

# The Effect of Carrier Properties on the Admix Performance of a Xerographic Developer

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## Abstract

During xerographic development, charged toner particles are removed from a xerographic developer, and to balance this loss an equivalent amount of fresh toner is dispensed into the developer. Since uncharged or poorly-charged toner particles tend to develop in the non-image "background" areas of a latent xerographic image, the dispensed toner particles must be rapidly brought to a charged state in order to avoid "background" development. Normally, the "added" toner and the "incumbent" toner (i.e., the charged toner particles already present in the developer) merge to a common level of charge, and the rate at which this merging process occurs (the so-called "admix rate") is an important functional property of any xerographic developer design, with a rapid rate being especially desirable.

In principle, the polarity, charge level, and the charge admix performance of any toner are functions of the chemical composition of the toner particles and of the xerographic carrier particles<sup>1,2</sup>. However, even for a single, apparently optimized xerographic toner/developer design, charge admix performance may also vary as a result of extrinsic factors. For example, for some developer designs, the admix rate can vary from acceptably fast to effectively zero under certain conditions; paradoxically, this latter admix failure mode actually occurs as a result of an ultra-rapid admixing process. In such a case, the added toner acquires a level of charge higher than that of the incumbent toner, and this increased charge is mirrored by an equivalent decrease in charge for the incumbent toner<sup>3-5</sup>. In an extreme failure condition, the populations of "added" and "incumbent" toner particles scarcely show any tendency to merge to a common intermediate level of charge, and the developer "stabilizes" with the carrier beads in charge equilibrium with coexisting high-charged added toner particles and low-charged incumbent toner particles.

For a single developer, the charging difference between the "aged" incumbent toner and the "fresh" added toner is the root cause for the above process, and normally such toner differences are reflected in toner charge values

that decline with developer mixing time<sup>5</sup>. However, in any two component developer, toner charge is also a function of carrier charging properties, and to illustrate the effect of carrier charge properties on toner charge and on toner charge admix, the present report details experimental data for a single "poor-admixing" toner paired with a range of carriers created by mixtures of "medium" and "high" charging carriers. Although the carrier changes created systematic changes in the charge level of the test toner, the toner admix performance remained as non-merging in all cases, indicating that this form of admix failure is indeed a function only of intrinsic toner properties. For the test developers, carrier mixtures designed to produce a high level of toner charge also produced a high level of overall charge stability as a function of developer mixing, and from normal charge-to-mass measurements such a result might be assumed to reflect a lack of carrier and toner aging. However, for the test toner, the subsequent admix performance remained as non-merging — apparently, for the high-charging developers, the mixing-induced declines in toner charging properties were coincidentally balanced by mixing-induced increases in carrier charging properties.

## Introduction

The average toner charge to mass ratio,  $q/m$ , is the most widely-used metric for the toner charging performance of a two-component xerographic developer, since it can be readily measured with a simple Faraday cage, and since it can be directly related to dot, line and solid image development<sup>6</sup>. Typically, the average toner charging properties decline with long-term production of xerographic images, and normally this decline reflects permanent, usage-induced changes to the triboelectric charging properties of the carrier particles<sup>7-10</sup>. However, toner charging properties can also be affected by usage-induced changes in the properties of the toners themselves<sup>2,5</sup>. For example, external additives can be lost from or become buried into the surface of toner particles, as a result of the mechanical agitation that a carrier/toner mixture receives in a xerographic development housing.

In such a case, toner "aging" will vary as a function of the residence time of the toner particles in the development housing, and can thus be quite variable. For high quality digital printing, toner usage per print may change by a factor of ten between text and pictorial images, and as a result the toner residence time, and hence toner "age", can alter significantly as a function of image type. Additionally, image-induced changes in toner usage will create corresponding changes in the amount of uncharged toner dispensed into the developer per print, and hence affect the charge admixing process between the charged "incumbent" toner particles and the uncharged "added" particles, for those cases where the admix process is a function of toner "age".

Accordingly, while the average  $q/m$  value of a toner and " $q/m$ -aging" performance are important factors, a full assessment of toner charging performance requires an additional measurement of a distributed charge property such as toner charge-to-diameter,  $q/d$ <sup>3-5</sup>. This is especially important for studies of xerographic background development, since this mode of development can be strongly affected by the population of particles in the low-charge/wrong-sign charge "tail" of a toner charge distribution<sup>11</sup>. In a normal, functional developer, this latter population represents only a minor fraction of the total number of toner particles, but the size of this latter population will increase during xerographic development if the rate of toner charge admixing is inadequate. In particular, under certain conditions, toner "aging" can strongly affect the admix rate, and in extreme cases can effectively drive the rate to zero<sup>3-5</sup>.

Now since the magnitude and polarity of the toner charging terms,  $q/m$  and  $q/d$  can also be altered via changes in the charging properties of the accompanying carrier beads, carrier properties can also affect the distributed charging properties of toner particles<sup>4</sup>. However, for cases where admix deficiencies are created via toner "aging", changes in carrier charging properties should not affect the underlying admix processes, and in this present paper this effect will be demonstrated via experimental data taken on a series of developers based on a common "aged" toner and a set of "medium-" to "high-" charging carriers.

## Experimental

The test toner was a negative-polarity polyester toner, jetted to about a 7 micron mean diameter, with external additives (lubricant, silica and titania) extensively blended onto the toner surface. The 65 micron diameter test carriers were based on a rough metallic, oxidized core, powder-coated at a nominal 1 wt%. Two test carriers were mixed in various ratios to produce a range of charging characteristics. Both carrier M and H were coated with a carbon-black-doped methacrylate resin, but for carrier H 20% of the coating was replaced with a higher charging resin (i.e., a resin designed to impart a higher level of negative charge to the test toner). Carriers M and H were mixed at 100:0; 80:20; 60:40; 50:50; 40:60; 20:80 and 0:100 in order to

create a range of charge levels from the single test toner. Sample developers were prepared at a 4 weight percent concentration of toner, and 200 grams of developer were vigorously mixed in 100 ml. glass jars on a paint-shaker. For all of the tests, the developer samples were conditioned at a controlled ambient of 20°C/ 50% relative humidity.

For studies of mixing time on  $q/m$ , total blow-off measurements were made at regular time intervals (e.g., 5, 15, 30, 45, 60, 75 and 90 minutes of mixing) on small samples of developer using a conventional Faraday cage/air-jet combination.

At the end of each mixing test, an "admix" test was made, with an additional 2 wt% of uncharged toner being added to the charged developer. The added toner was lightly mixed into the developer, and regular paint-shake mixing was then continued for 5 additional minutes. At short time intervals (e.g., 15, 30, 60, 90, 120, 180, and 300 seconds), a small sample of developer was examined using a "laminar air flow/transverse electric field" charge-spectrograph<sup>12</sup> to create a toner "smear", with particles displaced according to the magnitude and polarity of their  $q/d$  values. Image analysis of the "smear" was used to provide a quantitative map of toner particles on a  $q/d$  vs.  $d$  plane, and these data were used to generate a charge spectrum (e.g., an area-weighted spectrum of  $q/d$  vs. a peak-normalized population) and a  $q/d$  vs.  $d$  contour plot.

## Results

### (a) Effect of Carrier Mixtures on Triboelectric Charge Generation

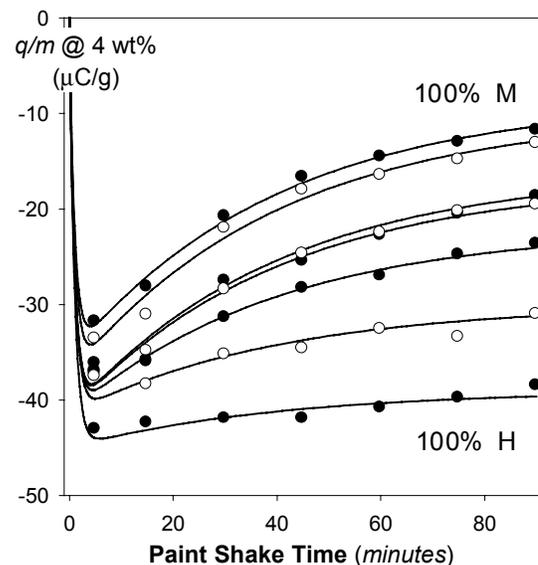


Figure 1.  $q/m$  vs. developer mixing time for 100%;80%;60%;50%;40%;20% and 0% of carrier M

Figure 1, the combined  $q/m$  data (corrected to a uniform 4 wt %) for the pre-admix paint-shake mixing experiments, shows that simple mixtures of carriers M and H were effective in creating a regular range  $q/m$  responses.

Indeed, the  $q/m$  data for any specific carrier mixture can be described by a simple weighted sum of contributions from the  $q/m$  responses of the component carriers. (Note, however, that the responses are specific to the 4 wt% toner concentration used in the experiments — mixing at lower toner concentrations, for example, produces an even greater level of  $q/m$  loss, and this effect has been discussed for similar developers in a previous report<sup>13</sup>.)

Besides producing the desired range of  $q/m$  values from a single toner, the mixtures of carriers also, coincidentally, produced a range of  $q/m$  loss as a function of developer mixing time — after 90 minutes of mixing, the developer based on 100% of carrier M showed a 68% loss in  $q/m$ , while the developer based on 100% of carrier H showed only a 12% loss, and all developers based on mixtures of these carriers showed proportional losses. Now, while losses in charging properties can be tracked using an intrinsic toner property, e.g.  $q/m$ , the observed losses could in fact reflect losses in either toner or carrier charging properties, or some combination of both. This can be made clear from the difference term ( $\phi_{toner} - \phi_{carrier}$ ) in a simple charging equation of the form<sup>2</sup>:

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

where,

$A'$  and  $C_0$  are constants, (governed by physical factors such as toner and carrier size and density, and by the physics of electrostatics),

$\phi_{toner}$  and  $\phi_{carrier}$  describe the charging tendency of the toner and carrier particles (functions of intrinsic properties such as surface composition — type and level of polymer, colorant, internal and/or external additives, and also of the effect of external factors such as ambient humidity on the intrinsic properties),

and  $(1 - \exp\{-\gamma \cdot t\})$  is a simple representation of the mechanics of developer mixing (i.e., the rate constant is a function of mixing efficiency).

While the constants  $A'$  and  $C_0$  can be estimated from the size and density of the test carriers and toner<sup>1,2</sup> (e.g.,  $A' = 110$  and  $C_0 = 1.5$  for the present materials), the  $\phi_{toner}$  and  $\phi_{carrier}$  values cannot be uniquely deduced from the experimental  $q/m$  data (since there is only one measured  $q/m$  value for two unknown parameters). Accordingly, Equation (1) can only be used with an assumed value for either  $\phi_{toner}$  or  $\phi_{carrier}$  as a starting point. An additional complication is that the experimental data clearly indicate that either  $\phi_{toner}$  and  $\phi_{carrier}$  (or both) "age" as a function of developer mixing time, i.e.:

$$\phi_i = (\phi_0 - \phi_\infty) \cdot \exp\{-k \cdot t\} + \phi_\infty \quad (2)$$

where  $\phi_{toner}$  or  $\phi_{carrier}$  vary exponentially with mixing time  $t$  from a zero-time value  $\phi_0$  to an eventual long-term value  $\phi_\infty$ . Table 1 shows a set of  $\phi$  values that describe the "100% carrier M" and "100% carrier H" experimental data,

all based on an initial, arbitrary assumption of 2.0 eV for  $\phi_{toner, \infty}$ .

Table 1

Condition of Carrier/Toner	100% Carrier M (eV)		100% Carrier H (eV)	
	$\phi_{toner}$	$\phi_{carrier}$	$\phi_{toner}$	$\phi_{carrier}$
New	0.47	2.345	0.47	2.645
"Aged"	2.00	2.550	2.00	3.900
New; de-tone/re-tone	0.47	2.400	0.47	1.845
"Aged"; de-tone/re-tone	2.00	2.650	2.00	3.750

As can be seen, almost all of the observed  $q/m$  "aging" observed in the test with 100% of the carrier M is assumed to be the result of a mixing-induced change in the  $\phi_{toner}$  value. This assumption is based on the fact that a repeat mixing test (with original carrier, but fresh toner) matched the original test. Similarly, the apparent  $q/m$  stability shown for the test based on 100% of carrier H is assumed to be the result of a coincidental balancing of the aging responses of the toner and the carrier, again based on the result of a repeat experiment. Effectively, the toner is assumed to age identically with both carriers, but the aging carrier H is assumed to become increasingly effective at imparting negative charge to the toner particles. Since this latter carrier is coated with a mixture of two resins, the assumed enhanced carrier "aging" could reflect a preferential, wear-induced change in surface composition. Alternately, it might be that the surface of carrier H is more receptive to the transfer of charge-enhancing (with respect to the carrier) components from the toner particles. Without further independent evidence, the results shown in Table 1 must be viewed merely as one of many possible models for the observed  $q/m$  aging data. Fortunately, post-mixing admix tests, as described in the following section, offer additional informative insights, since they allow the individual charging response of "new" and "aged" toner particles to be simultaneously evaluated.

## (b) Effect of Carrier Mixtures on Charge Admix Performance

At the 90 minute end-point of each mixing experiment, a small amount of toner was blown from the carrier beads into a charge spectrometer, to provide a pre-admix (i.e. at a nominal 4 wt% concentration) toner sample for a  $q/d$  evaluation. Figure 2, the resultant charge distributions for three representative ratios of carrier mixture, shows a unimodal distribution in all cases — i.e., there is no sign of individual contributions from the component carriers. The plot of mean  $q/d$  values versus the corresponding  $q/m$  values shown in Figure 2, shows a simple, linear relationship, consistent with:

$$q/m = q \cdot \left( \frac{6}{\rho \cdot \pi \cdot d^3} \right) = \left( \frac{q}{d} \right) \cdot \left( \frac{6}{\rho \cdot \pi \cdot d^2} \right) \quad (3)$$

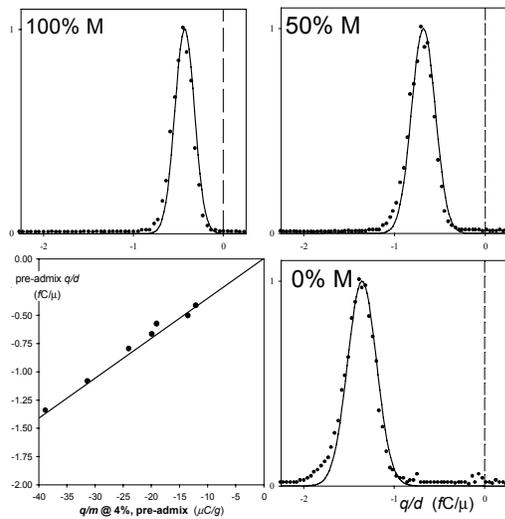


Figure 2. Representative charge spectra peaks for 100%, 50% and 0% carrier M after 90 minutes of mixing.

and for the present test toner, the relationship between  $q/m$  and  $q/d$  is:

$$q/m = 28.3 \cdot \left( \frac{q}{d} \right) \quad (4)$$

As detailed earlier, each test developer was subjected to a post-mixing admix test, with 2 wt% of uncharged toner being added to the charged developer. A typical set of admix data are shown in Figures 3a-c, where 3a shows the charge distribution peak(s), 3b shows the corresponding

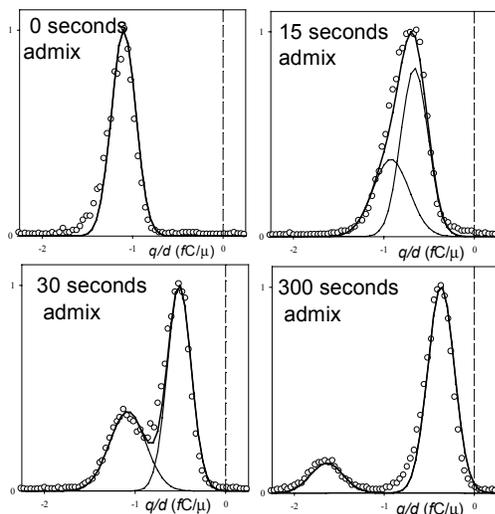


Figure 3a. Representative charge spectra peaks from the admix test of the 20% carrier M mixture, where the experimental curve envelopes have been separated into added and incumbent toner peaks.

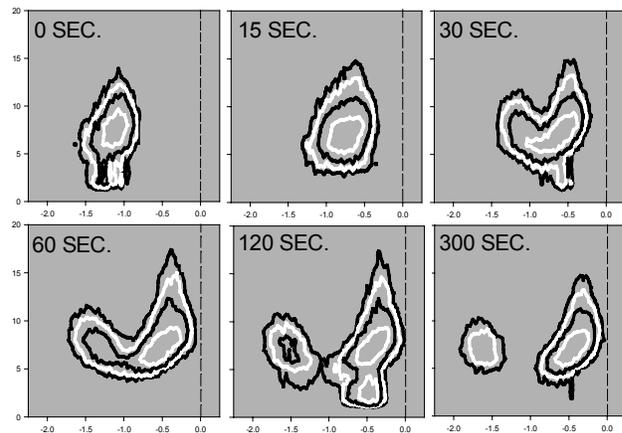


Figure 3b. Charge spectra contour plots on a toner size:charge per size plane, corresponding to the peaks shown in Figure 3a.

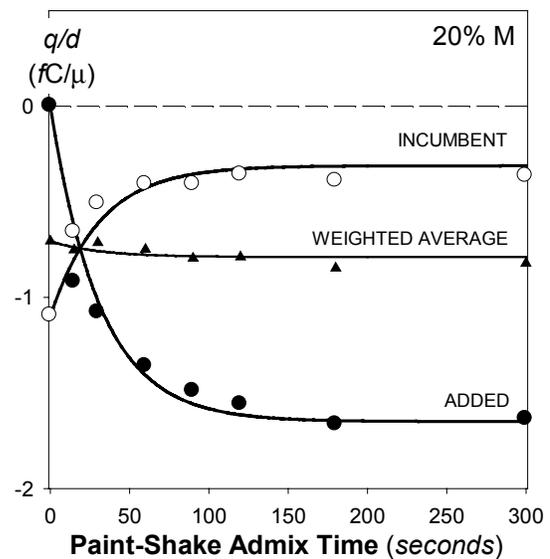
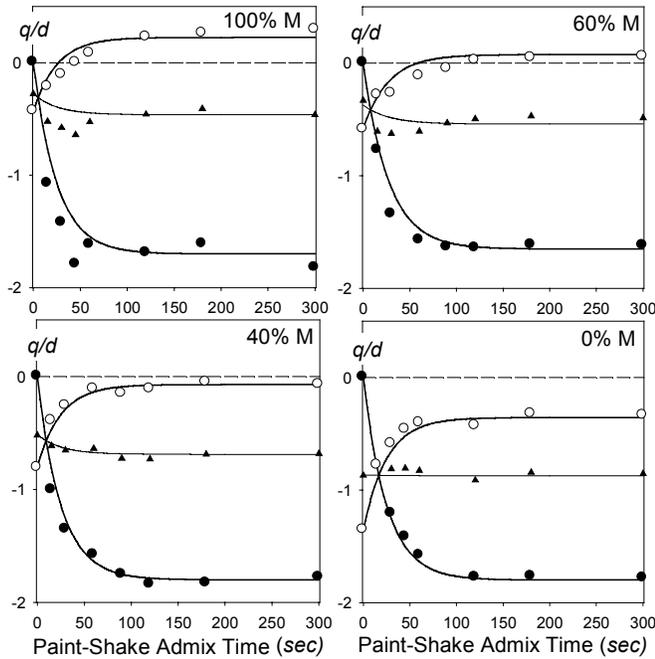


Figure 3c. Charge spectra peak positions for added and incumbent toner particles as a function of admix time, for the developer based on 20% of carrier M.

contour plots and 3c shows the aging profile for both incumbent and added toner particles. For this latter plot, a peak-fitting computer program was used to extract the individual component peaks from the total charge distribution envelope<sup>4,5</sup>, with the mean  $q/d$  values for each peak being plotted versus admix time in Figure 3c. Similar component peak plots for four other carrier mixtures are shown in Figure 4a-d, and in all cases it is clear that the added and incumbent toner populations remain charge-segregated regardless of the carrier particles used to charge the toners, and this unusual result will be discussed in the following section.



Figures 4a- d. Charge spectra peak positions for added and incumbent toner particles as a function of admix time, for the developers based on 100%, 60%, 40% and 0% of carrier M.

## Discussion

Toner particles can acquire charge via several pathways, and a total description of all aspects of the charging process will be necessarily quite complex<sup>3</sup>. However, for specific, well-defined charging conditions such as used in the present tests, a zero-order analysis can adequately illustrate the major effects.

For example, in the short-term, the present admix process may be assumed to involve only a redistribution of charges (i.e., no post-admix triboelectric charging in the conventional sense), and the pre- and post- admix charges can thereby be directly equated. Additionally, from a triboelectric charging equation such as Equation 1, there should be a simple relationship between the pre- and post-admix  $q/m$  value (or equivalently the average  $q/d$  value) of a developer. For example, at the end of the 90 minutes of paint-shake mixing, the test developers were typically at a final toner concentration of about 3.6 wt %, and the effect of an additional 2 wt% of toner can be predicted to be:

$$q/m_{3.6+2.0} = \left( \frac{3.6+1.5}{3.6+2.0+1.5} \right) \cdot q/m_{3.6} \quad (5)$$

where  $C_0$  has been set as 1.5,  
i.e.

$$q/m_{3.6+2.0} = 0.718 \cdot q/m_{3.6} \quad (6)$$

and since, for the present test toners,  $q/d$  is directly and linearly related to  $q/m$ , then

$$q/d_{post-admix} = 0.718 \cdot q/d_{pre-admix} \quad (7)$$

Now, the charge distribution spectra of the present tests clearly show segregated incumbent and added toner populations, and even for normal admix behavior (where the populations eventually coalesce<sup>3-5</sup>) such segregation is evident during the initial stages of the admix process. Accordingly, the total average charge properties for post-admix toners can be viewed as a simple population weighted average of the "added" and "incumbent" components, i.e. at any admix time,  $t$ , the following equality will be true:

$$q/d_{average,t} = \left( \frac{C_{inc}}{C_{inc} + C_{add}} \right) \cdot q/d_{inc,t} + \left( \frac{C_{add}}{C_{inc} + C_{add}} \right) \cdot q/d_{add,t} \quad (8)$$

where,

$C_{inc}$  and  $C_{add}$  are the incumbent and added toner concentrations,

$q/d_{average,t}$  is the average  $q/d$  value at admixing time,  $t$ ,

$q/d_{inc,t}$  and  $q/d_{add,t}$  are the  $q/d$  values for incumbent and added toner particles at admixing time,  $t$ .

For identical incumbent and added toner particles, the admix process will be complete when  $q/d_{inc,t}$  and  $q/d_{add,t}$  reach a common value, with the  $q/d_{average}$  value rising (for the case of 2 wt% of toner added to 3.6 wt% toner) from  $(3.6/5.6) \cdot q/d_{inc,0}$  to  $0.718 \cdot q/d_{inc,0}$ .

By contrast, the experimental data of the present study, shown in Figure 3c and Figures 4a-d, clearly represent an atypical mode of admix behavior, characterized by several key differences. The first important difference is the common, stable maximum level of charge acquired by the added toner particles (about  $-1.7 \text{ fC}/\mu$ ). Unlike the result predicted for "perfect admix" behavior, the observed value of  $-1.7 \text{ fC}/\mu$  is not some characteristic "shared" fraction of the pre-admix value — rather it is a value higher than that generated via triboelectric toner/carrier charging of any of the pre-admix test toners. As discussed by Gutman and Mattison<sup>3</sup>, the increased charge level for the added toner particles results from a toner-toner charge redistribution in the presence of attendant charged carrier beads. With this view, the eventual charge level attained by the added toner will be solely a function of a  $(\phi_{added \text{ toner}} - \phi_{incumbent \text{ toner}})$  term, independent of any  $\phi_{carrier}$  value, and for the present test toners, the common maximum value of charge for the toner particles added at 2 wt% to the "aged" incumbent toner particles will be

$$q/d_{added,\infty} = \left( \frac{(110) \cdot (0.47 - 2.00)}{(28.3) \cdot (2 + 1.5)} \right) \quad (9)$$

$$= -1.7 \text{ fC}/\mu$$

(where 110 =  $A'$ , 28.3 is the conversion factor from  $q/m$  to  $q/d$ , and 0.47 and 2.00 are the  $\phi_{added \text{ toner}}$  and "aged"  $\phi_{incumbent \text{ toner}}$  values — as initially assumed in the  $q/m$  model,

with values chosen to produce an internal consistency between the  $q/m$  and  $q/d$  calculations.)

Because the  $(\phi_{\text{added toner}} - \phi_{\text{incumbent toner}})$  term in the present tests has a large value (a common value for all tests, since all of the tests were based on a single toner), the added toner particles continue to acquire charge from the incumbent toner particles until the final  $-1.7 \text{ fC}/\mu$  value has been reached. For developers based on a medium-charging carrier (e.g., those rich in carrier M), this admix process drives the incumbent toner particles to very low or even reversal values of  $q/d$  (yet another example of inequitable sharing<sup>14</sup>), while high-charging carriers allow the incumbent toner to retain a finite level of charge.

The second important difference between the present data and "perfect" admix, lies in the value of the population weighted average  $q/d$  value. At equilibrium, for perfect admix, this weighted average is merely the final common  $q/d$  value shared by the identical incumbent and added toner particles. For the present tests, where a high-charging added toner is coupled with an "aged" incumbent toner, the population weighted average  $q/d$  value clearly varies with carrier charge — for developers based chiefly on the medium-charging carrier M,  $q/d_{\text{average}}$  is close in value to  $q/d_{\text{incumbent},0}$ , while for developers based on the high-charging carrier H,  $q/d_{\text{average}}$  is close to the "perfect" admix value of  $0.718 \cdot q/d_{\text{incumbent},0}$ , even though the actual admix is highly atypical.

The underlying cause for the above differences can most simply be explained in terms of  $q/d$  as a function of toner concentration and toner/carrier charging factors, using a  $q/d:C$  relationship diagram as shown, for example, in Figures 5a-b. In these figures, the  $q/d$  values for the incumbent toner particles are assumed to be related to toner concentration by:

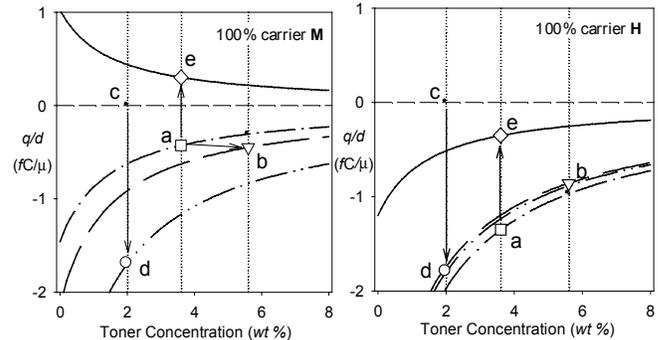
$$q/d = \left( \frac{A_q}{C + C_0} \right) \cdot (\phi_{\text{toner}} - \phi_{\text{carrier}}) \quad (10)$$

i.e., all combinations of  $q/d$  and  $C$  lie along a single  $q/d:C$  line. (The  $A_q$  value is simply the " $q/m$ -based"  $A'$  constant divided by 28.3 to produce a " $q/d$ -based" constant). For the added toner particles, the equivalent  $\Delta\phi$  term in Equation (10) will be  $(\phi_{\text{added toner}} - \phi_{\text{incumbent toner}})$ .

Figure 5a shows the  $q/d:C$  situation for a developer where the incumbent toner is "aged", and is coupled with carrier M. In this case, the added toner gains charge  $c$  to  $d$  from the "aged" incumbent toner, and this forces the latter toner particles towards zero charge along the path  $a$  to  $e$ . For the entire developer, the average  $q/d$  value appears to follow the path  $a$  to  $b$ , and the developer appears to generate an average  $q/d$  value (and hence average  $q/m$  value) that is almost independent of toner concentration, or is an increasing function.

By contrast, for the present experiments based on carrier mixtures rich in the high-charging carrier H, the pre-admix  $(\phi_{\text{incumbent toner}} - \phi_{\text{carrier}})$  value almost matches the  $(\phi_{\text{added toner}} - \phi_{\text{incumbent toner}})$  value, so that the "aged toner" and "added toner" components of the total developer appear

to follow a normal and common  $q/d:C$  (or  $q/m:C$ ) relationship, even though the pre- and post-admix charging processes are quite different (involving toner/carrier and toner/toner interactions, respectively). As a result, for this case, the addition of 2 wt% of toner to 3.6 wt% follows the form shown in Equation (7) despite the actual admix process being quite atypical. This behavior is illustrated in Figure 5b.



Figures 5a-b.  $q/d:C$  relationships for added and incumbent toner particles, pre- and post-admix, for developers based on 100% of carrier M and carrier H respectively.

In general, the relationship between the final average  $q/d$  value,  $q/d_{\text{average},\infty}$  and the pre-admix value,  $q/d_{\text{incumbent},0}$  can be expressed (for 2wt% added into 3.6wt% and  $C_0 = 1.5$ ) as

$$q/d_{\text{average},\infty} = \left( \frac{(3.6 + 1.5)}{(3.6 + 2 + 1.5)} \right) \cdot q/d_{\text{incumbent},0} \cdot \delta \quad (11)$$

where  $\delta$  is a factor that accounts for the enhanced or degraded post-admix average  $q/d$  (or  $q/m$ ).

For cases where both the carrier and toner remain unaged,  $\delta=1$ , and the admix will be normal (i.e., the two toner populations will collapse to a common  $q/d$  value). For cases with no carrier aging, but where the incumbent toner is "aged" during the pre-admix mixing,  $\delta > 1$  (because of the difference between the incumbent and added toner), and the admix will be atypical. For cases where toner aging is exactly offset by an equivalent carrier enhancement,  $\delta=1$ , but the admix will be atypical (because of differences between the incumbent and added toner).

As can be seen from Equation (11), the  $\delta$  factor can be directly related to the ratio of the final post- and pre-admix average  $q/d$  (or equivalently,  $q/m$ ) values. For example, if the pre- and post-admix  $q/m$  values are identical (despite the addition of the admix toner), then this can be taken as indirect evidence of an atypical admix event, and a post-admix charge spectrum may be expected to show two non-merging peaks.

Equation (11) can be used to predict another important post-admix value, namely the long-term  $q/d$  value of the incumbent toner,  $q/d_{\text{incumbent},\infty}$ , following the redistribution of charge between the incumbent and added toner particles.

For example, if Equation (8) (with time set as  $\infty$ ) is equated to Equation (11), then

$$q/d_{incumbent,\infty} = 1.117 \cdot q/d_{incumbent,0} \cdot \delta - \left(\frac{2.0}{3.6}\right) \cdot q/d_{add,\infty} \quad (12)$$

and this equation simplifies to the "typical" Equation (7) when  $\delta = 1$ , and  $q/d_{incumbent,\infty}$  equals  $q/d_{add,\infty}$ . For all other conditions, the equation predicts the change in the  $q/d$  of the incumbent toner as a result of a redistribution of charge between dissimilar incumbent and added toner, and the lines in Figures 3c, 4a-d were drawn using the values shown in Table 2, and the value of  $\delta$  was varied to obtain the best single fit to both the incumbent and added toner data. (From a complete experimental data set, the values for  $\delta$  can be directly obtained from the ratio of the post- and pre-admix  $q/m$  values as defined in Equation (11) — for example, for the 100% carrier H test, the pre-admix  $q/m$  value "corrected to 4 wt%" was  $-39.0 \mu\text{C/g}$ , and the post-admix  $q/m$  at 6% was  $-27.0 \mu\text{C/g}$ , giving a  $\delta$  value of 0.9, and the equivalent data for the 100% carrier M test were  $-12.5 \mu\text{C/g}$  at 4 wt% and  $-14.8 \mu\text{C/g}$  at 6wt%, for a  $\delta$  value of 1.6).

For calculations based on Equation (12), the key equations are:

$$q/d_{add,\infty} = -1.7$$

$$q/d_{average,0} = (3.6/5.6) \cdot (q/d_{incumbent,0})$$

$$q/d_{average,\infty} = 0.718 \cdot q/d_{incumbent,0} \cdot \delta$$

$$q/d_{average,t} = (q/d_{average,0} - q/d_{average,\infty}) \cdot \exp\{-\gamma \cdot t\} + q/d_{average,\infty}$$

$$q/d_{add,t} = (q/d_{add,\infty}) \cdot (1 - \exp\{-\gamma \cdot t\})$$

$$q/d_{inc,t} = (q/d_{average,t} - (2/5.6) \cdot q/d_{add,t}) \cdot (5.6/3.6)$$

As can be seen from Table 2, the value of  $\delta$  is highest for the carrier mixtures rich in carrier M, i.e., the mixtures that showed the greatest degree of "aging". The mixtures rich in carrier H gave  $\delta$  values close to 1, but still gave atypical charge admix — for these mixtures, the toner "aging" was offset by carrier "enhancement", but the toner "aging" still controlled the subsequent admix behavior.

**Table 2**

% as Carrier M	$q/d_{inc,0}$ fC/ $\mu$ (exptl. data)	$q/d_{add,\infty}$ fC/ $\mu$ (exptl. data)	$\delta$ (fitted)	$\gamma$ (sec) <sup>-1</sup> (fitted)
100	-0.43	-1.70	1.5	0.040
80	-0.50	-1.65	1.4	0.050
60	-0.58	-1.65	1.3	0.037
50	-0.67	-1.75	1.2	0.032
40	-0.80	-1.80	1.2	0.040
20	-1.10	-1.65	1.0	0.032
0	-1.35	-1.80	0.9	0.040

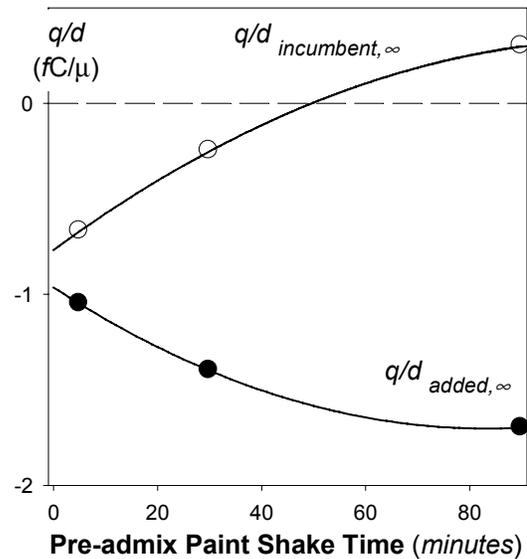


Figure 6. The long-term post-admix  $q/d$  values for incumbent and added toner as a function of the pre-admix mixing time.

As a final experimental example of the effect of toner "aging" on admix performance, Figure 6 shows the admix results for three levels of pre-admix mixing for the developer based on 100% carrier M. As expected, the reduced levels of pre-mixing produced a lower level of  $q/d_{add,\infty}$  and a reduced difference between the  $q/d$  values of the added and incumbent toners. However, as shown in Figure 6, an extrapolation of the data predicts that the test developer will give perfect admix only for the case of zero paint-shake pre-mixing. Evidently, the test toner is readily "aged" in the paint-shake mixer, and a less abusive mixer such as a roll mill would probably be necessary to produce a charged developer having a normal admix response<sup>5</sup>.

With "aged" toner as the root cause of atypical admix behavior, various strategies to minimize the effect can be proposed. From the toner viewpoint, a stable, robust design will be a key enabler. A tough toner binder resin would probably minimize the "burial" of external additives into the sub-surface of toner particles, but this rheological criterion is somewhat incompatible with overall "low-melt" toner fusing requirements. A toner free of external additives should be resistant to mechanically-induced surface-aging, but the total removal of external additives will probably adversely affect the toner performance in post-development subsystems such as image transfer and photoreceptor cleaning, especially if such sub-systems have been optimized for additive-toners. Toner external additives that produce a major increase in the total toner charging properties will be most likely to create toner "aging", since even a small loss of such additives will depress the overall toner charge characteristics<sup>2,13</sup>. Also, for toners that "age", charge-transfer-enhancing components will likely increase the rate and extent of atypical admix behavior.

From a xerographic hardware viewpoint, toner "aging" will normally increase as the size of the development housing is reduced, and this is an especial concern for full-color xerographic machines, where multiple housings must be accommodated in a limited space. Mixing dynamics within housings will also affect toner "aging" — while toner/carrier mixing zones may be gentle, other locations such as the magnetic brush trim region and development zone may be inherently abusive.

With respect to xerographic imaging process factors, the toner mean resident time in the development housing will affect the toner "aging" process, and this will involve factors such as the total mass of toner in the active developer, the rate of toner removal/addition (a function of developed image mass), and the imaging cycle strategy (e.g., the extent to which the developer is agitated during imaging and non-imaging intervals).

Image process control strategies may also drive an "aging" toner to a run-away, non-functional state — if the output image density declines as a result of an atypical admix process (e.g., via reduced development from the "high-charged" added toner), then closed-loop feedback to the toner dispenser will accelerate the admix failure and thereby lead to a further decline in development. Finally, if the toner "aging" process is sensitive to the concentration of toner in the developer, then the operational set-point may affect the toner charge admix behavior.

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### Biography

Robert Nash received his Ph.D. in Physical Chemistry from the University of Bristol, England. He joined the Xerox Corporation in 1970, and is currently a Principal Scientist in the Materials Technology and Concepts group. His research and modeling studies have focused on the design and evaluation of xerographic toners, carriers and developers, with especial emphasis on "aging" mechanisms. Starting with the 4th. International NIP Congress in 1988, he has yearly presented the results of his studies at the IS&T NIP Conference. In 1990, he served as Publication Chairman for the 6th. NIP Congress, and in 1992 he was Chairman of the IS&T Honors & Awards Committee. In 1999, he was named as a Fellow of the IS&T.

For the past fifteen years, he has traveled yearly to Japan for technology interchanges between the Xerox Corporation and Fuji Xerox. For the past two years he has been on an expatriate assignment at Fuji Xerox, Takematsu, Japan, as the Senior Manager, Resident for the Xerox Supplies Development, Manufacturing and Supply Chain Operations organization. In this assignment, he is broadening his area of interest to include the science and technology of photoreceptor design and manufacture.

In their spare moments, he and his wife Ann are now enjoying developing a cross-cultural garden (English/Welsh/Japanese) around their hillside home at Hakone Itabashi, Odawara, and are gradually adapting to a sub-tropical style of horticulture after many cold years in USDA zone #5.