Effects of Carbon Black on Toner Tribocharging in Two-Component Electrophotographic Developers

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Abstract

A steady-state version of the surface state model of tribocharging is developed and compared to the effects of carbon black on tribocharaging of two-component developers. In this model, the rate of charging of the toner and the rate of discharging of the toner, because of increased conductivity related to the carbon content of the toner, are assumed to be equal at steady state.

Carbon black was found to have the following effects on the triboelectric properties of model toners made from carbon black in a polymer binder:

- 1. Increasing the carbon black content causes the absolute value of the charge-to-mass of model toners to decrease when the toner is charged positively or negatively using poly(methylmethacrylate) coated carrier or poly(vinylidine fluoride) coated carrier.
- 2. The ratio of q/m when the toner is charged positively to q/m when the same toner is charged negatively is a constant.
- 3. Increasing the carbon black content causes the absolute value of the slope and the intercept of linear plots of mass-to-charge as a function of the mass ratio of toner to carrier to increase.

The model predictions agree with these observations.

Introduction

Black electrophotographic toners most frequently contain 5-10% of carbon black as a pigment in a polymer matrix. Despite the extensive application of black toner, only a few papers have appeared in the published literature

describing the influence of carbon black on the triboelectric properties of black toners.¹⁻⁵ The results presented in these papers differ widely. The purpose of this paper is to present some new experimental results related to the triboelectric effects of carbon black in toner and to compare them to a modified version of the surface state model of tribocharging, which takes into account back-flow of charge because of toner conductivity.

Experimental

Materials

Ten model toners were made at different concentrations of Black Pearls 430 carbon black (0 to 40 wt%) in a styrenebutylacrylate copolymer (75/25) matrix . The carbon black was melt-compounded in the polymer at 150°C and ground to 10 μ m volume average particle size. These toners were charged against two carriers. The first was a poly(vinylidine fluoride) coated iron-strontium ferrite (30 μ m average volume diameter). The second carrier was made from the same ferrite but coated with poly(methylmethacrylate). The former carrier caused the toners to charge positively, while the latter caused them to charge negatively.

Charge Measurements

The toners were mixed with the carriers at a series of toner concentrations ranging from a toner-carrier mass ratio (T/C) of 0.05 to 0.30. The mixtures were shaken for 2 min in wrist shaker and mixed for 30 s in a magnetic stirrer at 2000 rpm. This time was determined to be sufficient to bring the toner charge to its maximum value. The toner charge-to-mass ratio, q/m, was determined by removing the toner electrostratically.⁷ TC series plots (m/q vs T/C) were then made for each toner and carrier combination. All toner concentration series plots were linear.

DC Bulk Conductivity Measurements

Bulk DC conductivity was measured using a Keithly 617 Electrometer provided with an external variable voltage supply to generate voltages up to 2 kV. Current response as a function of time was measured during application of the electric field of constant magnitude.¹⁰

Results and Discussion

Charging Behavior

Figure 1 shows the toner concentration series plots for a representative subset of the toners charged positively against the poly(vinylidine fluoride)-coated carrier. The plots are linear with correlation coefficient $R^2 > 0.85$. It can be seen from the figure that as the carbon concentration increases, the slope of the toner concentration series plots increase. Figure 2 is similar to Fig. 1, but for a subset of the toners charged negatively against PMMA-coated carrier. As with the positively charged toner, the plots are linear, and the slopes and intercepts of the TC series increase as the carbon black concentration increased.



-1.00 0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4 Toner / Carrier ■ No Ca □ 10% CB ● 20% CB ○ 25% CB ▲ 30% CB △ 40% CB

Figure 2. Toner concentration plots for negative toner.

Figure 3 is a plot of q/m all ten toners charged negatively as a function of q/m of the same toners charged positively. The q/m values were interpolated to T/C = 0.15 using least squares linear fits to TC series. There is an excellent linear correlation between the positive and negative q/m measurements. The intercept is nearly zero.



Figure 3. Negative q/m as a function of positive q/m.

ConductivityMeasurements

Figure 4 shows the DC conductivity of the toners used in this study as a function of carbon black concentration. The data show that bulk conductivity begins to increase when the carbon concentration reaches 10 wt%. This concentration is referred to as the "percolation limit." Below the percolation limit, carbon black particles or clusters of particles are separated widely enough that they do not contribute to the bulk electrical conductivity.¹¹



Figure 4. Conductivity as a function of carbon black content.

It is interesting to compare carbon black concentration dependence of q/m of the toners to their electrical conductivity. Even at 1 wt% loading, q/m is less than for the polymer alone. At 10 wt% carbon loading, |q/m| is about 40% of |q/m| of the unpigmented polymer. At 25 wt%, |q/m| is about 10% of |q/m| of the unpigmented polymer.

Thus, at loadings well below the percolation limit, carbon black has a major effect on charging.

Extension of the Surface State Model

In this section, the high density limit of the surface state model is combined with a steady-state charging model of tribocharging proposed by Matsui and Oka.⁹ As with the "high density of states limit" of surface state models, they assumed that the driving force for exchange of charge is the difference in work functions between the toner and the carrier. In their view, the charge is determined by a balance between the rate of charging and the rate of loss of charge because of the low resistance of the toner caused by the presence of the carbon black. Their analysis is incomplete, however, because they did not include the effects of electric potential between the toner and carrier particles generated by exchange of charge. The present analysis follows Matsui and Oka's approach, but also includes electric field effects.

The rate of charge generation, dQ/dt can be written as a balance between charged species moving between the toner and the carrier over an energy barrier and ohmic back-flow of the charged species:

$$\frac{dQ}{dt} = -e\beta \exp\left[-\frac{(\varepsilon - \phi_t)}{kT}\right] + e\beta \exp\left[-\frac{(\varepsilon - \phi_c + V)}{kt}\right] - V\sigma \qquad (1)$$

In Eq.(1) Q is the charge transferred to a single carrier particle, t is the time, β is a kinetic parameter, ϵ is the height of the energy barrier to charge transfer, ϕ is the work function, V is the potential generated by the transfer of charge between the toner and the carrier, σ is the conductivity of the contact (1/ σ is the resistance to backflow of charge), k is Boltzmann's constant, and T is the absolute temperature. The subscripts, t and c, refer to toner and carrier, respectively.

At steady state, dQ/dt = 0, and

$$V\sigma = -e\beta \exp\left[-\frac{(\varepsilon - \phi_t)}{kT}\right] + e\beta \exp\left[-\frac{(\varepsilon - \phi_c + V)}{kt}\right]$$
(2)

In the high density of states limit of the surface state model, V is the electrical potential between the toner and the carrier as a result of the transfer of charge and is given in reference 7 as:

$$V = -\frac{d}{3\varepsilon_0} q'_m \left(r_t \rho_t + T'_C r_c \rho_c \right)$$
(3)

Equation (3) can be substituted into Eq. (2) and rearranged:

$$\frac{q'_{m}}{d\sigma} = -\frac{3\varepsilon_{0}\beta'}{d\sigma} \left(r_{t}\rho_{t} + \frac{T}{C}r_{c}\rho_{c}\right)^{-1} \bullet \left[1 - \exp\left\{-\left[\phi_{t} - \phi_{c} - \frac{q}{m}\bullet\frac{d}{3\varepsilon_{0}}\bullet\left(r_{t}\rho_{t} + \frac{T}{C}r_{c}\rho_{c}\right)\right]/kT\right\}\right]$$
(4)

In Eq. (4) the charging rate, $e\beta \exp[-(\epsilon-\phi_t)/kT]$, has been replaced by β' . This equation can be solved for q/m numerically.

However, in order to get a clearer picture of the behavior of q/m as a function of σ and T/C, the exponential expression can be approximated by the first two terms of its series expansion. Solving for q/m:

$$q_{m}^{\prime} \cong -\frac{3\varepsilon_{0}}{d} \left(\frac{\phi_{t} - \phi_{c}}{r_{t}\rho_{t} + T_{C}^{\prime}r_{c}\rho_{c}} \right) \bullet \left(\frac{1}{\frac{\sigma kT}{\beta^{\prime}} + 1} \right)$$
(5)

Numerical calculations confirm that the charging behavior predicted by Eq. (5) is similar to that predicted by Eq. (4). The predicted q/m values differ by less than a factor of 2 when $\sigma kT/\beta' \ll 1$ and converge as $\sigma kT/\beta'$ increases.

Eq. (5) is the same as the high density of states limit of the surface state model, except for the factor $1/(\sigma kT/\beta' + 1)$. In the limit of $\sigma kT/\beta' <<1$, Eq. (5) gives the same relationship between q/m and T/C as the high density of states limit of the surface state model. That is, m/q is a linear function of T/C, and the slope and intercept depend only on the particle sizes and mass densities. This is to be expected since large values of $\sigma kT/\beta'$ means that there is no back-flow of charge. As $\sigma kT/\beta'$ increases, but is still smaller than 1, q/m will decrease as linearly as $1 - \sigma kT/\beta'$. In the limit of $\sigma kT/\beta' >>1$, Eq. (5) has the same form as Matsui and Oka's model. That is, q/m is proportional to $\beta'\sigma kT$.

If two different carriers of the same particle size are used to charge the same toner, the ratio of the charges is given by

$$\begin{pmatrix} q \\ m \end{pmatrix}^{-} = \frac{\phi_t - \phi_c^+}{\phi_t - \phi_c^-} \begin{pmatrix} \frac{\sigma kT}{\beta^{-,}} + 1 \\ \frac{\sigma kT}{\beta^{+,}} + 1 \end{pmatrix} \begin{pmatrix} q \\ m \end{pmatrix}^+$$

$$\cong \frac{\phi_t - \phi_c^+}{\phi_t - \phi_c^-} \begin{pmatrix} \frac{\beta^{+,}}{\beta^{-,}} \end{pmatrix} \begin{pmatrix} q \\ m \end{pmatrix}^+$$
(6)

In Eq. (6) the "+" and "-"signs refer to carrier which charges the toner positively and negatively, respectively. Equation (10) predicts that, when $\sigma kT/\beta' >> 1$ (expression on the far right side of Eq. (6)), the ratio of q/m when the

toner is charged positively to q/m when the toner is charged negatively is just the ratio of the respective charging rates. That is, the ratio is a constant.

Equation (5) predicts a behavior not predicted by Matsui and Oka, namely, that as carbon black concentration increases, the absolute value of the slope and intercept of the TC series plots should increase.

Summary and Conclusions

Matsui and Oka's charging model has been extended to include the toner concentration dependence of tribocharging and the charge-limiting effects of electric fields generated by charge transfer. The charging measurements presented in this report are generally in agreement with four predictions of the extended model.:

- Toner concentration plots are linear regardless of the polarity of q/m or the magnitude of the conductivity parameter, σ (see Figures 1 and 2).
- At the same concentration in the toner, carbon blacks with larger work functions (higher surface acidity) should cause q/m to be more negative. The data of Julien and Oka and Matsui illustrate this.^{1,5}
- Figure 4 shows that addition of carbon black to the toner causes conductivity to increase. As $\sigma kT/\beta'$ increases, the absolute value of the slope and intercept of TC series plots is predicted to increase. Figures 1 and 2 confirm this behavior.
- Finally, Eq. (6) predicts a linear relationship between (q/m) and (q/m)⁺ if the work functions remain constant. This behavior is illustrated by Figure 3. The slope of 0.63 indicates that the rate of charging of the toner when it is charged negatively is slower than when it is charged positively.

One puzzling feature of the experimental results is that carbon black present at levels below those necessary to influence the bulk electrical conductivity of the toner have a significant effect on q/m. This region of carbon black concentration is important because typical black toners are filled with 6-10 wt% of carbon black. One possible explanation of this anomaly is that even at low carbon black concentrations, localized clusters of carbon black particles form, which give rise to local regions of higher conductivity that are electrically isolated from one another by the polymer. Thus, the local conductivity of the toner may be high at the point of contact between the toner and the carrier, even though bulk conductivity of the toner is low. The model represented by Eq. (5) and Eq. (6) may have another application. It is often said that high relative humidity causes tribocharging to be reduced because water adsorbed on the contacting surfaces leads to increased surface electrical conductivity. If this is so, then Eq. (5) predicts that both positive and negative tribocharging should be reduced. Furthermore, the slope and intercept of TC series plots using carriers that charge the same toner positively and negatively should increase. Some results of Veregin and coworkers suggest that this is so.¹²

References

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Biography

Dr. Anderson holds BS, MS and PhD degrees from Stanford University. He is currently on the research staff of Heidelberg Digital where he works on the physics and materials science of triboelectricity and electrophotography. Dr. Anderson is also part time Associate Professor at Empire State College, State University of New York.