

Quantitative Triboelectric Series and Their Applications

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Abstract

The charging behavior of toner particles in two-component electrophotographic developers is consistent with the surface state model of tribocharging. This model provides a basis for determining triboelectric series, which can be used to predict the magnitude of charge exchanged between particles, provided the model parameters are known for each material. In this paper, 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, for example, 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 ability to predict tribocharging behavior of individual components in a multicomponent developer mixture is, therefore, very useful in explaining observed developer failures and identifying potential problems.

Introduction

One approach toward understanding triboelectrification has been the construction of triboelectric series.[1] 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." 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 a 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.

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.[2-6] The model has proven to fit charging in two-component mixtures well.

Analysis of the equilibrium charge exchanged between the toner and the carrier leads to the following relationship between the mass-to-charge ratio of the toner particles, m/q, and the mass ratio of toner-to-carrier in the developer, T/C: [5]

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

In Eq. 1, d is a characteristic separation distance between the particle surfaces during charging, ε_0 is the permitivity of free space, ϕ 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, ρ 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.[2-7] 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.[3-9]

The reciprocal of Eq. 1 gives the relationship between charge-to-mass, q/m, the densities of states and the work functions.[5] The sign of the difference between the work functions determines the sign of the charge on the toner. 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 larger work function will charge negatively. Thus, listing materials in ascending order of work functions produces a tribo-electric series. Eq. 1 in conjunction with experimental charge measurements can be used to assign values to N_t, N_c, ϕ_t, and ϕ_c. The procedure used 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 is 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 ϕ_t, ϕ_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 ϕ_t, ϕ_c, N_t, and N_c were the best fit set found from regression as indicated above.

Multicomponent Powder Mixtures

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

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

$$\sum_i f_i \left(q/m\right)_i = \frac{3\varepsilon_o}{d} \sum_i f_i \left(E_f - \varphi_i\right) \times \left[\left(\frac{\varepsilon_0}{N_i e\, d} + 1\right) r_i \rho_i\right]^{-1} = 0. \qquad (2)$$

In Eq. 2 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. Solving for E_f:

$$E_f = \frac{\sum_i f_i \varphi_i \left[\left(\frac{\varepsilon_0}{N_i e\, d} + 1\right) r_i \rho_i\right]^{-1}}{\sum_i f_i \left[\left(\frac{\varepsilon_0}{N_i e\, d} + 1\right) r_i \rho_i\right]^{-1}} \qquad (3)$$

Substituting Eq. 3 into Eq. 2:

$$(q/m)_j = -\frac{3\varepsilon_0}{d}\left(\varphi_j - \frac{\sum_i f_i \varphi_i \left[\left(\frac{\varepsilon_0}{N_i e\, d} + 1\right) r_i \rho_i\right]^{-1}}{\sum_i f_i \left[\left(\frac{\varepsilon_0}{N_i e\, d} + 1\right) r_i \rho_i\right]^{-1}}\right) \times \left[\left(\frac{\varepsilon_0}{N_j e\, d} + 1\right) r_j \rho_j\right]^{-1} \qquad (4)$$

The reciprocal of Eq. 4 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.

Table I. Materials

Carriers

1. Aged poly(vinylidine fluoride) coated ferrite (2 wt%).*
2. Fresh poly(vinylidine fluoride) coated ferrite (1 wt%).
3. Fresh poly(vinylidine fluoride) coated ferrite (2 wt%).
4. Aged poly(vinylidine fluoride) coated ferrite (1 wt%).*
5. Uncoated ferrite.

Toners

1. Cyan polyester-amide toner.
2. Magenta polyester toner.
3. Cyan polyester toner.
4. Black polyester toner.
5. Black styrene-acrylic toner.
6. Yellow styrene-acrylic toner.

*- washed with solvent to remove residual toner.

The techniques used to make m/q measurements as a function of T/C are described in ref. 10. 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.

Results and Discussion

Three 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. Three toners (1, 2 and 3) and three carriers (A, B, and C) were mixed to form several two and three-component mixtures. TC series were determined for each of the mixtures. The data from the TC series were used to establish the work functions and the densities of states for the six materials. The results are shown in Table II, 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.

Table II. Charging Parameters

Material	Work Function	Density of States
Example One		
1	0.000	1.06×10^{11}
2	0.016	1.34×10^{11}
3	0.228	1.43×10^{11}
A	0.311	1.16×10^{11}
B	0.449	8.58×10^{10}
C	0.749	1.04×10^{11}
Example Two		
D	0.000	1.57×10^{10}
3	0.840*	$1.79 \times 10^{11*}$
4	0.876	3.33×10^{11}
E	1.058	1.13×10^{11}
Example Three		
6	0.000	1.33×10^{11}
5	0.275	2.37×10^{11}
F	0.402	1.41×10^{11}
G	0.454	1.65×10^{11}

**The parameter values for toner #3 differ from those in Example One because the regressions were carried out on different data sets.*

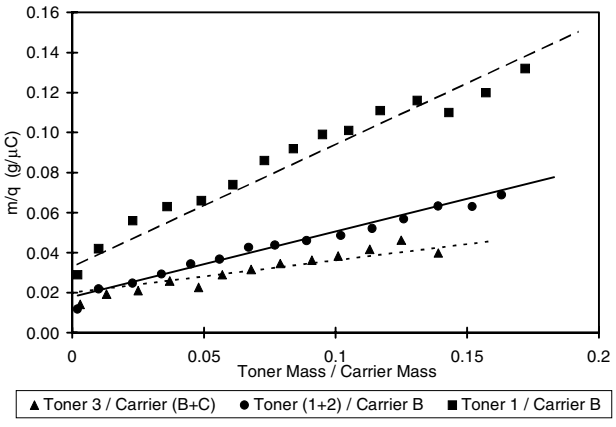

Fig. 1. TC series: The plots are linear as predicted by Eqs. 1 and 4. The lines in the figure are calculated from the work functions and densities of states determined from the two-component mixtures.

Three examples of these TC series are presented in Fig. 1. 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 4, 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. Toners 1 and 4 were used, one at a time, to determine TC series using carrier-ferrite mixtures. Figure 2 shows how the TC series for toner 4 changed as more uncoated ferrite was mixed with carrier D.

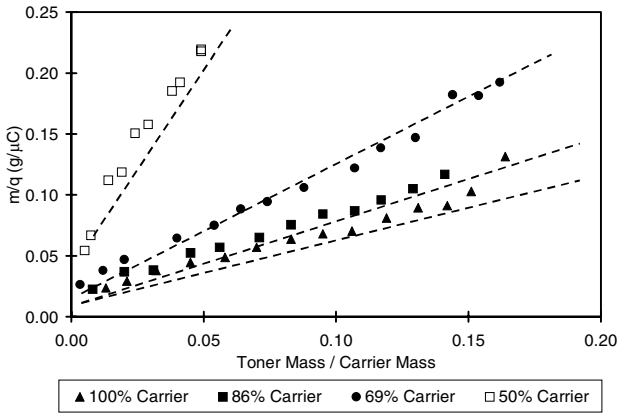

Fig. 2. TC series for toner 4 charged against carrier D- carrier E mixtures. The lines in this figure were drawn based on work functions and densities of states estimated from the TC series obtained using only carrier D and those obtained using a 50-50 mixture of carriers D and E.

The figure shows that the calculated m/q values for the other mixtures agree quite well with the measured values. Q/m for two samples made using the uncoated ferrite, E, were also measured. These latter charges were of the opposite polarity from the data on the carrier-ferrite mixtures, yet the measured and predicted charges are in good agreement.

Example Three

A third experiment was carried out to verify the expectation from Eq. 4 that two toners on a single carrier interact triboelectrically. Two-component TC series were made from toners 5 and 6 on carriers F and G. Work functions and densities of states of the materials found from charge measurements made with these developers were used to calculate the expected q/m for mixtures of toners 5 and 6 on carrier F as a function of the composition of the mixture. These calculations predicted that q/m of toner 5 (black) should be negative when less than 50% of toner in the mixture was toner 5 (black). To verify this prediction, developers were made with mixtures of toners 5 and 6 on carrier F with different mass ratios of the toners. The percent of black toner (toner 5), that was negatively charged, was determined by setting the polarity of the electric field to collect negative toner only in the charge measurement. Figure 3 shows the results. It can be seen that the percent of black toner (toner 5) which was negative decreased rapidly as the concentration of black toner (toner 5) increased, as predicted by the model.

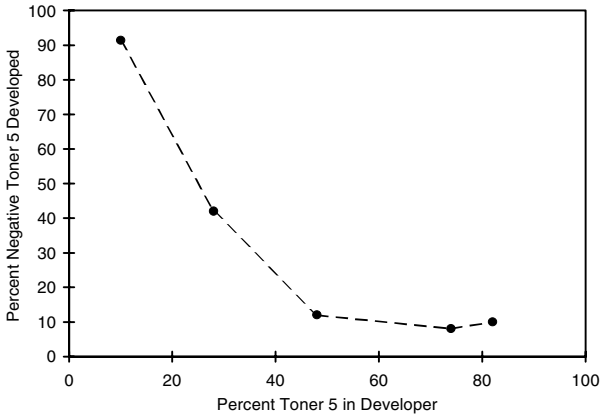

Fig. 3. Percent of negative toner as a function of yellow toner content. It can be seen that the percent of black toner (toner 5) which was negative decreased rapidly as the concentration of black toner (toner 5) increased, as predicted by the model.

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 be possible to predict the charging behavior of any mixture of a set of materials using Eq. 4. 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.

The ability to calculate charging in multicomponent mixtures from data obtained in two-component experiments is useful in a number of situations. For example, 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. 4, if the work functions and densities of states of the two toners and the carrier are known from two-component experiments. Example 3 illustrates 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 both toners of mixing them on a common carrier are of interest. This situation can be analyzed using in the same way as cross contamination. Example three is an illustration of incompatible toners, which could lead to toner dusting as one toner replaced the other.

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Biography

Dr. Anderson holds BS, MS and PhD degrees from Stanford University. He is currently on the research staff of Heidelberg Digital where he works on the physics and materials science of triboelectricity and electrophotography.

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