

The Effect of Toner Blend Conditions on Charge Admix Performance

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Abstract

Even for a fixed composition, the charging performance of a toner may show discernable differences between different production batches, and this can be a practical problem for commercial toners that are produced in multiple, worldwide production facilities. This effect may be especially evident in toners based on external additives — variations in the level and distribution of external additives can be a major source of variability in toner performance, since external additives enhance the basic properties of the base toner. As a result, the additive-blending production process can be a significant source of toner performance variability. Furthermore, toner particles experience additional mixing forces during the final packaging operation, during the developer production process (i.e., during the production mixing of toner and carrier particles to create a final developer at a specified toner concentration), and during actual operation in a xerographic development module, and these secondary mixing events can also create changes in toner performance.

While external toner additives can affect several key toner properties such as flow, cohesivity, humidity sensitivity, cleanability, etc., the effect of minor variations in blend conditions on performance is often most evident from a toner's charge admix response. This latter property is a measure of the rate at which uncharged, dispensed toner equilibrates with charged toner in a working developer). Since uncharged or poorly-charged toner particles will tend to develop in background, non-image areas, a rapid rate of charge admix is necessary for acceptable xerographic performance.

In this present study, charge admix measurements on a single toner design were used to illustrate how changes in toner blend conditions can create a range of charge admix performance, from unacceptably slow to an excellent rapid rate. The major blender topics considered include modes of mixing, along with a range of blend conditions for a single blender.

Introduction

While the basic charging performance of a xerographic toner can be assessed via the average toner charge to mass

ratio, q/m , a more detailed assessment requires an additional measurement of a distributed charge property such as toner charge-to-diameter, q/d .¹⁻⁵ 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.⁶ In a normal, functional developer, this latter population represents only a minor fraction of the total number of toner particles; however, during the xerographic development process (where uncharged toner particles are added from the toner dispenser to the incumbent, charged toner particles in the working developer) the size of the low-charge/wrong-sign toner population will increase if the charge-admix rate (i.e., the rate at which the uncharged dispensed toner particles equilibrate with the incumbent toner particles) is excessively slow. To alter the charge-admix characteristics of a toner, components such as charge control additives and external particulate additives are frequently incorporated into the overall toner design. However, minor changes in additive level (e.g., as a result of batch-to-batch variations during toner manufacturing) may produce a range of toner charging characteristics, and thereby alter the charge-admix rate for dispensed toner. This may be especially significant during the initial operation of a xerographic developer, since (because of manufacturing and product distribution logistics) the dispensed toner and the "blended developer" toner will never be from a common production batch. Additionally, even after extended xerographic operation (i.e., where the dispensed toner has completely replaced the initial toner in the developer) there can still be a charging mismatch between the dispensed and incumbent toner particles, if the latter particles are "aged" (i.e., undergo usage-induced changes in surface composition) by the mechanical forces present in the development housing.³

For surface-additive toners, the blending step in the toner manufacturing process is a major controlling factor for toner surface composition, and is thus a potentially important factor for charge-admixing. Indeed, charge-admix performance can be used to identify subtle differences between various toner blending strategies and processes, and this present report illustrates this point through an assessment of blender-induced changes in admix performance for a single test toner design.

Experimental

The test toner was a black, negative-polarity, wax-containing toner, jetted to an 11-micron mean diameter, with external additives (0.75 wt% of a 16 nm fumed silica and 0.4 wt% of sub-micron fluoropolymer spherical particles) blended onto the toner surface. Several batches of test toner were prepared using a variety of toner/additive blending schemes (see later). For admix charging evaluations, a control toner was mixed with a solution-coated 100-micron diameter ferrite carrier. A standard admix-charging test developer was prepared at a 3.5 wt% weight percent concentration of the control toner, and was charged by an initial 30 minutes of agitation in a closed xerographic development housing. For the charge-admix measurements, 100 gm of the "housing-charged" standard developer was roll-milled for an additional 15 minutes in a glass jar, after which 1 wt% of a test toner was added to the charged developer. The added toner was lightly mixed into the developer, and roll-mill mixing was then continued for 2 additional minutes. (The admix protocol was designed as a stress condition, so that the admix process would occur at a measurably slow rate in order to accentuate differences in toner admix behavior). At short time intervals (e.g., 0, 15, 30, 45, 60, and 120 seconds), toner was blown from a small sample of developer and examined using a "laminar air flow/transverse electric field" charge-spectrograph⁷ 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).

The test toners were blended in two types of blender: (a) a V-Cone blender, where small stainless steel blending balls were used to agitate the toner plus external additives as these powders flowed between the two arms of the mixer during each inversion of the V-shaped mixing chamber; (b) a horizontal, mechanically-agitated fluid-bed mixer, where toner plus external additives were blended via mixing elements mounted on a horizontal high-speed rotating shaft. Two types of mixing protocol were studied: (a) a single-step blend procedure, where the toner and additive particles were blended at their final concentration; (b) a masterbatch procedure, where an initial blend step was used to create an additive-rich blend (e.g., with an additive level ten to twenty times that of the final target value), and a second blend step was used to "dilute" the masterbatched material with additive-free toner in order to create the final target additive level for the total load of toner in the blender.

For the control toner used in the present tests, the external additives were applied using a two-step masterbatch blending procedure in a production-scale V-cone blender.

Theory

For any particular two-component xerographic developer, the toner q/m value can be related to toner and carrier physicochemical properties via a simple charging equation of the form^{8,9}:

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

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), and C is the toner wt % concentration in the developer,

ϕ_{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).

After an extended mixing time, t , the $q/m:C$ relationship can be simply related as:

$$q/m_t = \left(\frac{A_t}{C + C_0} \right) \quad (2)$$

where, all of the physicochemical charging terms are combined into the A_t parameter. (For the present test toner/carrier pair, $A_t = -110 \mu C/g \cdot \text{wt}\%$ and $C_0 = 2 \text{ wt}\%$).

In general, for a charge-active external additive,

$$\phi_{toner} = \theta \cdot \mu_{ext. add.} + (1 - \theta) \cdot \mu_{base toner} \quad (3)$$

where θ is the fraction of the toner surface covered by additive, and $\mu_{ext. add.}$ and $\mu_{base toner}$ are characteristic charging terms for the additive and toner, respectively.⁹

For additive particles randomly distributed on a toner surface, θ (and thence q/m) will be linearly related to the wt % concentration of the additive in the toner/additive blend,⁹ hence the potential impact of the toner blending process on the triboelectric charging performance of an additive-based toner.

For any fixed toner size and composition, the mean q/d value will be directly relatable to the average q/m value, via:

$$q/m = q \cdot \left(\frac{6}{\rho \cdot \pi \cdot d^3} \right) = \left(\frac{q}{d} \right) \cdot \left(\frac{6}{\rho \cdot \pi \cdot d^2} \right) \quad (4)$$

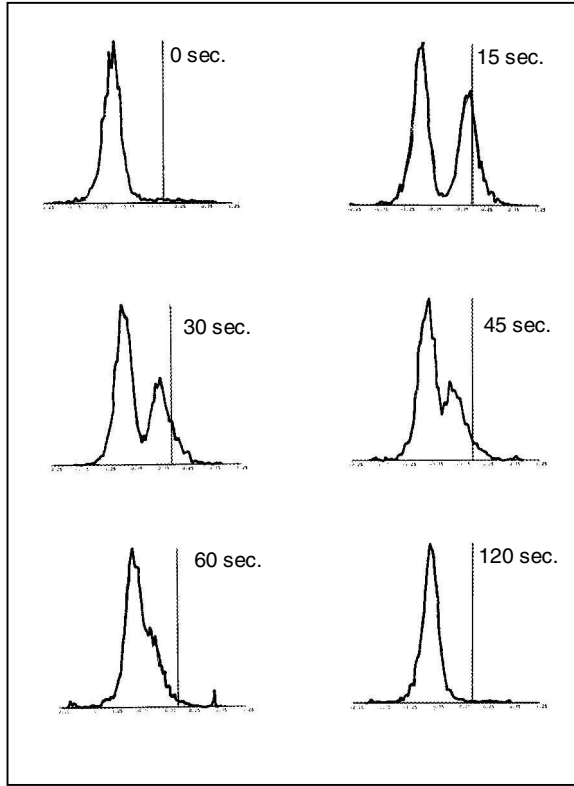


Figure 1. Charge-admix spectra for the addition of 1 wt% of uncharged production-scale fluid bed-2-step-blended toner (small peak) into a charged production-scale V-Cone-2-step blended toner at 3.5 wt% toner concentration (large peak), for the listed admix times from 0 to 120 seconds.

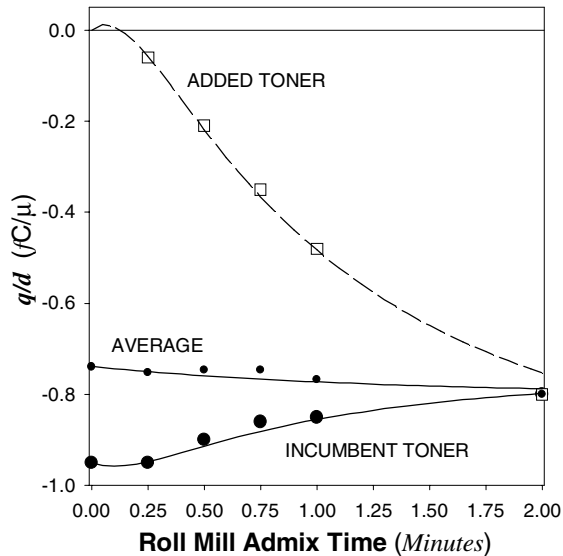


Figure 2. q/d vs. admix time for the added (square symbol) and incumbent (round symbol) populations from the charge spectra shown in Figure 1 for the production-scale fluid-bed-2-step blended toner. The small black points are the calculated weighted average q/d values for the entire toner population.

so that blender-induced changes in q/m should produce parallel changes in q/d . However, while q/m values are averages of total toner charge divided by total toner mass, q/d values (as obtained from charge spectral measurements) can be expressed in terms of average values or in terms of specific populations of toner particles in the total sample. For example, in charge-admix tests, where uncharged toner is added to charged toner in a charged developer, the charge spectrum may be resolvable into distinct contributions from the added and incumbent toner particles, especially (as in this present study) if the admixing process occurs slowly. Figure 1, illustrates this point, for the case of a production-scale toner (blended in a two-step masterbatch procedure in a horizontal fluid-bed mixer) admixed into a developer based on the production V-cone-blended control toner. For this test, the low-charged added toner particles slowly attain a common charge with the incumbent toner particles, and Figure 2, a plot of the individual q/d values, shows that the increase in the q/d value of the added toner particles is matched by a decline in the q/d of the incumbent toner particles. For reference, the calculated weighted average q/d values are also plotted in Figure 2 — as can be seen, these average values (and the corresponding average q/m values) are much less informative than those of the individual toner populations. (For a common standard deviation, the height of the individual incumbent and added toner peaks shown in Figure 1 should be in a ratio of 3.5 to 1. However, since low-charged toner is most readily removed from a developer during a charge spectrum measurement, a toner sample that is air-injected into the spectrograph may have an enriched added toner population, and the experimental data in Figure 1 shows this type of enhancement. However, such an enrichment will not affect the component peak positions, so that the q/d values in Figure 2 do represent the true state of the total toner population).

For the ideal case where added and incumbent toner particles are identical, then the admix process can be described in terms of a toner charge redistribution process in the presence of charged carrier particles,^{1,3,4} and the pre- and post-admix charges can thereby be directly equated. Similarly, from a triboelectric charging equation such as Eqn. 1, there should be a simple relationship between the pre- and post-admix q/m values (or equivalently the average q/d values) of a developer. For example, in the present admix tests 1 wt % of uncharged toner was admixed into a 3.5 wt % test developer, and from Eqn. 2 the eventual effect of this additional 1 wt% of toner can be predicted to be:

$$q/m_{3.5+1.0} = \left(\frac{(3.5 + 2)}{(3.5 + 1.0 + 2)} \right) \cdot q/m_{3.5} \quad (5)$$

where C_0 has been set as 2, i.e.

$$q/m_{3.5+1.0} = 0.846 \cdot q/m_{3.5} \quad (6)$$

or equivalently,

$$q/d_{\text{post-admix}} = 0.846 \cdot q/d_{\text{pre-admix}} \quad (7)$$

where Eqns. 5, 6 and 7 are applicable to the state of a developer after long-term admixing, and are simply expressions for the commonly-observed inverse relationship between q/m (or q/d) and the toner concentration, C .

For an admix process such as shown in Figures 1 and 2, the total average charge properties for the 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 true⁴:

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

where,

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

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

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

For a normal admix process, $q/d_{\text{inc},t}$ and $q/d_{\text{add},t}$ will reach a common value, with the q/d_{average} value rising (for the case of 1 wt% of toner added to 3.5 wt% toner) from $(3.5/5.5) \cdot q/d_{\text{inc},0}$ (i.e., the time-zero average of the uncharged and charged toners) to $0.846 \cdot q/d_{\text{inc},0}$ (i.e., the eventual common, equilibrated-charge condition), and the admix process can be categorized in terms of the rate of equilibration or the time required for complete equilibration. While external factors such as mixing efficiency will affect the admix rate, the properties of toner component materials may also be significant if they affect the rate and extent of the charge-equilibration process. In the extreme case where added and incumbent toner particles are not totally identical, then the toner admix process can be quite complex. For an added toner that is less triboelectrically active than the incumbent toner, the added toner particles may only charge to a post-admix level that is lower than that expected for normal charge equilibration with the incumbent toner.¹ Conversely, a highly-charging added toner may acquire a high post-admix charge level, and thereby drive the incumbent toner particles to a below-average charge level.^{1,3,4} In both of these atypical cases, the added and incumbent toner particles will equilibrate as two separate charge populations. 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 1wt % added into 3.5 wt % and $C_0 = 2$) as:

$$q/d_{\text{average},\infty} = \left(\frac{(3.5 + 2)}{(3.5 + 2 + 1.0)} \right) \cdot q/d_{\text{incumbent},0} \cdot \delta \quad (9)$$

where δ is a factor that accounts for the enhanced or degraded post-admix average q/d (or q/m).⁴

For cases where the added and incumbent toner particles are identical, $\delta=1$, and the admix will be normal (i.e., the two toner populations will collapse to a common q/d value). For cases where the incumbent toner is much less triboelectrically-active (e.g. is "aged" during the pre-admix mixing step), $\delta > 1$ and the admix will be atypical with the added toner equilibrating at a higher charge level than the incumbent toner — for $\delta < 1$, the reverse will be true.

From a detailed set of experimental admix charging data, the $q/d_{\text{inc},0}$, $q/d_{\text{add},\infty}$ and $q/d_{\text{av},\infty}$ values can be used to generate q/d vs. admixing times that fit the entire data set, where $q/d_{\text{add},t}$ is assumed to rise as a saturating exponential function from zero to $q/d_{\text{add},\infty}$ and $q/d_{\text{inc},t}$ is assumed to vary exponentially from $q/d_{\text{inc},0}$ to $q/d_{\text{av},\infty}$, with $q/d_{\text{inc},t}$ being deduced from the weighted $q/d_{\text{add},t}$ and $q/d_{\text{av},t}$ values according to Eqn. 7. Typical results from such an analysis scheme are shown in Figure 2 and in the similar style of data plots presented in the following Results section of this present report.

Experimental Results

Control Production V-Cone Toner

Figure 3 shows the charge spectra for an admix test of the control toner (masterbatch in a production V-cone / dilution blend in a production V-cone). Even for this toner, the spectra are visibly bimodal for the 30 and 45 second admix measurements, and this reflects the severity of the test protocol (1 wt % of added toner into 3.5 wt % of charged incumbent toner, with gentle roll-mill mixing being used to homogenize the sample). Figure 4 shows the q/d values of the added and incumbent toner populations, obtained from the spectra of Figure 3. (In general, the charge spectral peaks conform individually to a simple gaussian distribution, with a standard deviation of about $0.14 \text{ fC}/\mu$, so that component peaks effectively merge into a single peak if they are separated by $0.25 \text{ fC}/\mu$ or less).

The significant admix differences evident from Figures 2 and 4 include:

- The added production scale fluid-bed toner particles tend to charge weakly positive at short admixing times, even though the toner is designed to generate a negative triboelectric charge against the test carrier.
- The admix rate constant of the production scale fluid-bed toner is 2.5 times lower than that of the production scale V-cone toner.
- The q/d of the added production scale fluid-bed toner particles appears to extrapolate to a long-term value that is more negative than that of the production scale V-cone toner (i.e., the production scale fluid-bed toner is intrinsically more negative than the V-cone toner).

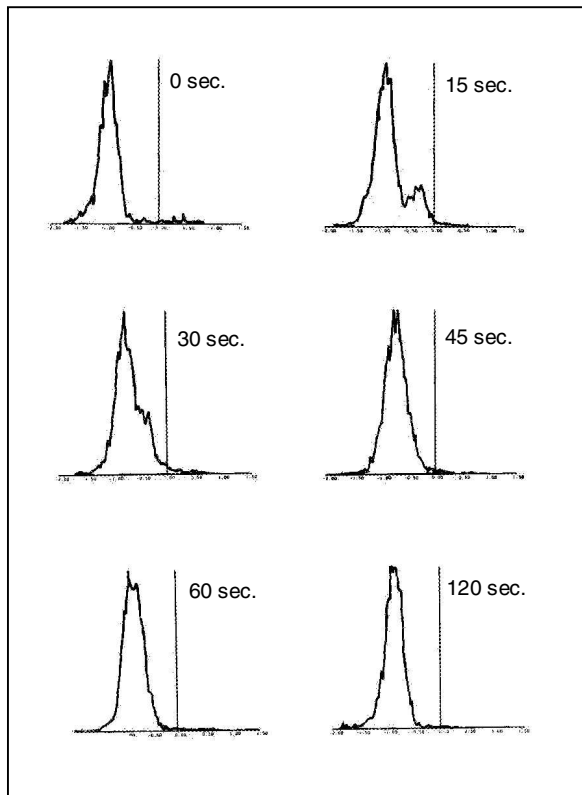


Figure 3. Charge-admix spectra for the addition of 1 wt% of uncharged production-scale V-Cone-2-step-blended toner (small peak) into a charged production-scale V-Cone-2-step blended toner at 3.5 wt% toner concentration (large peak) for the listed admix times from 0 to 120 seconds.

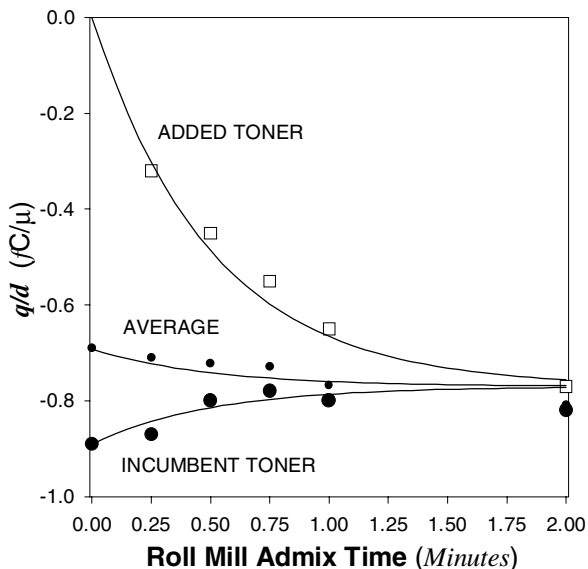


Figure 4. q/d vs. admix time for the added (square symbol) and incumbent toner (round symbol) populations from the charge spectra shown in Figure 3 for the production-scale V-Cone-2-step blended toner. The small black points are the calculated weighted average q/d values for the entire toner population.

The overall effect of the above differences between the two blended toners is that the production scale V-cone toner is effectively admixed in about half the time required for the production scale fluid-bed toner.

Single-Blend Step Fluid-Bed Toner

From the experimental data shown in Figure 5, it is clear that an unoptimized single-blend toner (90 seconds in a pilot-scale fluid-bed blender) can produce an extremely poor charge admix response. In Figure 5, the initial q/d values for the added toner are all strongly positive, indicating that the external additives are not homogeneously distributed on the toner particles. The long-term q/d value for the added toner is only $-0.6 fC/\mu$, well below the $-0.8 fC/\mu$ value expected for perfect admix. Overall, the experimental data indicate that the external additive on the single-blend toner is only partly effective at producing a negative-charging toner, for the blend conditions used in the single-blend test.

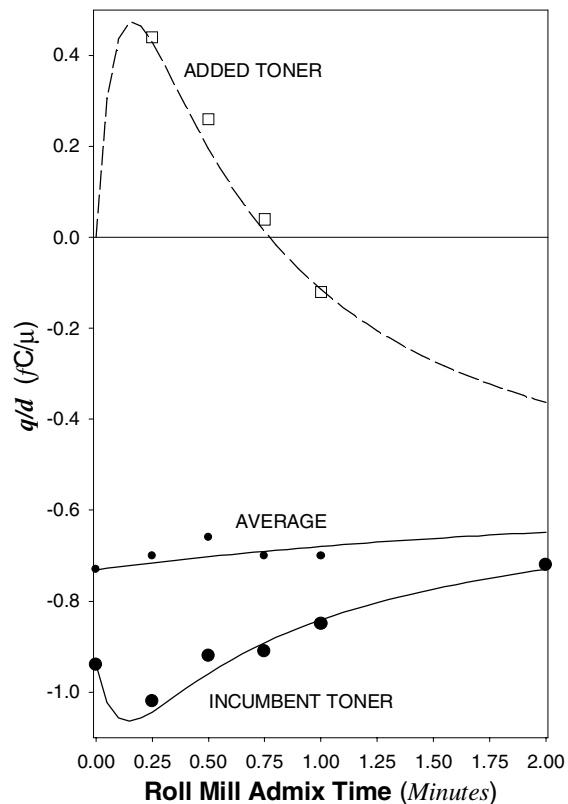


Figure 5. q/d vs. admix time for the added (square symbol) and incumbent toner (round symbol) populations from admix charge spectra taken on a pilot-scale single-step fluid-bed blended toner.

Reduced Blend Fluid Bed Toner

While a brief blending of toner and additive particles will produce a non-homogeneous toner, an extended blend time to ensure homogeneity may also create a sub-optimum toner, since over-blending may result in additive loss (burial) from the toner surface. Ideally, for process

latitude and stability, a range of blender settings that yield an in-specification product should separate the conditions for under- and over-blending. For toner blends created in a fluid bed mixer, a reduced blend time was found to be an effective means to match the performance given by a V-cone blender, and Figure 6 shows the admix charging data for a toner masterbatched in a fluid bed mixer, and diluted in a fluid bed mixer for one fifth the standard processing time.

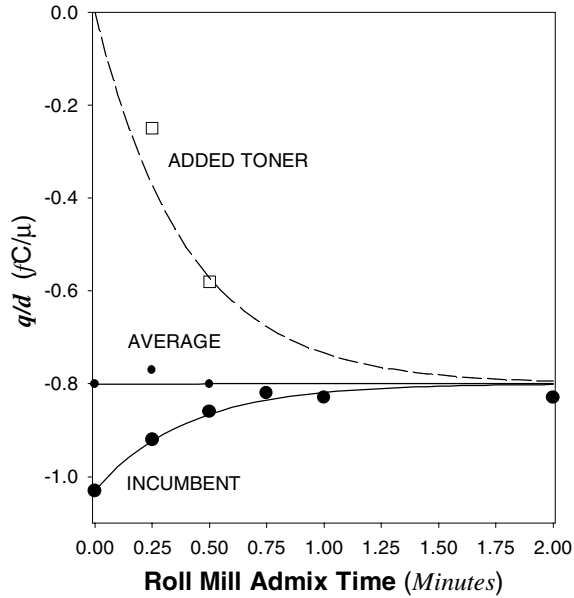


Figure 6. q/d vs. admix time for the added (square symbol) and incumbent toner (round symbol) populations for a 2-step fluid bed blended toner with a reduced dilution/blend processing time.

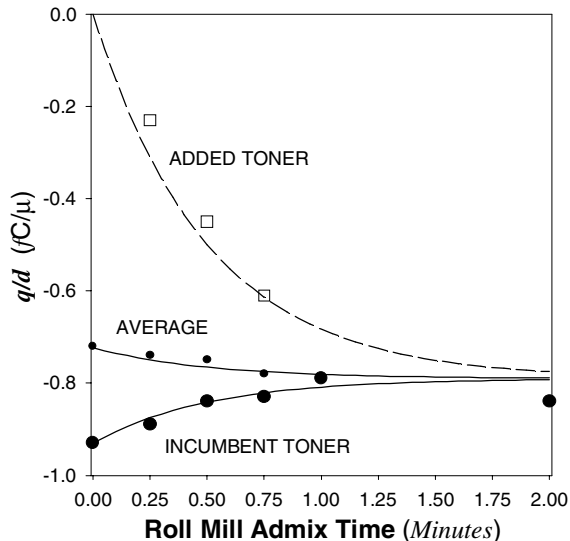


Figure 7. q/d vs. admix time for the added (square symbol) and incumbent toner (round symbol) populations for a 2-step fluid-bed blended toner. Before the admix test, the developer was tribo-charged by 30 minutes of mixing in a development housing, followed by 15 minutes of roll milling ($q/m = -21 \mu\text{C/g}$ at 3.5 wt%).

Pre-Mixing Effects On Charge Admix

For the present study, a standard 30 minutes of mixing in a development housing followed by 15 minutes of roll milling was used to ensure that the pre-admix developer sample was fully-charged (typical level: $-21 \mu\text{C/g}$ at 3.5 wt% of toner). Figure 7 shows a typical slow charge admix result for a pilot scale 2-step fluid-bed blended toner tested using the standard pre-admix charging times of 30 minutes + 15 minutes.

By contrast, when the pre-admix developer was only mixed for 15 minutes of roll milling, then the pre-admix charge was reduced to $-17 \mu\text{C/g}$ at 3.5 wt% toner concentration, and under such conditions the “poorly-admixing” pilot scale 2-step fluid-bed blended toner gave an ultra-rapid admix (see Figure 8) when added to the reduced-charge developer.

The large difference in admix behavior shown between Figures 7 and 8 for a single test toner illustrates the potential effect of test protocol on evaluation studies. With the 15 minute pre-admix roll mill procedure, very little distinction can be made between the admix performance of a range of test toners — in all cases the admix performance is excellent. This result also highlights the importance of matching bench test conditions to those present in actual xerographic machines, and coincidentally illustrates how toner performance may vary within a family of xerographic machines.

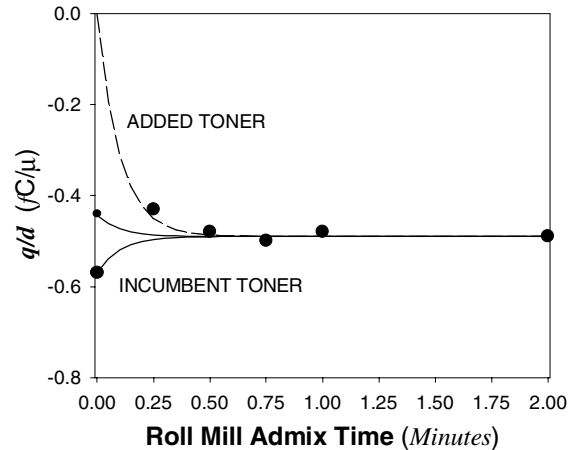


Figure 8. q/d vs. admix time for the added (square symbol) and incumbent toner (round symbol) populations for a 2-step fluid-bed blended toner. Before the admix test, the developer was tribo-charged by 15 minutes of roll milling ($q/m = -17 \mu\text{C/g}$ at 3.5 wt%).

Summary and Conclusions

Though toner components such as external additives can enhance many key properties of a xerographic toner, they can also be a significant source of variability in toner performance. Even for a fixed toner design, variability in manufacturing processes such as additive/toner blending may create a range of toner performance, and the present

experimental study demonstrates this effect for the case of charge-admix performance. Though the examples presented represent relatively major variations in blender operating conditions, the results confirm that consistent blender operation can be key to the production of a uniform toner product. For cases where external additives enhance the charge-admix performance of a xerographic toner, performance may even be subtly degraded during post-blending operations such as transport to and through toner packaging, storage, etc. For a toner having a limited xerographic latitude, these latter changes may be sufficient to degrade the performance of production-scale toners below the level identified during initial laboratory-scale testing (where test toners are typically processed in small-scale blenders, and are immediately evaluated in bench-scale devices). Ideally, a toner design should produce a wide latitude for performance, so that minor variabilities in production processes will not be significant; however, the recent digital imaging improvements that have enabled pictorial-quality xerographic imaging, have also greatly increased the specified performance requirements for toners, while at the same time the digital-driven trend towards compact, high-productivity development housings has increased the stresses that toners must withstand during use — all in all, the creation of a stable blended toner remains as a difficult, multi-dimensional task for toner designers and blend process technologists. Finally, for xerographic research scientists, a deeper understanding of the controlling factors for charge-admix performance (level, modes, rate of charging, etc.) would be a useful extension to the present-day theoretical and experimental studies that are largely focused on relatively simple macroscopic triboelectric charging processes.

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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. From 1998 until the end of 2000 he served an expatriate assignment at Fuji Xerox, Takematsu, Japan, as the Senior Manager, Resident for the Xerox Supplies Development, Manufacturing and Supply Chain Operations organization. He retired from Xerox in 2002, and currently provides a consulting service on a variety of subjects, ranging from xerographic materials to cross-cultural interactions with Japan His research and modeling studies at Xerox were 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, and in 2002 he received, jointly with John Bickmore, IS&T's Chester Carlson Award.