# Recent Advances In Our Understanding of Toner Charging

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## Abstract

Correct toner charging, its sign, magnitude, and distribution, are critical parameters in any electrophotographic development system. This review summarizes recent advances in our understanding of the physics and chemistry governing the toner charging process. These advances include (1) the experimental demonstration that toner charging data are consistent with the theory that toner particles charge up until a material dependent electric field is created at the surface of the toner particle, (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.

## Introduction

The primary material property that determines the behavior of any electrophotographic development system is the toner charge distribution.[1] The toner charge-to-mass ratio (Q/M) determines the amount of toner developed and toner with the wrong sign charge is known to degrade image quality. Despite the importance of this toner property, its optimization remains a highly empirical process, with its consequent large costs in terms of time and testing. A fundamental understanding of the material parameters that determine toner charging would be a revolutionary advance in the electrophotographic technology. Several recent advances in our understanding of toner charging, which bring this fundamental understanding closer, are reviewed here.

## 1. Electric Field Theory of Toner Charging

It has been known for some time that toner charging in a dual component system, which charges toner particles by mixing them with much larger particles called carrier beads, can be described by two theories. Both of these theories can account for the dependence of Q/M on carrier and toner diameter and toner concentration C (the ratio of toner mass to carrier mass). But the theories are very different conceptually.

In the first theory,[2] sometimes called the low density surface state theory, it is postulated that the toner and carrier have surface states that exchange charge until their surface "work functions" are equilibrated. In this theory, it is assumed that there are $N_t$ ($N_c$) states per unit energy per unit area on the toner (carrier) and that charge is exchanged to fill the states between the carrier "work function" $\phi_c$ and the toner "work function" $\phi_t$. After equilibration, it can be shown that the inverse of the charge-to-mass ratio M/Q is given by

$$\frac{M}{Q} = RC(\frac{\rho_c}{3\Delta\phi eN_c}) + r(\frac{\rho_t}{3\Delta\phi eN_t}) \qquad (1)$$

where R (r) is the carrier (toner) radius, $\rho_{c(t)}$ is the carrier (toner) density, and $\Delta\phi$ is the difference between the carrier and toner "work functions." This equation suggests that a measurement of M/Q plotted against C will be a straight line with a slope proportional to R and an intercept proportional to r. These predictions are in accord with numerous experimental observations.[2,3]

In the second theory,[4] the electric field theory, sometimes called the high density surface state theory, charge is exchanged until an electric field is created at the surface of the toner particle to offset the difference in "work functions" at the interface ($\phi_c - \phi_t$). The electric field $E_e$ in the interface is $(\phi_c - \phi_t)/ez$, where z is the distance between the insulators at which charge exchange ceases. One of the first people to suggest this idea was Kondo[5]; the most thorough calculation of the electric field at the surface of a toner particle is given by Gutman and Hartmann.[6] Based on this model, it can be shown that

$$\frac{M}{Q} = RC(\frac{\rho_c}{3\varepsilon_0 E_e}) + r(\frac{\rho_t}{3\varepsilon_0 E_e}). \qquad (2)$$

Note this equation also predicts that M/Q plotted against C will be a straight line with a slope proportional to R and an intercept proportional to r.

It was suggested[3,4] that these two models can be distinguished experimentally by calculating the slope to intercept ratio of M/Q vs. C. The slope-to-intercept ratio is determined entirely by known parameters, $R\rho_c/(r\rho_t)$, in Eq. (2); it is determined by the product of this parameter and $N_t/N_c$ in Eq. (1). When experimental data were compared with these predictions[3] it was found that in virtually all published experiments the results agreed with the electric field theory within a factor of two with no adjustable parameters. One must therefore conclude either (1) that the surface state density on the carrier and toner particles are equal ($N_c$=$N_t$) within a factor of two, for all of the different toner-carrier systems characterized, taken with different toners and carriers at different laboratories, which seems improbable, or (2) that the electric field theory is the correct description of the data. The value of the electric field can be determined by comparing the experimentally observed slopes or intercepts to the expressions in Eq. 2. It is about 10 V/μm, within a factor of about 2 or 3, and varies among materials. This result represents the first quantitative agreement between theory and any insulator charging experiment, with no adjustable parameters.

Attempts to understand the material properties that determine this electric field have not yet been successful. The difficulty is that the electric field predicted (1000 V/μm) using reasonable estimates of the parameters is orders of magnitude higher than observed (10 V/μm). This results from assuming a typical solid state work function difference of $\Delta\phi$ = 1 eV and a tunneling cutoff distance of z =1 nm. This makes it difficult to associate these parameters with material parameters, which is the goal of a microscopic theory of insulator charging.

Attempts to understand the fundamental basis of this model are further complicated by the empirical observation that the sign of insulator charging, and in particular toner charging, appears to be determined by the acidic or basic nature of the material. One model suggests that the acidic or basic groups promote water absorption on the surface, which provides $H^+$ and $OH^-$ ions which can transfer between materials.[7] Another, used sometimes to explain how charge control agents operate, envisions small mobile ions of the charge control agent CCA diffusing from the toner surface to the carrier particles.[8] Some workers have observed the small mobile ion of the CCA on the carrier by surface science tools. However, there are several difficulties using these ideas to explain toner charging. First, they are inconsistent with the almost universal observation that the toner charge depends on toner concentration.[1-3] This observation means that the mechanism determining the magnitude of the toner charge is directly affected by the number of toner particles on the carrier. A diffusion mechanism by itself cannot account for this observation. Furthermore, simple calculations reveal that if a surface science tool, even with sensitivity of 0.1%, detects CCA atoms on the carrier surface there are at least 100 atoms detected for every charge exchanged, i.e. mostly likely the surface science tool is detecting toner contamination on the carrier, not the charge species responsible for charging. It would appear that the empirical observation of the correlation of charging sign with the acidic nature of a material or the presence of a small mobile molecule of the CCA on carrier particles may identify a source of ions useful for toner charging but does not identify the mechanism determining the magnitude of the charge exchanged.

## 2. Surface "Work Function"

Both of the theories of toner charging discussed above include a term $\Delta\phi$ which represents the difference in surface "work functions" of the carrier and toner. The words "work function" have been put in quotes because of the conceptual problems of identifying a work function in an insulator, i.e. a work function assumes that an uppermost filled electronic state exists, which requires thermodynamic equilibrium among electronic states, something impossible in an insulator due to the low mobility of carriers. Recognizing this problem, Nash and coworkers[9] have called $\phi$ the "charging tendency" of toner or carrier. They[10] expressed Q/M in an empirical equation (which was extensively tested experimentally)

$$\frac{Q}{M} = \frac{A'(\phi_t - \phi_c)}{C + C_0} \tag{3}$$

where $C_0$ and $A'(\phi_t - \phi_c)$ are parameters fit to data. Note that Eq. 3 is consistent with Eq. 2 but not Eq. 1. Later, Gutman and Hartmann[6] made another advance in the theory of toner charging. They suggested that $\phi$ could be expressed as a surface area weighed sum of the "work functions" of the constituents

$$\phi = \sum P_i \phi_i$$

where $P_i$ is the fractional area of constituent i with "work function" $\phi_i$. Nash and coworkers[9,11] then added the idea that $P_i$ can be time dependent, producing "work functions" which appear to change with time. For example, toner impaction on the carrier (a usual failure mode in which the toner sticks to the carrier near the end of life), can change the $\phi$ of the carrier particles as the area that toner occupies changes with time. Q/M vs. time and Q/M vs. C curves were successfully fit with this concept.[9,11] Likewise, experiments in which CCA from toner poisoned the carrier surface, silica particles from the toner transferred to the carrier surface, etc. were explained. Nash et al.[11] suggest that even observations of Q/M independent of C or Q/M increasing with C (not readily understood in the context of Eq. 1 or 2) can be rationalized if the time dependence of the fractional area coverage of constituents is taken into account.

The successful description of such complicated toner charging data using the Gutman and Hartmann hypothesis that

$$\phi = \sum P_i \phi_i$$

plus Nash's idea of time dependent fractional area coverage are important advances in our understanding of toner charging phenomena, allowing an understanding of complicated toner charging behaviors observed in machine applications. Since $\Delta\phi$ appears in both Eq. 1 and Eq. 2, these ideas do not distinguish between the two theories of toner charging. Using the typical assumed values (p. 115 of ref. 11) of A' (70 %μC/g-eV with C in units of % or 0.70 μC/g-eV with C in fractional units) one can calculate z (the distance at which tunneling charge transfer stops) by associating A' with the appropriate terms in Eq. 2, the electric field theory of toner charging,

$$A' = \frac{3\varepsilon_0}{R\rho_C e z}.$$

Using R=50 microns and $\rho_C$=7.8 g/cm$^3$, the value of z obtained is 97.2 nm, much larger than is physically reasonable (for example, tunneling is usually assumed to stop at 1 nm). This only indicates in a slightly different form what was already noted earlier - that quantitative association of the parameters, obtained by fitting data to charging theories, with materials properties is not yet possible. For those interested in a microscopic theory of toner charging, the central issue noted in Section 1 above (understanding the materials origin of $E_e$) can be recast in Nash's language: what materials property determines the two parameters in the theory, z and the "charging tendency." Combining the "charging tendency" of 0.75 eV assumed in Ref. 11 with z gives $E_e$. It is 7.7 V/µm. Since A' is arbitrarily chosen, one could choose a new A' 97.2 times larger, giving z=1 nm, a more "reasonable" result. Now the charging tendency becomes 0.75 eV/97.2 = 7.72 meV, much smaller than is physically reasonable. Of course $E_e$ remains unchanged, 7.7 V/µm.

## 3. Air Breakdown Effects

The value of the electric field at which toner charging ceases is about 10 V/µm, not too far from the electric field at which air breaks down. (Paschen breakdown occurs at 3 V/µm at large air gaps and at higher fields as the air gap is reduced.) It is therefore of interest to consider whether toner charging is due to air breakdown. The role of return currents caused by air breakdown as particles separate has been discussed recently by Matsuyama and Yamamoto.[12] These experiment were done with insulating particles making a single contact to a metal plate. They assumed that during contact sufficient charge is transferred to cause gaseous breakdown during separation. The maximum final charge on the particle is then determined by the particles potential curve being tangent to Paschen's curve. Therefore the final particle charge (if it is determined by air breakdown) is uniquely determined by its diameter and dielectric constant. For 3.2 mm diameter polymer particles used in the experiment quantitative agreement between theory and experiment was obtained. For a 10 micron polymer particle such as toner, the final particle's predicted Q is 0.25 pC and Q/M is 500 µC/g, if air breakdown limits the charge. This value is obviously much higher than is generally observed. Experimental observations of toner charge after contact with a metal plane have been done[13] with "double blow-off" experiment. (Toner is blown out of a blowoff cage towards a piece of metal. Then it is blown off the metal. The charge arriving and leaving the metal plate is measured.) The observation of toner leaving the metal with Q/M of 20 µC/g indicates that if air breakdown limits toner charge it limits Q/M to some value greater than 20 µC/g.

As mentioned above, an air breakdown mechanism of toner charging predicts that the toner charge is uniquely determined by the toner diameter and dielectric constant. Yet it is well known that toner charge is highly variable among different toner-carrier mixes and even within a mix (see below). These well-known results would appear to indicate that toner charging cannot be determined by gaseous breakdown. Some other mechanism is controlling toner charging in the practical case.

## 4. Charge Distribution Intrinsically Wide

It has long been the goal of electrophotographers to measure the toner charge distribution. This is a challenging problem because of the difficulty of collecting a representative sample of toner without altering the toner charge (which can occur if toner particles interact with each other or the walls of the charge measuring device). Recently, a quantitative charge spectrometer QCS[14] was discussed which produces data from a monocomponent development system in which the calculated average Q/M equals the Q/M measured independently (with a vacuum pencil). In addition the amount of wrong sign toner detected was equal to the amount of wrong sign toner developed on the photoreceptor under reverse bias conditions (which is expected to develop out the wrong sign toner). The amount of wrong sign toner for an acceptable commercially available toner was observed to be on the order of 0.1% weighted by area.

The toner charge distribution determined from such a QCS has been shown in a monocomponent development system to shift upon application of an electric field during charging, consistent with the idea expressed in Eq. 2 that toner charging is an electric field driven process. The observed distributions are very wide. In fact, one can describe the distribution by saying that the standard deviation is equal to about 1/3 the mean value. It is not at all clear why this should be the case, especially in light of the fact noted above that the average Q/M has been shown to be determined by an electric field at the surface of the toner particle. Confirmation of this result can be found in the literature of metal-insulator charging. Experiments done by Lowell[15], using two planes were analyzed statistically. He also found that the standard deviation equals about 1/3 the mean; indeed his charge distributions look similar to observed toner charge distributions (compare Fig. 3 of Ref. 15 with Fig. 3 and 16 of Ref. 14) even to the extent that wrong sign charges are seen. It appears that a wide charge distribution may be fundamental to insulator charging.

The wrong sign toner charge distribution observed with this quantitative charge spectrometer is also of interest. One could imagine that it might be due to another mechanism, which would be visible as an additional peak in the charge distribution, or as a result of the statistically wide distributions observed, in which case it would appear as a part of the tail of the distribution. The observation is that wrong sign toner is simply a part of the tail of the distribution. Therefore it appears that wrong sign toner is due to a statistically wide charging process. Further confirmation of this result can be experimentally obtained by collecting the wrong sign toner (from the cleaner after printing many white pages) and putting the collected toner back into the development system. If the wrong sign toner were special in some way, subsequent prints should exhibit reversal printing (since all the toner would be wrong sign). On the other hand if the wrong sign toner were normal except for having been part of the statistical tail of the distribution, subsequent prints should be normal. In unpublished experimental results obtained by the author on a nonmagnetic monocomponent development system, the observation is that the prints were normal. One might envision the insulator charging process as analogous to gas dynamics - there always exists a wide velocity (charge) distribution which is intrinsic to the statistical behavior of the gas molecules (insulating materials) at a finite temperature (after contacting other insulators or metals). If this analogy is correct, the question then becomes what property of the charge exchange process corresponds to temperature.

## Conclusion

In summary, significant progress has been made in our understanding of toner charging in recent years. We now know that toner charges up until an electric field is created at the surface, whose value is material dependent and is about 10 V/μm, within a factor of 2 or 3. Associating this electric field with material properties has not yet been successful. Associating it with a surface "work function" has conceptual difficulties (it is not clear a work function can be defined for such insulating materials) and numerical difficulties (making reasonable assumptions for work function differences leads to results orders of magnitude larger than observed). Associating this electric field with a "charging tendency" is useful because it emphasizes that the material property may be a chemically related. It has been clearly shown that the "charging tendency" can be expressed as a time dependent area weighed sum of the toner constituents, which allows the description of many complicated time dependent charging phenomena, and further emphases that there is clearly material properties affecting the charging process. The charging process is almost surely not due to air breakdown effects. The toner charge distribution appears to be intrinsically wide, which results in the production of wrong sign toner which is known to degrade image quality.

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## Biography

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Lawrence B. Schein received his Ph.D. in solid state experimental physics from the University of Illinois in 1970. He worked at the Xerox Corporation from 1970 to 1983 and at the IBM Corporation from 1983 to 1994. He is now an independent consultant. He has helped implement development systems in IBM laser printers, has proposed theories of most of the known electrophotographic development systems, and has contributed to our understanding of toner charging and charge transport mechanisms in photoreceptors. He is the author of “Electrophotography and Development Physics,” a Fellow of the Society of Imaging Science and Technology, recipient of the Carlson Memorial Award in 1993, a Senior Member of the IEEE, and a member of the American Physical Society and the Electrostatics Society of America.