# A Method for Quantitatively Determining Triboelectric Series and Its Applications in Electrophotography

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The charging behavior of toner particles in two-component electrophotographic developers is consistent with a thermodynamic model of charging. This model, often referred to as the "surface state model," provides a basis for determining triboelectric series. It can also be used to predict the magnitude of charge exchanged between particles provided the model parameters are known for each material. The surface state model was used in conjunction with triboelectric measurements to demonstrate this capability. Model parameters were determined experimentally from two-component mixtures made from several carriers and toners. The model was then used to calculate charging in three-component mixtures of the same toners and carriers. Excellent agreement was found between calculated and experimental charge-to-mass ratios. Multicomponent developer mixtures may arise in many practical situations, such as the introduction of new toner formulations into an existing product, cross-contamination of developers in multicolor copiers, and changes in the charging properties of toners and carriers resulting from developer aging in service. The presence of more than two components in a developer often causes developers to fail. The ability to predict tribocharging behavior of individual components in a multicomponent developer mixture is very useful in explaining observed developer failures and identifying potential problems. Several applications of surface state models in practical situations are discussed.

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## Introduction

Triboelectrification, charging by rubbing two materials together, is the oldest known manifestation of electricity. In spite of this long history and the recent rapid advances in electronic technology, triboelectricity remains one of the least understood electrical phenomena. There is no consensus on what charged species are exchanged or on the mechanism where charging occurs. Nonetheless, tribocharging of powders can be controlled very precisely making it possible to use tribocharged particles to make high quality images in electrophotographic copiers and printers.

One approach toward understanding triboelectrification has been the construction of triboelectric series. It has long been known that it is possible to arrange materials in a sequence such that a material higher in the sequence charges positively against one lower in the sequence. These sequences are known as "triboelectric series." An example of a triboelectric series is shown in Fig. 1.[1] Using triboelectric series, it is possible to predict the sign of the charge on particles of a particular material in a mixture of two materials. For example, poly(methylmethacrylate), which is at the top of the series, charges positively against poly(vinylidine fluoride), which is at the bottom of the series. Thus, triboelectric series are useful when determining the sign of the charge on a material in a mixture of two powders. They are of little help, however, in finding the magnitude of the charge or in predicting tribocharging behavior in multicomponent powder mixtures.

Julien took a major step in this direction by showing that tribocharging of toners containing different carbon blacks can be correlated with the contact potential of the carbons.[2] His approach cannot be extended to other toners because of the difficulty of determining contact potentials or surface chemical potentials of insulating materials. It was recently shown that the surface state model of tribocharging can be used to determine relative work functions of toners by analyzing the charging of toner against a series of carriers with different triboelectric properties.[3] The relative work functions

Poly(methylmethacrylate)
Polyester
Poly(styrene)
Poly(ethylene)
Uncoated sponage iron
Cellulose nitrate
Poly(vinylidene fluoride)

**Figure 1.** Triboelectric series obtained by charging a reference toner against sponge iron carrier particles coated with a variety of materials. (Abstracted from Ref. 1.)

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determined from the surface state model are linearly correlated with Julien's measured contact potentials.[4] Although work functions established in this way can be used to construct triboelectric series, these series cannot be used to estimate charge-to-mass ratios in electrophotographic developers unless the work function of the carrier is also known.

The purposes of this investigation are: (1) to demonstrate that the surface state model of triboelectrification of two-component mixtures of powders can be used to establish triboelectric series for both toners and carriers; (2) to show how this information can be used to predict charge-to-mass ratios in two- and three-component powder mixtures; and (3) to suggest potential applications of these results to electrophotographic developers.

## Charging in Powder Mixtures

### Two-Component Powder Mixtures

The surface state model treats charging as the exchange of charged species (electrons or ions) between carrier and toner surfaces. The amount of the charge exchanged is determined by thermodynamic equilibrium of the charged species in energy states available to them on the surface of the toner and the carrier.[5–9] The model has proven to fit charging in two-component mixtures well.

There are several versions of surface state models that give equivalent descriptions of tribocharging[5–9] that can be adapted to the analysis given below. The particular version of the surface state model used in this article was developed by Anderson[8] and was used because it incorporates both the high and low density of states limits described below. It uses two parameters to characterize the triboelectric properties of each material and was found to fit the data better than the high density of states limit which uses only one parameter. This point is discussed further below.

Analysis of the equilibrium charge exchanged between the toner and the carrier leads to the following relationship between the mass-to-charge of the toner particles, $m/q$, and the mass ratio of toner-to-carrier in the developer, T/C: [8]

$$m/q = \frac{-d}{3\varepsilon_0(\phi_t - \phi_c)}\left(\left\{\frac{\varepsilon_0}{N_t e d}+1\right\}\rho_t r_t + T/C\left\{\frac{\varepsilon_0}{N_c e d}+1\right\}\rho_c r_c\right) \quad (1)$$

In Eq. 1, $d$ is a characteristic separation distance between the particle surfaces during charging, $\varepsilon_0$ is the permittivity of free space, $\phi$ is the work function in ev, $r$ is the particle radius, $N$ is the density of surface states in numbers/m$^2$/ev, $-e$ is the charge on the electron, $\rho$ is the mass density of the particles, and T/C is the mass ratio of toner to carrier. The subscripts, $t$ and $c$, refer to the toner and carrier, respectively. This equation predicts a linear relationship between $m/q$ and T/C. The slope and intercept depend upon the difference in work function between the toner and the carrier, the surface area of the particles, and the densities of surface electronic states. Plots of this type are referred to below as "TC series." Experiments using two-component mixtures by a number of workers have borne out the general features of this model.[5–10] For example, the linear relationship between $m/q$ and T/C and the dependence of the slope and intercept of Eq. 1 on particle size are well established.[6–12]

The reciprocal of Eq. 1 shows how charge-to-mass, $q/m$, is related to the densities of states and the work functions.[8]

$$\frac{q}{m} = \frac{-3\varepsilon_0(\varphi_t - \varphi_c)}{d}\left\{\left[\frac{\varepsilon_0}{N_t e d}+1\right]r_t\rho_t + T/C\left[\frac{\varepsilon_0}{N_c e d}+1\right]r_c\rho_c\right\}^{-1} \quad (2)$$

Equation 2 predicts that the sign of the difference between work determines the sign of the charge on the toner functions of the toner and the carrier. If the work functions are known, they can be used to rank order materials in a triboelectric series. In a two-component mixture, the material with the higher, larger work function will charge negatively. Thus, listing materials in ascending order of work functions produces a triboelectric series. If, in addition, the densities of states are known or if the high density of states limit applies, then Eq. 2 can be used to predict $q/m$.

Two limiting cases of Eq. 1 have been discussed. If $\varepsilon_0/N_t\ e\ d >> 1$ and $\varepsilon_0/N_c\ e\ d >> 1$ then Eq. 1 reduces to

$$m/q = \frac{-1}{3(\phi_t - \phi_c)}\left[\left\{\frac{\rho_t r_t}{N_t e d}\right\} + T/C\left\{\frac{\rho_c r_c}{N_c e d}\right\}\right] \quad (3)$$

Equation 3 is referred to as the "low density of states limit." If $e_0/N_t\ e\ d << 1$ and $e_0/N_c\ e\ d << 1$ then Eq. 1 reduces to

$$m/q = \frac{-d}{3\varepsilon_0(\phi_t - \phi_c)}(\rho_t r_t + T/C\ \ \rho_c r_c) \quad (4)$$

Equation 4 is referred to as the "high density of states limit."

Equation 1 in conjunction with experimental charge measurements can be used to assign values to $N_t$, $N_c$, $\phi_t$, and $\phi_c$. The procedure is as follows: First, TC series plots are determined experimentally for a set of materials of interest. For example, in the simplest case, TC series plots can be determined for the four two-component mixtures which can be made from two toners and two carriers. An initial guess is made for the work functions and densities of states of the four materials. Next, Eq. 1 is used to calculate $m/q$ for the TC series of each mixture. The RMS error between the measured and calculated $m/q$ values are then determined. A small random change in each of the parameters is made. If the RMS difference between the measured and calculated $m/q$ values is larger for the modified parameters, they are discarded and the original guess is saved. If the modified parameters improved the RMS difference, they are saved. The saved set is then used as the basis for the next search. These steps are repeated until a minimum in the RMS difference is found. Several sets of initial guesses should used to insure that the best fit set of parameters have been found.

The work functions found are not unique. It is clear from Eqs. 1 and 2 that adding a constant to all of the work functions does not change the results. Furthermore, for a given set of data, examination of Eq. 1 shows that the values of $\phi_t$, $\phi_c$, $N_t$, and $N_c$ found, depend upon each other and the value of $d$. In this study $d$ was taken to be $10^{-9}$ m, and the values of $\phi_t$, $\phi_c$, $N_t$, and $N_c$ were the best fit set found from regression as indicated above.

### Multicomponent Powder Mixtures

In developing the model that leads to Eq. 1, it was assumed that all the particles in a mixture are in chemical

**TABLE I. Materials**

| Carriers | Toners |
|---|---|
| A. Aged poly(vinylidine fluoride) coated ferrite (2 wt%).* | 1. Cyan polyester–amide toner. |
| | 2. Magenta polyester toner. |
| B. Fresh poly(vinylidine fluoride) coated ferrite (1 wt%). | 3. Cyan polyester toner. |
| | 4. Black polyester toner. |
| C. Fresh poly(vinylidine fluoride) coated ferrite (2 wt%). | 5. Cyan polyester–amide toner recovered from aged developer. |
| D. Aged poly(vinylidine fluoride) coated ferrite (1 wt%).* | 6. Yellow polyester toner recovered from aged developer. |
| E. Uncoated ferrite. | 7. Black styrene–acrylic toner. |
| | 8. Yellow styrene–acrylic toner. |

* washed with solvent to remove residual toner.

equilibrium. In a two-component mixture this means that the mixing of the powder during charging is vigorous enough that the entire surface of each component of the mixture comes into frequent contact with the other surfaces. This assumption can be used to extend the model from two-component to multi-component mixtures. Gutman and Hartmann used similar reasoning to describe the charging behavior of heterogeneous surfaces.[6]

During charging of a multi-component mixture, charges (assumed in this model to be electrons) are exchanged among the components that become charged. However, charge conservation requires the mixture to have no net charge. Overall, charge neutrality can be expressed as:

$$\sum_i f_i \left(q/m\right)_i = \frac{3\varepsilon_o}{d} \sum_i f_i \left(E_f - \varphi_i\right) \left[\left(\frac{\varepsilon_0}{N_i e\, d} + 1\right) r_i\, \rho_i\right]^{-1} = 0. \quad (5)$$

In Eq. 5 $E_f$ is the equilibrium Fermi level of the mixture, and $f_i$ is the mass fraction of component $i$ in the mixture, and the other parameters are as defined above.

$$\text{Solving for } E_f: \quad E_f = \frac{\sum_i f_i\, \varphi_i \left[\left(\frac{\varepsilon_0}{N_i e\ d} + 1\right) r_i\, \rho_i\right]^{-1}}{\sum_i f_i \left[\left(\frac{\varepsilon_0}{N_i e\ d} + 1\right) r_i\, \rho_i\right]^{-1}} \quad (6)$$

The charge to mass of a particular component in the mixture, $(q/m)_j$, can be written as:

$$(q/m)_j = -\frac{3\varepsilon_0}{d} \left(\varphi_j - E_f\right) \left[\left(\frac{\varepsilon_0}{N_j e\ d} + 1\right) r_j\, \rho_j\right]^{-1} \quad (7)$$

Substituting Eq. 6 into Eq. 7:

$$(q/m)_j = -\frac{3\varepsilon_0}{d} \left( \varphi_j - \frac{\sum_i f_i\, \varphi_i \left[\left(\frac{\varepsilon_0}{N_i e\ d} + 1\right) r_i\, \rho_i\right]^{-1}}{\sum_i f_i \left[\left(\frac{\varepsilon_0}{N_i e\ d} + 1\right) r_i\, \rho_i\right]^{-1}} \right) \left[\left(\frac{\varepsilon_0}{N_j e\ d} + 1\right) r_j\, \rho_j\right]^{-1} \quad (8)$$

The reciprocal of Eq. 8 predicts that $m/q$ for each component of a mixture should be a linear function of its mass fraction.

## Experimental

The toners and carriers used in this study are described in Table I. All the toners were approximately 10 μm in diameter and the carriers were all approximately 30 μm in diameter. The techniques used to make $m/q$ measurements as a function of T/C are described in Ref. 10. Namely, developer samples were agitated in an ac coil by the magnetic field for 30 s to tribocharge the toner. After charging, approximately 0.15 g of developer was placed in a stainless steel dish. A permanent magnet was rotated (2000 rpm) under the dish to agitate the developer. A dc electric field (approximately 2000 V/cm) was applied between the dish and a flat metal plate above the dish and separated from it by about 1 cm. The electric field and rotating magnet were switched on for a preset time interval. When both the rotating magnetic field and the electric fields are applied, toner is released from the carrier by the magnetic agitation and transported to the plate by the electric field. The carrier remains on the dish. This procedure was repeated 10–15 times to remove all of the toner from the carrier in increments. The time intervals were chosen such that approximately 1 mg of toner was collected in each increment. The charge on the toner collected on the plate was measured with an electrometer, and the weight of the toner collected on the plate was determined. The amount of toner removed and its $m/q$ were recorded. In all cases, the charge on the toner was positive, and the charge on the carrier was negative. These data were used to construct TC series. Figure 2 is an illustration of the TC series plots.

## Results and Discussion

Four examples are described below. Each set was chosen to illustrate a different aspect of the application of triboelectric series to represent the charging properties of two and three component mixtures of toners and carriers.

***Example One.*** The first example verifies that triboelectric series can be used to calculate the charging behavior of two and three-component mixtures.[15] Three toners and three carriers were used (see Tables I and II). They were mixed to form several two and three-component mixtures. TC series were determined for each of the mixtures using the method described above (see Table II). The data from the TC series were used to establish the work functions and the densities of states for the six materials. Two approaches were followed. In the first approach, only the two-component mixtures were used to estimate work functions and the densities of states,

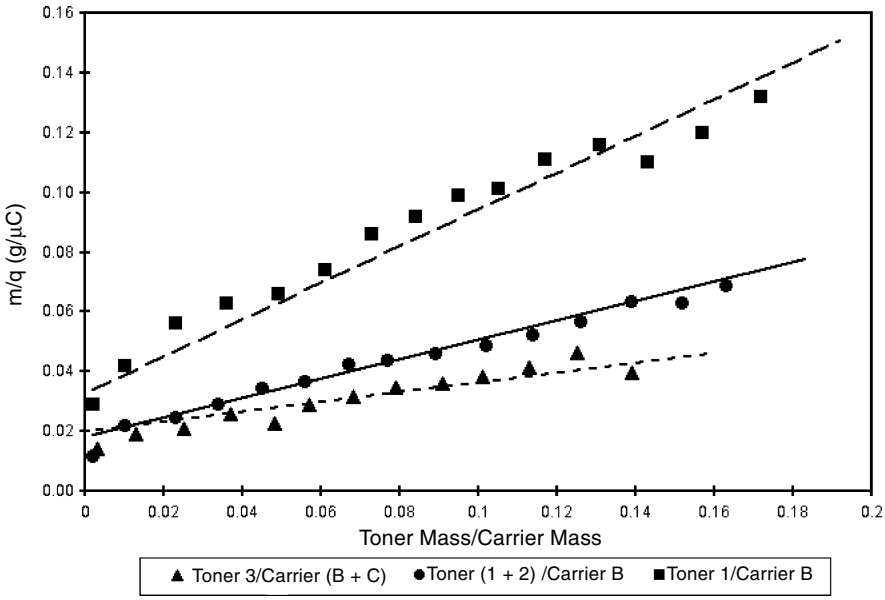


**Figure 2.** Toner was removed in 10–15 increments until all of the toner was removed from the carrier. The plot shows $m/q$ of each increment removed as a function of the toner concentration in the developer during the removal of the increment. Three examples of the TC series are presented above in the figure. The plots are linear as predicted by Eq. 2 and Eq. 3. The lines in the figure are calculated from the work functions and densities of states determined from the two-component mixtures.

**TABLE II. TC Series Tested**

| TC Series | 1st Toner | 2nd Toner | 1st Carrier | 2nd Carrier |
|---|---|---|---|---|
| 1 | 1 | | A | |
| 2 | 1 | | B | |
| 3 | 1 | | C | |
| 4 | 2 | | B | |
| 5 | 2 | | C | |
| 6 | 3 | | B | |
| 7 | 3 | | C | |
| 8 | 3 | | B | C |
| 9 | 2 | | A | B |
| 10 | 1 | | A | C |
| 11 | 2 | 3 | C | |
| 12 | 2 | 3 | B | |

**TABLE III. Work Functions and Densities of States for the Materials Used in Example One**

| | Two-component Mixtures | | Three-Component Mixtures | |
|---|---|---|---|---|
| Material | Work Function (eV) | Density of States (eV cm$^2$)$^{-1}$ | Work Function (eV) | Density of States (eV cm$^2$)$^{-1}$ |
| 1 | 0.000 | $1.06 \times 10^{11}$ | 0.000 | $1.06 \times 10^{11}$ |
| 2 | 0.016 | $1.34 \times 10^{11}$ | 0.0437 | $1.64 \times 10^{11}$ |
| 3 | 0.228 | $1.43 \times 10^{11}$ | 0.235 | $1.36 \times 10^{11}$ |
| A | 0.311 | $1.16 \times 10^{11}$ | 0.356 | $5.57 \times 10^{10}$ |
| B | 0.449 | $8.58 \times 10^{10}$ | 0.471 | $7.67 \times 10^{10}$ |
| C | 0.749 | $1.04 \times 10^{11}$ | 0.779 | $9.28 \times 10^{10}$ |

which were subsequently used to predict charging in three-component mixtures. In the second approach, TC series for both the two and three-component mixtures were used to find the work functions and the densities of states. The best work functions and densities of states for the 6 materials studied using both methods are compared in Table III. They are arranged in order of increasing work function as a triboelectric series.

In the mixtures containing two toners, equal amounts of magenta and cyan toners were mixed with a single carrier. The colors were chosen so that the color of the toner removed could be used to determine the ratio of the two toners as they were separated from the carrier. In this test, the color remained that for the 50–50 mixture. That is, the two toners were removed from the carrier at the same rate. These mixtures were treated as two-component mixtures. The carrier was treated as one component and the toner mixture was treated as the second component. The calculated $q/m$ of the combined toners was the weighted average of $q/m$ calculated for the two toners. For mixtures of two carriers and one toner, only the toner $q/m$ was calculated.

Three examples of the TC series are presented in Fig. 2. The plots are linear as predicted by Eqs. 1 and 8. The lines in the figure are calculated from the work functions and densities of states determined from the two-component mixtures. The measured and calculated $q/m$ values for both the two and three-component mixtures are compared in Fig. 3. The overall RMS difference between the measured and calculated $q/m$ values was 7% when the work functions and densities of states found using all the data were used and 12% when only the two-component data were used. This experiment shows that charging measurements of two and three-component mixtures are well represented by Eqs. 1 and 8, respectively.

***Example Two.*** A second set of experiments was carried out to examine the effects of carrier variations on charging behavior. In these experiments mixtures of poly(vinylidine fluoride)-coated ferrite, D, and uncoated ferrite, E, were used as the carriers. Two toners were used, one at a time, to determine the charging behavior of the carrier-ferrite mixtures. The materials are described in Table I. Figure 4 shows how the TC series for toner 4 changed as more uncoated ferrite was mixed with carrier D. The lines in this figure were drawn based on

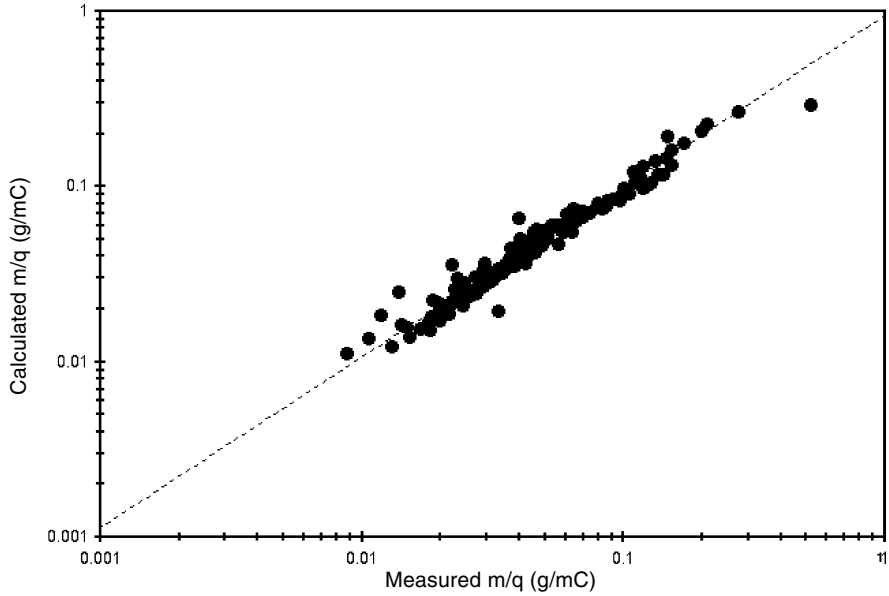


**Figure 3**. The measured and calculated $q/m$ values for both the two and three-component mixtures are compared in Fig. 3. The overall RMS difference between the measured and calculated $q/m$ values was 7% when the work functions and densities of states found using all the data were used and 12% when only the two-component data were used.

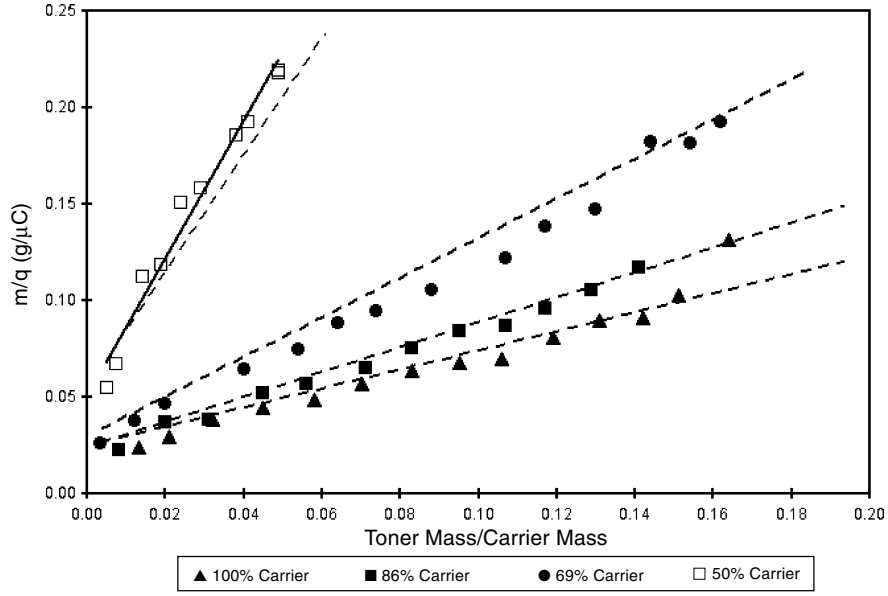


**Figure 4.** Toner concentration series plot for a single toner on carriers consisting of mixtures of poly(vinylidine fluoride)-coated ferrite, D, and uncoated ferrite, E. The lines in this figure were drawn based on work functions and densities of states estimated from the TC series obtained, using only the carrier and those obtained using a 50–50 mixture of carrier and ferrite. The figure shows that the calculated $m/q$ values for the other mixtures agree quite well with the measured values.

**TABLE IV. Work Functions and Densities of States for the Materials Used in Experiment Two**

| Material | Work Functions (eV) | Densities of States (eV cm$^2$)$^{-1}$ |
|---|---|---|
| E | 0.000 | $1.57 \times 10^{10}$ |
| 4 | 0.840* | $1.79 \times 10^{11}$* |
| 3 | 0.876 | $3.33 \times 10^{11}$ |
| D | 1.058 | $1.13 \times 10^{11}$ |

* Value for toner #1 differs from Table III because the regressions were carried out for different data sets.

work functions and densities of states estimated from the TC series obtained using only the carrier and those obtained using a 50–50 mixture of carrier and ferrite (see Table IV). The figure shows that the calculated $m/q$ values for the other mixtures agree quite well with the measured values. Figure 5 compares the measured and calculated values of $q/m$ including two made using the uncoated ferrite. These latter charges were of the opposite polarity from the data on the carrier-ferrite mixtures, yet the predicted charges agreed quite well. The coefficient of variation, $r^2$ is 0.91 between the measured and calculated values of $m/q$.

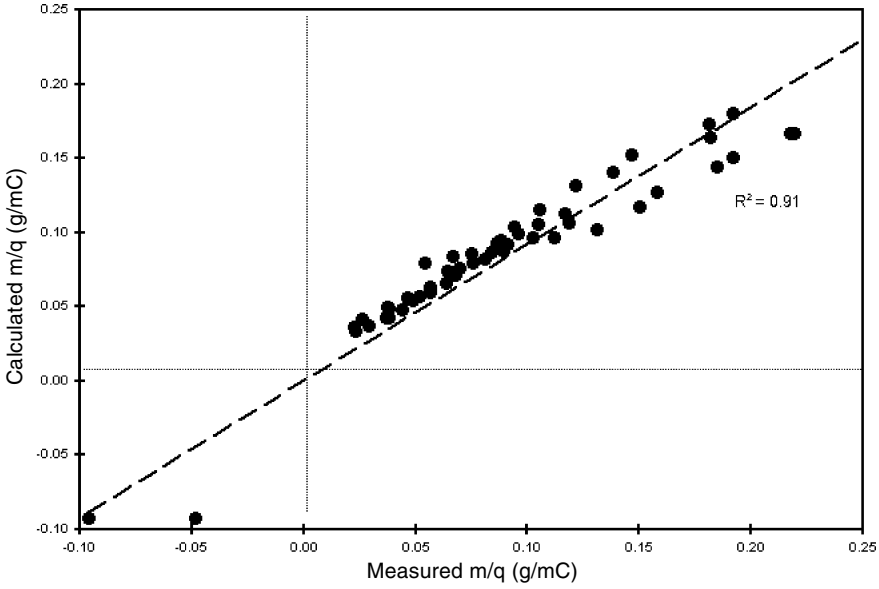


**Figure 5.** This figure compares the measured and calculated values of $q/m$ including those made at one toner concentration on the uncoated ferrite. These latter charges were of the opposite polarity from the data on the carrier–ferrite mixtures, yet the predicted charges agreed quite well.

**TABLE V. Work Functions and Densities of States for the Materials Used in Example Three**

| Material | Work Functions (eV) | Densities of States (eV cm$^2$)$^{-1}$ |
|---|---|---|
| 2 | 0.00* | 1.06 x 10$^{11*}$ |
| 6 | 0.327 | 2.11 x 10$^{11}$ |
| 5 | 0.371 | 5.82 x 10$^{11}$ |
| B | 0.443 | 8.80 x 10$^{10*}$ |
| C | 0.457 | 6.96 x 10$^{11*}$ |

* Values differ from those in Table III because the regressions were carried out for different data sets.

***Example Three.*** The third and fourth experiments were carried out to verify the expectation from Eq. 8 that two toners on a single carrier interact triboelectrically. In the first of these sets, the work functions and densities of states for two colored toners of quite different triboelectric properties were estimated from two-component mixtures. These parameters were used to calculate $q/m$ for mixtures of two toners on a single carrier. The toners used in the third and fourth experiments are described in Table I. The work functions and densities of states found for the materials used in the third experiment are listed in Table V. The materials are listed in order of increasing work function forming a triboelectric series. From the table it can be seen that the work function of toner 5 lies between the work functions of toner 2 and carrier C. It is expected that, in a three-component mixture of these materials, $q/m$ of toner 2 should be positive, and the charge-to-mass of carrier C should be negative. $Q/m$ of toner 5 may be either positive or negative and should be smaller than that of toner 2.

Figure 6 is a plot of the incremental removal of toner from a 50–50 mixture of toners 2 and 5 on carrier C. The squares are the measured $m/q$ values of the toner as it is removed. (The first increment is represented by the square at the highest toner to carrier mass ratio.) From the color of the toner removed, it could be seen that only toner 5 (cyan) was removed in the first 5 increments. The next few increments were mixtures of both toners, while the last 8 increments were only toner 2 (magenta). The dashed line represents $m/q$ of toner 5 calculated from the work functions and densities of states listed in Table V assuming that there was no interaction between the toners, and that the charge on the cyan toner was determined solely by charging against the carrier. It can be seen that because of the triboelectric interaction between the two toners, the measured $m/q$ is greater. The solid line in the figure is the calculated $m/q$ of the toner including toner–toner interactions and assuming that all of the cyan toner was removed before the magenta toner. This calculation gives a much better fit to the experimental data and illustrates the effect of toner–toner triboelectric interactions on the charge of toners in a three-component mixture.

***Example Four.*** The fourth example is similar to the third in that two toners with different work functions were mixed on a single carrier.[8] Toner concentration series were made from toners 7 and 8 on carriers F and G. The work functions and densities of states of the materials found from charge measurements made with these developers are shown in Table VI. These parameters were used to calculate the expected $q/m$ for toners 7 and 8 on carrier F as a function of the composition of the mixture. The total toner–carrier ratio was held constant for the series at 0.15. From Fig. 7 it can be seen that $q/m$ of toner 7 (black) is predicted to be negative when more than 50% of toner in the mixture is toner 8 (yellow). To verify this prediction, developers were made from toners 7 and 8 on carrier F with different mass ratios of toner 7 to toner 8. The percent of black toner (toner 7), that was negatively charged, was determined by setting the polarity of the electric field to collect negative toner. Figure 8 shows the results. It can be seen that the percent of black toner (toner 7) which was negative increased rapidly as the concentration of yellow toner (toner 8) increased, as predicted by the model.

## Theoretical Significance

The main purpose of this article is to demonstrate that the surface state model of tribocharging can be used to construct triboelectric series that permit calculation of

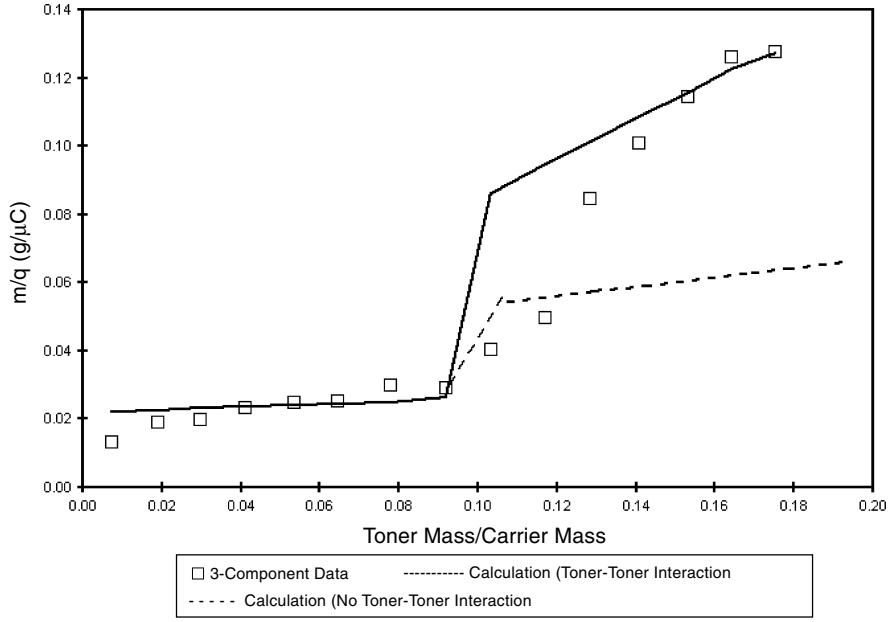


**Figure 6**. Toner concentration series plots for a 50–50 mixture of toners 2 and 5 on carrier C. The squares are the measured $m/q$ values of the toner as it is removed. Only cyan toner (toner 5) was removed in the first 5 increments. The next few increments were mixtures of both toners, while the last 8 increments were only magenta toner (toner 2). The dashed line represents $m/q$ of toner 5 calculated assuming that there was no interaction between the toners, and that the charge on the cyan toner was determined solely by charging against the carrier. These calculations are much lower than the $m/q$ measurements for the cyan toner from the toner mixture, illustrating the effect of toner–toner triboelectric interactions. The solid line is the calculated $m/q$ using Eq. 8 assuming that none of the magenta toner was developed until all of the cyan toner was removed. This calculation gives a much better fit to the measured $m/q$ values.

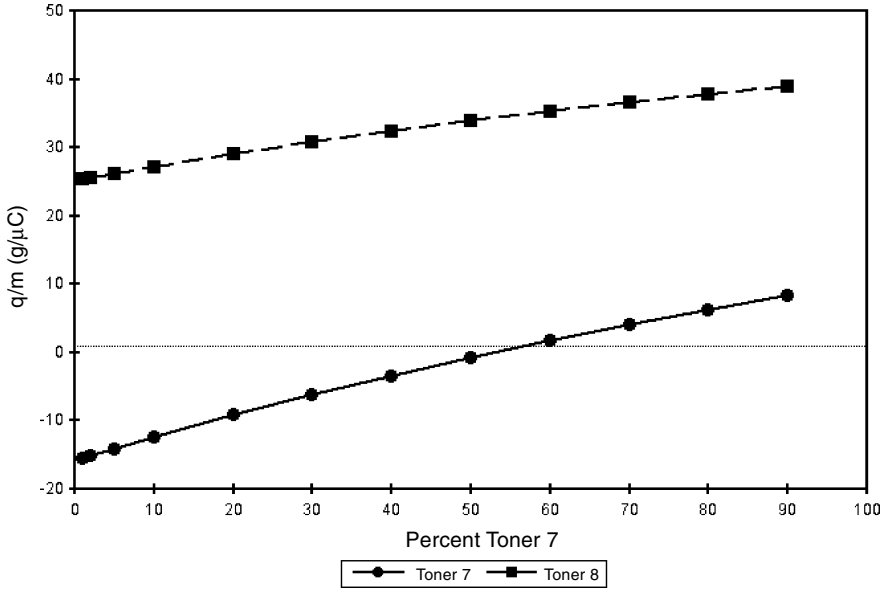


**Figure 7.** Calculated $q/m$ values for mixtures of toners 7 and 8 on carrier F. The work functions and densities of states used for these calculations are shown in Table V. The total toner/carrier ratio was held constant for the series at 0.15. It can be seen that $q/m$ of toner 7 (black) is predicted to be negative when more than 50% of toner in the mixture is toner 8 (yellow).

**TABLE VI. Work Functions and Densities of States for the Materials used in Example Four**

| Material | Work Functions (eV) | Densities of States (eV cm$^2$)$^{-1}$ |
|---|---|---|
| 8 | 0.00 | $1.06 \times 10^{11}$ |
| 7 | 0.343 | $1.88 \times 10^{11}$ |
| F | 0.503 | $1.12 \times 10^{11}$ |
| G | 0.567 | $1.31 \times 10^{11}$ |

the tribocharge of each component in a multi-component mixture. However, the results also have theoretical significance. From a theoretical point of view, the observed correlation between the calculated TC series and the experimental data shows that the surface state model represents the charging properties of powder mixtures very well. This has several implications for the charging process.

First, the surface state model of charging can work with multicomponent mixtures only if the mixing is such that each particle encounters all of the components of

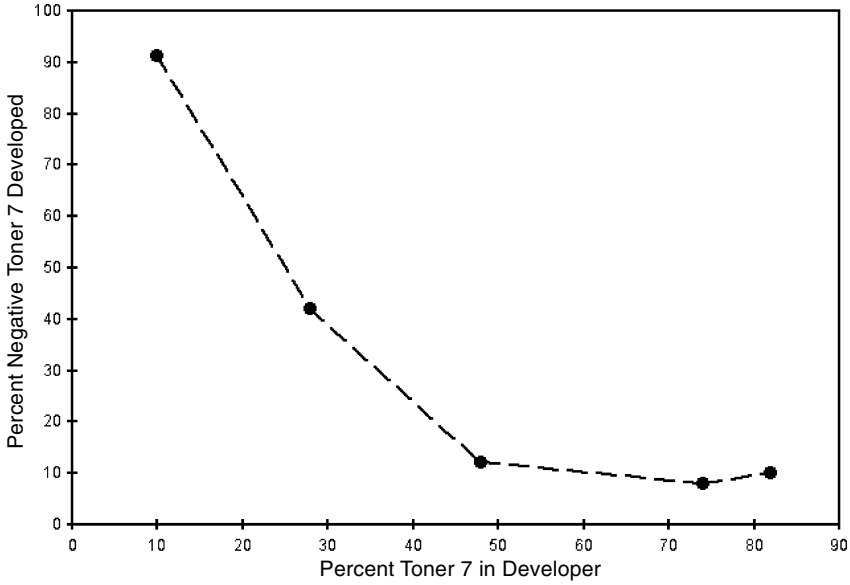


**Figure 8.** The percent of negatively charged, black toner (toner 7) was determined as above with the polarity of the electric field set to collect negative toner and is shown in this figure. The percent of black toner (toner 7) which was negative was found to increase rapidly as the concentration of yellow toner (toner 8) increased above 50%, confirming the predictions of the model.

the mixture. If this were not the case, then Eq. 8 could not be used to represent charging in a three-component mixture. Thus, agreement between the model and the charging behavior of three-component mixtures implies that complete mixing of the components has occurred.

Second, the ability to describe charging of different combinations of a set of materials by assigning work functions and densities of states to each material demonstrates that the properties of a material which control tribocharging are inherent to each individual material. Tribocharging of a pair of materials is a function of the work functions and densities of states of both materials. These parameters are a characteristic of each material itself and do not depend upon the identity of the other materials in a mixture. This is consistent with the notion of a triboelectric series.[2]

Finally, it may be asked if either the analysis or the experiments reported here help to resolve whether tribocharging of powder mixtures is best represented by the high density of states limit, the low density of states limit, or an intermediate case. In this article, $d$, the characteristic charging distance, was taken to be 1 nm. In order for the high density of states limit of the model to fit the data with this value for $d$, $\phi_t - \phi_c \cong 0.01$ eV which is of the order of $kT$ at room temperature. This is too small to be reasonable. If $d \cong 30$ nm, then $\phi_t - \phi_c \cong 1.0$ eV. Using the work functions found for this value of $d$ and Eq. 4, calculated values of $m/q$ for two component mixtures from example one agree with the experimental values to within about 40%.

Equation 4 also predicts that the ratio of the slope to the intercept of the TC series plots is given by $\rho_c r_c / \rho_t r_t$. For the materials in this study ($\rho_c = 3.5$ g/cm$^3$, $\rho_t = 1.0$ g/cm$^3$), $\rho_c r_c / \rho_t r_t \cong 10.5$. The average of the measured values is 29; the standard deviation is 25, and the range is 5.9 to 102. Castle and Schein have claimed that most measured slope-to-intercept ratios for published TC series plots fall within a factor of 2 of the value predicted by Eq. 4.[14] Some of these data fall well outside that range.

In the intermediate case, $\varepsilon_0 / N_t e\, d \cong 1$ and $\varepsilon_0 / N_c e\, d \cong 1$. Thus, $N_c = N_t \cong 5 \times 10^{12}$ eV$^{-1}$cm$^{-2}$. If $d$ is 1 nm, then $\phi_t - \phi_c \cong 0.01$ eV, which is too small. If $d$ is 60 nm, then $\phi_t - \phi_c \cong 1$ eV as in the high density limit.

When Eq. 1 is used to estimate the densities of states and the work functions with $d = 1$ nm without restricting the magnitude of the densities of states as was done above, the estimated densities of states are about 1 order of magnitude lower and $\phi_t - \phi_c \cong 1$ eV. The smaller densities of states mean that $\varepsilon_0 / N_t e\, d >> 1$ and $\varepsilon_0 / N_c e\, d >> 1$. Therefore, the estimates of the parameters given above could also have been made using the low densities of states limit as in Eq. 3. Although the parameters are different, the calculated values for $m/q$ using Eq. 1 are the same using either the intermediate case with $d = 60$ nm or the unrestricted case with $d = 1$ nm. The calculated values of $m/q$ agree with the measured values within about 10%. The calculated slope to intercept ratios agrees with the measured values to within about 25%.

The differences between the model predictions and the experimental data suggest that, at least for the systems studied here, the high density of states limit is not as good a representation of the charging behavior as Eq. 1. For this reason, Eq. 1 was used to find the charging parameters of the individual materials and to calculate the charging behavior of two- and three-component mixtures.

## Practical Applications

Once the work functions and densities of states have been assigned to all of the components by the methods outlined above using two-component mixtures, it is possible to predict the charging behavior of any mixture of a set of materials using Eq. 8. Therefore, it is not necessary to measure the charging behavior of all possible combinations and mixtures of materials. Rather, TC series determined for subset of mixtures, which contains each of the materials, are sufficient for assigning work functions and densities of states and therefore, for calculating charging behavior of any mixture of components from the set.

From a practical point of view, the ability to calculate charging in multicomponent mixtures from data obtained in two-component experiments is useful in a number of situations.

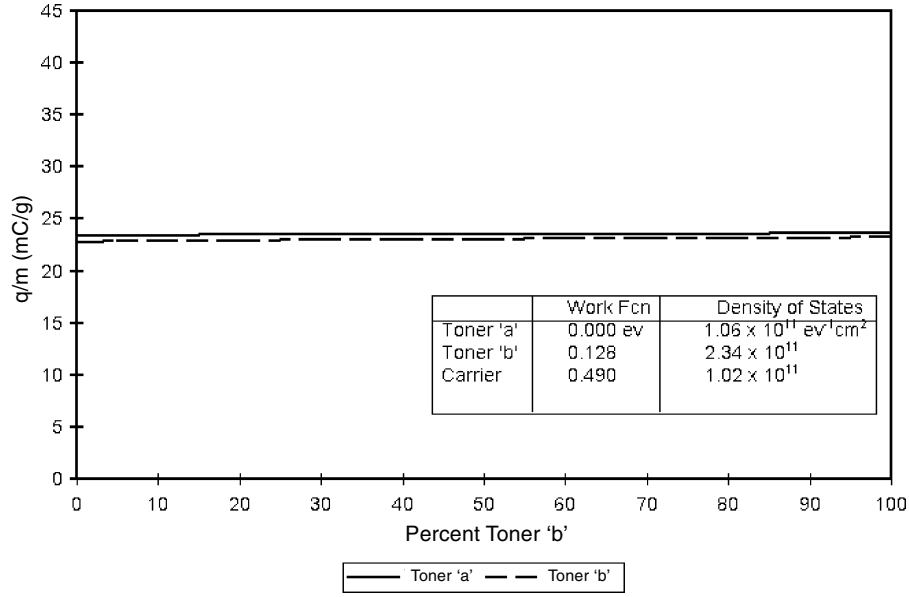


**Figure 9**. In this figure $q/m$ of a mixture of two toners was calculated as a function the concentration of one of the toners in the developer. (The total concentration of toner was held constant. T/C = 0.15.) Despite the fact that the toners have different work functions, they have the same $q/m$ over the entire range of composition on this particular carrier. This is not the case for all carriers. Should the carrier have either a higher or a lower work function, then $q/m$ of the two toners is no longer the same (see Figs. 10 and 11). This illustrates the difficulty in replacing one toner with another.

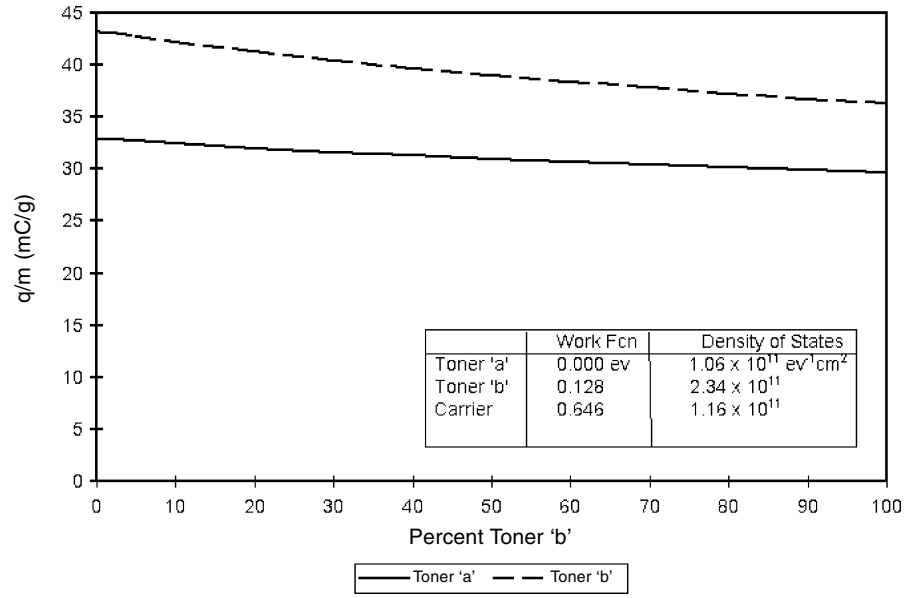


**Figure 10**. The calculated behavior of the same two toners as in Fig. 9 is different if the work function of the carrier is changed. In this case, the work function was increased to 0.646 eV, and toner 'b' has a higher $q/m$ than toner 'a'.

In multicolor copiers and printers where small amounts of toner from one development station may contaminate the toner in a second station, it is desirable to be able to predict $q/m$ of the contaminating toner. This situation can be analyzed using Eq. 8 if the work functions and densities of states of the two toners and the carrier are known from two-component experiments. Experiment four is an example of a cross-contamination problem.

If a different toner formulation is to be introduced into an existing product as the new material displaces the old in a developer station, it is possible that wrong-sign or low charging toner may be produced. Therefore, the effects on $q/m$ of mixing both toners on a common carrier are of interest. This situation can be analyzed in the same way as cross contamination. Experiment four is an example of incompatible toners which would lead to dusting as one toner replaced the other. Figure 9 is a hypothetical case illustrating this behavior. In this figure, $q/m$ of each of the toners was calculated as a function of its concentration in the developer. Despite the fact that the toners have different work functions, they have the same $q/m$ over the entire range of composition on a particular carrier. However this is not the case for all carriers. Should the carrier have either a higher or a lower work function, then $q/m$ of the two toners is no longer the same (see Figs. 10 and 11). This illustrates the difficulty in re-

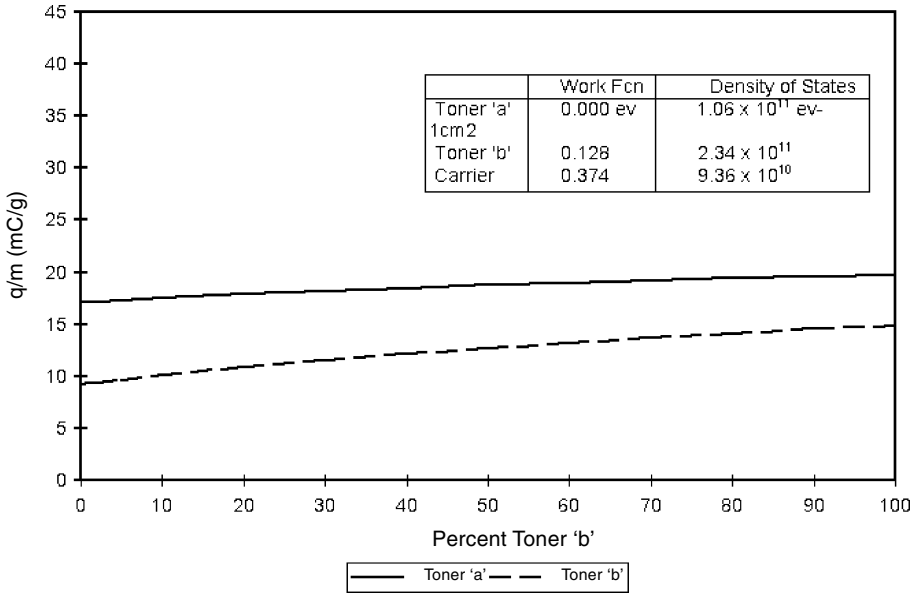


**Figure 11**. If the work function of the carrier is decreased to 0.374 ev, the same two toners as in Fig. 9 now charge in the opposite order. Toner 'a' has a higher $q/m$ than toner 'b'.

placing one toner with another. Matching the $q/m$ of the two toners on a fresh carrier does not guarantee that $q/m$ will match as the carrier ages. In order to avoid undesirable interactions, the work functions of the two toners should be as similar as possible.

Recently, Nash has shown that a similar approach can be used to model the charging behavior of developers made from toners with surface additives and the effects of developer age and relative humidity on tribocharging. His studies are a valuable resource for understanding the charging behavior of developers containing components with heterogeneous surfaces.[16,17]

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