Comparison of Triboelectric Measurements of Two-Component Xerographic Developers with the Continuous and Patchy Charge Models

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The two-component xerographic developer charging model of Gutman and Hartmann offers two alternative formulations of the interfacial electric field between toner and carrier, based on the assumption of either a continuous charge distribution on the surface of the toner, or a non-uniform patchy charge distribution. They found that m/q:C measurements on some developers were better described by one version of the model, while measurements on other developers were better described by the other version. In this study, we investigate when each version is applicable. We do this by comparing the two versions of the model with measurements of many different developers prepared with toners and carriers having different physical and chemical formulations that alter how charge is distributed throughout the developer. We found that the carrier surface formulation does not influence which version of the model better fits the data, nor does toner polarity. The main influence is the toner formulation, which creates different toner surface structures that presumably have intrinsically different toner surface charge distributions. We find that the patchy charge version fits the measurements if the carbon black is a minor component on the toner surface and an extremum in the triboelectric series. In contrast, the continuous charge version fits the data if the resin is a major component on the toner surface and also an extremum in the triboelectric series. Also, the continuous charge version of the model fits measurements of toners formulated with a charge control additive (CCA), consistent with the assumption that the particular CCA is uniformly distributed over the toner surface. In addition, we compare the two versions of the model to previously published measurements on a variety of toners with structures similar to those mentioned above, and find that the two versions fit the measurements in a similar pattern.

Journal of Imaging Science and Technology 47: 229–238 (2003)

Introduction

In commercial xerographic equipment with two-component development, the mass of toner particles developed on the photoreceptor depends on the quantity of charge on the toner particles. This is controlled by the triboelectric properties of the toner particles and carrier beads. The triboelectric properties can be characterized by measuring the toner charge-to-mass ratio, q/m, using the blow-off technique. For many developers, the inverse of the charge-to-mass ratio, m/q, is found to vary approximately linearly with toner concentration, C, equal to the mass-of-toner divided by the mass-of-carrier. The slope of the line drawn through the measurements on a plot of m/q versus C is related to the compositions of the toner particles and carrier beads; the intercept on the toner concentration axis depends on the sizes of the toner particles and carrier beads.[1]

To interpret the relationships governing the triboelectric charging of toners and carriers, Gutman and Hartmann (G–H)[1,2] have proposed a physical model that assumes field-dependent contact electrification as the basic contact charge exchange mechanism. The electric field in the gap in the region of contact between a toner particle and carrier bead, E_g, is the sum of the fields due to the contact charge density exchanged during the contact plus the "external field" called the "toner-carrier interfacial field" due to charges outside the region of contact. These include charges from previous contacts distributed on the carrier bead, the toner particle and neighboring toner particles. The derivation of the theoretical relationship between m/q and C depends on the details of this toner–carrier interfacial field. From their physical model, the slope of the line is denoted by A_0^{-1}, where

$$A_0 = \frac{a}{s}\frac{4\pi R^2}{M}\frac{\varepsilon_0}{ed}\left(\sum_j^{TS} P_j\mu_j - \sum_i^{CS} P_i\mu_i\right) = \frac{a}{s}\frac{4\pi R^2}{M}\frac{\varepsilon_0}{ed}\left(\Phi_t - \Phi_C\right) \quad (1)$$

and, where a is the microscopic area of contact of asperities between toner and carrier, s is the area of localized conductivity on the surface of the toner particle, R is the radius of the carrier bead, M is the mass of the carrier bead, e is the electronic charge, d is the electronic tunneling length, $P_{i(j)}$ are contact probabilities for the constituent materials, $\mu_{i(j)}$ are characteristic energy levels for the constituent materials, TS and CS are sums over the constituent materials on the toner and carrier surfaces, re-

Original manuscript received September 18, 2002

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spectively, and $\Phi_{t(C)}$ are the weighted chemical potentials of the toner or carrier. In deriving Eq. 1, G–H assumed the high density of states limit for the formulas that describe microscopic contact electrification. Nash[3] and co-workers have investigated the effect of systematic changes in the constituent materials of toners and carriers on their triboelectric properties. They show that while a developer is being mixed or used in a machine, the values of the contact probabilities may change and this phenomenon must be understood in order to interpret measurements using the G–H model. If the time dependence of the P's is not understood and taken into account during an experiment, the dependence of m/q on C will appear to be anomalous. Gutman and co-workers have recently discussed this situation.[4]

From a plot of m/q versus C, one finds an offset to the toner concentration that is the extrapolated intercept on the C axis and denoted C_0. The theoretical value of this parameter depends on the details of the interfacial electric field. G–H developed two models for the electric field depending on the assumptions they made about the distribution of the charge on the toner particles. The first model was named the "continuous charge model" because the toner charge was assumed to be distributed uniformly on the toner surface. The second model was named the "patchy charge model" because the toner charge was assumed to be concentrated in localized, or patchy, areas on the toner surface. For the electrostatics, they assumed that subsequent contacts of the toner with the carrier will involve charged areas of the toner surface in the continuous model and uncharged areas of the toner surface in the patchy model. These two models lead to different values for C_0. One or the other version of the model could represent different sets of data, but no general trend emerged. We have been curious under what circumstances, which of the two versions of the model might be applicable.

As a starting point, we recalled an experiment by P. Julien and co-workers.[5] They published results for an admix mode they called "toner charge sharing." In this mode the toner particles, which are added to a charged developer ("added toner"), obtain their charge from the incumbent toner particles, which give up some charge, without the carrier initially playing any role. This is in contrast to another admix mode in which the added toner gains its charge from the carrier surface. Their mechanism for charge sharing requires that i) the charge reside on the carbon black, ii) the carbon black is an extremum in a triboelectric series, and iii) the carbon black is not well dispersed within the toner or on the surface, such that there are local regions of conductivity. Their conclusions were based on an experiment using carriers with either a positive or negative coating and a set of toners made with blends of a positive and a negative polymer (which were near the positions of the positive and negative carrier coatings in a triboelectric series) and a carbon black that was in the middle of this triboelectric series. They observed fast admixing times when the carbon black was an extremum (the toner resin blend was between the carbon black and the carrier coating) in the triboelectric series and slow admixing times when the carbon black was between the toner resin blend and the carrier coating in the triboelectric series. Since the charge sharing admix mode presumes the toner charge resides primarily on the carbon black, it seemed that such a toner would be a good candidate to observe the patchy version of the G–H model when the toner was charged negatively and the continuous version of the G–H model when the toner was charged positively.

In this study we compare the electric field models to several sets of data to determine under what circumstances each version of the model applies. In the following sections, we briefly review the G–H model, describe experiments for several sets of developer materials and compare the two versions of the G–H model with this data and other published data.[6]

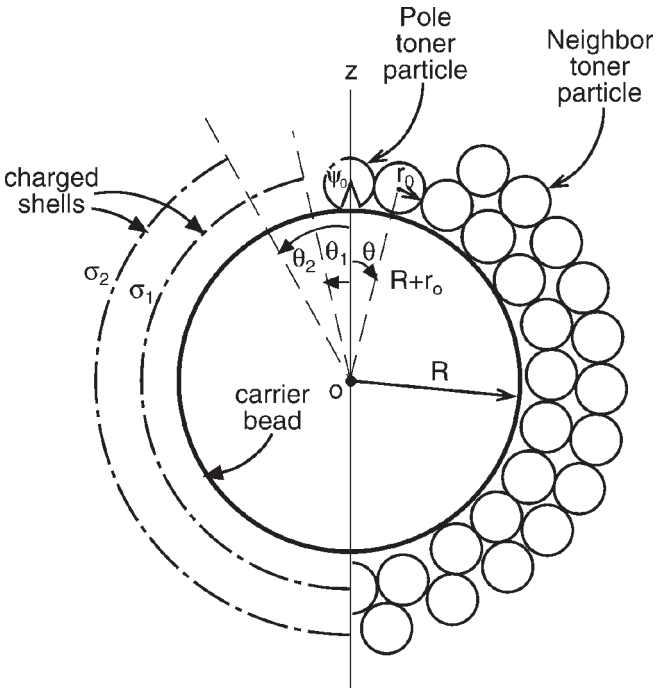

Figure 1. Geometry of the physical model for the patchy charge version. The right-hand side shows the assumed locations of toner particles; the left-hand side represents the electrostatic model. For the continuous charge version, $\Psi_0 = 0$.

Gutman–Hartmann Physical Model for Two-Component Developer Charging

The geometry of the G–H physical model for the patchy charge distribution is shown in Fig. 1. An objective of the model is to calculate the value of the electric field at the point of contact between the toner particle at the pole and the carrier bead. The field is the sum of contributions from charges on the "pole" toner particle, the charges on the carrier bead and the neighboring toner particles. The toner particles in the layer closest to the carrier surface are represented by a spherical shell of charge surrounding the carrier bead and located at $(R + r_0)$, but open at the pole to accommodate the toner particle under study. The toner particles in the second layer are represented by a second shell of charge surrounding the carrier bead and located at $(R + 3r_0)$, but also open at the pole. The radial position of the second layer depends on how the toner particles pack on the carrier bead surface. G–H found that the theoretical results are not very sensitive to the location of the second layer of charge because the layer is relatively far away from the contact point. The first layer can accommodate at most $n_{\text{mono}} = 4p_f R^2/r_0^2$ particles where p_f is the packing factor, approximately 0.5 to 0.6. The remaining $(n - n_{\text{mono}}) = n_2$ particles go into the second layer. Once the second layer is filled, in principle a third layer could be populated. In the present study, we will assign particles to the first layer until it is full and then assign all the remaining particles to a second layer.

G–H developed two versions of the model based on different assumptions about the details of how the charge is

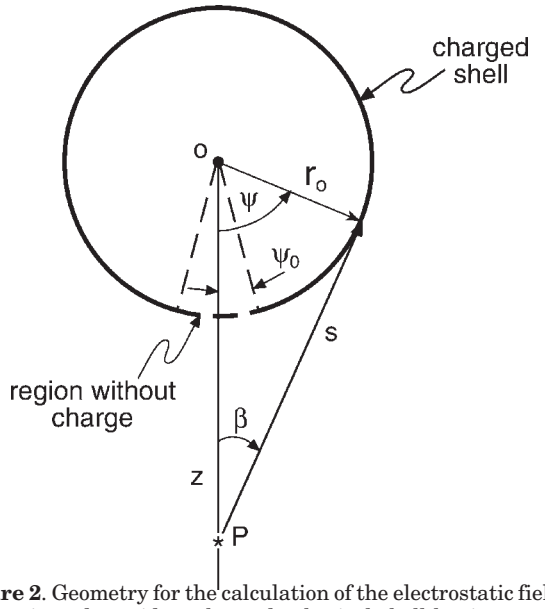

Figure 2. Geometry for the calculation of the electrostatic field on the z-axis and outside a charged spherical shell having a region without charge that subtends an angle, Ψ_0.

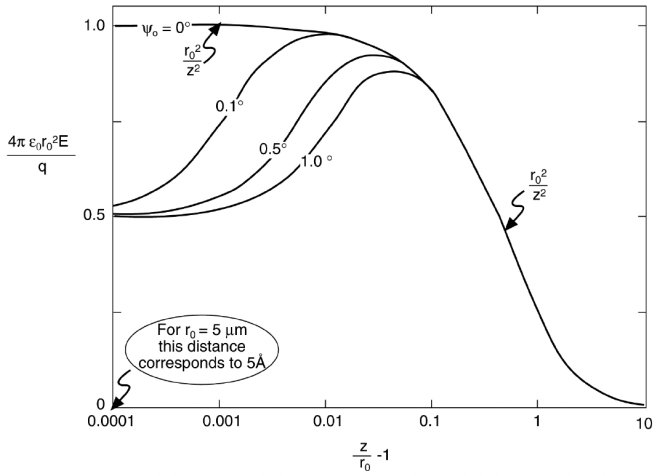

Figure 3. Calculated electrostatic field as a function of the distance, $(z - r_0)$, from the surface of a spherical shell of radius, r_0. The shell has a small region without charge that subtends an angle, Ψ_0, as shown in Fig. 2. The curve labeled $\Psi_0 = 0$ (no missing charge) is the function r_0^2/z^2. As an example, if $z/r_0 = 1.0001$ and $r_0 = 5$ μm, then the distance from the surface is 5 Å.

distributed on the toner particle, which, in turn, affects the toner–carrier interfacial electric field. These two forms of the model are named 'continuous charge model' and 'patchy charge model'. For the continuous charge model, the charge on the toner particle is assumed to be a uniform spherical shell of charge. Consequently, the charge on the toner particle can be represented by a point charge at the center of the toner particle and at a distance, r_0, from the surface of the carrier. In the patchy charge model, the charge on the pole particle is represented as a shell of charge except in the region of contact, Fig. 2. The effect of this small, initially uncharged area is to reduce the field, E_g, in the region of contact. The amount of reduction depends on the angle subtended by this initially uncharged area on the toner surface as shown in Fig. 3. G–H showed that the shell representing charge on the toner surface could be approximated by a ring of charge with radius, r_0, at a distance, r_0, from the carrier surface.

For both cases, the interfacial electric field that results from a consideration of the contribution of all the charges on toner and carrier, is

$$4\pi\varepsilon_0 E = -\frac{q}{r_0^2} f_1(1)\left[1 - G_1(n_1) - G_2(n_2)\right] + \frac{Q}{R^2} \qquad (2)$$

and

$$G_1(n_1) = \frac{n_1}{2f_1(1)} \int_{\cos\theta_1}^{-1} f_1(u)du$$
$$G_2(n_2) = \frac{n_2}{2f_1(1)} \int_{\cos\theta_2}^{-1} f_2(u)du \qquad (3)$$

where $u = \cos(\theta)$, $f(u)$ is a dimensionless function related to the normal field at the surface of the toner particle, $f(u) = (4\pi\varepsilon_0 r_0^2/q)\partial\phi/\partial r\,|_{r=R}$, ϕ is the potential in the cavity generated by the charged toner particle, $f_1(1)$ is a dimensionless parameter related to the strength of the interfacial field at the pole due to the charge on the pole toner particle. The functions $f_1(u)$ and $f_2(u)$ depend on the assumptions of patchy or continuous charge distributions and are the strength of the interfacial field at the pole due to the charge in the shells that represent the remaining $(n_1 - 1)$ particles in the first layer and the n_2 particles in the second layer. The parameter, $f_1(1)$, is approximately unity for the patchy charge model and approximately 2 for the continuous charge model.

When Eq. 2 for the interfacial field is substituted into the G–H physical model2, q/m is given by

$$\frac{q}{m} = \frac{A_0}{C + \Omega_0(C)}(1 - \exp(-t/\tau)) \qquad (4)$$

where A_0 is defined by Eq. 1, and for $n < n_{\text{mono}}$

$$\Omega_0(C) = \frac{r_0\rho_t}{R\rho_C} f_1(1)(1 - G_1(n))$$

and for $n > n_{\text{mono}}$

$$\Omega_0(C) = \frac{r_0\rho_t}{R\rho_C} f_1(1)(1 - G_1(n_{mono}) - G_2(n - n_{mono}))$$

where the number of toner particles, n, and the toner concentration, C, are related by $n = CM/m$, and m and M are the toner and carrier masses, respectively. For long mixing times, $t > \tau$, a simplified expression for m/q, to compare with experimental values, can be obtained from Eq. 4:

$$\frac{m}{q} = \frac{1}{A_0}(C + \Omega_0(C)) \ . \qquad (5)$$

The dependence of $\Omega_0(C)$ on the toner concentration, C, causes a plot of m/q versus C to be slightly non-linear. It is difficult to detect the non-linearity unless a wide range of

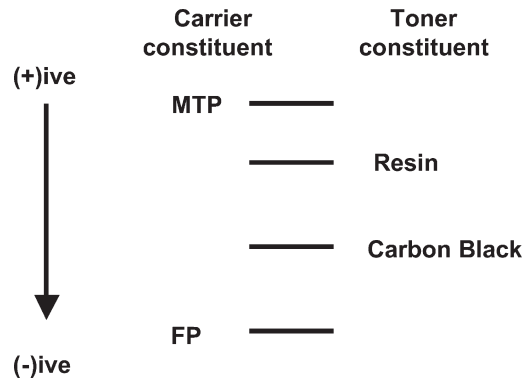

Figure 4. Triboelectric series for the constituent materials used in the charge sharing experiment.

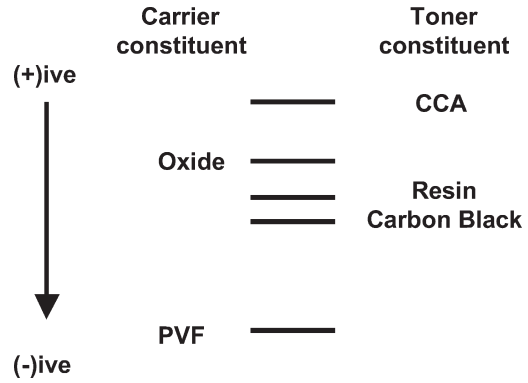

Figure 5. Triboelectric series for the constituent materials used in the 2×2 matrix experiment.

toner concentration is investigated and there is good measurement precision.[2] In the analysis of triboelectric data the term, $\Omega_0(C)$, is often approximated by a constant, called C_0, and in this approximation, m/q is written as

$$\frac{m}{q} = \frac{1}{A_0}(C + C_0). \tag{6}$$

Experiment

Materials – Set 1: Charge Sharing Toner

Carriers: The carriers were made with a ferrite core having a density of ~5 g/cc and a diameter of about 84 μm by number. The core was coated with either a methylterpolymer (MTP) or a fluoropolymer (FP) to obtain positive and negative charging surfaces respectively.

Toner: The toner comprises a copolymer of styrene and *n*-butyl methacrylate and a 10% loading of a high surface area, acidic carbon black. The toner was classified to a particle size of about 8.9 μm by number. This toner formulation (*CS*) will have a toner charge-share admix response when the carbon black is not well dispersed and the toner is charged negatively.[5]

Developers: The developers were prepared by blending about 7 g of the toner with 100 g of either carrier in an 4 oz jar and mixing on a paint shaker for 60 min. Toner concentration and q/m measurements were made at 10 min intervals. The toner concentration of the two developers was changed by using the three step detoning procedure described below for the Set 2 Matrix, except the developers were mixed for 2 min on the paint shaker after each detoning step. The toner concentration and q/m were measured after the 2 min of mixing. While mixing individual developers at the desired toner concentrations would be another method to vary the toner concentration, the three step detoning procedure was used to maintain consistency in the experimental procedure.

Julien's triboelectric series[7] for these materials is shown in Fig. 4.

Materials – Set 2: 2 × 2 Matrix of Carrier Coating and Toner CCA

Carriers: The carriers were an atomized iron-grit powder with volume median diameter of 158 μm and either uncoated, C1, or powder coated with about 0.2% polyvinylidene fluoride (PVF), C2.

Toners: The toners comprise styrene/*n*-butyl methacrylate copolymer melt-mixed with 5 wt.% of an unoxidized carbon black, T1; and with 2 wt.% of a long-chain alkyl pyridinium salt charge control additive (CCA) to produce a positive polarity toner, T2, when mixed with the above carriers. The toner was micronized and classified to a volume median diameter of 11 μm. The carbon black in these toners is well dispersed, and based on data from P. Julien,[7] is near the resin in a triboelectric series. Consequently, toners T1 and T2 do not charge share when charged either negative or positive.

***Developer Preparation*:** The developers were prepared by blending 5 g of each toner with 100 g of each carrier in four 4 oz glass jars The developers form a 2×2 matrix of carriers and toners. The developers were then mixed on a roll mill for 300 min. Toner concentration and q/m measurements were made using approximately one gram samples taken from the individual developer at 5, 10, 15, 30, 60, 120, 240 and 300 min.

Subsequently, the toner concentration of each of the developers was decreased using a three step "detoning" procedure. First, a developer was split into two portions. Second, the toner was completely removed from one portion (the "detoned" portion) by a large-scale analogue of the blow-off procedure used for the q/m measurement. The vessel holding the developer beads was metallic and electrically "earthed" to dissipate the charge build-up on the carrier beads as the toner was removed. The vessel acted like an earthed Faraday cage. Third, the neutral carrier recovered from this "detoned" portion was added back to the other "toned" portion. The developer–carrier mixture was hand tumbled to distribute the carrier beads in the developer beads and then put on the roll mill to mix. Toner concentration and q/m samples were taken after 1, 2, 5 and 10 min of mixing. This three-step procedure was repeated to obtain the desired lower toner concentrations. The purpose of this detoning procedure was to change the toner concentration while maintaining the composition of the toner and carrier surfaces constant.[4]

The triboelectric series for the constituent materials used in the four developers is shown in Fig. 5. The series is based on Julien's work[7] and our experience. For the developers made with toner, T1, for the C1/T1 pair, the carrier surface oxide and the carbon black are the extremes of the triboelectric series. For the C2/T1 pair, the PVF coating and the toner resin are the extremes of the triboelectric series. For the developers made with toner, T2, for the C2/T2 pair, the PVF coating and the CCA are the extremes of the triboelectric series. For the C1/T2 pair, it is more difficult to determine the toner extremum of the triboelectric series *a priori* because the carrier oxide is between the toner CCA and

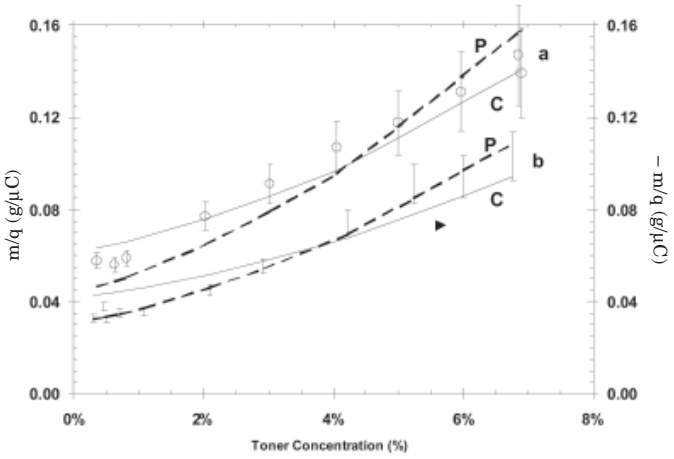

Figure 6. *m/q* versus toner concentration for the CS toner. The toner charges positively against the FP carrier (a) and negatively against the MTP carrier (b). The continuous model is a better fit to the data for the FP carrier; the patchy model is a better fit to the data for the MTP carrier. The error bars represent either ±5% of the *q/m* value or ±1 μC/g whichever is greater.

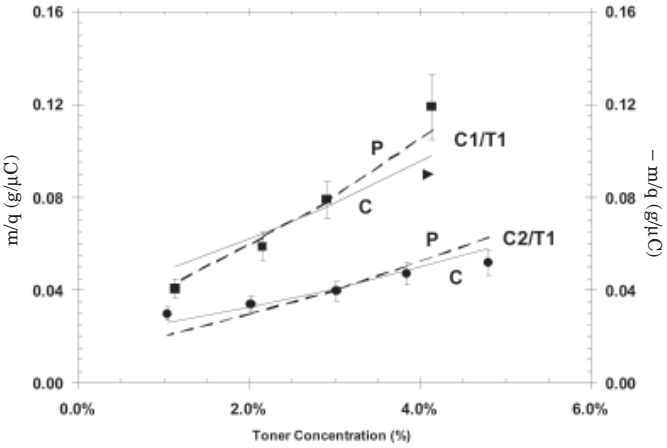

Figure 7. *m/q* versus toner concentration for the toner T1 (without CCA). The toner charges negatively against the uncoated carrier core, C1, and positively against the PVF coated carrier, C2. The patchy (P) model is a better fit to the data for carrier C1; the continuous (C) model is a better fit to the data for carrier C2. The error bars represent either ±10% of the *q/m* value or ±1 μC/g whichever is greater.

carbon black. Knowing the toner charged positively for this pair from a prior experiment, the carrier oxide and the toner CCA are the extremes of the triboelectric series even though the CCA is the least toner constituent material.

Results

Measurements with the Charge Sharing Toner

With a charge spectrograph,[8] we verified the toner had fast charge sharing admix response when charged negatively, and slow admix response when charged positively using a procedure similar to that used in Ref. 5.

Following the initial period of mixing to ensure the developers were fully charged and stable, the developers were detoned to obtain *q/m* as a function of toner concentration. The data for both developers are displayed as *m/q* versus toner concentration in Fig. 6. The error bars represent either ±5% of the *q/m* value or ±1 μC/g whichever is greater. The continuous and patchy G–H models were calculated for these materials. The parameter A_0 was used to adjust the model curves to the data. When the toner was charged negatively, the patchy model (dashed line) is a better fit to the data. For the toner charged positively, the continuous model (solid line) is the better fit to the data.

The A_0 values for both models were selected to simultaneously minimize the standard deviations for both *m/q* and *q/m*. For the model that does not fit the data, one can minimize the standard deviation of *m/q* by adjusting A_0 so that the curve goes through the high *m/q* points (low *q/m* values). Likewise, one can minimize the standard deviation of *q/m* by adjusting A_0 such that the curve goes through the low *m/q* points (high *q/m* values). The alternate model curve, which does not fit the data as well, is a compromise between the curves for low standard deviations of *m/q* and *q/m*. There is not an A_0 value that will make the alternate curve pass through all the data. For the model curve that does represent the data, the A_0 value is the best value for low standard deviations of *m/q* and *q/m*.

Measurements with the 2 × 2 Matrix of Carrier Coating and Toner CCA

The *m/q* data for the matrix of materials are displayed in Figs. 7 and 8. The error bars represent either ±10% of the *q/m* value or ±1 μC/g whichever is greater. Figure 7 shows the

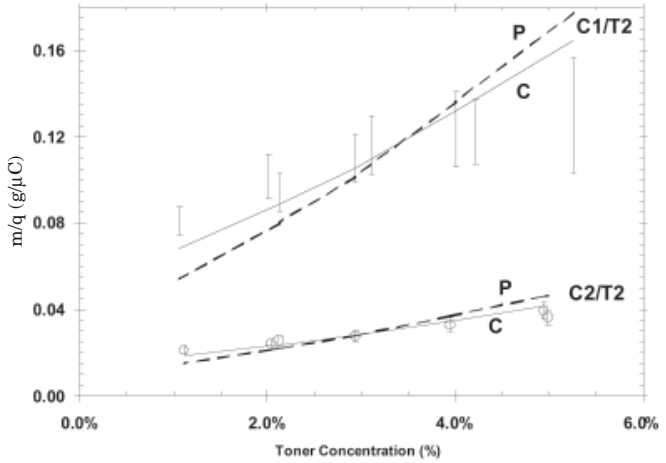

Figure 8. *m/q* versus toner concentration for the toner T2 (with CCA). The toner charges positively against both the uncoated carrier core, C1, and against the PVF coated carrier, C2. The continuous (C) model is a better fit to the data for both carriers. The error bars represent either ±10% of the *q/m* value or ±1 μC/g whichever is greater.

data for the toner without the charge control additive, T1. This toner charges negatively against the uncoated carrier core, C1; and, charges positively against the coated carrier, C2. The curves are the continuous (solid line) and patchy (dashed line) G–H models. The parameter, A_0, was used to adjust the position of the curves in *m/q:C* space. For the C1/T1 carrier–toner combination, the patchy model is the better representation of the data. For the C2/T1 carrier–toner combination, the continuous model is the better representation of the data. The A_0 values are the best values for small standard deviations of both *m/q* and *q/m*. For the alternate model curves, which do not represent the data very well, there is no value of A_0 that will make the curve pass through the data. One can minimize the standard deviation of either *m/q* or *q/m* but then the curve does not pass through the low *m/q* points or the high *m/q* points. The A_0 value chosen for this situation is the best compromise.

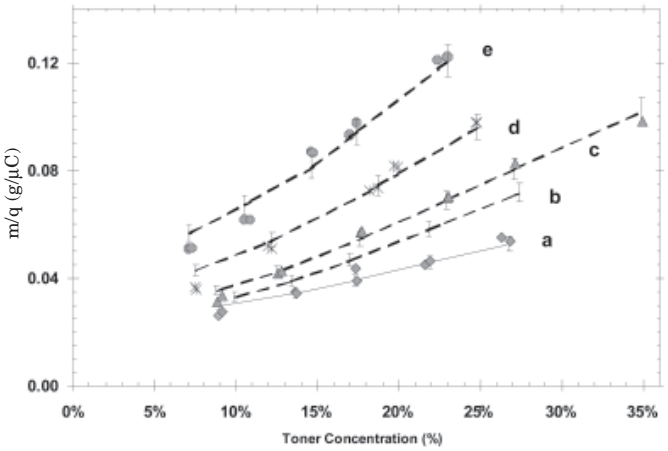

Figure 9. The curves are the G–H patchy model fit to the data from Ref. 6 for the 1 to 10% carbon black loaded toners, which were charged negatively by the PMMA carrier: (b) 1%, (c) 2%, (d) 5%, (e) 10%. The curve for the 0% toner (a) is the G–H continuous model. The bars indicate a range about the model values of ±5% or ±0.2 μC/g whichever is larger.

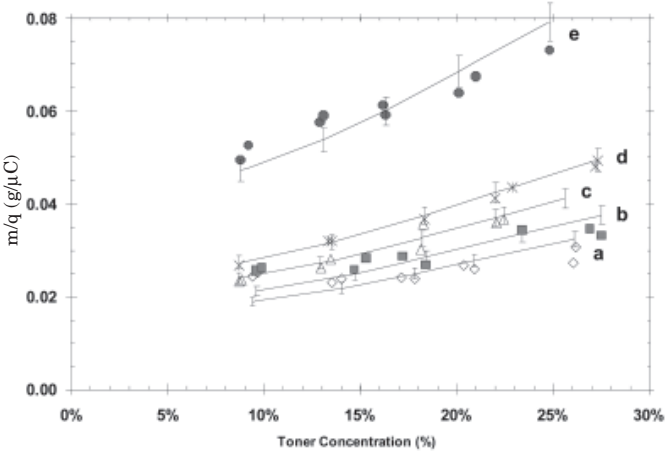

Figure 11. The curves are the G–H continuous model fit to the data from Ref. 6 for the 0 to 10% carbon black loaded toners, which were charged positively by the FP carrier: (a) 0%, (b) 1%, (c) 2%, (d) 5%, (e) 10%. The bars indicate a range about the model values of ±5% or ±0.2 μC/g whichever is larger.

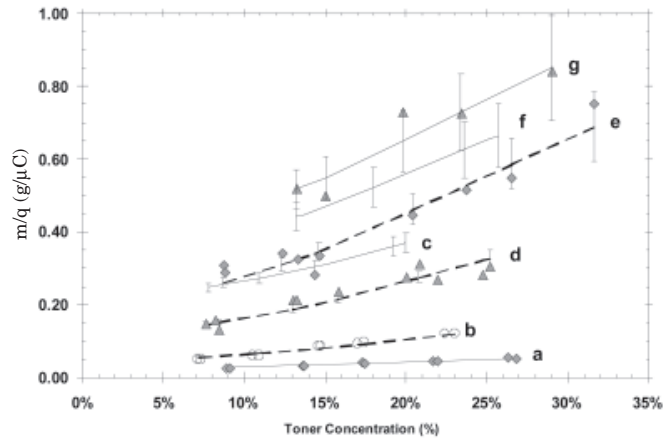

Figure 10. The curves are the G–H model fit to the data from Ref. 6 for the 0 and 10 to 40% carbon black loaded toners, which were charged negatively by the PMMA carrier: (a) 0%, (b) 10%, (c) 15%, (d) 20%, (e) 25%, (f) 30%, (g) 40%. Curves a, c, f and g are the G–H continuous model; curves b, d and e are the G–H patchy model. The bars indicate a range about the model values of ±5% or ±0.2 μC/g whichever is larger.

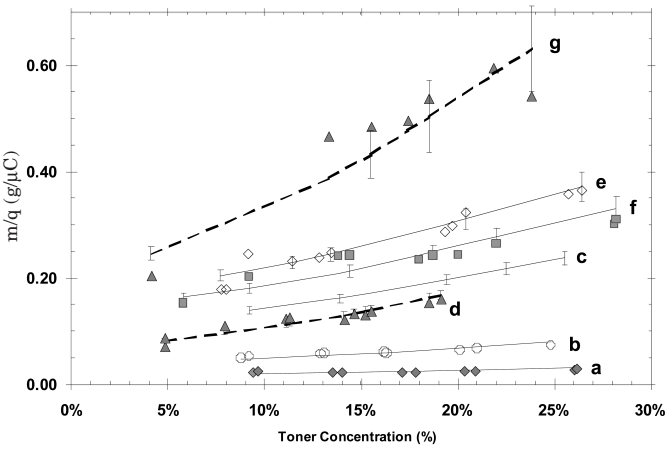

Figure 12. The curves are the G–H models fit to the data from Ref. 6 for the 0 and 10 to 40% carbon black loaded toners, which were charged positively by the FP carrier: (a) 0%, (b) 10%, (c) 15%, (d) 20%, (e) 25%, (f) 30%, (g) 40%. Curves a, b, c, e and f are the G–H continuous model; curves d and g are the G–H patchy model. The bars indicate a range about the model values of ±5% or ±0.2 μC/g whichever is larger.

Figure 8 shows the data for the toner with the charge control additive, T2. This toner charges positively against both carriers, albeit the coated carrier imparts more charge as expected. The continuous charge model is the better representation of the data for both carriers.

Comparison of the Continuous and Patchy Versions of the G–H Model to the Data of Anderson (Ref. 6)

J. Anderson[6] has published data for a series of toners in which the carbon black loading was varied from 0 to 40%. The 10 toners were mixed with a carrier that would charge them either positively (FP) or negatively (PMMA). We reproduce his data in Figs. 9 through 12. We calculated the patchy and continuous G–H models for the data based on the published toner and carrier sizes and used the A_0 parameters to adjust the model curves to the data. The better curve for each toner–carrier pair was selected based on the smallest standard deviations for m/q and q/m. In most cases the decision was straight forward. The better curves are shown in the figures. Figure 13 shows the 10% toner data and both the continuous and patchy charge models. The continuous model is a better representation of the data when the toner is charged positively and the patchy model is better when the toner is charged negatively.

The A_0 values and standard deviations of m/q and q/m for the continuous and patchy models, for Materials Set 1, Set 2 and for the data of Anderson are listed in Table I. An asterick in the table indicates the model that we judged to better represent a data set based on the standard deviations of both m/q and q/m.

TABLE I. A_0 Parameters and Standard Deviations for the Two Models

Carrier/ Toner	Continuous Version of the Model				Patchy Version of the Model			
	A_0	Std Dev m/q	Std Dev q/m		A_0	Std Dev m/q	Std Dev q/m	
Charge Sharing Toner Experiment								
MTP/CS	–100	9.296×10^{-3}	4.83		–67	3.579×10^{-3}	1.32	*
FP/CS	68	6.762×10^{-3}	1.21	*	47	1.423×10^{-1}	4.10	
2x2 Matrix of Carrier Coating and CCA in Toner								
C2/T1	105	3.776×10^{-3}	2.90	*	80	7.651×10^{-3}	7.62	
C1/T1	–55	1.398×10^{-2}	3.10		–40	6.569×10^{-3}	1.24	*
C2/T2	150	2.890×10^{-3}	3.59	*	112	6.139×10^{-3}	8.39	
C1/T2	39.7	1.932×10^{-2}	1.47	*	31	2.918×10^{-2}	3.37	
Carbon Black Loading Experiment (data from Ref. 6)								
Toner Charged Negatively								
PMMA/0%	–715	1.989×10^{-3}	1.828	*	–520	2.074×10^{-3}	1.835	
PMMA/1%	–613	6.612×10^{-3}	4.141		–421	2.733×10^{-3}	3.061	*
PMMA/2%	–495	6.419×10^{-3}	3.811		–371	2.432×10^{-3}	1.393	*
PMMA/5%	–395	9.205×10^{-3}	4.114		–287	3.871×10^{-3}	2.134	*
PMMA/10%	–303	1.111×10^{-2}	2.605		–213	5.137×10^{-3}	1.295	*
PMMA/15%	–83	1.770×10^{-2}	0.199	*	–58	2.582×10^{-2}	0.371	
PMMA/20%	–118	2.473×10^{-2}	0.750		–85	2.457×10^{-2}	0.490	*
PMMA/25%	–70	5.642×10^{-2}	0.292		–49	3.799×10^{-2}	0.310	*
PMMA/30%	–55	1.608×10^{-2}	0.059	*	–40	2.695×10^{-2}	0.094	
PMMA/40%	–47	4.683v	0.121	*	–35	6.364×10^{-2}	0.158	
Toner Charged Positively								
FP/0%	1140	3.470×10^{-3}	6.51	*	810	5.297×10^{-3}	10.19	
FP/1%	1020	3.155×10^{-3}	4.62	*	680	6.278×10^{-3}	6.74	
FP/2%	885	1.573×10^{-3}	1.51	*	608	3.036×10^{-3}	2.90	
FP/5%	773	8.534×10^{-4}	0.59	*	576	3.203×10^{-3}	3.33	
FP/10%	450	4.212×10^{-3}	1.21	*	318	8.563×10^{-3}	2.73	
FP/15%	153	2.756×10^{-2}	0.79	*	110	4.082×10^{-2}	1.28	
FP/20%	195	9.869×10^{-3}	1.19		129	8.976×10^{-3}	0.84	*
FP/25%	100	1.718×10^{-2}	0.38	*	71	2.987×10^{-2}	0.47	
FP/30%	118	2.155×10^{-2}	0.40	*	85	3.987×10^{-2}	0.77	
FP/40%	58	5.932×10^{-2}	0.72		42	5.791×10^{-2}	0.41	*

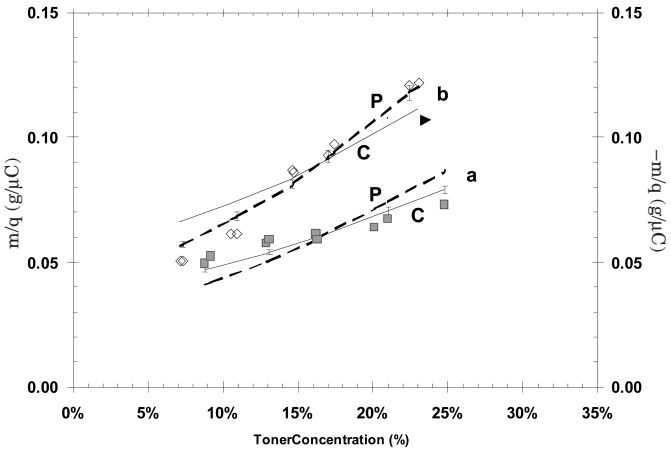

Figure 13. A comparison of the G–H continuous (C) and patchy (P) models fit to the data for the 10% carbon black toner charged positively against the FP carrier (a) and negatively against the PMMA carrier (b). The error bars indicate a range about the model values of ±5% or ±0.2 μC/g, whichever is larger.

Discussion

Charge Sharing Toner

In Table I, the A_0 values for both versions of the model are listed for each set of data. The source of the two different A_0 values is the requirement that the curve must pass through the data points and the calculated $\Omega_0(C)$ values. The $\Omega_0(C)$ values were obtained from the calculations of the toner–carrier interfacial electric field and were different for the patchy and continuous charge models. The A_0 value is then used to position the model curve through the data in m/q:C space, i.e., A_0 is used as a fitting parameter. The reciprocal of the A_0 value is the slope of the curve. As an example, consider the data for the negatively charged toner in Fig. 6. The curve for the continuous charge model does not pass through the data very well, whereas the curve for the patchy model does. We note that the standard deviations for the model that better fits the data were comparable to our measurement precision, indicating very good fits.

The data in Fig. 6 are consistent with our hypothesis that, for a charge sharing toner, the patchy charge model would better represent the data when the toner was negatively charged and the continuous charge model would be

a better representation of the data when the toner was positively charged. Since the carbon black loading was 10% by weight and moderately dispersed, the surface of the toner should consist of mostly resin with local areas of carbon black. From Julien's triboelectric series,[5,7] shown in Fig. 4, we infer that when the toner was negatively charged, the carbon black was more negative than the resin and controlled the charge on the toner. The areas of carbon black had large negative charge compared to the negative charge on the resin. Since these areas are scattered on the toner surface, the charge would appear "patchy". Likewise, when the toner was positively charged, we infer that the resin was more positively charged than the carbon black. Since the resin comprises most of the toner surface, the charge would appear to be more continuously distributed. The results of fitting the G–H models to the data are consistent with these ideas. The patchy model fits the data better when the carbon black is a minor constituent on the toner surface and an extremum in the triboelectric series. The continuous model fits the data better when the resin is a major constituent on the toner surface and is an extremum in the triboelectric series

2 × 2 Matrix of Carrier Coating and Toner CCA

One might think that the carrier formulation may influence which version of the model better describes the data, e.g., the MTP coating on the positive carrier might be less continuous (or more patchy) than the FP coating on the negative carrier. The 2 × 2 matrix was done to evaluate(i) the effect of a uniform or non-uniform distribution of materials on the carrier surface, (ii) the effect of a low loading of a carbon black that is both well dispersed on the toner surface and slightly more negative than the toner resin in a triboelectric series, and (iii) the effect of an ionic charge control additive. The carrier, C1, the core material, has a homogenous oxide surface (uniform surface), whereas the coated carrier, C2, has a very heterogeneous surface, consisting of islands of very electronegative coating and large areas of oxide (a non-uniform surface with several materials). Regarding the toners used in the matrix, the toner without the charge control additive, T1, has a surface with discrete areas of carbon black. For toner, T2, it is believed from our experience that the ionic CCA is uniformly dispersed on the surface of both resin and carbon black

Figure 7 displays the data and models for the developers made with toner T1. The patchy charge model is consistent with the data for the developer C1/T1 (uniform carrier surface), whereas the continuous charge model is consistent with the data for the developer C2/T1 (non-uniform carrier surface). For developer C1/T1, in which the carbon black is the minor constituent material and an extremum in the triboelectric series, Fig. 5, we expect the patchy model to apply. For developer C2/T1, in which the resin on the toner surface is the major constituent material and an extremum in the triboelectric series, Fig. 5, we expect the continuous model to apply. Both of these results are consistent with the charge sharing toner experiment. Even when the electronegative PVF carrier coating, which imparts the positive charge to the toner, is non-uniformly distributed on the carrier surface, the continuous model fits the data. The applicable model does not depend on the carrier surface.

Figure 8 displays the data for the developers made with toner T2, containing the positive charge control additive, CCA. In both developers the toner was positively charged and the CCA is the toner extremum material in the triboelectric series, Fig. 5. For both developers made with toner, T2, the continuous model applies, from which we infer that the CCA is uniformly distributed on the toner surface. If the CCA were not uniformly distributed, one might expect that the patchy charge model would better fit the data, as in the case when the carbon black is a minor toner constituent and an extremum in the triboelectric series. Again, there is no correlation between the choice of charge model and the surface of the carriers.

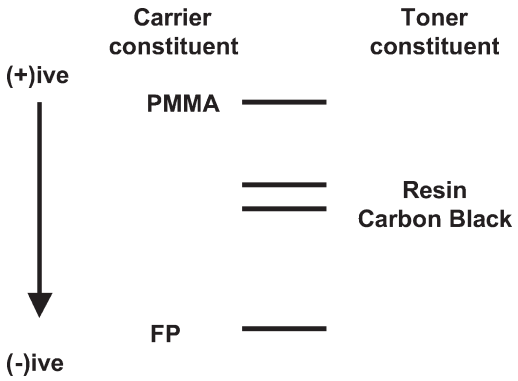

Figure 14. Hypothetical triboelectric series for the constituent materials used in the carbon black loading experiment from Ref. 6.

Data of Anderson (Ref. 6)

The results of fitting the G–H model to Anderson's data[6] are listed in Table I. For both toner polarities, the magnitudes of the A_0 values decrease with increasing carbon black loading. These A_0 values seem to be inconsistent with the idea of a triboelectric series, in agreement with Anderson's conclusions. To explain this result, he proposed that the conductive nature of the carbon black introduces a "backflow" of charge when the toner particles are being charged. This backflow of charge is a result of the conductive nature of the carbon black.

The G–H model offers an alternate explanation for the apparent lack of consistency of the A_0 values with a triboelectric series. In Eq. 1, A_0 is inversely proportional to s, the area of local conductivity on the toner surface. Below 10% carbon black loading, Anderson proposed that localized clusters of carbon black form and these clusters give rise to regions that are electrically isolated from one another. Above a 10% carbon black loading, the localized areas of conductivity become electrically connected forming larger areas of localized conductivity and conductive paths in the toner particles. Hence, for all carbon black loadings, it seems reasonable to hypothesize that the size of these localized regions of conductivity are dependent on the carbon black loading, i.e., s increases with carbon black loading.[9] From Anderson's conclusion that the weighted chemical potentials of the toners, Φ_t, are independent of the carbon black loading, it follows that, independent of the toner polarity, the quantity, $(\Phi_t - \Phi_C)/s$, and, hence, A_0, would decrease as the carbon black loading is increased.

The assumed triboelectric series for these developers is shown in Fig. 14. From Julien's work,[7] we have assumed that the carbon black is somewhat more negatively charging than the toner resin and both resin and carbon black are between the PMMA and FP carrier coatings. If Φ_t is independent of carbon black loading, then from Eq. 1, the chemical potentials of the carbon black and the resin are approximately equal, $\mu_{CB} \cong \mu_R$. As the carbon black loading is increased, the surface of the toner changes from resin as the major constituent material to a nearly equal mixture of resin and carbon black and eventually to carbon black as the major surface constituent material but $(\Phi_t - \Phi_C)$ remains nearly constant.

There is a pattern as to which version of the G–H model better fits the data. When the resin and FP carrier coating are the extremes in a triboelectric series, the toners are charged positively. The continuous charge model fits the measurements when the resin is the major surface constituent material at low carbon black loading. As the carbon black loading increases, we would expect to find some loading at which the resin becomes the minor surface constituent material and the carbon black is the major constituent material. When the resin is the minor constituent material we might expect the patchy model to fit the data. For a 40% loading we found the patchy model fits the data. We do not have an explanation for the 20% toner.

When the carbon black and PMMA carrier are the extremes in the triboelectric series, the toners are charged negatively. In the case of the 0% toner, when the surface is uniformly resin, one would expect the continuous model to apply. Our goodness of fit criterion slightly favors the continuous model but the patchy model is almost as good. The patchy model fits the data when the carbon black is the minor constituent material on the toner surface, with the exception of the 15% toner, for which we do not have an explanation. Eventually the carbon black may become the major constituent material on the toner surface, as discussed above. For the 30% and 40% loading, we found that the continuous model better represents the data.

With our assumption that the carbon black is somewhat more negatively charging than the toner resin, Anderson's data offers a good example of the conditions under which the continuous and patchy charge models should apply. All the experiments, in fact, suggest the following rules. When the major constituent material on the toner surface is an extremum in a triboelectric series for the developer materials, the continuous model applies. And, when the minor constituent material on the toner surface is an extremum in a triboelectric series for the developer materials, the patchy model applies.

Other Models

G–H's assumption of electric field dependent contact charging leads to the model prediction of the nearly linear dependence of m/q on toner concentration. The assumptions and geometry used for the electric field calculation lead to refinements of the predicted dependence of m/q on toner concentration. The simplest geometry is that of a uniform, spherical charge distribution on the toner surface. G–H were motivated to look at the geometry for a patchy toner surface charge by the work of Hays[10] on toner adhesion to substrates. He found that the electrostatic force of adhesion could be greatly increased depending on the toner surface charge distribution and the size of the area of contact. The toner charging process leads to a patchy toner surface charge. As we have observed in this study, if the data have very much scatter, one can still observe the nearly linear dependence of m/q on toner concentration but it is difficult to distinguish which version of the model provides the better fit.

An electric field model for triboelectric charging, which incorrectly represents the electric field at the carrier surface as

$$E = \frac{1}{4\pi\varepsilon_0}\left(\frac{Q}{R^2} - \frac{q}{r^2}\right), \qquad (7)$$

is similar to the continuous version of the G–H model, in that both are based on the assumption and geometry of uniform spherical charge distributions on the surfaces of the toner and carrier. However, such a model is not correct because the electric field for two point charges does not satisfy Maxwell's equations when the carrier bead is composed of a conductive or dielectric material. (See Appendix.*) The effect of a "patchy" toner surface charge distribution (Figure 1) on the electric field at the point of contact can only be discovered by solving Maxwell's equations for that geometry. G–H found that the patchy toner surface charge distribution predicted a steeper dependence of m/q on toner concentration than the continuous toner surface charge distribution. The difference in the two versions of the G–H models is manifested by a factor of two in the term, C_0, as discussed in Ref. 2.

Summary

A key assumption in the G–H model is electric field-dependent triboelectric charge exchange. Two models were derived by G–H for the electric field based on the assumption of 1) a continuous charge distribution on the toner particle or, 2) a "patchy" charge distribution on the toner particle. Developers were formulated with various toners and carriers having different surface structures and triboelectric properties to investigate under what circumstances the two electric field models applied. Beginning with Julien's proposal that charge sharing admix response requires the carbon black to be an extremum in a triboelectric series, we measured the m/q:C response of a charge sharing toner. When the carbon black was an extremum, the patchy charge model applied; when the resin was an extremum, the continuous charge model applied. We then investigated the role of the carrier and the use of a charge control additive in the toner. We found that the carrier surface did not affect which model provides the better fit. The patchy model provided the better fit only when the carbon black was an extremum in a triboelectric series. For either carrier, the continuous model provided the better fit for the toner with the CCA implying the CCA was uniformly distributed on the toner surface. Finally, with the data of Anderson,[6] we confirmed that when either the resin or the carbon black is the major toner surface constituent and an extremum in a triboelectric series, the continuous model better represents the measurements. Conversely, when either the resin or the carbon black is the minor toner surface constituent and an extremum in a triboelectric series, the patchy model better describes the data.

* The *Apppendix can be found on the IS&T website (www.imaging.org) for a period of no less than two years from the date of publication.*

Acknowledgement. We are deeply grateful to Dr. J. Anderson for providing the tabulated data from his work of Ref. 6 and reproduced in Figures 9 through 12. We also thank Dr. G. C. Hartmann for a careful reading of this article and helpful discussions.

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