

Electrical Conduction in Moderately Conductive Xerographic Carriers and Developers

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Abstract

A planar-electrode method was used to identify the charge transport mechanisms in moderately conductive carriers and developers via DC current-voltage (I-V) and transient measurements. High-voltage I-V behaviour of coated carriers is non-linear due to trap-controlled space charge limited conduction in the insulative coating, and the Poole-Frenkel conduction of the core. It is shown that I-V data for carriers and developers can be potentially used to determine various material parameters such as coating thickness, surface coverage and toner conductivity.

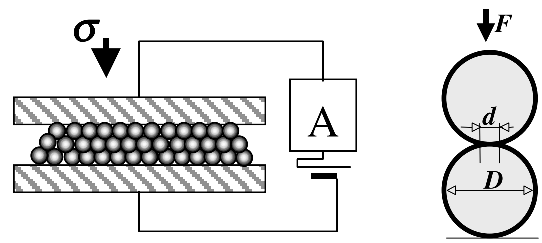
Introduction

The property conventionally referred to as electrical conductivity represents at least two separate concepts: Ohmic current density in a unit DC electric field, and the ability of a substance to dissipate localized space charge. Both concepts are of equal significance for xerographic powder materials, i.e., toners, carriers and developers. The contact development process used in many xerographic printers requires moderately conducting developers that are able to support stable development currents, with high rates of residual triboelectric charge dissipation required to facilitate the development process. The focus of this study is to identify the intrinsic processes of charge transport, accumulation and relaxation in model xerographic materials.

Experimental

Iron oxide carrier core with an average particle diameter of 35 µm was coated with 1, 1.25 and 1.5 wt. % polymethyl methacrylate (PMMA) by using the available coating process[1]. Preliminary SEM studies showed that the coating material formed a continuous thin layer on the carrier surface. Experimental developers were prepared by mixing uncoated carrier core with polyester cyan toner with an average particle size of 7 µm. Toner conductivity was adjusted by using surface additives. The materials were conditioned at a relative humidity of 15 % for 4 hours prior to measurement.

Two-probe I-V measurements were conducted on 3-mm thick piles of carriers and developers sandwiched between two parallel planar electrodes (Figure 1 a). A load of 10 kPa was applied to the upper electrode for good inter-particle contacts. Transients were measured by applying 1-minute high-voltage pulses, followed by short-circuiting the voltage source and measuring the transient currents with a Keithley electrometer.



(a) (b)

Figure 1. Schematic of the planar-electrode method (a) and the individual inter-particle contact (b)

The intimate inter-particle contact was the main concern of the present method. In order to be able to deduce information about intrinsic conduction mechanisms in the individual particle, it is important to minimize the series inter-particle contact resistance. The series resistance decreases with increase in size of the inter-particle contact (d) (Figure 1 b) which, in turn, relates to the particle diameter (D), applied load (σ), particle elastic modulus (E) and compact porosity (φ) as follows[2]:

$$(d/D)^3 = 0.225(1 - \nu^2)\sigma/E\phi^4 \qquad (1)$$

The load was chosen sufficiently low to avoid powder close packing that could modify powder surface properties and mechanically damage the coating. Preliminary studies conducted on the carrier coated with 1 wt. % PMMA showed that loads of up to 15 kPa do not change its apparent density. The free-flow apparent density of this specimen was 2.05 g/cm^3 while its picnometric density was 4.4 g/cm^3.

Results and Discussions

Insulative Carrier Coatings

Figure 2 shows the low-voltage DC I-V curves measured in the carrier coated with 0, 1, 1.25 and 1.5 wt. % PMMA. For uncoated core, current increases linearly with voltage up to 100 V, with a constant conductance of 10−4 S. Further increase in voltage results in a rapid non-linear increase in current. For 1 wt. % coating, the I-V dependence is linear only below 12 V, and then becomes quadratic between 12 and 100 V, as indicated by the slope of the I-V curve plotted in the logarithmic coordinates (Figure 2). The quadratic I-V behaviour is typical for space charge limited conduction3. Since the core remains a linear conductor within 12 – 100 V, it is believed that space charge injection occurs from the relatively conductive core into the insulative thin coating in the vicinity of the inter-particle contact points.

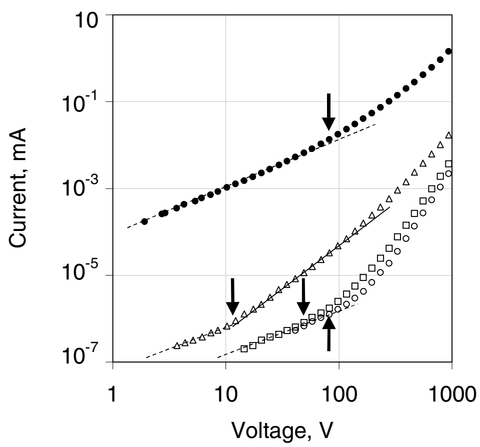


Figure 2. I-V dependencies of the piles of carrier coated with 0 (●), 1 (Δ), 1.25 (□), and 1.5 (○) wt. % PMMA. Slopes of 1 and 2 are shown with the dashed and solid lines, respectively. Arrows indicate the onset of non-linearity

Similarly to the carrier coated with 1 wt. % PMMA, the departure from I-V linearity in the carriers coated with 1.25 and 1.5 wt. % PMMA is attributed to the onset of space charge limited currents. However, the expected quadratic I-V dependence is obscured by the high-voltage non-linearity of the core.

Square roots of the voltages corresponding to the onset of the space charge injection process (V_{SC}) determined from the data in Figure 2 are plotted in Figure 3 as a function of coating weight. It should be pointed out that, at small coating weight percentages, coating thickness changes almost linearly with its wt. %. The behaviour shown in Figure 3 agrees with the theoretical predictions for planar insulative films[3] showing that space charge onset voltage is proportional to a square of the thickness of the insulator layer. Although, in the present coated powder, the relationship between V_{sc} and coating thickness can be significantly modified due to particle roughness, coating non-uniformity and the presence of uncoated patches or loose coating material, V_{sc} measurement can be potentially used as a method to determine coating thickness.

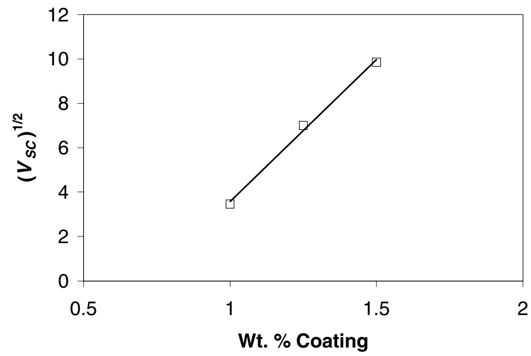


Figure 3. Space charge onset voltage vs. coating weight.

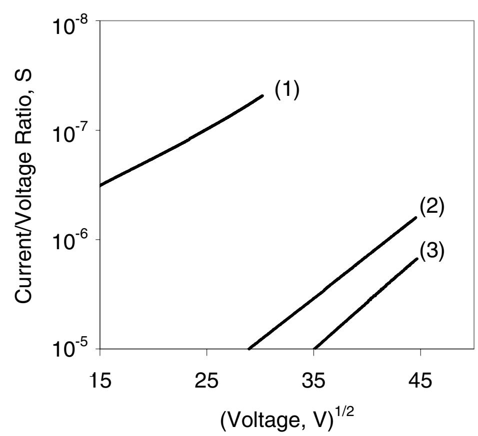


Figure 4. Poole-Frenkel plots for an estimate of the Poole-Frenkel coefficient B = 0.130 $V^{-1/2}$ for uncoated core (1); 0.177 $V^{-1/2}$ at 1 % coating (2) and 0.198 $V^{1/2}$ at 1.5 % coating (3).

The high-voltage portion of the I-V curves in Figure 2 can be best fitted with the Poole-Frenkel dependence:

$$I \propto V exp(BV^{1/2}) \quad (2)$$

The Poole-Frenkel coefficient B in Eq. (2) calculated from the slope of the Poole-Frenkel plots (Figure 4) increases with coating weight, changing from 0.130 $V^{-1/2}$ for the uncoated core to 0.177 $V^{-1/2}$ at 1 wt. % coating, and 0.198 $V^{-1/2}$ at 1.5 wt. % coating. It should be pointed out that B is the core material parameter, and thus, cannot be modified simply due to the presence of the coating. The apparent change of B can be only attributed to a change in effective local electric field applied to an individual particle. The effective electric field is reduced if the particle has conductive contacts with its nearest neighbours. Maximum of field reduction is observed in uncoated core that results in a decrease in effective local field and consequently the lowest apparent Poole-Frenkel coefficient. For coated carrier, there is still a finite probability of conductive contacts that can reduce the effective field. Since the number of conductive contacts in coated carrier depends on its surface coverage, the apparent Poole-Frenkel coefficient potentially can be used to determine coating quality.

Further I-V analysis shows a notable I-V hysteresis in the specimen with 1 wt. % coating, when voltage is ramped from 0 to 2000 V within a total time of 5 minutes, and then lowered to 0 V within 1 minute (Figure 5). The low-voltage Ohmic behaviour observed at increasing voltage was not detected at decreasing voltage. The current at decreasing voltage is ~ 10 times higher than during the initial increase in voltage. This I-V hysteresis is attributed to the presence of long-life trap sites in the coating polymer that affect the magnitude of the space charge limited currents. The initially unsaturated traps reduce the mobility of the injected charge. Trap saturation at high voltages, and the subsequent increase in charge mobility, results in higher space-charge currents at decreasing voltage, provided that trapped charge lifetime is sufficiently long.

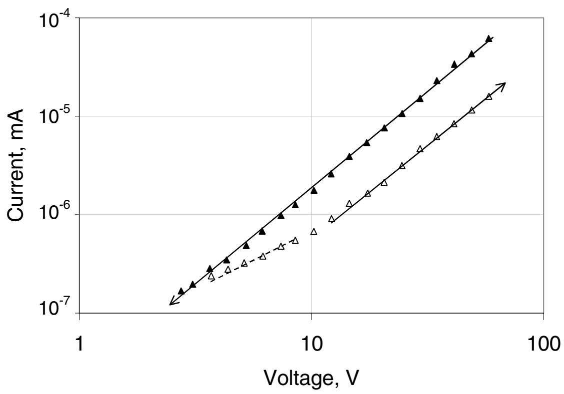


Figure 5. I-V dependence of carrier coated with 1 wt. % PMMA, at increasing (•) and decreasing (•) voltage.

The presence of trap-controlled currents in the PMMA coatings was further verified via transient measurements (Figures 6 and 7). It should be pointed out that the capacitance measured using the set-up shown in Figure 1 at 1 kHz and 1 V was ~ 70 pF, regardless of carrier coating weight. Thus, under normal conditions, 100 ms would be sufficient to restore zero current through the powder piles (with an electrometer internal resistance of 100 MΩ). Preliminary transient studies of the uncoated core showed that zero current restores within 50 – 100 ms, for the amplitude of the applied voltage pulse varying between 10 and 1000 V. Contrarily, coated carrier shows much greater transient time than expected from its capacitance, as indicated by the data in Figures 6 and 7. The transient time to a great extent depends on the voltage pulse amplitude: for instance, the time required for current decay from 10^{-5} to 10^{-7} mA changes from 1.8 s for a 10 V pulse to ~ 25 s for a 1200 V pulse. The observed voltage dependence of transient time can be interpreted as a result of both increase in injection levels and increase in mobility with voltage. Both factors are known to affect transient time for trap-controlled conduction[4]. It is seen in Figure 6 that the most significant change in transient time occurs at pulse amplitudes between 200 and 400 V which may indicate that the trap saturation process occurs within this voltage region.

Similarly, the decrease in transient time with increasing coating weight at the same pulse amplitude (Figure 7) is most likely associated with the reduction in transverse electric field in thicker coatings which subsequently leads to lower injection levels and lower mobility.

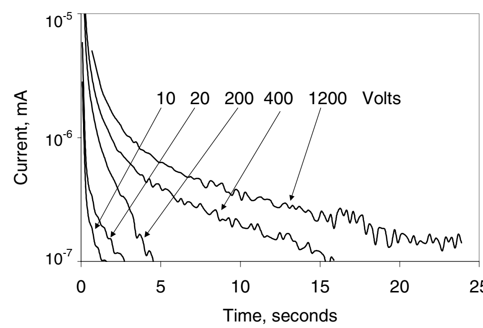


Figure 6. Transients in carrier coated with 1 wt. % PMMA at various pulse amplitudes.

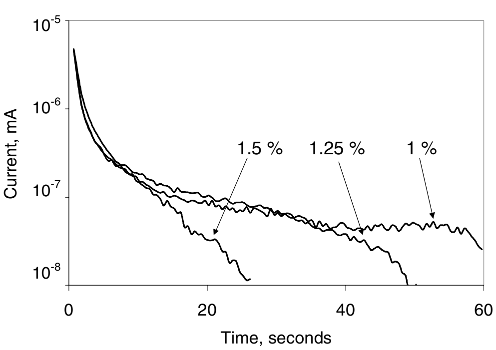


Figure 7. Transients in carriers with different coating weights (pulse amplitude = 800 V).

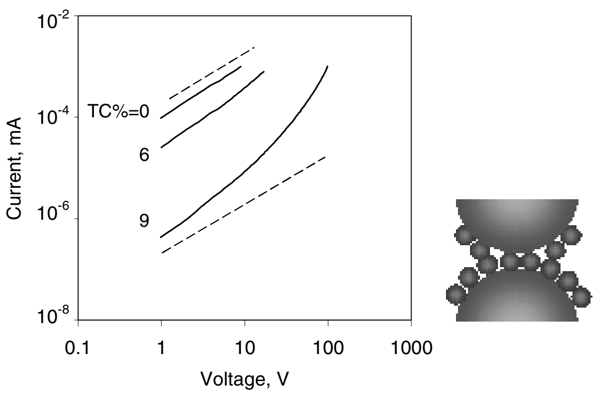
Moderately Conductive Developer

The change of the I-V behaviour of the developer based on conductive carrier core and moderately conductive toner with toner concentration (TC) is shown in Figure 8-a. As discussed above, the core is an Ohmic conductor at voltages below 100 V. The linear I-V behaviour persists at a TC of 6 %, while at 9 % the I-V dependence becomes apparently non-linear, with a significant drop in current. Finally, at 12 % TC, the DC current falls below the meter limit of 10-8 mA.

As was done previously, the change from Ohmic to non-linear behaviour is attributed to the occurrence of a new conductance mechanism. Thus, at 6 % TC and below, current percolates through contacts between carrier particles, while the much less conductive toner serves as an electrically insignificant (separating) phase. At 9 % TC, the apparent breakage of percolation conduction indicates the possibility of toner monolayer formation at the carrier surface. For the simplest monolayer configuration shown in Figure 8-b, electric current passes through a series of carrier-toner contacts. For such a case, the individual resistance of a toner particle between two "polar" contacts can be evaluated using a series equivalent circuit:

$$R_T \sim (V/I)(D/L) \qquad (3)$$

where I and V are the measured voltage and current values from a linear I-V region, D is the carrier particle diameter, and L is the developer pile thickness. Substituting the values for 1 V into Eq. (3) gives resistance of 3×10^7 Ω for an individual toner particle. The non-linear charge transport in an individual toner particle will require further studies.



(a) *(b)*

Figure 8. I-V curves for a developer containing a conductive carrier and moderately conductive toner (dashed lines indicate linear I-V dependence) (a) and a schematic of monolayer conduction (b)

It should be pointed out that monolayer TC estimated for toner particles close-packed on the surface of the carrier particles with the given size and density is ~ 20 %. The critical TC at which percolation conduction is blocked by toner monolayer is ~ approximately half monolayer TC, since the configuration shown in Figure 8-b requires only half monolayer to block percolation conduction in the developer.

Conclusions

Current-voltage and transient behaviour of moderately conducting carriers and developers was studied by the planar electrode method. Non-linear high-voltage I-V behaviour in carrier with insulating coating is dominated by transverse space charge limited currents in the coating and Poole-Frenkel conduction in the core. The presence of intrinsic unsaturated long-life traps was detected in PMMA coatings. I-V data for carriers can be used to evaluate carrier coating surface coverage and thickness.

DC conduction in developers containing conductive carrier core and moderately conducting toner depends on toner concentration. Percolation conduction at low TC disappears at higher TC when toner particles form a monolayer on carrier surface.

References

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Biography

Vladislav Skorokhod received a Ph.D. in Materials Engineering from Queen's University (Canada) in 1998. Since 1999, he has worked in the Xerox Research Centre of Canada. His work has primarily focused on the development of new xerographic powder materials, functionalization and electro-physical properties of polymers, and physics of fine powders. Previous work included microstructural design, processing and properties of functional and structural ceramics.