CCA Effects on the Triboelectric Charging Properties of a Two-Component Xerographic Developer

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Charge control agents (CCA's) are frequently added to toners to create a desired charge level and polarity. Triboelectric charging tests on model, CCA-surface-treated toners and carriers indicate that CCA transfer between toner particles and carrier beads can be a controlling factor for the magnitude and polarity of toner charge — in extreme cases, toner polarity can even be reversed as a result of CCA transfer. The tests also indicate that the transfer process, and hence the final charging properties of a toner can be significantly affected by the concentration of the toner in a xerographic developer.

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Introduction

The sign and magnitude of toner chage-to-mass ratio, q/m, can be manipulated by the addition of charge control agents to the toner recipe (CCA's—typically salts formed from bulky inorganic or organometallic ions paired with small counterions[1]). While CCA's are usually melt-mixed into the bulk of the toner resin matrix, they are presumed to affect toner charging performance via their partial presence at the toner surface.[2,3] Indeed, some CCA effects are best explained in terms of CCA transfer from toner particles to the surface of the carrier beads. For example, for a model negative polarity toner, the sign and magnitude of q/m has been linearly related to the amount of CCA species transferred to the carrier surface.[4] (Interestingly, in the cited study, the developer was examined at a single toner concentration, and the q/m:CCA effect was studied for a range of q/m values created over a range of mixing times, i.e., the CCA transfer varied as a function of mixing time). An additional example of CCA/carrier effects can be deduced from charging data taken on a developer based on a positive-charging toner,[5] for that system, the sign of the toner charge actually reverses at low toner concentrations, (i.e., the extent of CCA transfer from the toner particles to the carrier beads is a function of the toner concentration.) Similarly, an indirect example of CCA transfer to carrier particles is the enhanced developer conductivity that can result when a conductive carrier is paired with a CCA-containing toner[6] (an effect where the carrier packing density is enhanced by the lubricating effect of the transferred surface CCA).

To illustrate the importance of CCA/carrier effects on the triboelectric charging performance of CCA-based toners, experimental toner charging data will be presented and analyzed, using model developers based on CCA-containing toners, on matching base CCA-free toners, and on toners and carriers directly treated with CCA's.

Theory

Conceptually, toner triboelectric charging can be simply expressed as a product of terms related to the physics and chemistry of charging and to the mechanics of mixing,[7,8] e.g.,

$$q/m = (A'/(C + C_0)) \cdot (\phi_{toner} - \phi_{carrier}) \cdot (1 - exp\{-\gamma \cdot t\}) \quad (1)$$

physics chemistry mechanics

where q/m is the toner charge to mass ratio, at a toner weight % concentration of C, and A' and C_0 are constants related to the size and density of the toner and carrier particles. The rate constant γ defines the rate of triboelectric charging, and is related to the mode of the toner/carrier mixing process. The ϕ_{toner} and $\phi_{carrier}$ terms represent the charging tendency of the toner and carrier particles, and the relative magnitude of these two terms directly governs the polarity of the toner particles, and also affects the magnitude of the toner charge.

The constant A' in Eq. 1 can be related to the physical properties of a carrier bead as follows[7]:

$$A' = \frac{4 \cdot \pi \cdot R^2 \cdot \varepsilon_0}{M \cdot e \cdot d} \quad (2)$$

where R and M are the carrier radius and mass, ε_0 is the electric constant (8.85×10^{-12} F/m or C^2/J.m) , e is the elementary charge (1.602×10^{-19} C) and d is the charge tunneling cutoff distance (assumed to be 1 nm).

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For a 100 μm diameter steel carrier bead, R is 5×10^{-5} m and M is 4 μg , so that A' in units of $\mu C.g^{-1}.eV^{-1}$ is:

$$A' = \left(\frac{4 \cdot \pi \cdot \left(5 \times 10^{-5}\right)^2 \left(m^2\right) \cdot 8.85 \times 10^{-12} \left(C^2 / J \cdot m \right)}{4 \times 10^{-6}(g) \cdot 1.602 \times 10^{-19}(C) \cdot 1 \times 10^{-9}(m)} \right) \cdot \left(1.602 \times 10^{-19} \left(J / eV \right) \cdot 10^6 \left(\mu C / C \right) \right) \quad (3)$$

Thus, $A' = 70\ \mu C.g^{-1}.eV^{-1}$

The constant C_0 in Eq. 1 can be related to the density and radius values of the toner particles and carrier beads by[7]:

$$C_0 \approx \frac{\rho_{toner} \cdot r_{toner}}{\rho_{carrier} \cdot R_{carrier}} \quad (4)$$

and for a 100 μm diameter steel carrier bead and a 9 μm toner particle, $C_0 \approx 1$.

Because the surface of toner and carrier particles are typically composed of several components, e.g., binder resin, pigment, coating, etc., the ϕ_{toner} and $\phi_{carrier}$ terms in Eq. 1 may be expressed in terms of surface-weighted contributions from the various components,[7–10] e.g.,

$$\phi = P_i \cdot \mu_i + P_j \cdot \mu_j + \ldots\ldots \quad (5)$$

where the total sum of the fractional weights, P_i, P_j etc., equals unity, and the parameters μ_i and μ_j etc. are characteristic charging factors for the various surface components.

Frequently, the mechanical forces of the triboelectric mixing process affects the surface composition of toner and carrier particles, i.e., the P_i, P_j values are functions of the mixing time, and the resultant q/m values can be complex non-linear functions of mixing time.[5,8,10]

For a CCA-containing toner, the ϕ_{toner} term can be expressed as

$$\phi_{toner} = P_{CCA} \cdot \mu_{CCA} + (1 - P_{CCA}) \cdot \mu_{toner}$$

or

$$\phi_{toner} = P_{CCA} \cdot (\mu_{CCA} - \mu_{toner}) + \mu_{toner} \quad (6)$$

where the charging contributions from the toner binder resin, pigment etc., are all combined in a single composite μ_{toner} term. Eq. (6) is not based on any particular charge exchange mechanism, it merely indicates that a CCA affects the tendency of a toner to accept or donate charge.

The effect of a CCA on toner polarity will depend on the relative magnitude of the μ_{CCA} and μ_{toner} terms; e.g., if $\mu_{CCA} > \mu_{toner}$ then Eqs. (1) and (6) indicate that ϕ_{toner} will increase as the surface content P_{CCA} increases, and that the toner q/m will become increasingly positive. Experimentally, however, levels of CCA above some optimum value can sometimes lead to a decline in q/m,[2] and for a carrier–toner pair that produces a positive polarity toner, this CCA effect may reflect a CCA-driven increase in the value of $\phi_{carrier}$, as given by

$$\phi_{carrier} = P_{CCA} \cdot \mu_{CCA} + (1 - P_{CCA}) \cdot \mu_{carrier}$$

or,

$$\phi_{carrier} = P_{CCA} \cdot (\mu_{CCA} - \mu_{carrier}) + \mu_{carrier} \quad (7)$$

where, in this case, P_{CCA} is the fraction of the carrier surface covered by CCA that has transferred from the toner particles, and where $\mu_{CCA} > \mu_{carrier} > \mu_{toner}$. For the case where CCA is partially transferred from the toner to the carrier particles, there will be an attendant decline in ϕ_{toner} if the P_{CCA} term of the toner is decreased by the transfer process, and this will also contribute to a decrease in q/m.

If a toner-to-carrier CCA transfer process actually reaches an equilibrium state, then the toner q/m value will eventually stabilize, and such behavior has indeed been observed in long term toner throughput aging experiments with CCA-based toners.[2,3,11]

In general, P_{CCA} at any mixing time, t, (for both toner and carrier particles) can be described by:

$$P_{CCA,t} = (P_{CCA,0} - P_{CCA,\infty}) \cdot exp\{-k \cdot t\} + P_{CCA,\infty} \quad (8)$$

where $P_{CCA,0}$ and $P_{CCA,\infty}$ are the values of P before and after extended mixing. As a result, ϕ_{toner} and $\phi_{carrier}$ will vary as

$$\phi_{toner,t} = (\phi_{toner,0} - \phi_{toner,\infty}) \cdot exp\{-k_{toner} \cdot t\} + \phi_{toner,\infty} \quad (9)$$

$$\phi_{carrier,t} = (\phi_{carrier,0} - \phi_{carrier,\infty}) \cdot exp\{-k_{carrier} \cdot t\} + \phi_{carrier,\infty} \quad (10)$$

and these non-linear changes in ϕ_{toner} and $\phi_{carrier}$ will produce non-linearities in q/m as a function of mixing time. (For complex interactions, where changes in ϕ_{toner} and $\phi_{carrier}$ may reflect simultaneous, consecutive and/or reversible processes, a comprehensive kinetic equation will contain many terms[11,12]; however, for any particular fixed condition, experimental charging data can often be described by simple expressions based on relationships such as those in Eqs. (9) and (10)).

Now, while substitution of the terms in Eqs. (9) and (10) into Eq. (1) will produce a non-linear equation for q/m as a function of mixing time, experimental q/m data can only be used to deduce values of the difference term ($\phi_{toner} - \phi_{carrier}$), and individual values of ϕ_{toner} and $\phi_{carrier}$ can only be obtained with respect to some arbitrary reference. Despite this critical limitation, an in-depth analysis of q/m data from CCA-based developers can yield informative mechanistic insights, and this approach will be illustrated in the Results and Discussion section of this present report.

Experimental

A nominal 9 μm black toner was prepared by melt-mixing, jetting and size-classification, and approximately 0.25 wt% of a positive CCA was blended into the toner resin matrix in the melt-mix step. For diagnostic tests the toner was also prepared in a CCA-free state. A surface-CCA-treated toner was also prepared from the latter base toner: 0.05 g of the positive CCA was blended with 50 g of base toner, with small stainless steel balls being used to facilitate the blending process.

The test carrier was prepared from nominal 100 μm steel carrier beads, powder coated with an approximately 1:1 PMMA/ fluoropolymer mixture. A CCA-coated version was also prepared: 2000 g of the polymer coated carrier were roll-milled with 0.1 g of the positive CCA. Finally, an aged sample of the test carrier was recovered from a developer that had been used for an extended print test with the melt-mixed-CCA toner.

For q/m generation, developer samples were conditioned at 16° C/20% relative humidity, and were agitated on a paint shaker. At regular time intervals, small

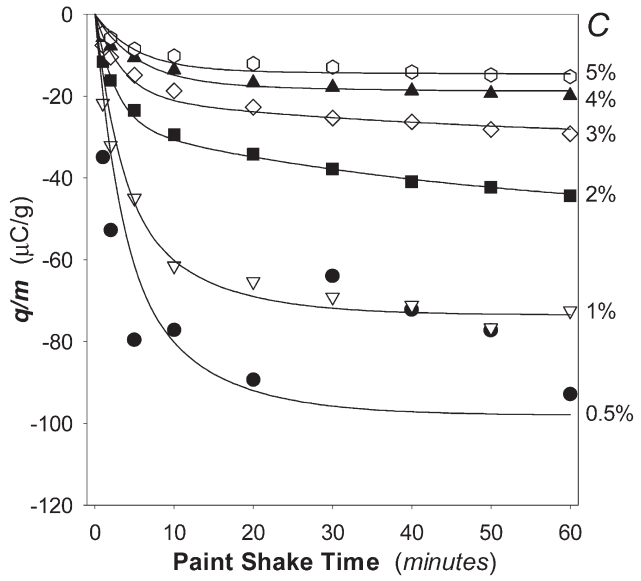

Figure 1. Charge-to-mass-ratio data for the CCA-free base toner with the test carrier (negative at all toner cocentrations).

samples were removed for q/m evaluation using a total blow-off procedure.

Results and Discussion

Triboelectric Charging Over a Range of Fixed Toner Concentrations

Frequently, the q/m response of a developer is evaluated only at a single toner concentration, and only after a single "standard" mixing time. However, toner/carrier interactions can be strongly affected by the level and duration of the mechanical mixing forces, so that experimental kinetic q/m data taken over a range of toner concentrations can reveal interactions that cannot be deduced from "single-point" measurements. In this regard, the behavior of CCA-based toners can be especially complex, and the unusual test data described in the following section highlight the utility of multi-point measurements.

Test 1. CCA-Free Base Toner With Test Carrier

Figure 1 shows q/m data taken at a series of fixed toner concentrations from 0.5 wt% to 5 wt% for the base, CCA-free toner and the test carrier. As can be seen, this developer produces a strongly negative polarity toner.

At long-mixing times, Eq. (1) can be rearranged to give

$$(\phi_{toner} - \phi_{carrier}) = (q/m)\cdot(C + C_0) / A' \qquad (11)$$

For the test developer, $A' = 70\ \mu C.g^{-1}.eV^{-1}$ and $C_0 = 1$, and with ϕ_{toner} set at an arbitrary reference value of 0 eV, then the experimental data can be fitted using the $\phi_{carrier}$ values listed in Table I. From these values, by definition, $\phi_{carrier} = 1.15$ eV, and $\phi_{toner} = 0$ eV.

Test 2. Melt-Mixed-CCA Toner with Test Carrier

Figure 2 shows the q/m data at high toner concentrations for a developer based on the test carrier and the toner melt-mixed with about 0.25 wt% of a positive CCA. Using the 1.15 eV value for $\phi_{carrier,0}$ (as deduced from Test 1), the data in Fig. 1 yield $\phi_{toner,0} = 1.80$ eV for the melt-mixed-CCA-based toner.

TABLE I. CCA-Free Base Toner with Test Carrier

C wt%	$\phi_{carrier,\infty}$ eV	$\phi_{carrier,0}$ eV	$\phi_{toner,\infty}$ eV	$\phi_{toner,0}$ eV	k_{toner} min^{-1}	$k_{carrier}$ min^{-1}	γ min^{-1}
5	1.25	1.15	0	0	0	0.05	0.15
4	1.35	1.15	0	0	0	0.05	0.2
3	1.80	1.15	0	0	0	0.02	0.3
2	2.20	1.15	0	0	0	0.02	0.4
1	2.10	1.15	0	0	0	0.1	0.4
0.5	2.10	1.15	0	0	0	0.1	0.4

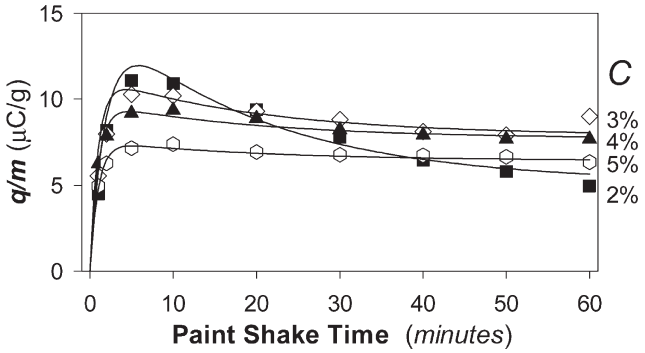

Figure 2. Charge-to-mass-ratio data at high toner concentrations for melt-mixed-CCA toner with test carrier (expanded q/m scale). (Note that q/m is positive at all of the high toner concentrations)

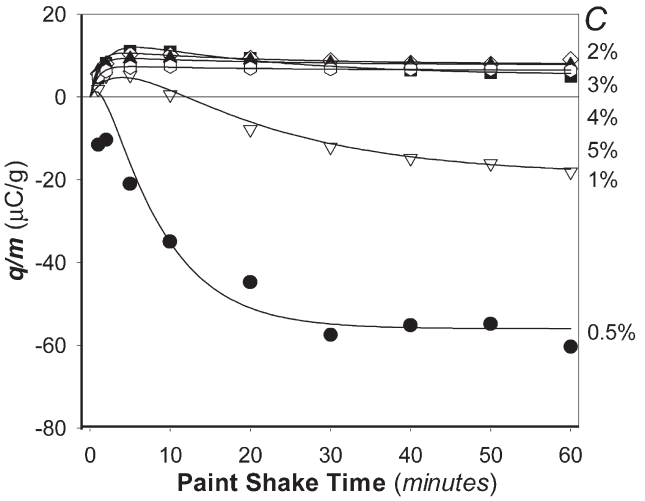

Figure 3. The entire q/m data set for the melt-mixed-CCA toner with the test carrier. (Note the reversal in q/m polarity at low toner concentrations)

However, as shown in the total data set in Fig. 3, the developer based on the melt-mixed-CCA-based toner apparently produces a positive toner polarity only at high toner concentrations. In a previous report,[5] we hypothesized that a CCA-transfer carrier enhancement process was necessary to produce a positive toner polarity; however, diagnostic tests made for the present report now suggest that anomalous negative toner polarities seen at low toner concentrations are in fact the result of a carrier poisoning effect, caused by CCA transfer to the carrier surface, and Table II lists the results of an analysis based on this hypothesis.

The analysis indicates that CCA transfer to the carrier is most severe at low toner concentrations, even

TABLE II. Melt-Mixed-CCA Toner with Test Carrier

C wt%	$\phi_{carrier,\infty}$ eV	$\phi_{carrier,0}$ eV	$\phi_{toner,\infty}$ eV	$\phi_{toner,0}$ eV	k_{toner} min^{-1}	$k_{carrier}$ min^{-1}	γ min^{-1}
5	1.15	1.15	1.70	1.80	0.05	0	1
4	1.15	1.15	1.70	1.80	0.05	0	1
3	1.15	1.15	1.60	1.80	0.05	0	1
2	1.15	1.15	1.37	1.80	0.05	0	0.5
1	1.35	1.15	0.80	1.80	0.06	0.5	0.15
0.5	2.00	1.15	0.80	1.80	0.15	0.5	0.15

TABLE III. Surface-CCA-Treated Base Toner

C wt%	$\phi_{carrier,\infty}$ eV	$\phi_{carrier,0}$ eV	$\phi_{toner,\infty}$ eV	$\phi_{toner,0}$ eV	k_{toner} min^{-1}	$k_{carrier}$ min^{-1}	γ min^{-1}
5	1.15	1.15	4.50	4.50	0.05	0	0.7
4	1.15	1.15	4.50	4.50	0.05	0	0.7
3	1.15	1.15	4.50	4.50	0.05	0	0.7
2	1.45	1.15	4.30	4.50	0.05	0.5	1
1	2.10	1.15	4.10	4.50	0.06	0.5	1
0.5	2.20	1.15	3.60	4.50	0.15	0.5	1

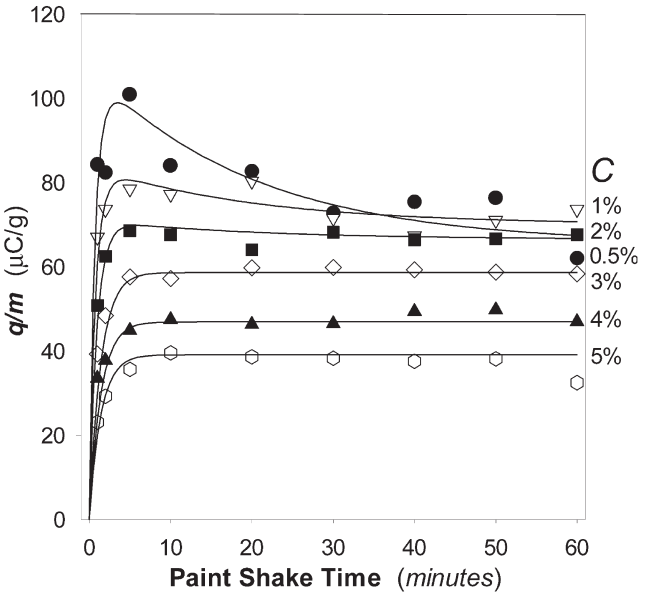

Figure 4. Charge-to-mass-ratio for surface-CCA-treated base toner with the test carrier. (Note that q/m is positive at all toner concentrations).

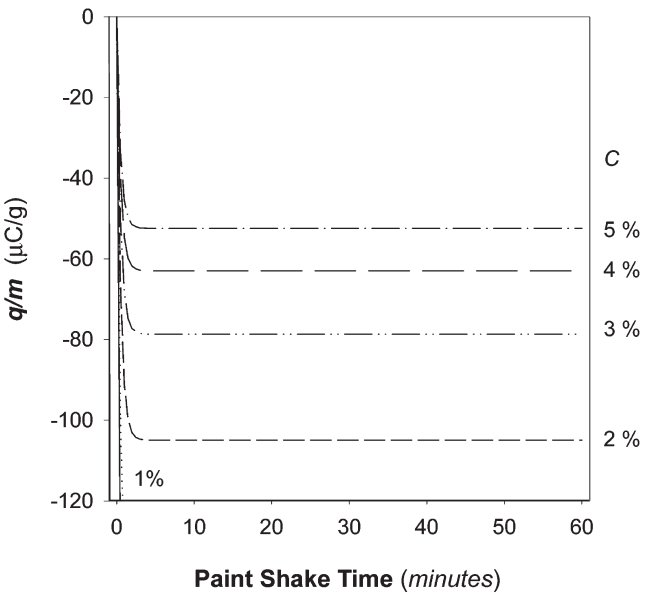

Figure 5. The predicted q/m: C response for CCA-free base toner with surface-CCA-coated carrier, based on ϕ_{toner} = 0 eV and $\phi_{carrier}$ = 4.5 eV.

though such concentrations expose the carrier beads to the lowest total concentration of CCA from the toner particles. One possible explanation is that increased mechanical/frictional forces at low toner concentrations enhance the CCA transfer process. Significantly, developer aging experiments using CCA-containing toners have shown a similar effect[11]—developer aging was found to be most severe at a constant low toner concentration.

Given a value for μ_{CCA}, Eqs. (6) and (7) can be used to convert the ϕ values in Table II into CCA surface coverage values. From a diagnostic test (discussed in the next section), μ_{CCA} can be deduced to be 4.5 eV, and this value yields a CCA surface coverage of about 40% for the melt-mixed-CCA test toner. In the lowest toner concentration tests, this level falls to about 20%, e.g.,

$$\phi_{toner,\infty} = P_{CCA}\cdot(4.5 - 0) + 0\ , \quad (12)$$
so for $\phi_{toner,\infty}$ = 0.8 eV, P_{CCA} = 0.18.

Similarly, the carrier surface becomes 25% contaminated with CCA, e.g.,

$$\phi_{carrier,\infty} = P_{CCA}\cdot(4.5 - 1.15) + 1.15, \quad (13)$$

so for $\phi_{carrier,\infty}$ = 2.0 eV, P_{CCA} = 0.25.

As a consequence, the increase in $\phi_{carrier}$ to 2.0 eV and the decrease in ϕ_{toner} to 0.80 eV, produce a highly negative toner charge for the predicted q/m value at a toner concentration of 0.5 wt%, e.g., $70\cdot(0.8 - 2.0)/(0.5 + 1) = -56$ μC/g.

Test 3. Surface-CCA-Treated Base Toner

The q/m data in Figure 4 are for the surface-CCA-treated toner with the test carrier. By comparison with the previous results from the CCA-free and melt-mixed-CCA toners, it is clear that a low level of CCA can have a major effect on both toner polarity and charge level, when it is directly applied to the toner surface.

A 1.15 eV value for $\phi_{carrier,0}$, as deduced from the previous tests, yields a value of 4.5 eV for $\phi_{toner,0}$ for the surface-treated toner tests, and the total analysis is given in Table III. If the initial CCA surface coverage on the toner is assumed to be 100%, then ϕ_{CCA} = 4.5 eV by definition.

As in the previous tests, the test data at high toner concentrations show only a minor degree of CCA transfer to the carrier surface. At the lowest 0.5 wt% toner concentration, the CCA coverage on the carrier is deduced to be about 30%, while the CCA coverage on the toner drops from 100% to 80%.

Test 4. Surface-Treated Carrier with CCA-Free Base Toner

According to Eq. (7), a surface-coating of CCA on the carrier surface should increase the value of $\phi_{carrier}$ (up to 4.5 eV for a monolayer coverage), and thereby reduce the q/m level of any toner below that obtained with a

TABLE IV. Surface-Treated Carrier with CCA-Free Base Toner

C wt%	$\phi_{carrier,\infty}$ eV	$\phi_{carrier,0}$ eV	$\phi_{toner,\infty}$ eV	$\phi_{toner,0}$ eV	k_{toner} min^{-1}	$k_{carrier}$ min^{-1}	γ min^{-1}
5	1.50	4.50	4.50	0	2	1	2
4	1.50	4.50	4.50	0	2	1	2
3	1.40	4.50	4.50	0	2	1	2
2	1.60	4.50	4.30	0	2	1	2
1	2.30	4.50	4.10	0	2	1	2
0.5	3.06	4.50	3.60	0	2	1	2

TABLE V. Surface-CCA-Treated Carrier with Melt-Mixed-CCA Toner

C wt%	$\phi_{carrier,\infty}$ eV	$\phi_{carrier,0}$ eV	$\phi_{toner,\infty}$ eV	$\phi_{toner,0}$ eV	k_{toner} min^{-1}	$k_{carrier}$ min^{-1}	γ min^{-1}
5	1.90	4.50	4.50	1.80	2	1	2
4	1.70	4.50	4.50	1.80	2	1	2
3	1.50	4.50	4.50	1.80	2	1	2
2	1.70	4.50	4.30	1.80	2	1	2
1	2.40	4.50	4.10	1.80	2	1	2
0.5	2.90	4.50	3.60	1.80	2	1	2

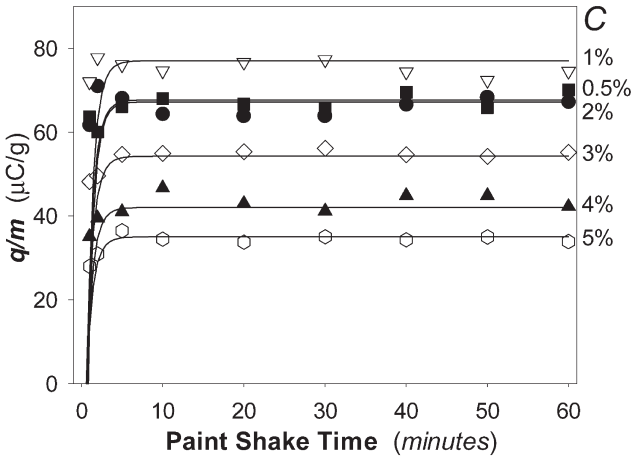

Figure 6. Charge-to-mass-ratio for CCA-free base toner with surface-CCA-coated carrier. (Note that q/m is positive at all toner concentrations, whereas the predicted q/m values in Fig. 5 are all negative).

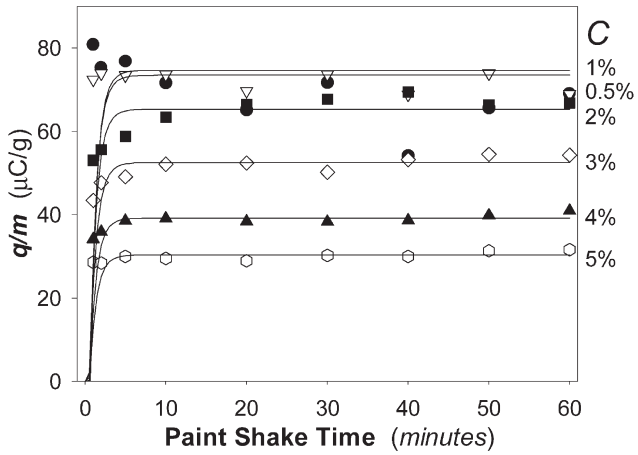

Figure 7. Charge-to-mass-ratio for melt-mixed-CCA toner with aged carrier. (Note that q/m is positive at all toner concentrations).

CCA-free version of the carrier. For the present CCA-free base toner, where ϕ_{toner} = 0 eV, a CCA-treated carrier should produce a highly negative toner charge, e.g., at 5 wt% toner concentration: $q/m = 70\cdot(0 - 4.5)/(5 + 1) = -52.5$ μC/g, and Fig. 5 shows the predicted q/m:C response at various values of the toner concentration.

However, for the test carrier coated with 0.0001g of a positive CCA per gram of carrier, the experimental q/m value is +35 μC/g at a 5 wt% toner concentration of the CCA-free toner, and the developer gives highly positive and stable q/m values at all toner concentrations, as shown in Fig. 6.

Apparently, the toner particles rapidly acquire a surface coating of CCA from the CCA-coated carrier beads, and this gain (coupled with a partial CCA-loss from the carrier beads) provides a high level of positive toner charge. The net effect on $\phi_{carrier}$ and ϕ_{toner} is listed in Table IV, based on an assumption that the carrier is initially 100% coated with CCA. These values indicate a CCA loss from the carrier of about 90% at high toner concentrations, and about 40% at the 0.5 wt% toner concentration.

Test 5. Surface-CCA-Treated Carrier with Melt-Mixed-CCA Toner

For this carrier/toner combination, the toner contains its own level of CCA and this therefore reduces the tendency for CCA transfer from the carrier surface. As a result, at high toner concentrations the developer based on the CCA-treated carrier and the melt-mixed-CCA toner actually gives a lower positive q/m value than that seen with the CCA-free toner when paired with the CCA-treated carrier.

Figure 7 shows the entire data set, and Table V lists the fitted values. For the surface-CCA-treated carrier, the controlling difference between the charging performance of the CCA-free and melt-mixed-CCA toner is the effect of these toners on the value of $\phi_{carrier,\infty}$ (compare Tables IV and V). The net result is a CCA loss from the CCA-coated carrier of about 80% at the highest toner concentrations with the melt-mixed-CCA toner (compared with the 90% loss deduced for the CCA-free base toner).

Test 6. Aged Carrier with Melt-Mixed-CCA Toner

When aged in a toner throughput imaging test, a carrier is exposed to a continual supply of fresh toner. As a result, in addition to any coating loss, the surface of a carrier may acquire a level of CCA from the toner particles, when aged with a CCA-toner. Figure 8 shows experimental q/m data for an aged version of the test carrier, paired with the test melt-mixed-CCA toner. Basically, this combination gives increased developer stability and a higher positive charging toner over that given with new carrier , e.g., see Test 2. Based on a value of 1.8 eV for $\phi_{toner,0}$, the data in Figure 8 yield a value of 0.95 eV for $\phi_{carrier,0}$, with only a minor change in both values throughout the test. Evidently the aged carrier can be viewed as being in equilibrium with the CCA level on the toner surface.

Test 7. Aged Carrier with CCA-Free Base Toner

For the combination of an aged carrier and a CCA-free toner, the experimental q/m data shown in Fig. 9 appear to show an initial CCA transfer from the aged carrier to the toner, and the deduced $\phi_{toner,0}$ value is close

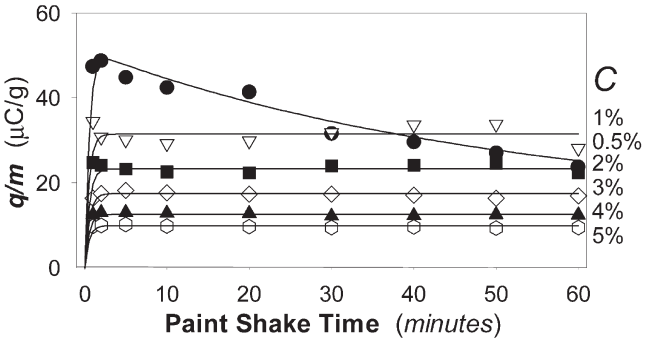

Figure 8. Charge-to-mass-ratio for melt-mixed-CCA toner with aged carrier. (Note that q/m is positive at all toner

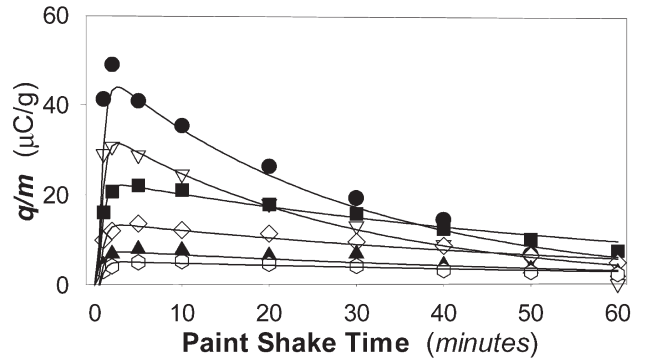

Figure 9. Charge-to-mass-ratio for CCA-free base toner with aged carrier. (Note that the q/m values are all positive at

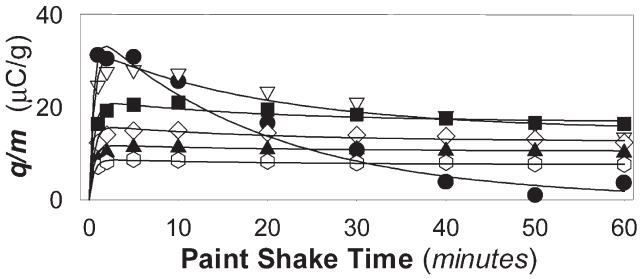

Figure 10. Charge-to-mass-ratio for melt-mixed-CCA toner with a 50:50 mixture of new and aged carrier. (At short mixing times, the q/m values increase regularly in the order of decreasing toner concentration)

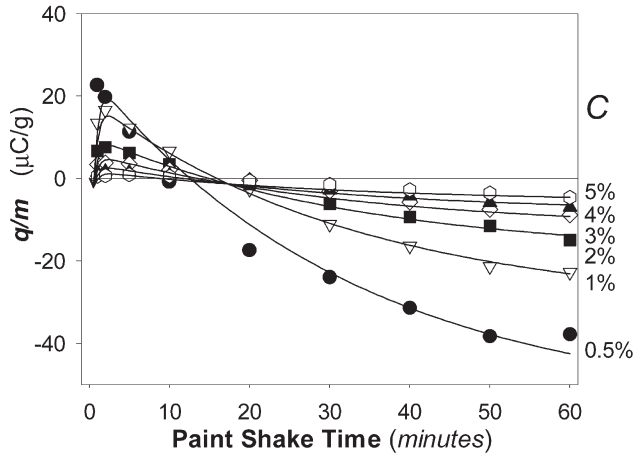

Figure 11. Charge-to-mass-ratio for CCA-free base toner with a 50:50 mixture of new and aged carrier. (Note the common q/m value after 17 min of mixing).

to that of the melt-mixed-CCA toner. (compare this result with that shown in Fig. 1, where the q/m values are all negative for the base toner with an new sample of the carrier). At long mixing times, however, the q/m values in test 7 tend towards zero for all toner concentrations, perhaps indicative of a convergence of the values of $\phi_{toner,\infty}$ and $\phi_{carrier,\infty}$ (as a result of an eventual loss of CCA from the toner surface).

Test 8. Melt-Mixed-CCA Toner with a 50:50 Mixture of New and Aged Test Carrier

As shown in Fig. 10, an equal mixture of new and aged carrier gives a stable, positive-charging developer with melt-mixed-CCA toner at all toner concentrations greater than 1 wt%. For this case, CCA transfer to the new carrier can potentially occur from the aged carrier and from the CCA-containing toner, in addition to transfer between the toner and the aged carrier. Overall, there does not appear to be any major change, except at the lowest toner concentrations, and even under such conditions the developer maintains a positive toner polarity. (The net result is similar to that based on a non-interacting 50:50 mixture of new and aged carrier).

Test 9. CCA-Free Base Toner with a 50:50 Mixture of New and Aged Test Carrier

In this test, the toner rapidly charges to a positive polarity, but the charge slowly changes to a negative polarity with extended developer mixing. Apparently, continued developer mixing causes a loss of surface CCA from the toner, thus leading to an eventual reversal in polarity. The existence of a common q/m value after about 17 minutes of developer mixing (see Fig. 11) indicates that the changes in q/m follow a common mechanism for toner concentrations from 1 to 5 wt%. The overall effect does not match a prediction based on a non-interacting 50:50 mixture of new and aged carrier—the CCA-free toner clearly receives CCA from the aged carrier.

The Effect of Changes in Toner Concentration on Triboelectric Charging

During xerographic image development, toner is removed from the developer, and this will lead to a decreased image density as a result of a reduced supply of toner, and an increase in q/m (since q/m is an inverse function of toner concentration). The developed toner is replaced by toner dispensed from a toner supply unit to maintain a constant image density. As a result, a developer's response to incremental changes in toner concentration, and to the addition of uncharged, dispensed toner, is an important factor for stable xerographic development [13–16]

Test 10. Incremental Addition of Uncharged Toner to a Developer Based on Melt- Mixed-CCA Toner and Aged Test Carrier

Figure 12 shows a set of toner additions to a developer based on the melt mixed-CCA toner and the aged version of the test carrier. The initial charging at a low toner concentration of 0.4 wt.% rapidly produces a high positive q/m value followed by a subsequent decline, and addition of uncharged toner, to create final toner concentrations of 0.8, 1.5 and 2.2 wt%, produces a series of stable

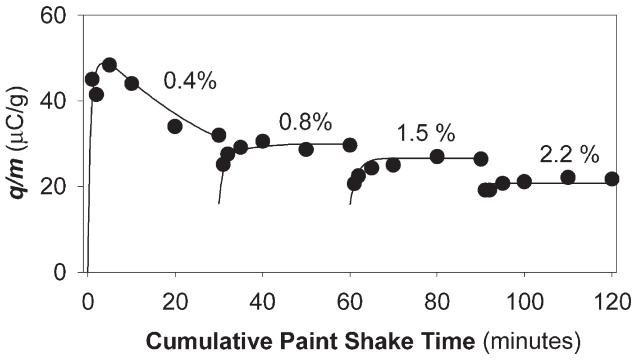

Figure 12. The q/m response of a developer based on melt-mixed-CCA toner and aged test carrier. The toner concentration of the developer was increased stepwise by the addition of uncharged toner.

positive q/m plateau values. Thus, apart from the response at 0.4 wt%, the developer shows a regular q/m:C relationship.

The initial results at 0.4 wt% match those seen in Test 6 at 0.5 wt%, but all subsequent results reflect the addition of uncharged toner to the test developer. During the initial stage of these additions, the charged toner already in the developer (the "incumbent" toner) must equilibrate with the added, uncharged toner particles. This process will alter the charge value of both incumbent and added toner particles.[13–16] From an average q/m viewpoint, the initial net result will be a simple weighted average of the component charge values, e.g., the increase in toner concentration from 0.4 to 0.8 wt% in Test 10 produces an initial change in q/m from +32 to +16 μC/g. However, for continued mixing, the q/m values will reflect any changes in the surface chemistry of the toner and carrier particles. For the present CCA-based toner, such changes will be driven by CCA-transfer mechanisms, and the net effect can be seen in the values for $\phi_{carrier}$ and ϕ_{toner} listed in Table VI.

To create the plots shown in Fig. 12, the measured average q/m values were assumed to be the sum of contributions from the charged/uncharged admix process and a subsequent mixing-generated charging process. For simplicity, the former process was modeled as a rapid exponential decrease from an initial post-admix, averaged q/m value, e.g., +16 μC/g after the first addition of uncharged toner, and the latter process was assumed to be governed by the $\phi_{carrier}$ and ϕ_{toner} values listed in Table VI. For the $\phi_{carrier}$ values, the $\phi_{carrier,0}$ value after the toner addition was taken as the $\phi_{carrier,\infty}$ value at the end of the previous mixing test. Similarly, the $\phi_{toner,0}$ values were taken as weighted averages of $\phi_{toner,\infty}$ and $\phi_{toner,dispensed}$, where the latter value is that of the fresh, dispensed toner, e.g., $\phi_{toner,dispensed}$ = 1.8 eV for the melt mixed-CCA toner. As can be seen from Table VI, there are only minor changes in ϕ_{toner} and $\phi_{carrier}$ for all toner concentrations above 0.5 wt%, and the developer q/m:C response is extremely regular.

Test 11. Incremental Addition of Uncharged Toner to a Developer Based on Melt-Mixed-CCA Toner and Unaged Test Carrier

Figure 13 shows the effect of increasing toner concentration increments on the q/m response of a developer based on the melt-mixed-CCA toner and the unaged test carrier. The initial test at 0.5 wt% toner concentration shows a major decline to a highly negative toner q/m value, even though the toner CCA was designed to produce a positive toner polarity. As discussed in the Test 2 section, this anomalous result is assumed to be the result of CCA-transfer mechanisms between the toner and carrier particles, and the $\phi_{carrier}$ and ϕ_{toner} values in Table VII reflect these processes modified by the addition of fresh toner. Once again, the q/m values from the tests at the higher toner concentration values are quite stable, and the final value of $\phi_{carrier}$ is close to that of the unused carrier.

TABLE VI. Incfremental Addition of Unchanged Toner to a Developer Based on Melt-Mixed-CCA Toner and Aged Test Carrier

C wt%	$\phi_{carrier,\infty}$ eV	$\phi_{carrier,0}$ eV	$\phi_{toner,\infty}$ eV	$\phi_{toner,0}$ eV	k_{toner} min^{-1}	$k_{carrier}$ min^{-1}	γ min^{-1}
0.4	0.70	0.95	1.00	1.80	0.03	0.5	2
0.8	0.60	0.70	1.30	1.40	0.01	0.5	2
1.5	0.60	0.60	1.55	1.55	0	0	0.6
2.2	0.60	0.60	1.55	1.55	0	0	1

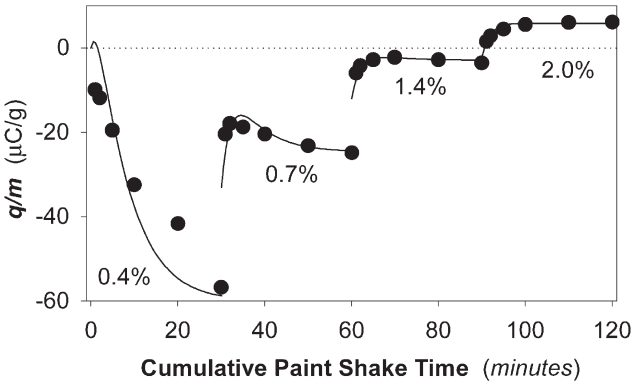

Figure 13. The q/m response of a developer based on melt-mixed-CCA toner and unaged test carrier. The toner concentration of the developer was increased stepwise by the addition of uncharged toner.

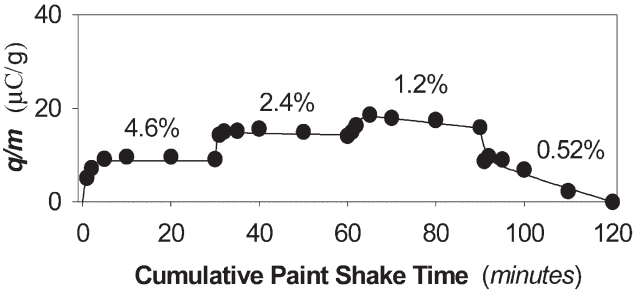

Figure 14. The q/m response of a developer based on melt-mixed-CCA toner and unaged test carrier. The toner concentration of the developer was decreased stepwise by a vacuum detoning of half of the developer.

Test 12. Incremental Removal of Charged Toner from a Developer Based on Melt-Mixed-CCA Toner and Unaged Test Carrier

Figure 14 shows the effect of toner removal (by vacuum de-toning half of the developer) on the q/m:C response of a developer based on the melt-mixed-CCA toner and the unaged test carrier. In this test, the

TABLE VII. Incremental Addition of Unchanged Toner to a Developer Band on Melt-Mixed-CCA Toner and Unaged Test Carrier

C wt%	$\phi_{carrier,\infty}$ eV	$\phi_{carrier,0}$ eV	$\phi_{toner,\infty}$ eV	$\phi_{toner,0}$ eV	k_{toner} min^{-1}	$k_{carrier}$ min^{-1}	γ min^{-1}
0.5	2.0	1.15	0.80	1.80	0.15	0.5	0.15
0.7	1.40	2.0	0.80	1.20	0.5	0.5	0.15
1.4	1.20	1.40	1.10	1.30	0.5	0.5	0.15
2.0	1.00	1.20	1.25	1.30	0.5	0.5	1

TABLE VIII. Incremental Removal of Charged Toner from a Developer Based on Melt-Mixed-CCA Toner and Unaged Test Carrier

C wt%	$\phi_{carrier,\infty}$ eV	$\phi_{carrier,0}$ eV	$\phi_{toner,\infty}$ eV	$\phi_{toner,0}$ eV	k_{toner} min^{-1}	$k_{carrier}$ min^{-1}	γ min^{-1}
4.7	1.10	1.10	1.80	1.80	0	0	1
2.4	1.10	1.10	1.70	1.80	0.01	0	1.5
1.2	1.20	1.10	1.40	1.70	0.01	0.01	0.5
0.52	1.70	1.20	0.90	1.40	0.01	0.005	1

changes in toner concentration simply create changes in the q/m value of the incumbent toner, generated by changes in $\phi_{carrier}$ and ϕ_{toner}, since the test developer is based only on the incumbent toner and test carrier at all times. As a result, at each reduction in toner concentration, $\phi_{toner,0} = \phi_{toner,\infty}$ and $\phi_{carrier,0} = \phi_{carrier,\infty}$, and Table VIII lists the values used to create the fit shown in Fig. 14. As can be seen, the test developer gives a "normal" response for a "positive-CCA-toner", i.e., q/m is positive and increases with decreasing toner concentration, except at the lowest toner concentration. At that latter condition, q/m decreases with mixing time, and approaches zero, whereas a "normal" response would have been an increase to a highly positive level. As shown in Table VIII, $\phi_{carrier} > \phi_{toner}$ at the lowest toner concentration, and this leads to the decline in toner q/m.

Summary and Conclusions

From the present experimental data set, it is clear that the charging performance of a toner can be greatly altered through the use of a CCA. However, it is also evident from the data that incorporation of a CCA can create an extremely complex charging behavior.

The tests based on CCA-surface-coated toners and carriers illustrate the major influence that surface-CCA can have on toner charge and on overall charge stability. These tests also reveal that transfer of CCA between toner and carrier surfaces (in both directions) can control the polarity and magnitude of toner charge.

Though complex, the charging behavior of CCA-based developers can be described by a self-consistent simulation model where added CCA alters the charging tendency of the toner and carrier surfaces. In this regard, the influence of CCA on toner charge appears similar to that seen with external additives such as TiO_2 and SiO_2.[5,8,10] However, a key difference between such latter particulate charge modifying additives and CCA's is that CCA's may function as surface active, film forming additives, and thereby be especially effective in transfer processes even at low additive concentrations.

Finally, in actual operational conditions, toner particles are continually removed from a developer as a result of xerographic development, with fresh toner being added to counter this loss. As a result, processes such as CCA transfer may be affected by the rate of toner throughput in an imaging developer, and the present data, taken under fixed batch conditions, should probably be only viewed as representative of the extreme condition of zero toner throughput for any conventional xerographic imaging system.

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