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Feature Article

Electric Field Theory of Toner Charging

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It is assumed in the electric field theory of toner charging that toner particles triboelectrically charge until a material-dependent electric field is created at the surface of each toner particle. This is also called the high-density limit of the surface state theory. There are now two independent published experimental tests that are consistent with this theory. These experimental tests are reviewed and analyzed. In addition, several topics related to this theory are discussed, including (1) progress towards a microscopic theory of toner charging, (2) limitations on one of the theories of toner adhesion, and (3) a proposed new theory of the source of wrong sign toner.

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Introduction

Significant progress has been made in understanding the mechanisms involved in triboelectric charging of insulating, toner particles. These advances, discussed in a recent review,[1] include

(1) the experimental demonstration that toner charging data are consistent with the electric field theory of toner charging,[2-4]
(2) the suggestion and verification that the surface "work function" of a toner can be expressed as a time-dependent surface area weighed sum of the "work functions" of the toner constituents,
(3) the experimental and theoretical studies showing that toner charging is not determined by air breakdown, and
(4) experimental measurements showing that the toner charge distribution is intrinsically wide, as though a statistical process underlies the charging process, with wrong sign toner resulting from the tail of the distribution.

Recently a second experimental test of the electric field theory of toner charging has been proposed and compared to experimental data.[5,6] This new proposed experimental test, as well as the original test,[2–4] was suggested in order to distinguish between the low-density and the high-density versions of the surface state theory. The high-density version of the theory (also called the electric field theory) assumes that toner particles charge until a material-dependent electric field is created at the surface of the toner particle. The low-density version of the theory assumes that the two contacting materials exchange charge between their surface states until the upper most filled levels are equilibrated.

The purpose of this article is to review these experimental tests and to provide a quantitative analysis of their ability to distinguish between the low- and the high-density versions of the theory. The second purpose is to begin to explore several topics related to the electric field theory of toner charging. First, we review the progress towards a microscopic theory of toner charging. A microscopic theory of toner charging, which relates the observed material-dependent electric field at which toner charging ceases to material properties, would be a major advance in the material science of electrophotography in particular, and in the field of triboelectricity in general. Second, agreement on the mechanism(s) of toner adhesion, while critical to the behavior of some of the electrophotographic subsystems, remains to be achieved. This theory of toner charging puts limits on one of the models of toner adhesion. Finally, combining this theory with a hypothesis of Gutman and Hartmann leads to a natural explanation for toner charge distributions and the existence of wrong sign toner in electrophotographic development systems.

Surface State Theory

In many electrophotographic systems, toner, which is approximately 10 microns in diameter, is triboelectrically charged by mixing it with much larger (100 micron diameter) particles called carrier beads. The basis of the surface state theory, which describes the triboelectric charging of toner particles, is shown in Fig. 1, which shows a macroscopic view of toner on carrier (Fig. 1a) and a microscopic view of a toner—carrier contact (Fig. 1b). Both the toner and carrier beads have surface states, represented by dashed lines, and filled states represented by a dot on the dash. The toner (carrier) surface states are filled to ϕ_1 (ϕ_2) before contact. (ϕ can be regarded as a "work function," but this concept has some difficulties when applied to insulators, as discussed in Ref. 1.) After contact, the surface states are filled to a common level. Due to the exchange of charge, an electric field E is created between the two surfaces. The voltage drop between the two surfaces is Ez, where

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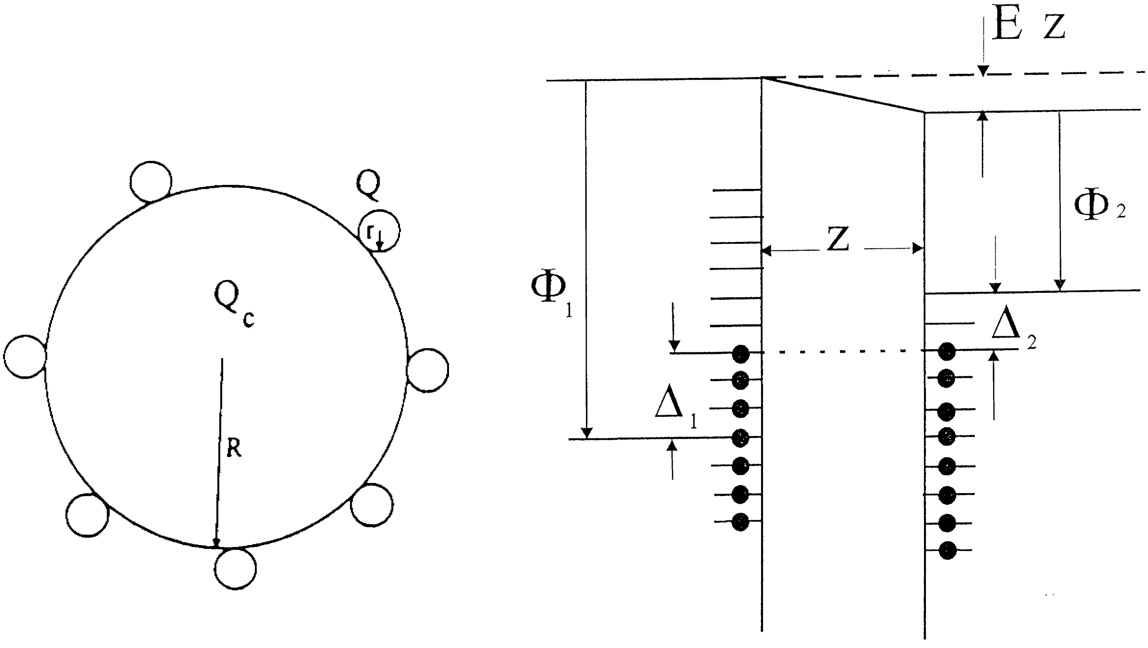

(a) (b)

Figure 1. (a) Macroscopic view of toner-carrier contact. (b) Microscopic view of toner-carrier contact (from Ref. 4).

z is the distance between the two surfaces at which charge exchange ceases. The low-density theory is the limit in which the voltage drop is negligible. The high-density theory is the limit in which the voltage drop dominates the physics of the charge exchange.

Anderson,[7] as well as Castle and Schein[4] and have shown that, in general, the mass-to-charge ratio, M/Q, in the surface state theory can be expressed as

$$\frac{M}{Q}=\frac{1}{3\Delta\phi}\left(\frac{1}{eN_t}+\frac{ez}{\varepsilon_0}\right)r\rho_t+C\frac{1}{3\Delta\phi}\left(\frac{1}{eN_c}+\frac{ez}{\varepsilon_0}\right)R\rho_c \qquad (1)$$

where e is the electronic charge, N_c (N_t) is the carrier (toner) surface state density (number per unit area per unit energy), ε_0 is the permittivity of free space, C is the toner concentration (ratio of toner mass to carrier mass), R (r) is the carrier (toner) radius, ρ_c (ρ_t) is the carrier (toner) density and $\Delta\phi$ is $\phi_1 - \phi_2$. $\Delta\phi/ez$ is the electric field E_e (the effective electric field) at which charging ceases in the high-density limit of the theory. This equation can be used to demonstrate the two experimental tests proposed to distinguish between the low- and high-density limits of the theory.

First, the equation describes a linear relationship between the M/Q and the toner concentration C. The slope to intercept ration S/I for this curve is given by

$$\frac{S}{I}=\frac{\left(\frac{1}{eN_c}+\frac{ez}{\varepsilon_0}\right)R\rho_c}{\left(\frac{1}{eN_t}+\frac{ez}{\varepsilon_0}\right)r\rho_t} \qquad (2)$$

This has two limits. In the high density limit ($1/eN<<ez/\varepsilon_0$) where N represents both N_t and N_c

$$\frac{S}{I}=\frac{R\rho_c}{r\rho_t} \qquad (3)$$

while in the low density limit ($1/eN>>ez/\varepsilon_0$)

$$\frac{S}{I}=\frac{R\rho_c}{r\rho_t}\frac{N_t}{N_c} \qquad (4)$$

These results provide an experimental test suggested by Schein.[2,3] Experimental observations of S/I can be plotted versus $R\rho_c/r\rho_t$, the prediction of the high-density version of the theory, which has no adjustable parameters. If agreement is obtained, than either $N_t = N_c$ for all of the carrier and toner mixtures (which seems unlikely) or the high-density theory is the valid description of the data. Such a plot is shown in Fig. 2 taken from an article by Castle and Schein.[4] Obviously, the data does not fall on an exact 45-degree line. There are observed deviations from the line, which could be due to a variety of reasons. A discussion of the possible reasons for the deviations is presented below.

The second experimental test to distinguish between the high- and the low-density limit was suggested by Anderson.[5,6] He noted that Eq. 1 suggests that a relationship exits between measurement of Q/M for two toners $(Q/M)_i$ and $(Q/M)_j$ charged against a series of carriers.

$$\left(\frac{Q}{M}\right)_i=\frac{a_j}{a_i}\left(\frac{Q}{M}\right)_j+\left(\phi_{ti}-\phi_{tj}\right)/a_i \qquad (5)$$

where

$$a_i=\frac{ze}{3\varepsilon_0}\left(\frac{\varepsilon_0}{N_{ti}e^2z}+1\right)r_{ti}\rho_{ti}+C\frac{ze}{3\varepsilon_0}\left(\frac{\varepsilon_0}{N_ce^2z}+1\right)R\rho_c \qquad (6)$$

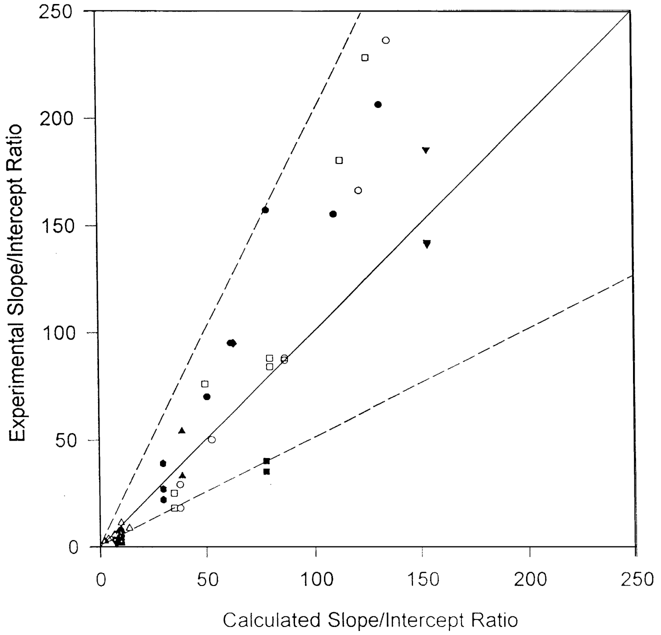

Figure 2. Comparison of experimental and calculated values of *S*/*I* from the high-density theory of toner charging (from Ref. 4).

with a similar equation for a_j. Assume that the experiment values of *Q*/*M* are obtained for constant toner size and density, constant carrier size and density, and constant toner concentration. The only parameters left to consider are N_c and N_t. A straight line can only be obtained for Eq. 5 if N_c is in the high-density limit (because the second term will be different for each carrier). If a slope of 1 is obtained between $(Q/M)_i$ and $(Q/M)_j$, this suggests $a_i = a_j$ which can only occur if $N_{ti} = N_{tj}$ (which seems unlikely) or the high-density limit applies. Part of the data analyzed in Ref. 6 are shown in Fig. 3 which are taken from data published by Law and Tarnawskyj.[8] In these data four different carriers were used (which had a systematic variation in the carrier coating) which represents the four points on each straight line. The *Q*/*M* was measured against these four carriers for pairs of toners. The toners had different silica concentrations, a surface additive used to enhance flow properties. The slopes of these and all of the curves analyzed by Anderson are shown in Table I. Much of the data has a slope of 1 within experimental error, which is consistent with the high-density limit of the surface state theory. Some of the data do not have a slope of 1 within the experimental error quoted, which is the standard error of the least squares linear fit to the data. In Ref. 6 it is concluded that "the charging behavior of these toners may not be determined by the high density of states limit." However, a discrepancy between the observed slope and 1 could be due to a variety of reasons. An analysis of the possible reasons for the discrepancy is presented below.

Quantitative Analysis of Tests

First Experimental Test

Consider the first experimental test, comparing the experimental slope to intercept ratio of plots of *Q*/*M* versus *C*, the toner concentration, with the prediction of the high-density theory. In general, the theory (Eq. 1) predicts a *S*/*I* given by Eq. 2. Deviations from the pre-

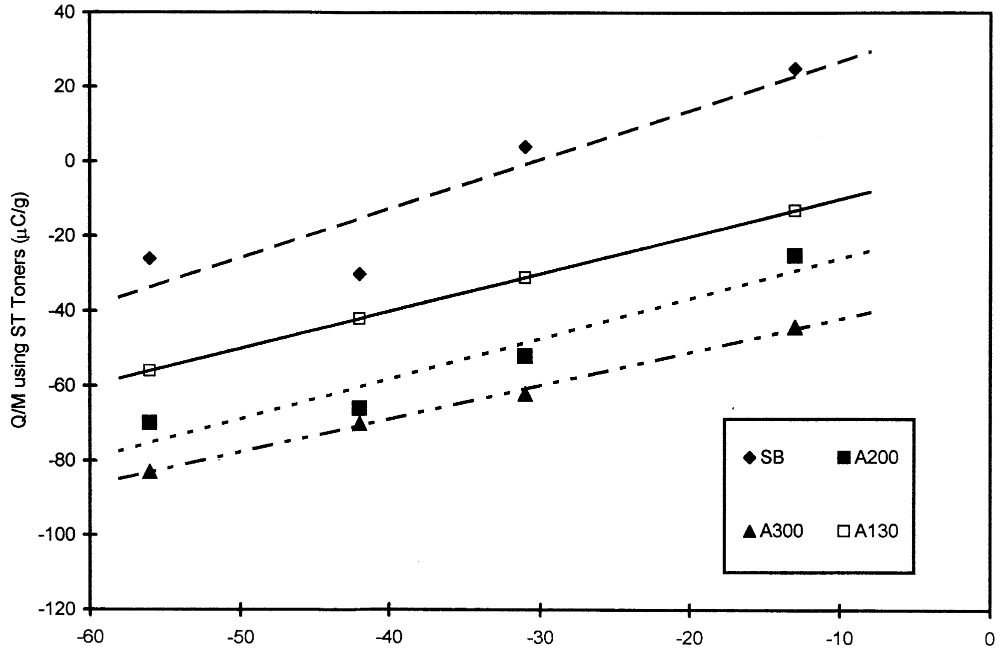

Figure 3. Q/M of four different toners plotted against A130 toner as suggested by Eq. 5 in the text. The four data point on each line represent 4 different carrier particles (which have systematic changes in their coating material). The A130 toner is a coated with an hydrophilic silica of nominal size 16 nm at 0.5% weight concentration. The SB toner is not treated with silica. The A200 and A300 toners are the same hydrophilic silica at 12 and 7 nm size at the same weight concentration. The lines are least squares it to the data. They show a linear correlation between *Q*/*M* measured on one toner against *Q*/*M* measured against another toner for various carrier particles (from Ref. 6).

TABLE I. Slopes observed by plotting A130 toner (used as reference) against other toners. A130, A200, and A300 are toners treated with hydrophilic silica with 16, 12 and 7 nm sizes. R972, R974 and R976 are hydrophobic silicas with 16, 12 and 7 nm size. R202, R805 and R812 are other hydrophobic silicas also with 16, 12 and 7 nm size. SB is untreated. All were mixed at 0.5% weight concentration (taken from Ref. 6).

Silica	Slope
SB	1.32 ± 0.34
R202	1.41 ± 0.25
A130	(reference) 1
A200	1.08 ± 0.21
R972	0.97 ± 0.24
R974	1.18 ± 0.02
A300	0.90 ± 0.03
R805	0.87 ± 0.19
R976	0.66 ± 0.10
R812	0.44 ± 0.09

dicted value of high-density theory could be attributed to $N_c \neq N_t$. However, several other factors need to be considered before this conclusion can be drawn. For example, it is well known that Q/M measurements[9] are generally not repeatable within ±10%. Second, for some toner carrier mixtures, inaccurate measurements can be obtained because all of the toner particles are not blown out of the blowoff cage.[9] This can occur if the toner is high charged (thus has high adhesion) or the air pressure is low. Another possibile source of error is carrier chips or small diameter carrier coming out of the cage adding to the mass measurements. Finally, the surface state theory is an equilibrium theory. It requires adequate mixing until Q/M does not change with mixing time, an experimental result not generally reported.

For the sake of discussion, assume none of these experimental errors are occurring. As one can see from Fig. 2 some of the data deviate from the predicted S/I by a factor of 2. What values of N_t and N_c could account for this observation? Slightly rewriting Eq. 2,

$$\frac{S}{I}\frac{r\rho_t}{R\rho_c} = \frac{\left(\dfrac{1}{eN_c}\dfrac{\varepsilon_0}{ez}+1\right)}{\left(\dfrac{1}{eN_t}\dfrac{\varepsilon_0}{ez}+1\right)} \qquad (7)$$

one can see that it has the form $(S/I)(r\rho_t/R\rho_c) = (a_1 + 1)/(b_1 + 1)$ where

$$a_1 = \frac{1}{eN_c}\frac{\varepsilon_0}{ez} \qquad (8)$$

and a similar equation for b_1 (with N_c replaced with N_t). Because the maximum deviation observed for S/I from the high-density prediction is 2, Eq. 7 becomes

$$2 = \frac{a_1 + 1}{b_1 + 1} \qquad (9)$$

or

$$a_1 = 2b_1 + 1. \qquad (10)$$

There are two cases to consider. If b_1 is small compared to 1, N_c is large and the high-density limit applies to the carrier. In this case $a_1 = 1$ and N_t is just at the exact boundary between the low and high-density limit. If b_1 is large compared to 1, then N_c is small and the low-density limit applies. Then $a_1 = 2b_1$ and N_t must equal exactly $2N_c$. Is this ratio of 2 realistic? Consider the source of surface state densities. They are surface states on the surface of an insulator which can hold charge. The upper limit is the number of molecules on the surface of solid, approximates 10^{14} to 10^{15} states/cm^2. (Because solid states energies are typically about 1 eV, this is equivalent to 10^{14} to 10^{15} states/cm^{2}eV.) Typically in semiconductors, surface state densities are reported as 10^{11} states/cm^2. To fit toner-charging data, it can be shown that numbers such as 10^{11} states/cm^2 are needed. What ratio between the surface states density on different materials is reasonable? With 3 to 4 orders of magnitude of variations possible, one could fairly say that a ratio of a factor of 10 variation is not unreasonable. The data shown in Fig. 2 has S/I equal to the predicted high-density theory within a factor of 2 for many toner-carrier mixtures. Therefore, either $N_c = N_t$ within a factor of 2 for all of these toner—carrier mixtures or the high-density theory applies. It seems an unreasonable coincidence to believe that $N_c = N_t$ within a factor 2. More reasonably, one or several of the experimental errors mentioned above could account for the factor 2 discrepancy observed in a few cases between the data and the high-density theory prediction.

For the low-density theory to be consistent with the data, with the density of states assumptions made above, the S/I ratio should differ from the predicted high-density value by factors of 10 for most of the toners.

Second Experimental Test

Consider the second experimental test, comparing the slope of $(Q/M)_i$ versus $(Q/M)_j$ to 1. The experimentally observed slopes as reported by Anderson are shown in Table I. Many of the slopes are 1 within experimental error, as predicted by the high-density theory. Deviations from the predicted value of 1 of the high-density theory could be attributed to $N_{ti} \neq N_{tj}$. However, as discussed above, there are several other factors that need to be considered before this conclusion can be drawn:

1. Q/M measurements are generally not repeatable within ±10%.
2. in some cases all of the high charged toner particles are not blown out of the blowoff cage
3. carrier chips or small diameter carrier can be blown out of the cage,
4. adequate mixing until Q/M does not change with mixing time is required to compare data with the equilibrium surface state theory.

For the sake of discussion, assume none of these experimental errors are occurring. The slope is predicted to be (from Eq. 5 and 6).

$$\frac{a_j}{a_i} = \frac{\left(\dfrac{\varepsilon_0}{N_{ti}e^2 d}+1\right) r_{ti}\rho_{ti} + C\left(\dfrac{\varepsilon_0}{N_c e^2 d}+1\right) r_c\rho_c}{\left(\dfrac{\varepsilon_0}{N_{ti}e^2 d}+1\right) r_{ti}\rho_{ti} + C\left(\dfrac{\varepsilon_0}{N_c e^2 d}+1\right) r_c\rho_c} \qquad (11)$$

As can be seen from Table I, some of the data deviate from the predicted slope of 1. One even has by a slope of

0.44. What values of N_t and N_c could account for this observation? Note first that a straight line can only be obtained if N_c is in the high-density limit ($\varepsilon_0/N_c e^2 d << 1$). If N_c were in the low-density limit the data points would be scattered on the graph as each carrier N_c changed. Assuming N_c is in the high-density limit gives

$$0.44 = \frac{\left(\dfrac{\varepsilon_0}{N_{ti}e^2 d} + 1\right) r_{ti}\rho_{ti} + C r_c \rho_c}{\left(\dfrac{\varepsilon_0}{N_{tj}e^2 d} + 1\right) r_{ti}\rho_{ti} + C r_c \rho_c} \tag{12}$$

which becomes (using parameters from the original article,[8] $r = 4.5$ microns, $R = 65$ microns, $C = 0.02$, $\rho_t = 1.1$ g/cm^3 and $\rho_c = 7.8$ g/cm^3)

$$b_2 = 2.5 a_2 + 4.6, \tag{13}$$

where

$$a_2 = \frac{\varepsilon_0}{N_{ti}e^2 d} \tag{14}$$

with a similar equation for b_2 (with N_{ti} replaced with N_{tj}). Again, there are two cases to consider. If a_2 is small compared to one (N_{ti} is large), then b_2 is 4.6. In this case, toner i is in the high-density limit, and toner j has exactly 4.6 times the density of states as the crossover limit between the two theories. If a_2 is large (N_{ti} is small and in the low density limit), N_{tj} is 2.5 times N_{ti}. Again, we find the requirement that the ratio of the surface state densities has to be within an unreasonable close ratio to satisfy the experimental results. More reasonably, the data are described by the high-density limit and one of the several experimental errors mentioned above accounts for the discrepancy. For example, the largest discrepancy (0.44) occurs for toner with Q/M = 100 µC/g, which is very high charged toner and may not be completely blown out of the blowoff cage. In addition, if the 10% error is applied to the original data, the R812 slope changes from 0.44 ± 0.09 to 0.78 ± 0.23, which is consistent with the high-density limit.

For the low-density of states limit to be consistent with data, straight lines should not be obtained on plots such as Fig. 3. Instead, the data should be scattered as each carrier N_c varies, since it is reasonable to expect all of the materials to be in the same limit.

In an earlier article,[5] in which this experimental test was first described, slopes of 0.4 and 0.6 were obtained. The same discussion above applies. A reasonable interpretation of the data is that they are consistent with the high-density limit and deviations of the slopes from 1 are due to experimental error.

Discussion

The experimental evidence from two independent tests, as well as other experiments,[2-4] appears to be consistent with the electric field theory of toner charging. The theory can be written with the effective electric field E_e explicitly shown by taking the high density limit of Eq. 1 and identifying E_e with ($\Delta\phi/ez$)

$$\frac{M}{Q} = RC\frac{\rho_c}{3\varepsilon_0 E_e} + r\frac{\rho_t}{3\varepsilon_0 E_e} \tag{15}$$

Three topics related to this equation are discussed below.

Progress Towards a Microscopic Theory of Toner Charging

Given the remarkable success of the electric field theory of toner charging in accounting for a wide range of experimental data, it is reasonable to inquire as to what are the observed values of E_e, how does this field depend on material parameters, and how can it be accounted for based on the physical and chemical characteristics of the materials involved.

There are several ways to determine the effective electric field based on the equations given above. Perhaps the easiest and most reliable is to note in Eq. 15 that the slope of a measure M/Q versus C curve is $R\rho_c/3\varepsilon_0 E_e$. If R and ρ_c are known, E_e is readily calculated from the measured slope. Even if a complete curve of M/Q versus C is not available, E_e can still be calculated from a single measurement of Q/M if enough information is available. Solving Eq. 15 for E_e gives

$$E_e = \frac{Q/M}{3\varepsilon_o}\left(RC\rho_c + r\rho_t\right) \tag{16}$$

Schein[2,3] calculated E_e from M/Q versus C curves and noted its variation with charge control agent CCA concentration. His results are 8.8, 12.9, 21.3 V/µm for 0, 0.5 and 2.5% CCA in a styrene acrylic resin toner. Clearly the effective electric field depends on CCA concentration.

In 1978, Lee[10] published one of the earliest articles in the field to address the theory of toner charging. His Fig. 2 is for two different toner sizes on a steel carrier (density = 7.8 g/cm^3) coated with an aliphatic copolymer. E_e is 9.5 V/µm, taken from the slope, and is independent of toner diameter, consistent with the theory. In his Fig. 3 the two different toners used in Fig. 2 are mixed with a nonmetallic carrier (density 5.5 g/cm^3) coated with an aliphatic copolymer. E_e is 9.0 V/µm. In his Fig. 4 an aromatic polymer is coated on a nonmetallic carrier. The toner sign reverses and the E_e is –8.5 V/µm. Clearly, E_e can change and will even change sign as the polymer of the carrier changes. (The sign of E_e is ignored for the remainder of this article.)

In Fig. 3 of their 1992 article, Gutman and Hartmann[11] plotted Q/M versus C behavior of a series of toner with diameter from 5.8 to 15.1 µm. E_e is 5.3 ± 0.5 V/µm for all of the toners. Clearly, E_e does not vary with toner diameter, as shown earlier by Lee. In Fig. 2 of this article, a Xerox 914 toner was mixed with a carrier coated with a methyterpolymer whose thickness was varied. E_e changed from 6.5, to 9.7, to 12.1 V/µm. Therefore E_e varies with carrier coating thickness.

As discussed in an another study,[1] Nash and Bickmore[12] published a series of articles which successfully accounted for complicated time-dependent toner charging behavior by adding time dependence to the Gutman and Hartmann[10] hypothesis that the "work function" of a toner can be expressed as the area weighed sum of the "work functions" of the toner constituents. When this was done, familiar M/Q versus C curves were obtained. In Ref. 1 it was shown how to obtain E_e from their fitting parameters, A' and the "charging tendency." When this is done E_e turns out to be 7.7 V/µm for the data shown in Ref. 12. Note that while their fitting method requires some arbitrary assumptions, E_e is a fixed value for each toner-carrier system, unaffected by their arbitrary assumptions.

TABLE II. Calculations of E_e for hydrophilic and hydrophobic silicas with varying coverage. The carrier coating and silica weight percent were kept constant (data taken from Ref. 8).

Silica size	Surface coverage	hydrophilic silica		hydrophobic silica	
nm	m^2/g	Q/M μC/g	E_e V/μm	Q/M μC/g	E_e V/μm
16	120	55.3	32.8	80.3	47.6
12	170	69.2	41	90.5	53.6
7	250	82	48	100.9	59.8

TABLE III. Effect of % Kynar in carrier coating on E_e (data taken from Ref. 8).

% Kynar	Q/M μC/g	E_e V/μm
20	55.3	32.8
40	41	24
60	30	17.8
80	11	6.5

Anderson's analysis of Law's and Tarnowskyj's data is useful for verifying the consistency of the electric field theory of toner charging with data but is less useful for obtaining actual values of E_e. Note from his[6] Eq. 5 that only the *difference* in toner "work functions" are obtained from the S/I ratio of Q/M_i versus Q/M_j plots. However, using Eq. 16 above, together with Law and Tarnowskyj's data[8] it is possible to calculate E_e and to determine its sensitivity to several material parameters. Table II shows a hydrophilic and a hydrophobic silica the variation in E_e with silica size. (Silica are nm size particles added to the surface of the toner particles to enhance flow properties. They also affect charging. Because of their small size and the high-energy methods of addition, their adhesion to the toner particles is very large, making them permanent parts of the toner. Which surface is charged, the toner or the silica, has not been determined, to the author's knowledge.) For this experiment the carrier coating was fixed (20/80 Kynar/PMMA mix where Kynar is poly(vinylidene fluoride) from Pennwalt and PMMA is poly(methyl methacrylate)), and the silica concentration was fixed at 0.5%. Therefore the smaller silica had larger area coverage, as shown in the table. (The other fixed parameters were already quoted above.) Note that E_e increases between 25 and 50% as the area coverage increases by a factor of 2 for both types of silica. Table III shows the effect of changing the carrier coating: changing the Kynar concentration from 20 to 80% causes E_e to decrease. The effect of moisture was also tested. Changing from 20 to 80% RH changed E_e from 32.8 to 4.5 V/μm for the A130 silica.

Wu and coworkers[13] mixed a magnetic carrier with three different color toners and obtained the same E_e for all three mixes, 15.5 ± 0.4 V/μm.

Anderson has published extensive Q/M data. As an example, consider Ref. 7. In Fig. 3 of Ref. 7, Q/M versus C data are shown with 100 micron diameter carrier. Assuming $\rho_c = 5$ g/cm^3 gives $E_e = 12$ V/μm. From his Fig. 5, E_e of 5.6 V/μm is obtained. Figure 7 of Anderson's article is interesting because it appears to show measurements of the S/I ratio (for the same toner and carrier) that depend on CCA concentration, which is inconsistent with Eq. 3, the prediction of the high-density theory. These data are inconsistent with results published in Refs. 2 and 3, discussed above. Again, the discrepancy with high-density theory is small, which makes it difficult to believe that the data can be explained by the low-density theory.

In conclusion, E_e is about 10 V/μm within a factor of two for most materials tested so far (although values as high as 60 V/μm have been reported). It is interesting to note that E_e varies systematically with charge control agent concentration (Schein's data) or coverage (Law and Tarnawskyj's data), with systematic changes in the carrier coating material (Lee's data and Gutman and Hartmann's data), and with relative humidity changes (Law and Tarnawskyj's data).

Nonetheless, accounting for the absolute magnitude of E_e is difficult using normal solid state physics concepts. As pointed out before,[1] if one views E_e as the field built up to cancel a work function difference, it should equal the work function difference between polymers divided by the distance at which charge exchange stops. A solid state work function difference is 1 eV and tunneling stops about 1 nm, giving a predicted value of E_e of 1000 V/μm, much larger than observed. The identification of the material/physical parameters that can account for E_e is probably the key to a microscopic theory of toner charging.

Patch Model of Toner Adhesion

The theory of toner adhesion has been under discussion[14,15] for many years. Agreement on whether nonuniform charging of the toner surface area or van der Waals force dominate adhesion has not been achieved. The electric field model of toner charging discussed above places some limits on one of these models of adhesion.

It is generally assumed that a uniformly charged sphere (which is a first order model for a charged toner particle) brought into contact with a metal plane induces charge in the metal plane which leads to an electrostatic adhesive force F_e of

$$F_e = \frac{1}{4\pi\varepsilon_0}\frac{Q^2}{4r^2} \tag{17}$$

It is also well known that this force underestimates the measured force of adhesion of toner particles by a large amount, between a factor of 5 or 10 according to some authors.[14] In an attempt to account for this discrepancy, some authors have argued that the charge on the toner particle is non-uniformly distributed[14] and some authors have argued that van der Waals force dominates toner adhesion.[15]

One non-uniform toner charging model assumes that the toner is charged in patches, such that at the area of contact, a parallel plane approximation can be made.[14] In this region, charge exchanged between the metal and the toner sits opposite each other as in a capacitor structure with a charge per unit area of σ in a capacitor area of A_c. By assuming values of $\sigma = 1$ mC/m^2 and a ratio of $A_c/A_T = 0.2$ (where A_T is the total charged area), observed adhesions forces (100 nN) can be accounted for. However it has been pointed out[15] that such large values of σ lead to air electric fields of ($\sigma/2\varepsilon_0$) of 56 V/μm, far in excess of the 3 V/μm which can be sustained in large air gaps without Paschen breakdown. However, it is also well known that much larger electric fields can be sustained over small distances, so whether such large values of σ can be sustained has not been resolved.

This electric field theory of toner charging has some implications regarding the patch model of toner adhesion. Obviously, a large electric field is being assumed at the toner-metal interface. If such a large electric field exists, it should also occur at a toner–carrier interface. However, assuming such a large electric field at the interface leads to the prediction that toner charge-to-mass ratios are independent of toner concentration, which is inconsistent with extensive experimental data. This is shown as follow:

The demonstration of this statement requires only two calculations. First, let us define (following Ref. 14) $f = A_c/A_T = Q_c/Q$ where A_c is the contact area, A_T is the charged area, Q_c is the charge in the contact area, Q is the total charge on the toner particle. Define $\beta = A_c/A$ where A is the total area. Hays assumed f was to be 0.2 (in order to obtain large enough adhesion to match the experimental data), although the exact magnitude is not critical to this argument. β can be calculated from the Hertz theory of elastic contact: the contact radius r_H for a given load P is

$$\pi_H^3 = \frac{3}{4} P\pi \frac{1-\nu^2}{E} \tag{18}$$

where ν is the Poisson ratio (0.3) and E is the modulus of elasticity (3 Gpa), using numbers typical of polymers. If we chose a very large adhesion of 1000 nN, then r_H = 96 nm and

$$\beta = \frac{\pi r_H{}^2}{4\pi r^2} = 1.4 \times 10^{-4} \tag{19}$$

which is an upper bound for β given the assumed large adhesion. (Similar results are obtained with JRK theory for large forces. See for example Eq. 7 in Ref. 15.) This gives $f/\beta \approx 10^3$ with f = 0.2, as assumed in Ref. 14.

With f and β now known, the “patch” electric field σ/ε_0 can be added to the normally assumed electric fields at the toner–carrier interface:

$$E = \frac{1}{4\pi\varepsilon_0}\left(\frac{Q_B}{R^2} + \frac{Q_T}{r^2}\right) + \frac{\sigma}{\varepsilon_0} \tag{20}$$

where Q_B is the carrier bead charge and Q_T is the toner charge uniformity distributed around the toner particle. σ can be expressed as

$$\sigma = \frac{Q_c}{A_c} = \frac{fQ}{A_c} = \frac{fQ}{\beta A} = \frac{f}{\beta}\frac{Q}{4\pi r^2} \tag{21}$$

Assume the remainder of the charge is uniformly distributed around the toner particle

$$Q_T = Q - fQ \tag{22}$$

then substitution into Eq. 20 gives

$$E = \frac{1}{4\pi\varepsilon_0}\left(\frac{Q_B}{R^2} + \frac{Q - fQ}{r^2}\right) + \frac{f}{\beta}\frac{Q}{4\pi r^2} \tag{23}$$

which can be solved for M/Q using the usual assumptions ($Q_B = nQ$ where n is the number of toners on a carrier, $C = nm_T/m_C$ where m_T is the mass of a toner and m_T is the mass of a carrier, both assumed spherical), gives

$$\frac{M}{Q} = \frac{1}{3\varepsilon_0 E_e}\left[CR\rho_c + r\rho_t\left(1 - f + \frac{f}{\beta}\right)\right] \tag{24}$$

and the slope to intercept ratio of M/A versus C is

$$\frac{S}{I} = \frac{R\rho_c}{r\rho_t\left(1 - f + \dfrac{f}{\beta}\right)} \tag{25}$$

Because f/β is about 10^3, M/A is predicted to be almost completely independent of toner concentration in Eq. 24 (which is not observed) or the slope to intercept ratio, given by Eq. 25, is predicted to be 10^3 times smaller than is observed.[4]

Of course, non-uniform charge distributions can and probably do exist on toner particles. However, this argument suggests that non-uniform charge distributions that lead to electric fields at the interface that are much larger than the normal electric fields due to the toner and carrier charges uniformly distributed on their surfaces, do not occur.

Theory of Toner Charge Distributions and Wrong Sign Toner

As described above, the effective electric field was calculated from the data. It was shown that systematic variations were observed in E_e with systematic variations in charge control agent concentration and coverage, and with systematic changes in carrier coating material. Explanation of such observations were first suggested by Gutman and Hartmann,[11] who suggested that the “work function” ϕ of a toner can be expressed as surface area weighed sum of the “work functions” ϕ_i of the toner constituents, that is

$$\phi = \sum A_i \phi_i \tag{26}$$

where A_i is the area of each constituent. Reformulating Eq. 26 into the language of the electric field theory of toner charging, we obtain

$$E_e = \sum A_i E_{ei} \tag{27}$$

where E_{ei} are the effective electric fields of each toner constituent.

Of course, A_i is difficult to measure for charge control agents because they are chemicals mixed into bulk at the 1% by mass level. Nonetheless, Eq. 27 (or 26) does suggest a means of understanding the systematic changes observed in E_e.

Consider the implication of Eq. 27 on the question of the source of toner charge distributions. ϕ is identified with “the characteristic energy of a particle” on p. 339 of Ref. 11. Let us hypothesize instead that each toner constituent, within its own surface area on the toner particle, charges to a value determined by E_{ei}. This hypothesis leads to a theory of toner charge distributions: toner charge distributions are due to variations in A_i among toner particles.

This theory of toner charge distributions can be taken one step further to a theory of wrong sign toner. Wrong sign toner is well known to limit the behavior of development systems. We hypothesize that wrong sign toner is due to large enough variations in A_i that toner constituents, which charge to the opposite sign of the other toner constituents, dominate the toner charging.

Experimental verification of this theory of wrong sign toner would be useful. Measurements on the microscopic scale of charges on the surface of a toner particle appear challenging. However, a much simpler experiment can be conceived. The hypothesis above suggests that there exists in a batch of toner, some toner with its A_i such that it becomes wrong sign. Therefore wrong sign toner is special toner. Wrong sign toner can be collected in the cleaning station of an electrophotographic engine by, for example, running white pages only. Then this toner can be mixed with carrier particles and put back into a clean development system. If wrong sign toner is really special toner, then all of the toner in the new developer mix should be wrong sign and development should be reversed. (There is one report of this experiment in the literature in Ref. 1 done by the author. It was experimentally observed that the images were normal. However, the experiment was done with monocomponent development, which does not use carrier particles, and should be repeated, due to its importance.)

Conclusions

The two experimental tests of the electric field theory of toner charging have been reviewed. These experimental tests have been analyzed to determine how well they can distinguish between the low-density version and high-density version (also called the electric field theory) of the surface state theory of toner charging.

The first experimental test compares the slope-to-intercept ratio predicted by the electric field theory of toner charging to experimentally observed values. Much of the data agrees with the theory by a factor of less than 2. In a few cases, a discrepancy of about a factor of 2 is observed. Explanations for this discrepancy are:

1a. N_c is in the high density limit and N_t is at the exact boundary between the high and low density limits, or
2a. $N_t = 2\ N_c$, or
3a. The data are consistent with the high-density limit and experimental error accounts for the factor of 2 discrepancy observed in a few cases.

Based on the physical nature of surface states, it has been suggested that surface state densities should vary by factors of 10. Therefore if the low-density limit applies, then the S/I ratio should vary from the value predicted by the high-density theory by factors of 10 for most toners. As this is not observed experimentally, a reasonable explanation of the data is #3a above.

The second experimental test compares the slope of a plot of Q/M measured on one type of toner with Q/M measured on a second type of toner, both toners being charged against various carrier beads. The slope is predicted to be 1 if the high-density limit applies. Much of the data presented in the literature does have a slope of 1 within experimental error. Sometimes discrepancies are observed. A value of 0.44 has been reported. Explanations for this discrepancy are:

1b. N_c and N_{ti} are in the high density limit and N_{tj} = 4.6 times the limit at the boundary between the high and low density limit, or
2b. N_c is in the high density limit and $N_{tj} = 2.5\ N_{ti}$, or
3b. The data are consistent with the high-density limit and experimental error accounts for the discrepancy. For example, it has been pointed out that if ±10% measurement errors are added to the original data set, the slope changes from 0.44 ± 0.09 to 0.78 ± 0.23.

If the low density of state limits applies for one material, it should apply for all of the materials. Therefore, straight lines should not be obtained on plots such as Fig. 3. Instead the data should be scattered as each carrier N_c varies. If one allows that the carrier and toner can be described by different limits in the same experiment, and that the carrier is described by the high density limit, then the ratio of the densities of states of the two toners should vary by a factor of 10, given the nature of surface states. This predicts slopes on the data such as shown in Fig. 3 of 10. As neither of these predictions are observed experimentally, a reasonable explanation of the data is #3b above.

The effective electric fields E_e at which triboelectric charging of insulating toner particles ceases, have been calculated from available experimental data. E_e is about 10 V/µm within a factor of 2 for most materials tested so far (although values as high as 60 V/µm have been reported). Further measurements of this value are encouraged, especially under the conditions under which some material parameter is systematically varied. It is interesting to note that E_e varies systematically with charge control agent concentration (Schein's data) or coverage (Law and Tarnawskyj's data), with systematic changes in the carrier coating material (Lee's data and Gutman and Hartmann's data), and with relative humidity changes (Law and Tarnawskyj's data). Nonetheless, accounting for the absolute magnitude of E_e is difficult using normal solid state physics concepts. The identification of the material/physical parameters that can account for E_e is probably the key to a microscopic theory of toner charging.

This electric field theory of toner charging puts limitations on one of the theories of toner adhesion. Nonuniform charge distributions on the surface of a toner particle have been hypothesized to account for the large toner adhesion that have been experimentally observed. While non-uniform charge distributions are possible, if the non-uniformity is large enough to significantly affect the electric field at the interface between the toner and carrier particle, then such a theory leads to the prediction that the toner charge-to-mass ratio is independent of toner concentration, inconsistent with extensive experimental data.

Finally, a theory of toner charge distribution in general, and wrong sign toner in particular, have been suggested. They are due to variations in the area on each toner particle of constituents that have their own effective electric fields. An experimental test of this theory has been suggested.

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Authors Note

The reader may be interested in two articles that were published after this article was submitted which relate to the subject matter discussed. In James Q. Feng and Dan A. Hays' article,[16] non-uniform charge densities on the toner (in the shape of a dumb-bell) were assumed to calculate toner adhesion. Such non-uniform charge densities lead to large electric fields at the surface of the toner, as discussed in this article in the section, **Patch**

Model of Toner Adhesion. In J.H. Anderson's article,[17] it is pointed out that an analysis using the **Second Experimental Test** (as defined in this article) of published data of carbon black in toner leads to the conclusion that the electric field theory of toner charging describes the data.

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