaces of the carrier beads.

Metal-oxide conduction can be described by a Schottky model if the conduction is limited by the metal-oxide interfacial barrier; or, by the Poole-Frenkel model if the conduction is limited by the bulk oxide. Both models lead to the same form of the field dependent current density.

The relation between the current through a bed of developer consisting of many carrier beads and a single oxide layer is a complex problem, which we will not address explicitly. The work of Gutman and Hartmann[6] showed that the current flowing through the developer has the following dependence on the applied electric voltage

$$I=G_0(C)V\exp(BV^{0.5}) \qquad (1)$$

where $G_0(C)$ is the ohmic conductance which depends on toner concentration, V is the applied voltage, and B is the Poole-Frenkel related parameter, $(e^3/\pi\varepsilon l)^{0.5}/2kT$. We interpret l as the effective thickness of the oxide layer that simulates the cumulative effect of all the oxide surfaces on the carrier beads. Because all the measurements were made at room temperature, kT has been incorporated into the parameter B.

Experimental

A miniature magnetic brush conductivity cell, illustrated in Figure 1, was used. The cell includes a magnetic brush roll, made with a 3.8 cm diameter by 9.5 cm long nonmagnetic steel cylinder with a surface roughness, approximately 13 µm roughness, which assists in transporting the developer material. The cylinder is rotated by a motor at a surface speed of 25 cm/sec. Inside the cylinder there is a stationary magnetic field assembly designed to give the magnetic field profile shown in Figure 1. This magnetic field profile approximates the magnetic field used in xerographic development. A trim bar with an adjustable gap is located at the 3 o'clock position, where the tangential magnetic field is strong. The trim bar gap and the cylinder-to-electrode spacing were set to 2.54 mm. The cell holds about 50 cc of carrier or developer material. The top of the cell is a segmented flat plate with a rectangular measurement electrode surrounded by a guard electrode. The rectangular electrode is 0.5 cm wide by 6 cm long. It is located in the constant radial magnetic field region of the development zone. The current was measured with a Kiethly 610C electrometer.

The I-V curves were measured by putting 50 cc of developer material into the cell and rotating the steel cylinder for three minutes to form a uniform magnetic brush in the development zone. After the three minute conditioning process, the measurements can be done while the cylinder continues to rotate, "dynamic mode" or with the cylinder stopped, "static mode". In this work the measurements were made in the static mode. The cylinder was stopped, the voltage applied and the current reading was made 15 sec later. To measure the I-V characteristic, this process was repeated for each voltage step. The voltage was increased until breakdown occurred or until 1000v.

The 11 µm toner used in this study consisted of 93% resin, 5% carbon black and 2% of an alkyl pyridinium salt. The 158 µm carrier had 0.2% polyvinylidene fluoride powder coated on oxidized core. Developers were prepared by mixing 3 pph toner with carrier. The toner concentration of the developer was changed by a three step "detoning" procedure. First, the developer was split into two portions. Second, the toner was removed from one portion. Finally, the carrier recovered from this portion was blended back into the other portion and mixed for a short time.

Results

The I-V data for different toner concentrations are shown in Figure 2. The lines in Figure 2 are the Poole-Frenkel function, Eq. 1, fit to the data with a single value of B and with G_0 dependent on toner concentration. The values for B and G_0 are listed in Table 1. G_0 was found to depend on toner concentration by $G_0(C) = G_0(0)\exp(-\alpha C)$ where C is the toner concentration (weight of toner/weight of carrier), $G_0(0)$ is the ohmic conductance when C equals 0, and α is a parameter that characterizes the semi-logarithmic slope[6]. The value of α is $(3.1\pm0.2)\times10^2$ with an index of determination of 0.98.

The data in Figure 2 can also be plotted as the log(G) versus $V^{0.5}$, where G=I/V, as shown in Figure 3. In this plot, data that are consistent with the Poole-Frenkel function should form a straight line. For the voltage range 9 to 81 volts, the data are very linear for all the developers. However, for developers with toner concentrations greater than 1.3% and for voltages less than 9v, the data deviate from a straight line.

Table 1. Values of G_0, B, ΔV for Data in Fig. 1

Toner Concentration (pph)	G_0 (ohm)$^{-1}$	B (volt)$^{-0.5}$	$\Delta V = V_{Contact}$ (volt)
0.16	5.69×10^{-7}	0.50	--
0.55	2.33×10^{-7}	0.50	--
1.30	5.01×10^{-8}	0.50	1.42 ± 0.27
1.55	1.48×10^{-8}	0.50	1.20 ± 0.18
1.97	3.07×10^{-9}	0.50	1.43 ± 0.20
2.32	9.54×10^{-10}	0.50	1.35 ± 0.34
2.77	1.62×10^{-10}	0.50	1.15 ± 0.21

Discussion

The data in Figure 1 have been reported by Gutman and Hartmann.[6] In that work they disregarded the small discrepancies between the data and the Poole-Frenkel fits for the low voltages less than 9v. We will now examine the source of that discrepancy. There are several potential explanations for the discrepancy. First, as noted earlier, the relationship between a single oxide layer and the collection of oxide layers on the beads in a developer is complex; the Poole-Frenkel function derived for a single oxide film may not apply to the collection of layers on the carrier beads. However, G-H have found good agreement in the range 9 to 81v and four orders of magnitude of current. In addition, they found the Poole-Frenkel function fit the data for many other materials. We will continue to assume the Poole-Frenkel function is a good descriptor of the data.

A second potential cause of the discrepancy is a measurement problem with the small currents for voltages less than 9v. We note, however, that developers with higher toner concentration, lower conductivity, have comparable currents at higher applied voltages. These currents do fit the Poole-Frenkel function. Therefore there does not seem to be a problem measuring the current.

A third potential source of the discrepancy is the voltage across the developer sample is not equal to the applied voltage for the low conductivity developers. The ideal geometry that G-H assumed was a single oxide layer between electrodes. The ideal geometry also assumes the contacts are "ohmic," i.e., the electrode work function is less than the insulating oxide layer work function so that the electrode can readily supply electrons to the sample. In this case there is no voltage drop across the electrode-oxide layer contact. The importance of "ohmic" contacts is well known in thin film physics[7]. If the contact is not ohmic then there may be a voltage drop across the electrode-sample contact. Consequently, the voltage across the sample is less than, and not equal to, the applied voltage.

The equivalent circuit for the non-ideal G-H geometry is a voltage source connected across a series resistor combination consisting of the contact resistor and the sample resistor. The resistance of the contact resistor is determined by the Schottky model; the resistance of the sample resistor is determined by the Poole-Frenkel model.

From this equivalent circuit, the same current flows through both the contact and the sample. Hence, the voltage across the sample is the voltage required by the Poole-Frenkel function for that current. Given the current, the sample voltage can be obtained from the Poole-Frenkel function using the common value of B and the specific $G_0(C)$ for a particular developer obtained from the parametric fit to the data. The difference between the applied voltage and the calculated sample voltage is the voltage drop across the contact resistor, ΔV. A plot of current versus ΔV shows an initial increase in current to a constant ΔV, followed by about an order of magnitude increase in current at constant ΔV and then a decrease in the contact voltage at higher currents. This is illustrated in Figure 4 for the lower conductivity developers with toner concentrations greater than 1.3%. In this Figure, the current values have been normalized by the current measured at 1v. Table 1 lists the toner concentration and the average of the ΔV values for approximately a 10x increase in current for each developer. The average value ± one standard deviation of ΔV for all the developers with $C>1.3\%$ is also shown in Figure 4; the values are 1.32v±0.25v respectively.

We now offer a physical interpretation of the equivalent circuit and the data. The source of the contact resistor in the equivalent circuit is the barrier height at the contact between electrode and oxide layer. (Which, in this case, is not just the model oxide film but the actual oxide layers on the carrier beads contacting the electrodes.) At low voltages the conduction process is limited by the thermal excitation of electrons over the electrode-oxide barrier. This process is the Schottky model. Simmons[7] describes two processes that may occur as the voltage is increased. If the width of the barrier is thin enough, field emission of electrons from the cathode into the conduction band of the oxide layer can occur. If the bias voltage exceeds $3E_g/2$, E_g is the ionization potential of the atoms in the oxide, impact ionization can occur in the depletion region of the oxide layer. Both of these processes are characterized by a rapid increase in current. We believe this is the source for the order of magnitude increase in current at constant ΔV. Hence, the contact resistance is decreasing much more rapidly than the bulk resistance of the sample. Thus, the applied voltage is initially across the electrode-oxide contact. Then, as the contact resistance decreases, the applied voltage is split between the contact resistance and the sample resistance until finally the applied voltage is almost entirely across the sample. There is a transition from electrode limited conduction, Schottky model, to bulk limited conduction, Poole-Frenkel model. As the sample voltage approaches the applied voltage, ΔV approaches zero.

There are several possible reasons for the fact the highest conductivity developers only show the Poole-Frenkel conductivity. The first reason is the electrode condition was different and did not have a high barrier height when these developers were measured. The second possibility is the current density at the electrode-oxide layer contact was large enough, due to the higher bulk conductivity, that either field emission or impact ionization masked the Schottky effect and we only observed the Poole-Frenkel effect. While we cannot rule out the former, we suspect the latter is the correct explanation. We note that the current in the high conductivity developers exceeds the current at the transition to the Poole-Frenkel effect ($\sim 10^{-6}$ amp) in the 1.3% developer, which has the third highest conductivity.

Summary

In conclusion, we have presented I-V data for xerographic developers that are consistent with the Poole-Frenkel function in the voltage range of 9 to 81v. The data for the lower conductivity developers deviate from this function for voltages less than 9v. We proposed that this is due to a non-ohmic contact between the electrodes and carrier beads. The source for a contact resistance between the sample carrier beads and the electrodes is a difference in work functions of the electrode(s) and the oxide layers on the carrier beads. The equivalent circuit for the measurement consists of two resistors in series: a contact resistor governed by the Schottky effect and a sample resistor governed by the Poole-Frenkel effect. We found that the current across the contact resistor initially increases and then rises about an order of magnitude at a constant voltage drop across the contact resistor. This rapid increase in current causes the contact resistance to become less than the sample resistance, such that the voltage across the sample approaches the applied voltage. When this occurs the Poole-Frenkel effect is observed. The highest conductivity developers do not show this behavior due to a large current density even at the lowest applied voltages. Finally, the experimentalist should be aware of the possibility of the electrode-sample contact resistance especially when measuring developer conductivity at a single voltage.

References

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Biography

Edward Gutman received the B.S. and M.S. degrees from John Carroll University in 1965 and 1967. After receiving a Ph.D. in solid state physics from Iowa State University in 1970, he was a post-doctoral research associate at the University of Illinois. In 1972, he joined Xerox Corporation where his research interests have focused on the physics of the xerographic development process and the science of xerographic developer materials. In 1989, Dr. Gutman received the Xerox President's Achievement Award for his contributions to the design of xerographic developer materials. He holds several patents on xerographic developer materials or devices. Currently he is a Research Fellow in Xerox Supplies Development and Manufacturing Services. He is a member of the Society for Imaging Science and Technology and the American Physical Society.

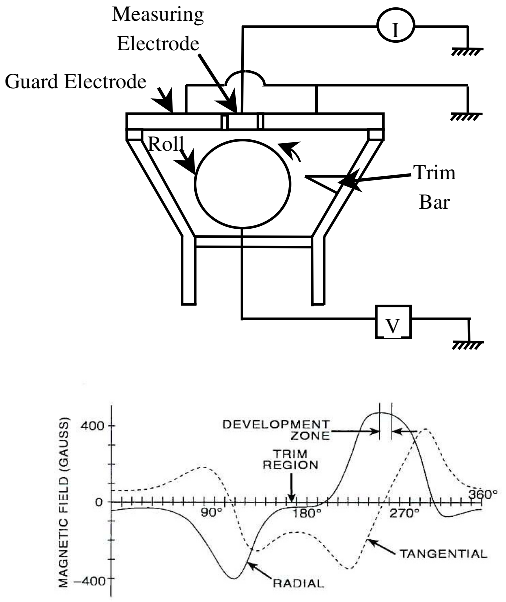

Figure 1. Diagram of the magnetic brush conductivity cell. The roll can be rotated. Inside the roll are two stationary magnets. The radial and tangential magnetic fields also shown.

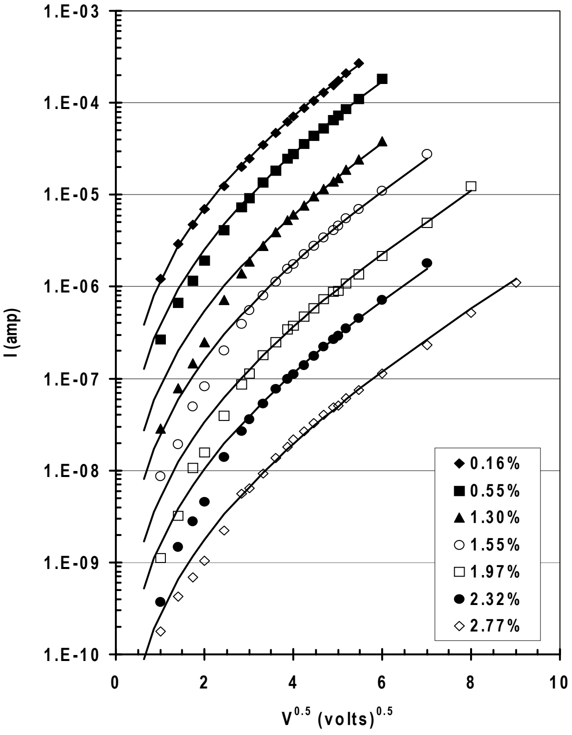

Figure 2. Current-Voltage measurements of a developer material for different toner concentrations. The solid lines are calculated with Eq. 1 for separate values of G_0 and a common value of B.

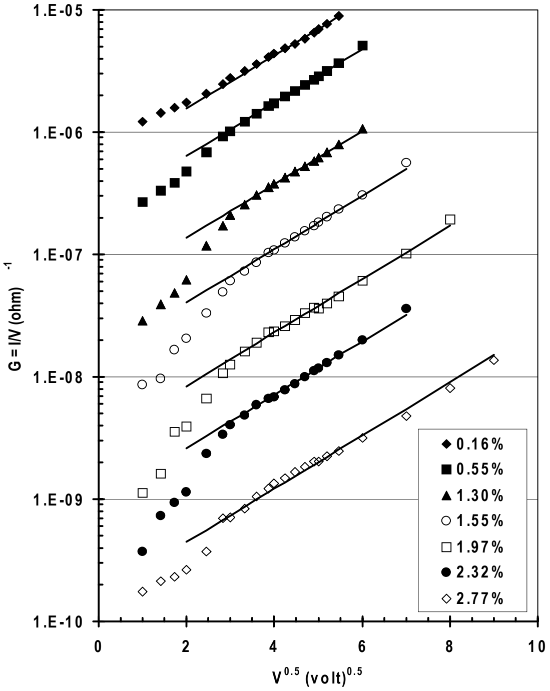

Figure 3. Conductance, G, as a function of voltage. In this plot, data which follow the Poole-Frenkel function form a straight line. For V>9v the data are very linear for all developers. For V<9v, the data for developers with C>1.3% deviate from a straight line.

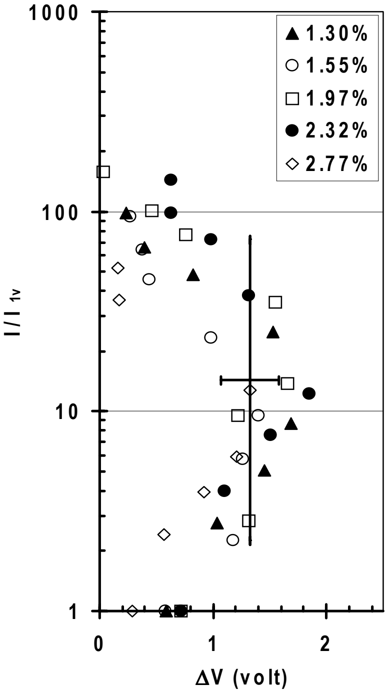

Figure 4. I normalized to the current at 1v versus ΔV, the voltage drop across the contact resistance. The current increases about an order of magnitude at a constant voltage drop. The average value of ΔV and one standard deviation are shown.