A Comparison of Experimental Data and Model Predictions for Tribocharging of Two-Component Electrophotographic Developers

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Abstract

Several models have been proposed to explain tribocharging of powders used in electrophotography. Some of these models have been developed quantitatively and can be used to make predictions of the charging behavior of powders. Recently Schein has examined the differences between the high- and low-density limits of surface-state charging models. Models based on either limit predict a linear relationship between mass-to-charge ratio *(m/q)* and toner-to-carrier mass ratio (m_t/m_c), in agreement with experiment. However, according to models derived from the high-density limit of surf states, the ratio of the slope to the intercept of plots of *m/q* versus m_t/m_c, γ, depends only on the particle size and the mass density of the materials. Thus, varying the chemical composition of one of the powders in a mixture should lead to a family of *m/q* versus m_t/m_c plots that have the same γ. On the other hand, according to models derived from the low-density limit of surface states, γ depends upon the chemical composition of the surfaces. In this study the predictions of a simple version of the surface-state charging model, as well as the high and low-density limits of the model, are compared with published data and with experiments carried out in our laboratories. Experimental γ values agree within a factor of 4 with those calculated from particle size and density using a high-density model of surface states. The data also show that systematic changes in the chemical composition of the powder surfaces cause systematic changes in γ that are more consistent with the full surface-state model. For charge-to-mass values calculated using the surface-state model to agree with measured values, the concentration of surface states must be approximately 10^{11} eV^{-1} cm^{-2} and the ratio of the separation between the particle surfaces beyond which no charging takes place and the work function difference between the surfaces must be unexpectedly large. This dilemma can also be resolved if only 1/1000 of the surface is available for charging.

Introduction

Triboelectrification, electrical charging by rubbing two materials together, is the oldest known manifestation of electricity. Despite this experience and the explosion of electronic technology, triboelectricity remains the least understood of electrical phenomena. There is no consensus on what charged species are exchanged or on the mechanism by which charging occurs.

The purposes of this study are:

1. To review the surface-state model of tribocharging of two-component electrophotographic developers.
2. To compare the predictions of this model with experimental studies of tribocharging.

In two-component electrophotographic development, toner particles are mixed with magnetic particles (carrier). The toner and carrier are chosen so that they exchange charge when they are brought together and become oppositely charged. Electostatic forces cause the smaller toner particles to adhere to the larger carrier particles. The two-component mixture is transported magnetically to the photoconductor and brushed against it. Toner is removed from the carrier and deposited on the photoconductor under the influence of the electrostatic fields associated with the latent image. The carrier is returned to the developer station, where it picks up fresh toner.

Toner particles are 10-15 μm in diameter and are made from a pigmented polymer to produce an image of the desired color. The rheology of the toner polymer is chosen so that the image can be thermally fixed to the paper. In most cases, pigmented polymer does not tribocharge properly for the operation of a copier. Additives, called charge control agents or charge agents, are therefore included in toner formulations to control the sign and magnitude of the toner charge. Toner particles are usually prepared by melt-compounding the toner constituents and grinding to the desired particle size.

Carrier particles range from 30 to 200 μm in diameter. They are made from ferromagnetic metals or oxides so that they can be used to transport the toner, be separated from the toner magnetically, and be retained in the copier. They are often coated with a polymer chosen such that the coated carrier imparts the proper charge to the toner particles.

Models of Charging Powders

Schein et al[1,2] and Gutman and Hartmann[3] have recently discussed surface-state models of tribocharging of two-component electrophotographic developers. Their framework will be used in this study to discuss charging behavior,

and an electronic mechanism will be assumed. The driving force for charge exchange between toner and carrier is the difference between the work functions of the two surfaces. Electrons will move from filled levels in the material with the smaller work function to empty levels in the material with the higher work function. Exchange of charge will cease when the Fermi levels of the two materials coincide. There are two contributions to the movement of the Fermi levels. Mechanism (1): as electrons move from one material to the other, the number of occupied levels in one material increases, while the number of empty levels in the other increases, causing the Fermi levels of the two materials to approach one another. Mechanism (2): the exchange of charge results in a potential difference between the two materials, which opposes further transfer of charge and moves the Fermi levels toward one another.

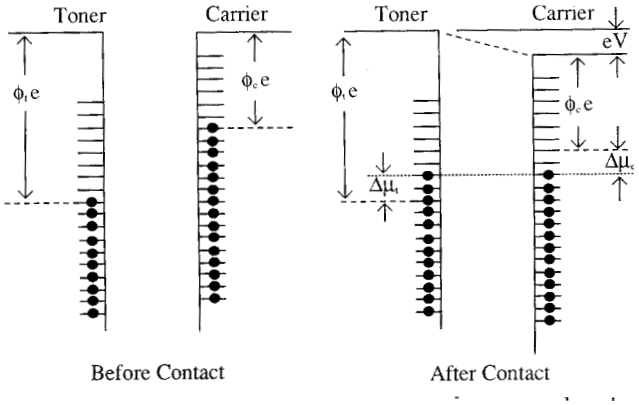

Figure 1. Energy level diagram for the surface-state charging model. Transfer of electrons from the carrier to the toner causes the Fermi energy of the toner to change by $\Delta\mu_t$ and the Fermi energy of the carrier to change by $\Delta\mu_c$. The transfer of charge also produces a potential difference between the toner and the carrier, V. The net effect is that the Fermi levels of the toner and carrier are the same after contact (dotted line).

The initial difference in work functions is equal to the total change in the work functions due to Mechanisms (1) and (2). (See Fig. 1.)

$$(\phi_t - \phi_c)e = \Delta\mu_t - \Delta\mu_c + eV, \tag{1}$$

where ϕ is the work function in volts, $\Delta\mu$ is the change in Fermi energy in eV, *–e is* the charge of the electron, and V is the potential at the surface of the carrier relative to that of the toner. The subscripts, *t* and *c*, refer to the toner and carrier respectively.

The changes in the Fermi energies due to Mechanism *(1),* $\Delta\mu_t$ and $\Delta\mu_c$, can be written in terms of the properties of the particles: the charge, *q*, the mass, *m,* the particle radius, *r*, the mass density, ρ, the specific surface area, $3/r\rho$, and the density of surface states, *N*, in units of number eV^{-1} cm^{-2}.

$$\Delta\mu_t = \frac{-q_t}{m_t}\frac{r_t\rho_t}{3N_t e}; \quad \Delta\mu_c = \frac{-q_t}{m_t}\frac{m_t}{m_c}\frac{r_c\rho_c}{3N_c e} \tag{2}$$

The potential difference between two oppositely charged, insulating spheres is

$$V = \frac{1}{4\pi\in_0}\left[\frac{-q_t d}{r_t(r_t+d)} + \frac{-q_c d}{r_c(r_c+d)}\right] \tag{3}$$

In Eq. 3 $\in_0$ is the permittivity of free space and *d is* the separation between the toner and the carrier when charging ceases. It is usually assumed that *d* represents the distance over which electron tunneling can occur.[1,2] Therefore, $d << r$, and Eq. 3 can be simplified to

$$V = \frac{1}{4\pi\in_0}\left[\frac{-q_t d}{r_t^2} + \frac{-q_c d}{r_c^2}\right] \tag{4}$$

Equation 4 can be rewritten in terms of the toner charge-to-mass ratio, q_t/m_t, by replacing the particle charges with the product of the *q/m* and the particle mass. (Note that the carrier charge-to-mass ratio is given by the toner charge-to-mass ratio times the ratio of toner mass to carrier mass in the developer.)

$$V = \frac{-d}{3\in_0}\frac{q_t}{m_t}\left[r\rho_t + \frac{m_t}{m_c}r_c\rho_c\right] \tag{5}$$

Eqs. 2 and 5 can be substituted into Eq. 1:

$$(\phi_t - \phi_c)e = \frac{-q_t}{m_t}\frac{r_t\rho_t}{3N_t e} - \frac{q_t}{m_t}\frac{m_t}{m_c}\frac{r_c\rho_c}{3N_c e} - \frac{ed}{3\in_0}\frac{q_t}{m_t}\left[r_t\rho_t + \frac{m_t}{m_c}r_c\rho_c\right] \tag{6}$$

Solving Eq. 6 for mass-tocharge, *m/q*, gives:

$$\frac{m_t}{q_t} = -\frac{d}{3\in_0(\phi_t - \phi_c)}\left[\frac{\in_0 r_t\rho_t}{N_t e^2 d} + \frac{m_t}{m_c}\frac{\in_0 r_c\rho_c}{N_c e^2 d} + r_t\rho_t + \frac{m_t}{m_c}r_c\rho_c\right] \tag{7}$$

Thus, the model predicts that *m/q* is a linear function of m_t/m_c, and that the slope and intercept of the line depend upon the particle sizes, the mass densities, and the densities of surface states.

High-Density Limit

Schein[2] has pointed out that most published models of tribocharging correspond to the limits of Eq. 7 when the density of states is very high or very low. If $\in_0/(de^2N_c) << 1$ and $\in_0/(de^2N_t) << 1$, then Eq. 7 reduces to

$$\frac{m_t}{q_t} = -\frac{-d}{3\in_0(\phi_t - \phi_c)}\left[r_t\rho_t + \frac{m_t}{m_c}r_c\rho_c\right] \tag{8}$$

This result is the same as that found by Kondo.[4] Gutman and Hartmann[3] have extended Kondo's calculations to take into account the influence of clusters of toner particles around a single carrier particle and polarization and image charge effects. Their work showed that these latter effects are relatively small.

Low-Density Limit

If $\in_0/(de^2N_c) >> 1$ and $\in_0/(de^2N_t) >> 1$, then Eq. 7 can be simplified to

$$\frac{m_t}{q_t} = \frac{-1}{3(\phi_t - \phi_c)e^2}\left[\frac{r_t\rho_t}{N_t} + \frac{m_t}{m_c}\frac{r_c\rho_c}{N_c}\right]. \quad (9)$$

This result is the same as that derived by Lee,[5] who considered only the changes in work function caused by the exchange of electrons between filled and empty levels on the two surfaces. It is also similar to the results of Anderson[6] and Anderson and Bugner,[7] which have the same functional form, although the initial assumptions and the interpretation of the parameters are somewhat different.

Comparison of the High- and Low-Density Limits

Kondo,[4] and more recently Schein[2] and Gutman and Hartmann,[3] have pointed out that the ratio of the slope to the intercept of Eq. 7, γ, is of particular interest because it can be used to assess the relative importance of the two terms of the expressions for the slope and intercept.

$$\gamma = \frac{r_c\rho_c(1+\epsilon_0/de^2N_c)}{r_t\rho_t(1+\epsilon_0/de^2N_t)} \quad (10)$$

In the high-density limit, the expression for γ reduces to

$$\gamma = r_c\rho_c / r_t\rho_t \quad (11)$$

Thus, in the high-density limit, γ is determined by electrostatics and is independent of both the work function difference and the densities of states. It depends only on the size and density of the particles and no other properties of the materials.

In the low-density limit, the expression for γ reduces to

$$\gamma = \frac{N_t r_c\rho_c}{N_c r_t\rho_t} \quad (12)$$

Thus, in the low-density limit γ depends not only on the particle sizes and densities, but also on the surface densities of states of the toner and the carrier.

The differences among Eqs. 10, 11, and 12 can serve as a means of determining whether or not models based on the low-or high-density limits are adequate to represent experimental data. If γ is found to be independent of materials composition, then the high-density limit models are satisfactory. If γ is dependent on materials composition, then either a low-density limit model or the complete model, Eq. 7, may represent the data better.

Measured Tribocharging Properties of Two-Component Developers

Experimental Methods

New charge-to-mass measurements reported in this study for developers with carrier particle sizes of 100 µm were made using the blow-off method described by Schein.[2] This method cannot be used for smaller carrier particles because they can escape from the measuring chamber through the screens along with the toner. For this reason, an electrostatic method of *q/m* measurement was adopted. This method is described fully elsewhere.[8] Briefly, a known mass of developer is placed between two metal electrodes separated by about 1 cm. An electric field of approximately 2 kV/cm is applied between the plates, and the developer is agitated simultaneously with either a rotating permanent magnet or an ac coil. Toner is freed from the carrier by the agitation and collected on the top plate by the electric field. The carrier remains on the lower plate. The charge and mass of the toner collected are measured and used to calculate *q/m* and m_t/m_c.

All particle sizes for the new measurements reported in this paper were made using a Coulter® Multisizer II (Coulter Electronics, Inc., Hialeah, FL).

Effects of m_t/m_c and Particle Size

Several workers have examined tribocharging in electrophotographic developer systems. Lee[5] examined the charging of toner against polymer-coated metal and insulator carrier particles. He found (Figure 2) that *m/q* of the toner was a linear function of m_t/m_c for m_t/m_c less than 0.1. (Plots of *m/q* versus m_t/m_c are hereafter referred to as "toner concentration series.") Schein[2] and Gutman and Hartmann[3] have reported similar results. Anderson has measured toner concentration series for toner/carrier ratios up to 0.4, using smaller carrier particles[6] (Figure 3). Recently, tribocharging in binary mixtures of fresh (unused) coated carrier particles, uncoated carrier, and aged (used) coated carrier have been studied. No toner is used in these experiments. Figure 4 shows that the linear relationship between *m/q* and the ratio of the masses of the two types of particles in a mixture extends over mixtures ranging in composition from 1:10 to 10:1. Thus, the linear relationship found by Lee[5] is well verified and followed by mixtures of powders in any proportion. This finding is in agreement with the predictions of Eq. 7 and high- and low-density limit models of tribocharging.

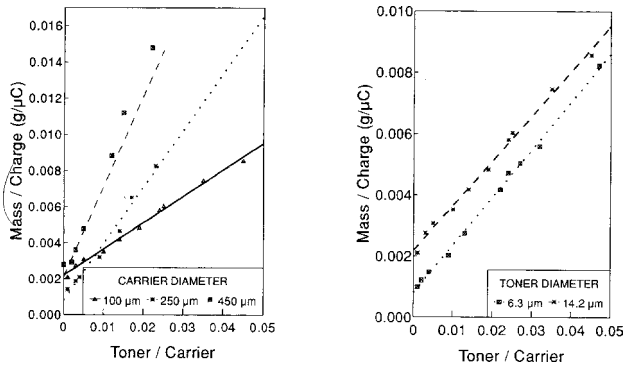

Figure 2. Toner concentration series for carrier and toner particle of different sizes. Increasing the carrier particle size causes the slope to increase while the intercept remains nearly constant. Increasing the toner particle size causes the intercept to increase while the slope remains nearly unchanged. (Figure taken from Ref. 5.)

Lee[5] also found that 14.2-µm toner charged lower than 6.3-µm toner. The slopes of the toner concentration series were the same for the two toners, whereas the intercepts on the *m/q* axis were different (see Figure 2). Gutman and Hartmann[3] have reported similar results.

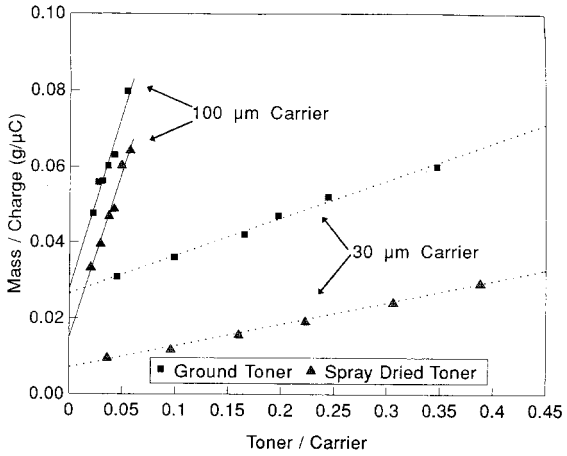

Figure 3. Toner concentration series made with two toners and two carriers. The toner concentration series using 100-μm carrier have larger slopes. The toner concentration series using the 30-μm carrier shows that the linear relationship between m/q and m_t/m_c extends to $m_t/m_c = 0.4$.

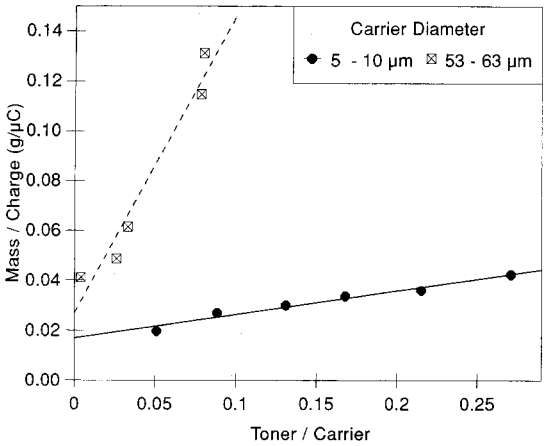

Figure 5. Toner concentration series for carriers of different particle sizes. The particle size of the 53-64-μm carrier was estimated from sieve analysis. The particle size of the 5-10-μm carrier was determined using the Coulter® Multsizer. The slope for the 5-10-μm carrier is 0.094; for the 53-63-μm carrier, the slope is 1.02.

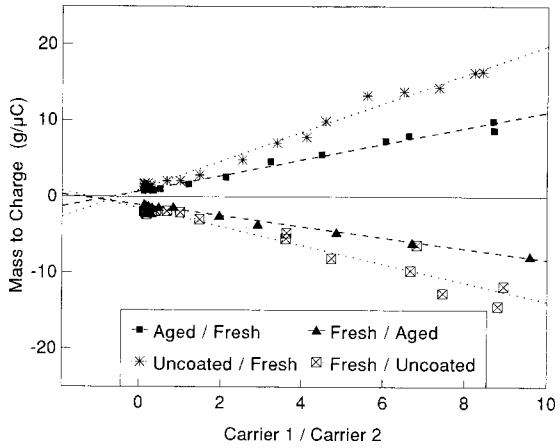

Figure 4. Concentration series for carrier-carrier charging. These data show that the linear relationships between m/q and the mass ratio of the two components extends over the composition range from 1:10 to 10:1.

Lee[5] also reported that when carrier particle size was increased, the slopes increased, while the intercepts on the *m/q* axis showed relatively little change (see Figures 2 and 3.) Increasing slope with increasing carrier size was also observed in this study (Figure 5). Again, this result agrees with Eq. 7 and models based on either the high-or low-density limits.

Materials Composition Effects

In this study, two types of experiments were carried out to examine the effects of changing the composition of the toner and carrier materials. In the first experiments, ferrite core was coated with series of blends of two polymers. The charging properties of these carriers were compared, using the same toner. In the second series of experiments, the concentration of charge agent in the toner was varied and charging properties of the toners were compared, using the same carrier.

In Figure 6, data taken from Ref. 6 are shown for charging of a common toner by a series of carriers coated with a blend of poly(methylfluorochloroethylene-*co*-vinylidene fluoride), PMVF, and poly(methylmethacrylate), PMMA. The reference toner was a styrene butylacrylate polymer containing a charge control agent and carbon black. From the figure it can be seen that *q/m* and the slope/intercept ratio, γ, declined as the concentration of PMMA in the blend increased. Overall, the ratio decreased by a factor of approximately four. A similar experiment was carried out using poly(vinylidine fluoride) (PVF)-PMMA blends. The toner for these experiments was a styreneacrylic polymer containing a blue pigment and both positive and negative charge agents. In this case, both *q/m* and γ increased as PMMA was added. When the PMMA concentration reached 60%, the polarity of the toner charge switched from positive to negative. Presumably this change occurred because the work function of the carrier coating decreased as PMMA was added until it became less than the work function of the toner. Beyond the point where the polarity of the toner changed, γ decreased again (see Figure 6). These experiments show that *q/m* and γ vary smoothly as the carrier core composition is changed. Because the toner and carrier particle sizes were constant in these experiments, the variations seen are the result of composition changes.

We have recently reported studies of the effect of changing the composition of the toner on charging behavior.[8,9] Figure 7 shows γ for toners made with different concentrations of charge control agent. In these experiments two chemically related charge control agents were examined in a polyester binder and a styrene-acrylic binder. The surface concentration of charge agent was determined by an extraction technique.[8,9] It can be seen from the figure that γ increases as the charge agent concentration increases.

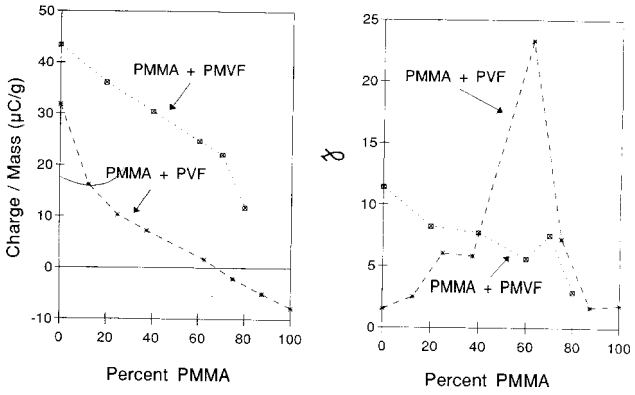

Figure 6. Charge-to-mass ratio at $m_t/m_c = 0.15$ and γ as functions of earner coating composition. These data show not only that q/m is a function of the composition of the carrier coating, but that γ is also.

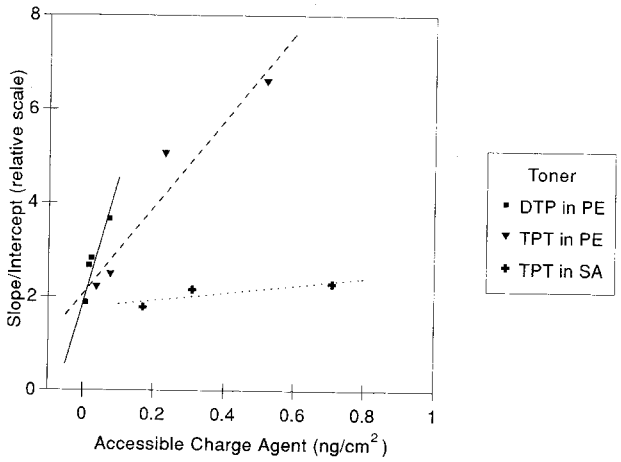

Figure 7. γ as a function of the surface concentration of charge agent. Two phosphonium salt charge control agents, dodecyltriphenylphosphonium tosylate (DTP) and methyltriphenylphosphonium tosylate (TPT), were made into toner, using a polyester (PE) binder. TPT was also used to make a toner with a styrene acrylic binder (SA).[8,9] The surface concentration of charge agent in these toners was measured by an extraction technique.[8,9] Toner concentration series were made using a 30-μm PVF-coated ferrite carrier. γ increased linearly as the concentration of charge agent increased for all three systems. Equation 10 predicts this behavior if the density of surface states on the toner is proportional to the surface concentration of charge agent.

Discussion

Particle Size and Toner Concentration

The agreement between the observed dependence of *m/q* on toner concentration and toner and carrier particle sizes and the relationships predicted by the surface-state model, Eq. 7, supports the basic assumptions of the model, namely:

1. Charging results from equilibrium exchange of charge between toner and carrier.
2. The specific surface areas of the toner and the carrier determine both the concentration of surface charging sites and the potential between the toner and the carrier generated when charge is exchanged.

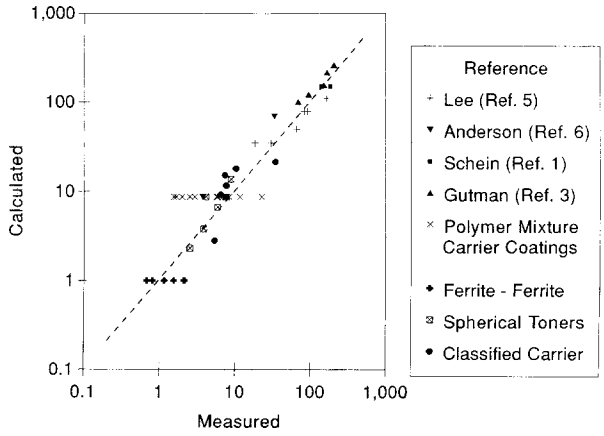

Figure 8. Measured values of γ versus values calculated from Eq. 11. This figure shows that although chemical composition variations affect γ, they are not as important as particle size. (Data for spherical toners were obtained using a series of toners, ranging in size from 8-50 μm, prepared by a limited coalescence technique.[10] The toners were made from an 80% styrene 20% butylacrylate copolymers without charge agent. The carrier used was 30-μm PVF-coated ferrite.)

As stated above, the dependence of the slope or the intercept of toner concentration series on particle size is the same for both the high- and low-density limits of the surface-state model. To differentiate between them, the influence of materials composition on charging behavior must be considered.

Slope/Intercept

Schein[2] reviewed several published data sets that allowed him to test the prediction of the high-density limit that γ can be calculated from particle size and mass densities alone. It is possible to extend Schein's comparison by adding the rest of Lee's data,[5] Gutman and Hartmann's data,[3] and the results presented above for ferrite-ferrite charging, for carrier particle size variations, and for toner and carrier composition changes. The measured γ values are compared in Figure 8 with the values calculated without considering materials composition, using Eq. 11. The data cover a range of more than two orders of magnitude and agree with the calculated values to within a factor of 4. This result is remarkable in that it demonstrates the possibility of calculating measured charging behavior to a first approximation without any adjustable parameters.

Figures 6 and 7 show that γ is not completely independent of the composition of the carrier and the toner. The observed variations might be dismissed as experimental error if it were not for the fact that they occur systematically as either the composition of the carrier coating or that of the toner is varied. Furthermore, it is reasonable to expect that the surface concentration of charging sites on the toner should increase as the surface concentration of charge agent increases, as shown in Figure 7. The observed variation of γ with materials composition is of second order, however.

These results are close to those predicted for the high-density limit. But, as Schein[2] noted, they are also compatible with the low-density limit if $N_t \approx N_c$ for all carriers and toners, which is highly unlikely. The observation that composition effects are of secondary importance suggests that perhaps the full model, Eq. 10, may best describe the experimental data. Deviation of γ from Eq. 11 by less than a factor of 10 implies that $\in_0/de^2N_t \approx \in_0/de^2N_c \sim 1$. Thus, $Nt \approx Nc \approx 5 \times 10^{12}$ eV^{-1} cm^{-2}. This is approximately 1/1000 the measured surface concentration of charge control agent for a typical toner.[8]

q/m Calculations

The surface-state model can also be used to estimate the magnitude of *q/m.* For a typical two-component developer, $r_t = 5$ μm, $\rho_t = $ I g/cc, $r_c = 50$ μm, $\rho_c = 7.0$ g/cc, and $m_t/m_c = 0.02$. The cutoff distance for electron tunneling, 10^{-7} cm, can be used as an estimate for *d.* The difference of the work functions of the toner and carrier surface, $\phi_t - \phi_c$, is of the order of one electron volt. The density of states may be taken to be approximately 5×10^{12} eV^{-1} cm^{-2}. For these values of the parameters the high-density limit, Eq. 8, gives $q/m \approx 2 \times 10^4$,(μC/g. For the low-density limit, Eq. 9 gives $q/m \approx 2 \times 10^3$ μC/g. These values are much greater than typical measured values for *q/m,* 10-50 μC/g. Thus, the surface-state model fails to estimate the magnitude of *q/m* correctly, using the set of assumptions above.

In the high-density limit, if the assumption that *d* is related to electron tunneling were incorrect, and *d* is larger, and/or if the work function difference were smaller, such that $d/(\phi_t - \phi_c) \sim 10^{-4}$, then the calculated magnitude of *q/m* would agree more closely with observed values. In the low-density limit, the densities of states would need to be ~ 10^{11} eV^{-1} cm^{-2} for the predicted value to agree with the experiment.

Gutman and Hartmann[3] have offered other suggestions. In their development of the surface-state model they included the analysis of multiple toner particles on a single carrier particle. They showed that this analysis introduces a correction that is about a factor of two to Eqs. 7 and 8. This correction is insufficient to account for the difference between model predictions and experimental results noted above. Gutman and Hartmann[3] also suggested that the total surface areas of the toner and the carrier are not available for charging. They included the ratio of the surface available for charging to total surface as a factor in their expression for *q/m*. If this approach is correct and the estimates for the other parameters given above are approximately correct, then only 1/1000 of the surface is available for charging.

Conclusion

Further experimental work is desirable to confirm the results related to materials composition presented here. Additional methods of estimating the density of surface states and the fraction of the surface that is actually charged need to be developed.

Acknowledgments

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