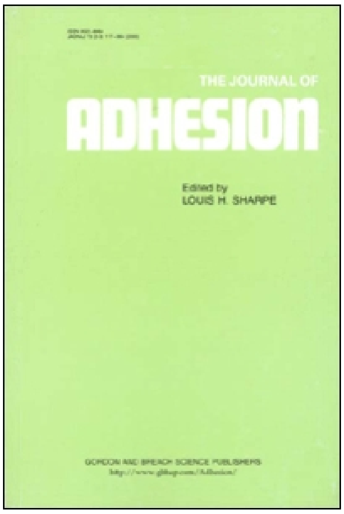

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Anderson, J. H. and Fox, Elizabeth(1995) 'Tribocharging of Three-Component Powder Mixtures', The Journal of Adhesion, 51: 1, 27 — 40

To link to this Article: DOI: 10.1080/00218469508009987

URL: http://dx.doi.org/10.1080/00218469508009987

J. Adhesion, 1995, Vol. 51, pp. 27–40
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Tribocharging of Three-Component Powder Mixtures

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(Received March 26, 1994; in final form July 9, 1994)

Adhesion of charged toner particles used in electrophotography is dominated by electrostatic forces. In this paper we discuss a model which describes the process by which toner particles acquire their electrostatic charge, tribocharging.

In previous papers, we have presented a model of tribocharging of two-component mixtures of powders based on the assumptions that:

1. The surface of each powder is populated with electron accepting and donating sites;
2. The density of states of the donating and accepting sites can be represented by narrow bands, all of which have the same energy; and
3. Charge is exchanged between donor and acceptor sites until thermodynamic equilibrium is established.

In this paper, we show how to extend this model to multi-component mixtures. The extended model can be used to calculate the charging behavior of three-component mixtures of electrophotographic toners and carriers based on measurements with two component mixtures. Experimentally-measured charging behavior agrees with the model predictions.

These results confirm it is possible to assign charging site densities to individual materials empirically. The site densities can then be used to predict charging behavior of the materials in mixtures which have not been studied experimentally. The success of the model also implies that toner particles migrate freely from carrier particle to carrier particle and that triboelectric interactions take place between toner particles of different compositions in mixtures.

KEY WORDS electrostatics; electrophotography; charged particles; charging models; powder mixtures; triboelectrification; toner; adhesion.

INTRODUCTION

Electrophotography

Electrophotography (xerography) depends upon the ability to control adhesion of electrically charged particles (toner) to charged surfaces. The process consists of six steps illustrated in Figure 1:

Charge — The photoconductor is charged uniformly using a corona discharge.
Expose — The photoconductor is exposed to the image to be produced. Exposed areas of the photoconductor are discharged leaving a latent image consisting of a charged pattern on the photoconductor.

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*Presented at the Seventeenth Annual Meeting of The Adhesion Society, Inc., in Orlando, Florida, U.S.A., February 21–23, 1994.

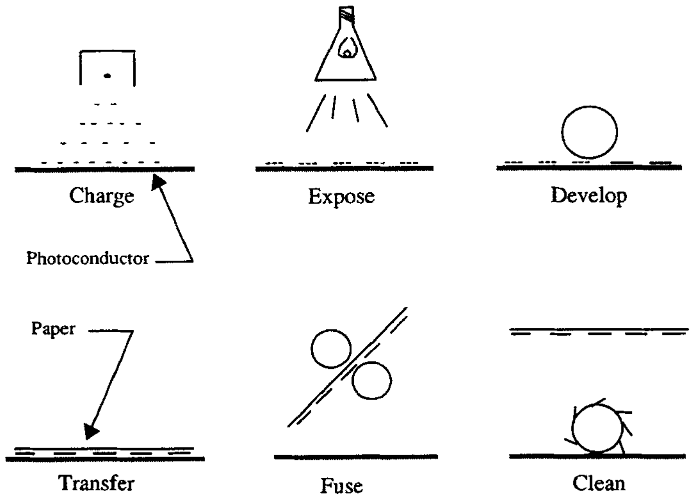

FIGURE 1 Schematic representation of the electrophotographic process showing the six steps in the process. The focus of this paper is on the tribocharging of the toner and carrier particles used in the development step.

Develop — Electrostatically-charged polymer particles (toner) of the appropriate color are brought into contact with the photoconductor and adhere to it where it is charged.
Transfer — The developed image is transferred from the photoconductor to paper or other surface.
Fuse — The image is fixed to the paper by heat and pressure.
Clean — Residual toner is removed from the photoconductor and the photoconductor is ready to make the next print.

In the development, transfer and cleaning steps, charged particles are either deposited on or removed from flat, charged surfaces. Thus, adhesion between charged particles and surfaces plays a pivotal role in electrophotography.

Under low external loads, theories of adhesion predict that surface forces make an important contribution to the work of adhesion.[1] However, Hays has shown that electrostatic forces dominate the adhesion of charged toner particles.[2] Thus, in order to understand the electrophotographic process fully, both the process by which toner particles acquire their charge (triboelectrification) and their adhesion to other charged surfaces must be understood.

Triboelectrification, electrical charging by rubbing two materials together, is the oldest known manifestation of electricity (Thales of Miletus, 600 BC). Amber was found to become electrified when rubbed and to attract lightweight objects. In spite of this long history and the recent explosion of electronic technology, triboelectricity remains the least understood of electrical phenomena. There is no consensus on what charged species are exchanged or on the mechanism by which charging occurs. Nonetheless, tribocharging of powders can be controlled very precisely, making it possible to use tribocharged particles to make high quality images in copiers and laser printers.

The purpose of this work is to discuss a model of triboelectrification of two-component mixtures of powders developed earlier, to extend it to multi-component mixtures, and to determine whether the extended model is consistent with the measured charging properties of two- and three-component mixtures.

Triboelectrification in Electrophotography

In many high-speed copiers, the toner particles are brought into contact with the photoconductor by mixing them with magnetic particles (carrier). The mixture of toner and carrier in the copier is often referred to as the "developer." The toner and carrier are chosen so that they exchange charge and become oppositely-charged when they are mixed together. Electrostatic forces cause the smaller toner particles to adhere to the larger carrier particles. The two-component mixture is transported magnetically to the photoconductor and brushed against it. Toner is removed from the carrier and deposited on the photoconductor under the influence of the electrostatic fields associated with the latent image. The carrier is returned to the developer station where it picks up fresh toner.

Toner and Carrier Properties

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

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

CHARGING IN TWO-COMPONENT MIXTURES

Several models of triboelectrification have been proposed to explain the charging of two-component electrophotographic developers. One of them, referred to hereafter as the "surface state model",[3] has a simple form and has proven to fit charging in two-component mixtures well. This model treats charging as exchange of electrons between carrier and toner surfaces. The amount of the charge exchanged is determined by thermodynamic equilibrium of electrons in energy levels available on the surface of the toner and the carrier.

A useful form of the surface state model has been developed by Anderson and Bugner.[4,5] The model is based on the assumptions that:

1. The surface of each powder is populated with electron accepting and donating sites;
2. The density of states of the donating and accepting sites can be represented by narrow bands, all of which have the same energy; and
3. Charge is exchanged between donor and acceptor sites until thermodynamic equilibrium is established.

Analysis of the equilibrium charge exchanged between donating and accepting charge sites on both 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

$$\mathrm{m/q} = \mathrm{e}^{-1}\left[\frac{(D_c + A_c)}{S_t(D_t A_c - A_t D_c)} + \mathrm{T/C}\frac{(D_t + A_t)}{S_c(D_t A_c - A_t D_c)}\right] \tag{1}$$

In Eq. (1) A and D stand for the concentration per unit surface area of acceptor and donor electronic states, respectively. S is the specific surface area, and e is the charge on the electron. The subscripts t and c refer to toner and carrier.

This equation predicts a linear relationship between m/q and T/C. The slope and intercept depend upon the surface area of the particles and the concentration of donating and accepting sites on their surfaces. Plots of this type are referred to below as "TC series."

The specific surface area of monodisperse spherical particles is given by $3/r\rho$, where r is the radius and ρ is the mass density. Eq. (1) then becomes:

$$\mathrm{m/q} = \mathrm{e}^{-1}\left[\frac{r_t\rho_t(D_c + A_c)}{3(D_t A_c - A_t D_c)} + \mathrm{T/C}\frac{r_c\rho_c(D_t + A_t)}{3(D_t A_c - A_t D_c)}\right] \tag{2}$$

Equation (2) predicts that changing the carrier's particle size affects only the slope of the TC series, while changing the toner's particle size affects only the intercept. The slope is proportional to the radius of the carrier particles times their mass density, and the intercept is proportional to the radius of the toner particles times their mass density.

Experiments using two-component mixtures by a number of workers have borne out the general features of the model.[3-9] The linear relationship between m/q and T/C and the dependence of the slope and intercept of Eq. (2) on particle size are well-established.[3-9]

Determining Charging Site Densities

In earlier work it was shown that it is possible to use TC series to assign donor and acceptor charging site densities to toners and carriers.[10] The procedure used was as follows: First, TC series plots were determined experimentally for a set of materials of interest. For example, in the simplest case, TC series plots were determined for the four binary mixtures which can be made from two toners and two carriers. An initial guess was made for the relative acceptor and donor charging site densities on the four materials. Next, Eq. (1) was used to calculate m/q for the TC series of each mixture. The RMS error between the measured and calculated m/q values was determined. The best fit set of site densities was found by searching for a set which minimized the RMS difference between the measured and calculated m/q values.

The following search routine was used: An initial guess was made for the charging site densities. Small, random changes in each of the site densities were made. If the RMS difference between the measured and calculated m/q values was larger for the changed site densities, they were discarded and the original guess was saved. If the changed site densities improved the RMS difference, the set of changed sites were saved. The saved set was then used as the basis for the next search point. These steps were repeated until a minimum in the RMS difference was found. Several sets of initial guesses were used to insure that the best fit set of site densities had been found.

CALCULATION OF CHARGING PROPERTIES OF MULTI-COMPONENT MIXTURES

In developing the model which leads to Eq. (1), it was assumed that the charging sites on all particles in a mixture are in chemical equilibrium. Practically, this means that the mixing in the powder during charging is vigorous enough that the acceptor and donor charging sites on each component of the mixture come into frequent contact with one another. In order to extend the model from two-component to multi-component mixtures, one can treat the mixture as if it were a two-component mixture. The first component is one of the actual components in the mixture. The second, pseudo-component, is a composite of the other materials in the mixture. The acceptor and donor charging sites assigned to the pseudo-component are the weighted sums of the acceptor and donor charging sites, respectively, of the rest of the materials in the mixture. Thus, Eq. (1) can be rewritten as

$$\mathrm{m}_1/\mathrm{q}_1 = \mathrm{e}^{-1}\left[\frac{\sum m_i S_i D_i + \sum m_i S_i A_i}{[S_1(D_1 \sum m_i S_i A_i - A_1 \sum m_i S_i D_i)]} + \frac{m_1 S_1 (D_1 + A_1)}{[S_1(D_1 \sum m_i S_i A_i - A_1 \sum m_i S_i D_i)]}\right] \tag{3}$$

where m, e, S, D, and A are defined as in Eq. (1), and the subscript, 1, refers to the component of interest. The sums represent the charging sites on the pseudocomponent. The index, i, is summed over all actual components in the mixture except component 1.

Equation (3) can be simplified to

$$\mathrm{m}_1/\mathrm{q}_1 = \mathrm{e}^{-1}\frac{\sum f_j S_j (D_j + A_j)}{S_1[D_1 \sum f_j S_j A_j - A_1 \sum f_j S_j D_j]} \tag{4}$$

where f_j is the mass fraction of component j, and the sums are taken over all components in the mixture including component 1.

Equation (4) predicts that m/q for each component of a mixture should be a linear function of its mass fraction. The ratio of the slope to the intercept of the line gives the ratio of the total number of charging sites on the material of interest to the sum of the charging sites on all of the other components.

In many practical situations it is sufficient to know only the relative site densities for a set of materials. When this is the case, e^{-1} and the surface areas in Eq. (4) can be folded into the site densities simplifying the expression further:

$$m_1/q_1 = \frac{\sum f_j(D_j + A_j)]}{D_1 \sum f_j A_j - A_1 \sum f_j D_j} \tag{5}$$

In Eq. (5), m_1/q_1 is in units of grams per μ Coulomb, and the site densities, A and D, are now expressed on a relative scale.

EXPERIMENTAL

Materials

Three toners and three carriers were used in these experiments. They are described briefly in Table I.

Measurements

The techniques used to make m/q measurements as a function of TC are described in Reference 11. In brief: Developer samples were agitated in an AC coil by the magnetic field for 30 seconds to tribocharge the toner. After charging, approximately 0.15 gram 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 volts/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

TABLE I
Materials used

Carriers:	
A:	1 pph poly(vinylidine fluoride) on a 30 μm Iron-Strontium ferrite core.
B:	1 pph poly(vinylidine fluoride) on a 30 μm Iron-Strontium ferrite core. Removed from a full process test and washed with dichloromethane to remove residual toner.
C:	2 pph poly(vinylidine fluoride) on a 30 μm Iron-Strontium ferrite core.
Toners:	
1.	Cyan polyester amide toner.
2.	Magenta polyester toner.
3.	Cyan polyester toner.

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 T/C series. Figure 2 is an illustration of the TC series plots.

Site Densities

Twelve binary and ternary mixtures were constructed using the three toners and carriers as shown in Table II. TC series for each mixture were determined as described above. The data from all of the TC series were used to search for the set of charging site concentrations for the six materials which gave the smallest overall RMS difference between the measured and calculated m/q values. The mixtures containing two toners were a 50-50 mixtures of the toners. The colors, magenta and cyan, were chosen so that differences in the ratio of the two toners could be easily determined as they were removed from the carrier. In these experiments, the color

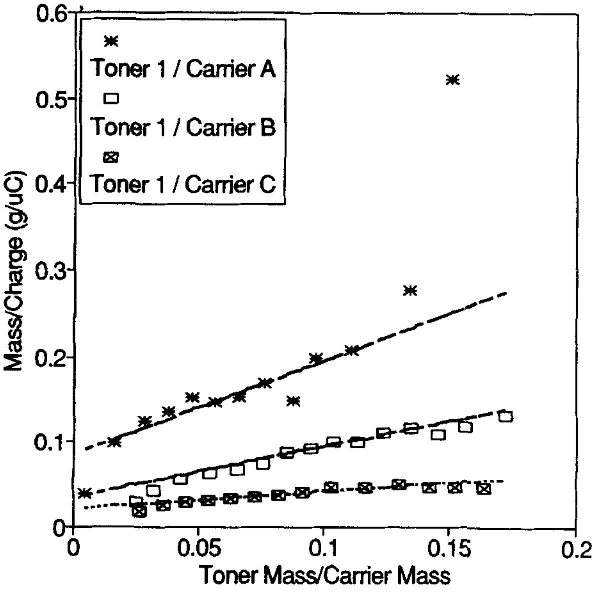

FIGURE 2 TC series for toner 1 on carriers A, B and C. Figures 2–4 illustrate the linear relationship between the m/q of the toner and the ratio of toner mass to carrier mass.

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	—

remained that for the 50-50 mixture. That is, the two toners were removed at the same rate from the carrier. In these mixtures, the carrier was treated as one component and the toner mixture was treated as the pseudo-component. For mixutres of two carriers and one toner, the carrier mixture was considered as the pseudo-component.

EXPERIMENTAL RESULTS

Figures 2–9 show the results of these measurements. In the figures, m/q is plotted as a function of the toner-to-carrier ratio, T/C, in the mixture. The lines in the figures were calculated using Eq. (5) and the best fit charging site densities, which are listed in Table III. Table IV gives the RMS differences for each TC series. With one exception (toner 2 on a 50-50 mixture of carriers A and B-Figure (6), the calculated lines fit the measured points quite well.

TABLE III
Charging Site Densities

Material	Acceptors*	Donors*
1	52	113
2	22	132
3	16	107
A	4.9	7.9
B	4.7	4.8
C	8.5	3.0

* Relative number per unit mass

Figure 10, which is a plot of measured *vs.* calculated q/m, illustrates how well the calculated q/m values match the measured values. In this figure there are 168 points with an average RMS error of 11.7%. Thus, experimental charging measurements of two and three-component mixtures are well represented by Eq. (5).

TABLE IV
RMS difference between measured and calculated TC series

TC Series	RMS Difference (%)
1	9.7
2	9.1
3	10
4	5.8
5	7.5
6	3.8
7	11
8	9.6
9	28.9
10	10.5
11	12.9
12	4.3

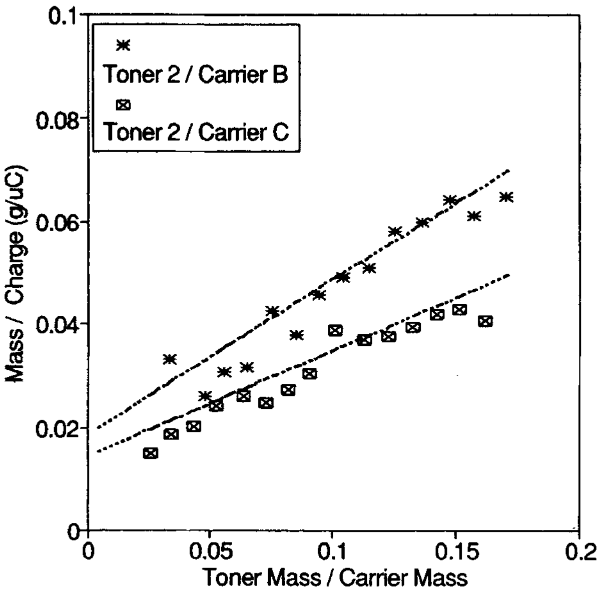

FIGURE 3 TC series for toner 2 on carriers B and C.

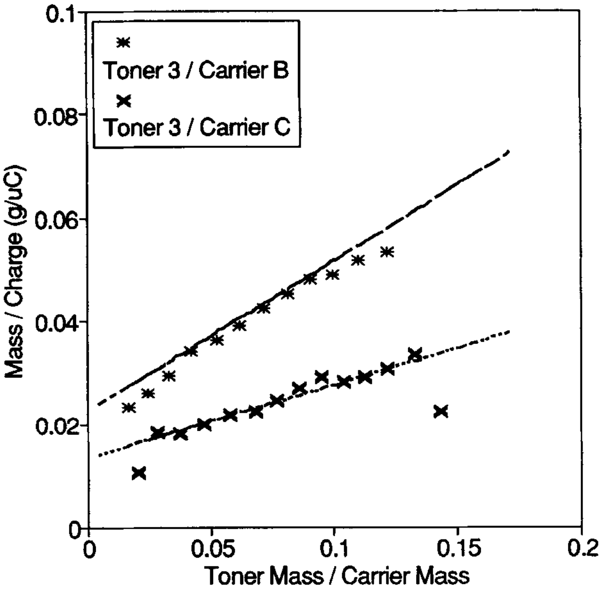

FIGURE 4 TC series for toner 3 on carriers B and C.

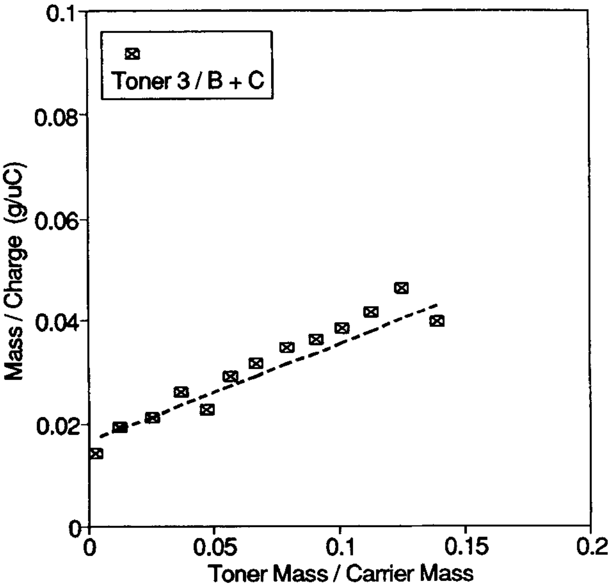

FIGURE 5 TC series for toner 3 on a 50-50 mixture of carriers B and C. Figures 5–9 illustrate that there is a linear relationship between m/q of the toner and the ratio of toner mass to carrier mass in three component mixtures.

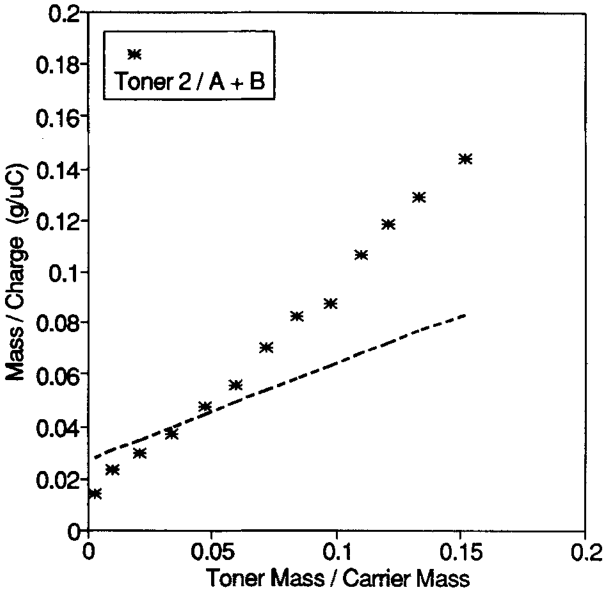

FIGURE 6 TC series for toner 2 on a 50-50 mixture of carriers A and B.

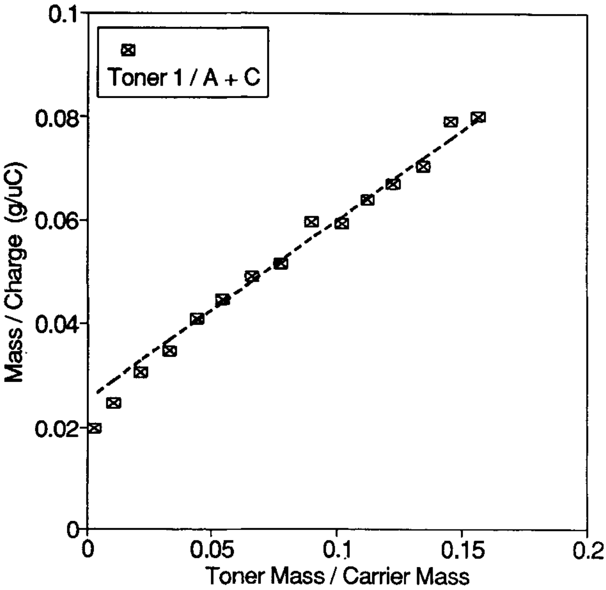

FIGURE 7 TC series for toner 1 on a 50-50 mixture of carriers A and C.

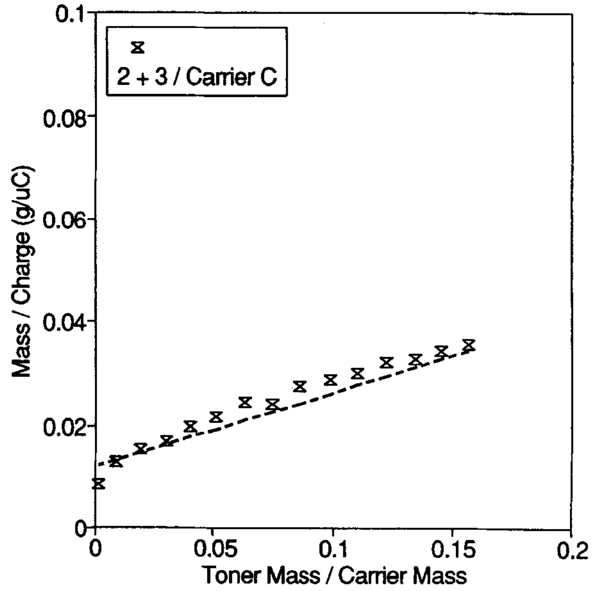

FIGURE 8 TC series for a 50-50 mixture of toners 2 and 3 on carrier C.

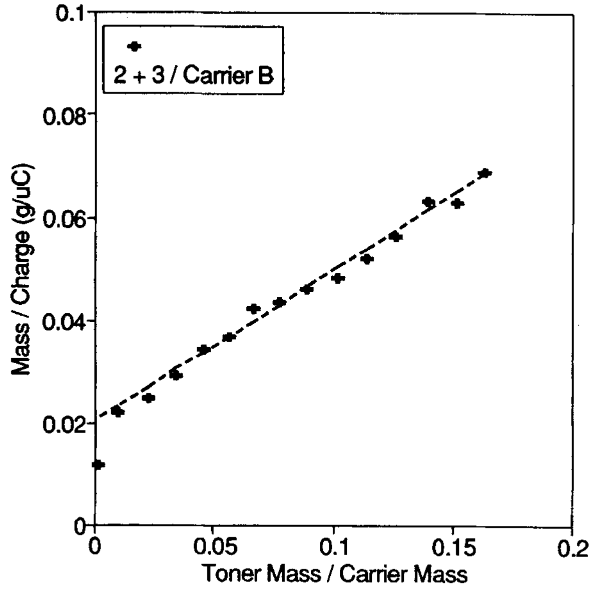

FIGURE 9 TC series for a 50-50 mixture of toners 2 and 3 on carrier B.

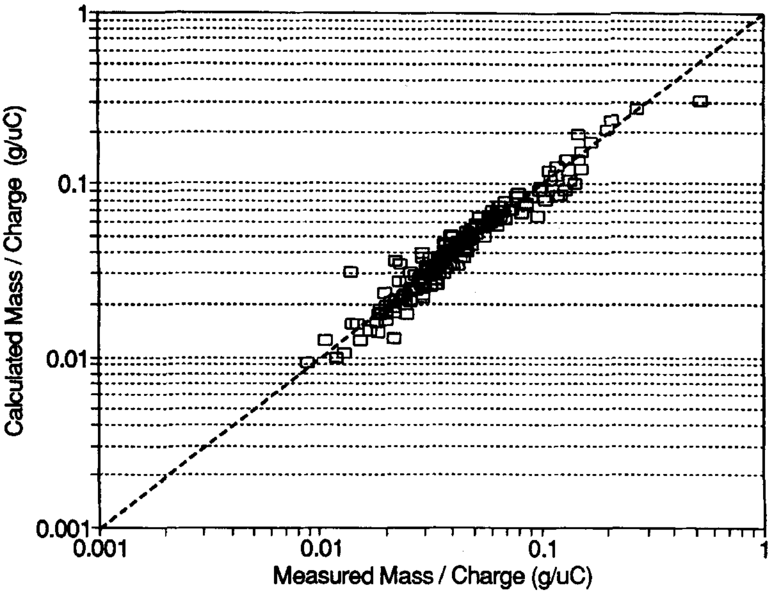

FIGURE 10 Scatter plot of measured *vs.* calculated m/q values. The RMS difference between the measured and calculated values is 11.7%.

CONCLUSIONS

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. Firstly, the surface-state model of charging can work with multi-component mixtures only if the mixing is such that each particle comes into contact with all of the components of the mixture. If this were not the case, then the weighted average of site densities could not be used to represent a mixture. Thus, agreement between the model and the charging behavior of three-component mixtures implies that complete mixing of the components has occurred.

Secondly, the ability to describe charging of different combinations of a set of materials by assigning charging site densities to each material demonstrates that the properties of a material which control tribocharging are inherent in each individual material. Tribocharging of a pair of materials is a function of the charging site densities of both materials. However, the charging site densities themselves are a characteristic of the material and do not depend upon the identity of the other materials in a mixture. This is consistent with the notion of a triboelectric series.[3]

Finally, the agreement between the surface-state model and experiment means that it should be possible to predict the charging behavior of any mixture of a set of materials if charging sites have been assigned to all of the components by the methods outlined above using binary mixtures. Therefore, it is not necessary to measure the charging behavior of all possible combinations and mixtures of materials. Rather, TC series determined for a subset of mixtures which contains each material are sufficient for assigning charging site densities and, therefore, for calculating charging behavior of any mixture of components from the set.

References

1. K. L. Johnson, K. Kendall and A. D. Roberts, *Proc. Roy. Soc. Lond.* **A324**, 301 (1971).
2. D. A. Hays, The Adhesion Society, *Proc. of the 17th Annual Meeting and the Symposium on Particle Adhesion*, pp. 91–93, Orlando, Florida, 20–23 Feb., 1994.
3. L. B. Schein, *J. Imaging Sci. Technol.* **37**, 1 (1993).
4. J. H. Anderson, *J. Imaging Sci.* **33**, 200 (1989).
5. J. H. Anderson and D. E. Bugner, *Proceedings of the 4th International Congress on Non-Impact Printing Technologies*, 1988, pp. 79–82.
6. A. Kondo, *Proceedings of the Technical Association of the Pulp and Paper Industry, 1980 Printing and Reprography Conference*, pp. 153–157.
7. J. H. Anderson, "A Comparison of Experimental Data and Model Predictions for Tribocharging of Two-Component Electrophotographic Developers", *J. Imaging Sci. and Technol.* **38**, 378 (1994).
8. E. Gutman and G. Hartmann, *J. Imaging Sci. and Technol.* **36**, 335 (1992).
9. L.-H. Lee, *Photographic Sci. and Eng.* **22**, 228 (1978).
10. R. A. Guistina, J. H. Anderson and D. E. Bugner, *J. Imaging Sci. and Technol.* **37**, 439 (1993).
11. J. H. Anderson, D. E. Bugner, L. P. DeMejo, R. A. Guistina and N. Zumbulyadis, *J. Imaging Sci. and Technol.* **37**, 431 (1993).