Toner Aging: Causes and Effects

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Abstract

In this review, a simple conceptual model for xerographic developer charging is used as a framework to illustrate key aspects of toner aging. Topics covered include: the effect of toner additives (external/internal) on charge level and charge admix; the effect of toner physical properties such as concentration and size on performance; the impact on toner aging of external factors such as toner throughput rate, relative humidity and process control strategies.

Introduction

The long-term aging of a xerographic developer is normally associated with a gradual usage-induced degradation of the charging performance of carrier beads. By contrast, aging effects associated with toner particles may occur at any time in the life of a developer, with seemingly stable operation being followed by a sudden catastrophic and irreversible failure mode. Modern, high-performance toners are typically based on a complex set of ingredients, with major charging and flow properties being controlled by relatively low levels of key components such as external additives and internal charge control additives. As a result, usage-induced changes in the effective level of such additives can create a significant toner aging effects, and attendant significant changes in image development performance.

Additionally, xerographic development itself can create variable changes in toner size, and thereby affect toner properties such as charging and adhesion. Problems associated with toner aging effects can be particularly evident in digital printing applications, where a variable coverage level of printed output can create a range of toner aging. This effect reflects the variations in the time that toner particles spend in an active development housing, since the mechanical abuse of toner particles can affect key toner properties such as charge level, charge admix and flow/cohesion.

External factors such as ambient relative humidity can also create sudden and potentially catastrophic changes in toner properties. Such cases can be an extreme challenge for stable process control —— non-linear responses to step-function changes in toner properties may in fact lead to a process control-induced runaway failure condition.

Framework Model

As detailed in previous reports [1,2], the toner charge-to-mass ratio ("tribo", ***q/m***) of a two-component xerographic developer can be simply related to key physical and chemical properties via:

$$\boldsymbol{q/m} = A' / (C + C_o) \,.\, (\phi_{toner} - \phi_{carrier}) \qquad (1)$$

where A' contains all of the physical charging factors (size, density, charge tunneling distance, etc.), C is the toner concentration (C_o is an offset term, that is a function of toner and carrier size/density), and ($\phi_{toner} - \phi_{carrier}$) represents the toner/carrier charging tendencies. The magnitude of ***q/m*** is a function of all of the terms in Eq. 1, but the polarity of ***q/m*** is set only by the difference term ($\phi_{toner} - \phi_{carrier}$).

Conceptually, the ϕ_{toner} and $\phi_{carrier}$ factors can be expressed as area-weighted sums of the various toner and carrier surface species:

$$\phi = \mathbf{P}_i.\mu_i + \mathbf{P}_j.\mu_j + \mathbf{P}_k.\mu_k + \ldots\ldots \qquad (2)$$

where the fractional areas, $\mathbf{P}_i$, $\mathbf{P}_j$, $\mathbf{P}_k$ sum to unity, and μ_i, μ_j, μ_k are charging factors for the various surface types.

From an aging viewpoint, "wear-induced" processes will affect the **P** terms, while external factors such as ambient humidity will affect the μ terms.

For any particular xerographic developer, Eq. 1 can be rearranged to give a general ***q/m*** aging metric A_t defined, at any aging time t, as:

$$\begin{aligned} A_t &= A' \cdot (\phi_{toner} - \phi_{carrier}) \\ &= (\boldsymbol{q/m}_t) \cdot (C_t + C_o) \qquad (3) \end{aligned}$$

However, though the A_t parameter can be directly calculated from the observed ***q/m*** and C values (plus an assumed fixed value for C_o), it cannot directly distinguish between carrier and toner aging processes since it implicitly includes the difference term ($\phi_{toner} - \phi_{carrier}$).

Examples of Triboelectric Charging and Toner Aging Behavior

Carrier Aging: Surface Composition

While the subject of the present report is toner aging, it will be instructive to consider carrier aging as a preliminary benchmark phenomenon.

Eq. 1 indicates that the ϕ_{toner} and $\phi_{carrier}$ terms have equivalent effects on the level and polarity of toner ***q/m***. For example, a toner will have a negative polarity if $\phi_{carrier} > \phi_{toner}$, and this condition can be readily achieved either via an increase in $\phi_{carrier}$ (e.g., a PMMA coating) or via a decrease in ϕ_{toner} (e.g., SiO_2 as a toner surface additive).

For ***q/m*** control via $\phi_{carrier}$, mixed carrier coatings [3] (e.g., PMMA + Kynar) or even simple physical mixtures of carrier types can be used. As shown in Fig. 1, the latter strategy can produce a sharp charge distribution (as expressed in terms of ***q/d***, the toner charge-to-size ratio) over a range of ***q/m*** values. Indeed, the fact that a carrier mixture can produce a functional average ***q/m*** value enables a zero rate of ***q/m*** aging to be achieved via the so-called trickle technology [4], where aged carrier beads are continually replaced by fresh beads, added as a toner-rich "replenisher".

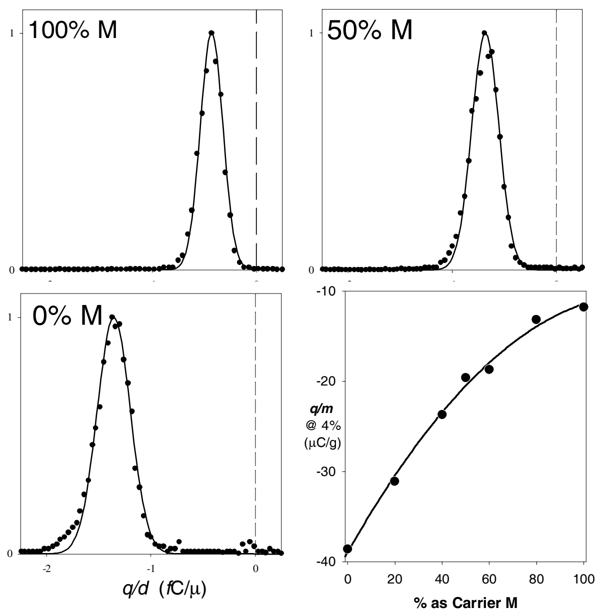

***Figure 1**. **q/d** spectra for a test toner with a high-charging (H) carrier, a medium-charging (M) carrier, and a 50:50 carrier mixture. The q/m data show a smooth increase from –38 μC/g to –12 μC/g.*

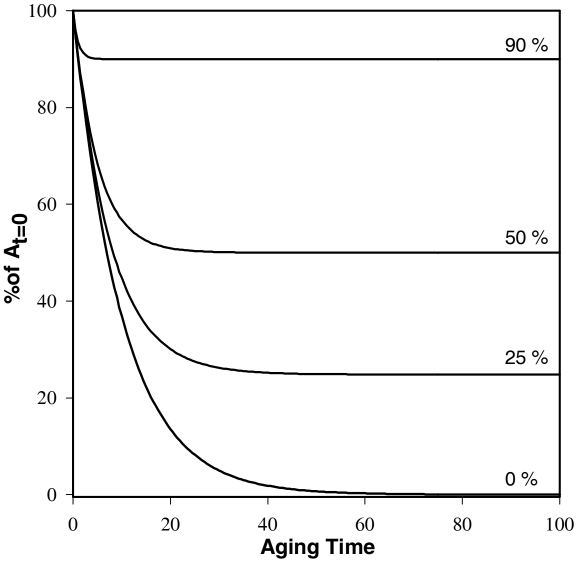

***Figure 2.** Triboelectric carrier aging for a range of replenisher ratios (e.g., the 90% line is for a 10% toner : 90% carrier mixture).*

With this strategy, the ***q/m*** aging will follow

$$A_t = A_0 - [A_0\cdot(1-exp\{-(k+r)\cdot t\})/(1+r/k)] \qquad (4)$$

where A_0 is the time-zero value, *k* is the carrier aging rate constant, and *r* is the carrier dispense rate constant (carrier dispense rate/total carrier mass in the sump). Fig. 2 shows A_t stabilization for various trickle rates.

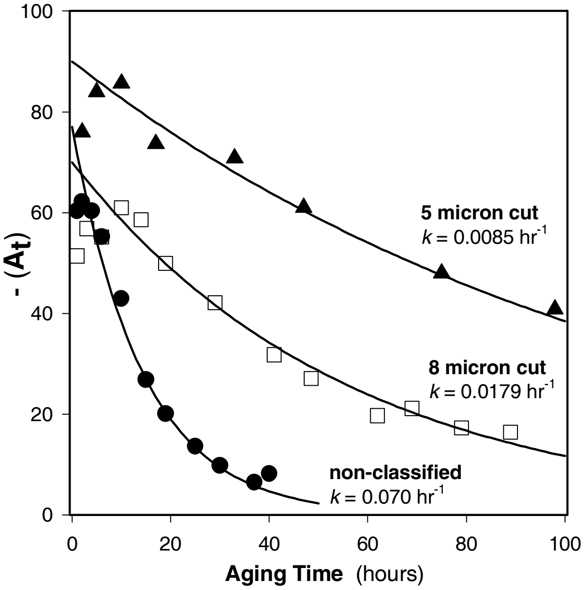

***Figure 3.** Triboelectric carrier aging for 3 levels of toner classification.*

In a non-trickle case, carrier aging is frequently most severe during conditions of normal toner throughput, where a constant toner flux provides a supply of "contaminants" to the carrier beads (for zero toner throughput — e.g., as in a bench-scale jar-mill study — the rate of carrier aging will fall to zero once the initial supply of "contaminants" is consumed). If the "contaminants" are merely fine toner particles (i.e., the toner particles that are most likely to become physically "welded" or "impacted" to a carrier's surface) then ***q/m*** as a function of aging time, t, will be:

$$\boldsymbol{q/m} = A' / (C + C_o) \cdot (\mu_{toner} - \mu_{carrier}) \cdot exp\{-k \cdot t\}$$

i.e.

$$A_t = A_{t=0} \cdot exp\{-k \cdot t\} \qquad (5)$$

where the ***q/m*** aging rate constant, *k*, is directly related to factors such as the mechanical mixing forces, the surface area of the carrier beads, and the level of toner "fines". Fig. 3 shows a typical A_t aging response for three levels of toner classification, driven by a carrier "surface impaction" aging process [5]. As shown, removal of toner fines can produce an eight times reduction in *k*, and hence a major increase in developer life.

Toner Aging: External Additives

(i) Charge Aging

Nano-sized particulates are added to the surface of toner particles to minimize particle-particle sintering, to promote powder flow, and to adjust toner charging properties (level and rate). The effect of such particulates on ***q/m*** can be simply assessed using Eq. 1 and 2:

$$\phi_{toner} = \mathbf{P}_{base} \cdot \mu_{base} + \mathbf{P}_{additive} \cdot \mu_{additive}$$

$$= \mathbf{P}_{add.} \cdot (\mu_{additive} - \mu_{base}) + \mu_{base} \qquad (6)$$

i.e., the effect on ϕ_{toner} (and thence on ***q/m***) will be directly related to the additive surface concentration, $\mathbf{P}_{add}$, and to the difference term ($\mu_{additive} - \mu_{base}$).

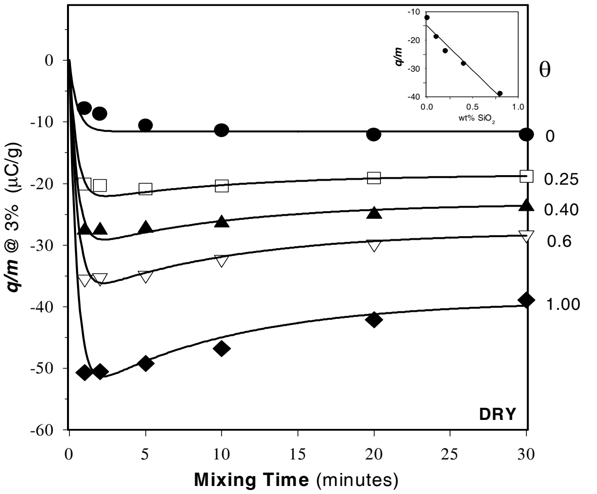

***Figure 4. q/m** of a negative polarity toner for various surface coverages, θ, of an 8nm SiO₂ external additive, at 60°F / 20% RH . The inset figure shows **q/m** vs. wt% SiO₂ (30 min. mixing data).*

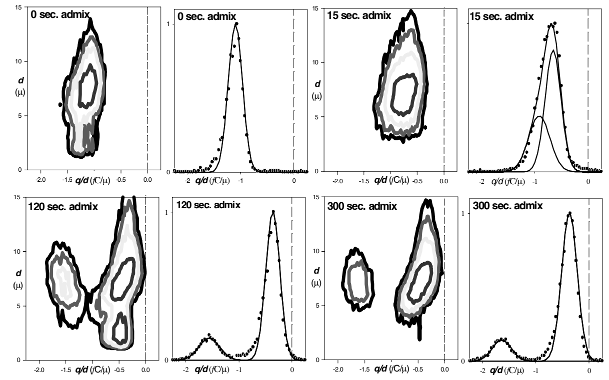

***Figure 5. q/d:d** contour plots and **q/d** spectra for pre-admix, 15 sec., 120 sec., and 300 sec. admix, for an "aged toner" developer.*

For example, in nominal ambient humidity, fumed SiO$_2$ enhances the negative charging level of a toner ($\mu_{SiO2} < \mu_{base}$), and Fig. 4 shows that the effect is directly proportional to the additive wt. % concentration (as expected for a surface area effect).

If external additives transfer to the surface of carrier beads, then Eq. 6 can be recast to indicate the effect on $\phi_{carrier}$, with the overall result being a reduction in ***q/m***. Carrier/external additive effects will be most evident in the extreme case where ***q/m*** is driven below the base toner level.

From a toner viewpoint, Fig. 4 shows that the external additive charging enhancement effect is not stable — with extended carrier/toner mixing, the external additive particles become buried in the sub-layer of the toner particles, and the toner ***q/m*** values decline towards the "additive-free" value. (The data in Fig. 4 were taken at a single fixed toner concentration — in general, the extent of additive burial will be a function of toner concentration, being most severe at low values).

Typically, the $\mathbf{P}_{add}$ term in Eq. 6 declines with mixing time to a limiting $\mathbf{P}_{add,\infty}$ value:

$$\mathbf{P}_{add,t} = (\mathbf{P}_{add,o} - \mathbf{P}_{add.\infty}) \cdot (exp\{-\beta.t\}) + \mathbf{P}_{add,\infty} \qquad (7)$$

and, as a result, the charging level of the "aged" toner particles is lower than that of the initial external additive-based toner particles.

Stress conditions for the additive burial process include low toner concentrations and low toner throughput in a xerographic development housing, with the highest burial rate occurring during initial mixing. At a low, constant toner throughput rate, the net effect of additive burial will be a steady decline in toner ***q/m*** and ***q/d*** towards some reduced steady-state condition. If, however, the toner throughput rate is abruptly increased (e.g., as triggered by a transition from text to pictorial imaging), then a flux of fresh, uncharged toner particles will be dispensed into the aged toner particles of the working developer. In such a case, the fresh toner particles may acquire charge from the aged toner particles via a rapid charge-sharing process [6-9]. (This toner charge-sharing process can be directly demonstrated via mixing experiments on unaged, but dissimilar toner particles — e.g., colored toner vs. black toner [7], or positive toner vs. negative toner [10]).

For toner-toner charge-sharing between aged and fresh toner particles, the post-admix average ***q/m*** value will be close to the value expected for normal charge admix (where the aged and fresh toner particles charge to a common intermediate level), and the admix process will appear to be normal in terms of ***q/m*** (e.g., for a mixture of negative and positive toners, the average ***q/m*** will be a simple linear function of the toner ratios [10]). Additionally, for short admix times, even the charge spectra will indicate a normal (albeit an ultra-rapid) charge admix process, with both toner populations having a common charge level (as indicated by a sharp, single peak in the ***q/d*** spectrum).

However, with continued admixing, the fresh toner particles will continue to acquire charge from the aged toner particles, and in extreme cases the latter particles can be driven to zero charge or even a wrong-sign condition. The ***q/d*** charge spectrum shown in Fig. 5 illustrates this atypical ***q/d*** response for the case of a fresh toner added to a developer having aged toner — after continued admixing, the added toner peak is centered at a high ***q/d*** value, while the incumbent toner particles have been driven to a low ***q/d*** level. Xerographically, the post-admix developer will give an increased level of non-image "background" development (from the low-charged toners) combined with a reduced level of image development (from the high-charged toners) — a failure condition driven by toner "aging".

Since the above processes are governed by differences between the incumbent and the added toner particles, several counter-strategies can be considered:

A reduction in the in-machine mechanical forces (e.g., "gentle" trim zones, development zones, mixing zones) would be beneficial, since it would enable a wide range of toner designs. This approach can be directly demonstrated via bench-tests based on "gentle" (e.g., a roll mill) vs. "severe" (e.g., a paint-shaker) mixers — indeed, many "fragile" toners actually show normal admix behavior when mixed on a roll mill [8].

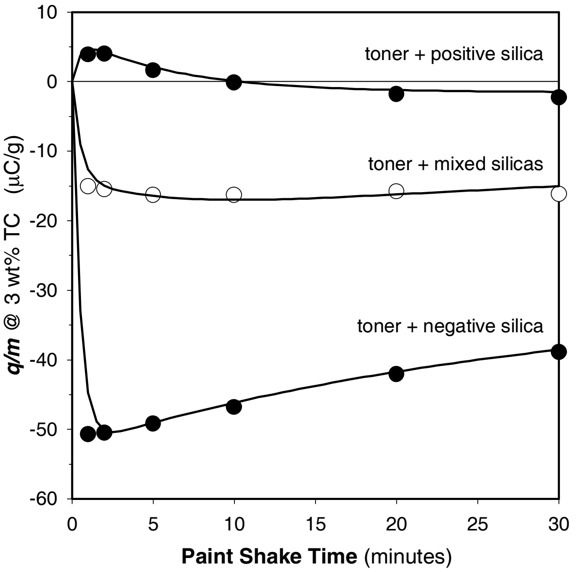

***Figure 6.** q/m stability created via a mixture of 0.6 wt% positive and 0.4 wt% negative SiO_2 external additives.*

Mechanistically, from a toner viewpoint, the key factor in atypical admix for toners based on external additives is the mismatch between the added and incumbent toners (i.e., between ϕ_{added} and $\phi_{incumbent}$), driven by the burial of charge-enhancing external additives. As shown by Eq. 4, the charge mismatch will be reduced if the ($\mu_{additive}$ - μ_{base}) difference term is minimized. For a negative polarity toner design, a CCA can be added to the toner to reduce the value of μ_{base}. Alternately, the value of $\mu_{additive}$ can be increased either by a change to a less negative additive (e.g. from SiO_2 to TiO_2), or by a change in the surface chemistry of the additive particles (e.g., from a conventional hydrophobic coating such as hexamethyldisilazane to a nitrogen-containing coating such as aminopropyltriethoxysilane).

At a higher level of complexity, multiple external additives can be combined to produce an effective overall value for $\mu_{additive}$. Fig. 6 illustrates this concept for a ***q/m***-stable negative polarity toner where burial of an 8 nm negative surface additive is balanced by burial of a 12 nm positive surface additive. In the example shown, the ***q/m*** of –10 μC/g at 3wt% toner concentration for the base toner was increased to –50 μC/g at a monolayer coverage of the 8 nm silica surface additive, and was decreased to + 5 μC/g when the negative silica was replaced by the positive silica at a surface coverage of about half a monolayer. A relatively stable ***q/m*** of –15 μC/g was produced from dual surface additives at 0.6 wt% of the positive additive and 0.4 wt% of the negative additive.

Practical toner designs are often based on multiple external additives that vary in particle size, composition (e.g., SiO_2, TiO_2, Al_2O_3, etc.) and surface chemistry, but the simple example shown in Fig. 6 illustrates the general concept for ***q/m*** stability via competing additive contributions. It should be noted, however, that in all cases of external-additive-driven toner aging, the degree of stabilization via multiple additives may be affected by the operational toner concentration, thereby limiting the latitude of stable designs.

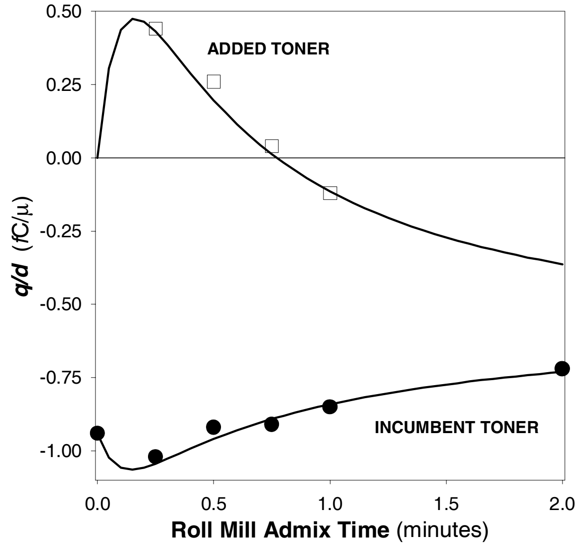

***Figure 7.** Slow admix for toners that differ only in their blend state.*

An additional potential problem with stabilization schemes based on CCA's or positive/negative additives is that toner aging may actually increase ***q/m*** over that of the unaged toner (e.g., if there is preferential loss of a positive additive from a negative toner) — in such a case, the charge admix process will be slow, with the added toner stabilizing at a reduced ***q/d*** level.

(Parenthetically, a similar mode of admix can be produced from unaged toners that are identical in composition but which differ in their additive blend state — Fig. 7 shows slow admix for toners that differ only in blend procedure [11]).

To increase the negative ***q/m*** level of an additive-stabilized toner, Eq. 1 indicates that an increase in $\phi_{carrier}$ (e.g., via a nitrogen-containing carrier coating) will change the ***q/m*** level without altering the stability achieved via mixed external additives. However, if such an enhanced carrier coating is not abrasion-resistant, then toner contamination by coating fragments will produce a long-term decrease in the incumbent toner ***q/m***, and will thereby lead to charge admix problems created by $\phi_{incumbent\ toner} > \phi_{added\ toner}$.

(ii) Cohesion Aging

Since external particulate additives promote the free-flowing character of toner particles, an age-induced decrease in the effective level of toner external additives will increase the overall cohesivity of the toner particles. This will be a particularly relevant problem for melt-mixed wax-containing toners since such toners are highly cohesive in their base, additive-free condition. From a xerographic viewpoint, toner flow aging will especially affect "carrier-less" marking technologies such as single-component and powder cloud development, leading to problems such as reduced image development, differential image density banding, and ghost images.

In particular, a stress condition for toner cohesion aging will be an extended print run of text images followed abruptly by continuous printing of high-coverage pictorial images [12,13]. During extended text printing at a low toner throughput rate, toner aging via additive burial will tend to increase developability via a reduction in ***q/m***, and decrease developability via an increase in toner cohesion — overall, the net effect will allow a set image output density to be maintained under process control (e.g., via adjustments to the electrostatic development potential); however, a transition to pictorial imaging will increase the toner throughput rate, and a combination of toner-toner admix problems (as discussed earlier) and increased toner cohesion will limit overall developability. Unlike a starvation condition, this type of reduced developability will occur despite an adequate supply of toner on the development roll or in a development magnetic brush.

For fresh toners, a high surface concentration of a small (e.g., 8 nm) fumed silica additive produces the lowest level of cohesion, but this enhancement is rapidly lost as the toner is mechanically aged (Fig. 8). Large fumed silica additive particles (e.g., 40 nm) provide a slower rate of toner cohesion aging than small additives (e.g. 8 nm), but a greatly increased wt% concentration is necessary to produce an equivalent toner surface coverage for large additives. Other additives such as 40 nm surface-treated TiO_2 have been shown to improve cohesion stability [14]. Ultra-large silica additives (e.g., 100-150 nm sol-gel silicas) also give a reduced rate of additive burial toner aging, but mainly provide a beneficial effect for xerographic transfer and photoreceptor cleaning [15].

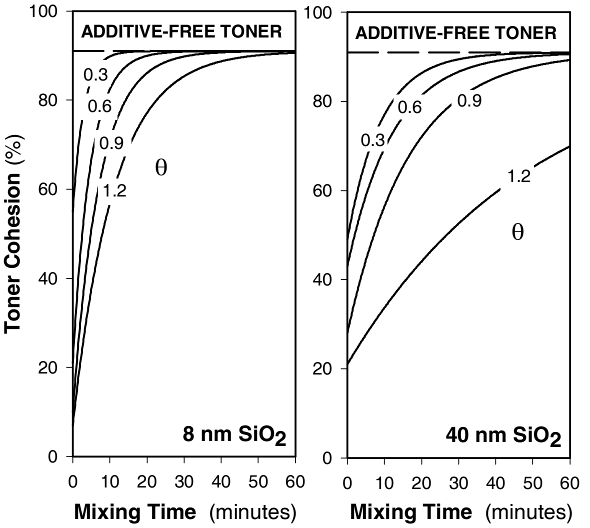

Figure 8. *The effect of external additive size and surface concentration on toner cohesion aging (left plot: 8 nm SiO_2 ; right plot: 40 nm SiO_2).*

Finally, for jetted toners, mechanical stress relaxation of the base toner resin matrix may continue post-production, and thereby create a degree of surface additive aging via toner-toner sintering. This "storage" aging [16] may be significant if the toner design has limited latitude, especially for donor roll-based xerography.

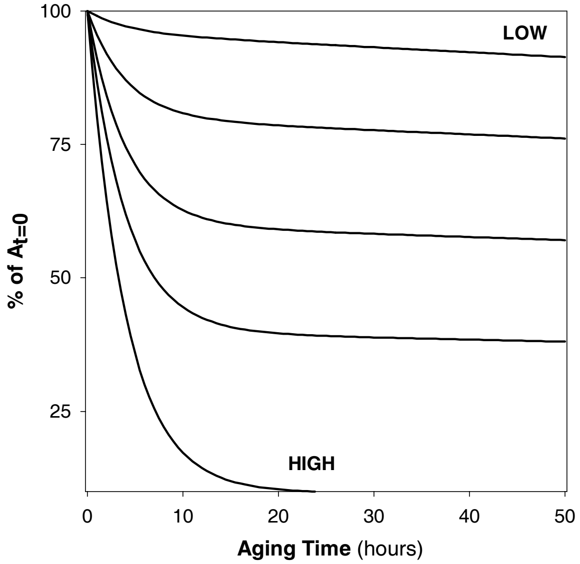

Figure 9. *CCA-induced A_t aging. The LOW response is typical of aging at low toner concentrations or high CCA levels; the HIGH response is typical of aging at high toner concentrations or low CCA levels.*

Toner Aging: Internal CCA's

(i) Charge Aging

The polarity and magnitude of toner charge can be conveniently adjusted via the addition of a charge control agent, CCA, (typically a molecule having a large electron-accepting or donating ion coupled with a small counter-ion) as an internal toner additive. While CCA's are typically added at about a 1 wt% level during the toner melt-mixing process step, CCA's govern toner charge as a surface effect [17-21] — as a result, the process of bulk addition of CCA to achieve an effective surface CCA level can lead to variable results as a function of base resin type, melt-mix conditions, and bulk CCA level. (Equivalent effects may be achieved via the direct surface addition of extremely low levels of CCA's, but this is not generally practical from a toner manufacturing viewpoint).

From an aging viewpoint, CCA effects can involve both toner and carrier surfaces. This can be directly demonstrated via the deliberate surface addition of low levels of CCA's to toners and carriers [18-21] — in particular, the charge polarity of a CCA-free toner can be rapidly transformed to that of a CCA-based toner, simply by mixing with a CCA-surface-treated carrier surface.

In general, the controlling mechanism for CCA-aided triboelectric charging involves a dynamic interchange of CCA between toner and carrier surfaces. As a consequence, CCA-based toners can sometimes produce an extremely high rate of ***q/m*** aging via a surface "CCA-poisoning" of the carrier beads — this effect is typically seen with high levels of toner CCA or under conditions of toner/carrier mechanical stress (e.g. at low toner concentrations, or in high shear development housings).

By contrast, under specific post-initial transient conditions, CCA-driven toner/carrier surface interactions may evolve to a equilibrium state that yields a stable ***q/m*** value and a zero rate of triboelectric aging, even for carrier beads having a high surface level of impacted toner [22,23]. In general, for CCA-based toners, the initial rate of ***q/m*** aging and the equilibrium ***q/m*** value will depend on factors such as the operational toner concentration and the toner CCA level, so that a single toner/carrier design may exhibit a range of aging responses (e.g., as shown schematically in Fig. 9).

In practical applications, various "pre-treatment" schemes based on CCA-rich/small-sized toners have been developed to adjust a CCA-based developer to a desired equilibrium state, in order to eliminate initial transient in-machine aging [24,25]. For black-only digital printing, such stabilization schemes can be quite effective; for full-color printing, however, a variable toner throughput rate may affect the degree of CCA-driven ***q/m*** aging. For example, a CCA-based developer that is ***q/m***-stable under conditions of high toner throughput (a CCA-effect on carrier charging) may be quite unstable at low toner throughput (a CCA-effect on toner charging). Alternately, for a CCA-based toner design where the CCA is quite labile, toner throughput may create a high ***q/m*** aging rate for a developer that is quite stable under zero-throughput conditions.

In certain cases, toner-production conditions may also produce unwanted side-effect chemical reactions in CCA-containing toners, thus producing a degree of post-processing toner aging. In addition to changes in CCA composition, this type of aging may involve CCA/binder resin effects — for example, certain CCA's can act as cross-linking agents for polyester resins [26].

Toner Aging: External Film-Forming Additives

(i) Charge Aging

Film-forming additives are added to toners to provide lubrication for photoreceptor blade-cleaning, to enhance developer conductivity via an increased carrier packing density [27,28], and to reduce the rate of toner impaction-driven ***q/m*** aging. Since film-forming additives affect both toner and carrier surfaces, the effect of such additives on ***q/m*** can be a complex and variable function of additive type and level — as with CCA's, surface equilibration may produce an overall stable result for a specific operational condition.

(ii) Toner/Developer Flow Aging

Film-forming toner external additives are often coupled with particulate toner external additives, to promote toner flow, to limit film build-up on photoreceptors, and to adjust toner ***q/m***. As a result, "external additive burial" toner aging will adversely affect the cohesive performance of such dual additive-type toners, leading to variable toner performance as a function of print mode, operational toner concentration, etc.

For developers based on toner with film-forming additives, an increase in packed density can produce an uneven developer flow and resultant variable image development [29]. Effectively, in such a case, the developer transitions from a free-flowing state to a tightly packed, highly-cohesive state. Stress conditions for such a failure mode include a high level of film-forming additive, a decreased level of particulate additives (e.g., via "burial"), and a high toner concentration. Interestingly, certain surface-active CCA's can also create developer flow aging, if the CCA transfer from the toner to the carrier beads is extensive enough to increase the developer packed density [30]. Toners based on internal or external waxes may also show this type of failure under stress conditions. In all cases, stable xerographic operation under automatic image density control will transition abruptly to a toner concentration runaway condition once developer flow becomes erratic, since the target patch developed by a "clumped" development brush will have a reduced average density. Diagnostically, this failure mode can be reversed via the addition of free particulate additives to the cohesive developer mass, but this is not a practical option. For certain toner designs, a reduction in the level of the film-forming additive is an effective countermeasure for developer cohesion problems [29].

Toner Aging: Ambient Relative Humidity

(i) Charge aging

The toner and carrier processes outlined thus far have all involved changes in the surface concentrations of key toner and carrier charging materials (i.e., the $\mathbf{P}_i$, $\mathbf{P}_j$ … terms in Eq. 2), and generally involve long-term irreversible effects (the exception being reversible CCA-driven effects). By contrast, ambient humidity affects ***q/m*** aging via reversible changes in the toner and carrier intrinsic chemical charging properties (i.e., the μ_i, μ_j …. terms in Eq. 2). Many external particulate toner additives are given a hydrophobic surface treatment, to ensure free-flowing powder performance over a range of humidities, but such treatments do not necessarily impart ***q/m*** humidity-stability to additive-based toners. The basic problem is that many toner and carrier component chemicals are affected by humidity, so that the humidity sensitivity of a total xerographic developer will governed by the combined effect of changes to all μ terms [31]. Since toner ***q/m*** after extended mixing can be expressed as:

$$\boldsymbol{q/m} = (A'/(C + C_o)) \cdot (\theta \cdot (\mu_{additive} - \mu_{toner}) + \mu_{toner} - \mu_{carrier}) \quad (8)$$

where θ is the toner additive surface coverage, one condition for humidity-insensitivity will be:

$$\theta \cdot \Delta\,(\mu_{additive} - \mu_{toner}) = -\,\Delta \cdot (\,\mu_{toner} - \mu_{carrier}) \quad (9)$$

where Δ is the change in the μ difference terms produced by a change in ambient humidity.

For multiple external additives, this stability scheme will be effective if the additives respond to humidity in an opposing fashion. However, as can be seen from Eq. 9, humidity stability will achieved only at a specific coverage of the external additives — toner-aging-induced changes in θ will alter the degree of humidity sensitivity.

Fig. 4 and 10 show an instructive example of humidity sensitivity created via the addition of a hydrophobic toner surface additive at various θ levels to an otherwise humidity-stable developer. At the low humidity condition shown in Fig. 4, the $(\mu_{additive} - \mu_{toner})$ term is large, as evident from the strong ***q/m*** response to additive level, whereas the limited ***q/m***:θ response at the high humidity condition, Fig. 10, indicates a reduced value for

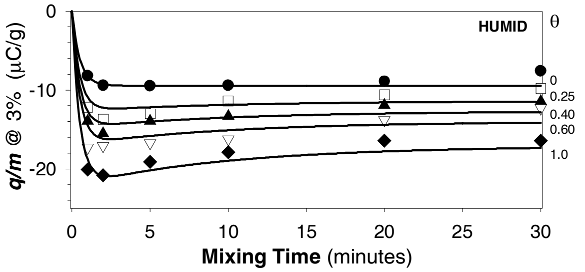

Figure 10. ***q/m*** *of a negative polarity toner for various surface coverages, θ, of an 8nm SiO_2 external additive, at 80°F / 80% RH. (Same test developer as in Fig. 4).*

the ($\mu_{additive} - \mu_{toner}$) term. The net humidity response created by the hydrophobic external additive is an increased **q/m** sensitivity to humidity (as judged by the **q/m_{dry}** : **qm_{humid}** ratio) as θ increases, with the additive-free toner being least sensitive to humidity.

From a xerographic performance viewpoint, **q/m** humidity sensitivity can produce wide and abrupt changes in developability, and for high-performance production printing the entire xerographic module must be maintained at a constant ambient condition to ensure satisfactory imaging stability. For typical office xerographic printing applications, a reasonable level of image stability can be achieved via process controls (see later).

Toner Aging: Size Effects

(i) Charge Aging

While the size distribution of xerographic toners are typically narrow (created either via a post-grind classification or directly for "chemical" toners), the selective xerographic development of "large" toner particles [32] can reduce the effective size of toner in a working developer by as much as 2μ. This physical form of toner "aging" can affect the overall development process, and can be especially significant during major transitions in toner throughput — during low area coverage imaging, small, higher charged toners will accumulate in a development brush or on a development roll, while for high area coverage imaging the size of the "working" toner will approach that of the dispensed toner. For xerographic processes based on uniformly-toned donor rolls, toner size variations can also occur from point-to-point across the roll — for example, small toner particles can accumulate at non-image roll locations, leading to defects such as "ghost" images following a transition from non-image to mid-range solid image development. For conventional two component developers, charge aging as a result of area coverage variations has been shown to be particularly severe for spherical toner particles, with shape modification (from round to "potato-shaped") being effective at reducing the effect [33].

From a charge admixing viewpoint, toner size is a significant factor [34,35]. For equivalent values of **q/m**, a small toner will have a lower **q/d** value than a large toner. For mixtures of large and small toners that have been separately charged, large toners rapidly lose charge and small toners gain charge [35]. When new, uncharged toner is added to a developer that contains charged aged toner at a low **q/d** level, the resultant **q/d** vs. **d** contour plot can be quite asymmetrical, with **q/d** in the aged toner region having a common value over a range of toner diameters (i.e. $q \propto d$) and with the added toner region initially showing enhanced **q/d** values for large diameter "new" toners. After extended admixing, the new and aged toner particles coexist as separate $q \propto d$ populations (see Fig. 5, for example).

Process Control for Aging Toners

(i) Process Control-Induced Toner Aging

Since xerographic developers, toners and even photoreceptors are not totally stable, key controlling factors for development must be adjusted under process control in order to maintain a specified image metric, starting from some initial start-up condition with new marking materials [36]. However, if the initial set-up procedure creates a significant degree of toner aging, then the process control strategy may fail to converge to a stable imaging condition. For example, for robust developer designs, an initial period of developer mixing at zero toner throughput will serve to create a well-charged developer, but for external additive-based developers this strategy may actually degrade developer imaging performance via toner aging.

For simple black-only xerographic printers, the major function of long-term process control is output image density maintenance as a function of A_t aging, with periodic sensing of the density of a control image patch being used to control toner concentration (which in turn controls **q/m**). This simple strategy, however, is not appropriate for a developer that is highly sensitive to ambient humidity. For such a case, the control point will shift to a low toner concentration in response to an increase in developability associated with a low value of **q/m** at a high humidity, and this set-point change may create further age-related problems.

A simple control scheme based on toner dispense will give varying levels of image density stability as a function of developer age — e.g., for a new developer, image density will vary smoothly with toner concentration, but for an aged developer small variations in toner concentration will create large image variations, since the set-point of an aged developer will lie in a region of low **q/m** and low toner concentration.

For a printer based on a conductive developer, a simple level of process control may provoke a cascading failure mode, where an increased toner concentration in response to a decline in image output density creates a reduced level of carrier conductivity and thereby further reduces the output density. A developer that generates developed background because of poor charge-admixing will also suffer a similar cascading type of failure under a simple toner concentration control strategy — the background development will increase the toner consumption rate and thence increase the toner dispense rate, which will further degrade the charge-admixing capability of the developer.

(ii) Control Strategies for Aging Toners

For full-color xerographic printers, each color xerographic module will have an individual response to the problems outlined in the previous toner aging discussion, and variable aging responses will create color shifts. Accordingly, for color applications, the outputs from multiple sensors (e.g., electrostatic voltmeters for photoreceptor control, densitometers for image density control, temperature and humidity sensors for ambient measurements, and magnetic permeability sensors for toner concentration sensing) are used for feedback to key actuators that control image development [36].

Since half-tone reproduction over a wide range is a key requirement for high quality digital imaging, a single ***q/m*** value at a fixed toner concentration represents the ideal developer set-point. Thus, rather than using toner concentration as a means to alter ***q/m***, toner concentration in high-performance printing is sensed and controlled strictly from a supply viewpoint. Typically, the digital image data stream to the printer is used to predict toner demand, with a concentration sensor used for periodic in-situ updates. For actual image sensing, multiple target patches are used to assess the imaging performance at key tone reproduction levels, with electrostatic settings being used for image adjustment. This type of control strategy is also appropriate for humidity-sensitive developers [37], provided that the required electrostatic adjustments do not exceed the capabilities of the photoreceptor.

However, an image density control strategy based on variable biases and/or photoreceptor image potentials will not be effective for cases where development is a saturating function of development electrostatics [13]. For simple developers, limited development at high development fields is characteristic of a high ***q/m*** value at a low toner concentration, but for development from a donor roll (e.g., single component or powder cloud development) a development shortfall following a transition from low to high area imaging is symptomatic of external additive-driven toner aging [12] (i.e. age-increased toner cohesion and/or age-induced creation of high-charged added toners).

From a process control viewpoint, the increased cohesivity of aged toners is a difficult challenge. Since external additive burial is the root cause of toner aging, a dispensing scheme for free additives (in addition to toner and carrier particles) has been modeled as an analog of the carrier trickle concept [12]. However, since commercial toner designs are typically based on precise loadings of carefully-blended multiple external additives, in-situ additive dispensing is probably not a practical strategy.

From a variable toner throughput viewpoint, a direct strategy would be the maintenance of the toner throughput above some critical low level via a periodic development of toner-consuming, inter-image patches [38]. Such an approach, of course, would represent a trade-off between toner utilization and imaging stability.

For charge-admix problems created at a transition from low to high toner throughput rates, the effect may be reduced via a proportional/integral toner dispense strategy, coupled with a dispenser design that disperse added toner evenly throughout the working developer [39]. Fig. 11 illustrates this concept, where a reduced level of added toner reduces the severity of the admix charge-through phenomenon. (The graphs give the ***q/d*** peak values for the incumbent and added toners —— for reference, the inset figures show the final, post-admix charge spectrum).

For donor-roll-based toner aging problems in general, a process control strategy based on a periodic total detone/retone process would minimize the accumulation of aged toner and thereby minimize image history defects such as banding, ghosting, etc. Again, drawbacks to this strategy would include reductions in productivity and toner utilization.

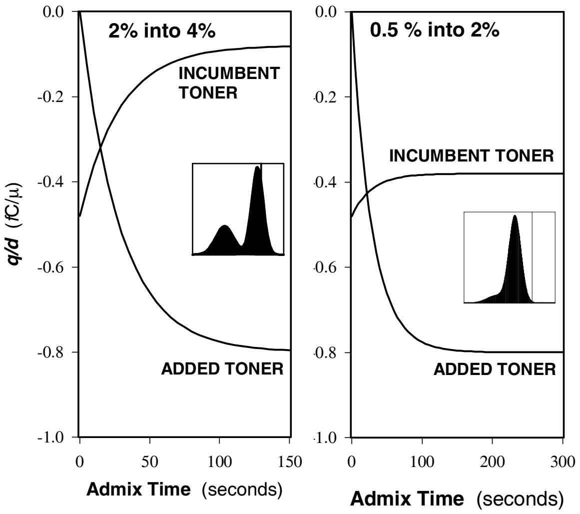

Figure 11. *Charge admix for two levels of toner addition (left plot: 2 wt% into 4 wt%; right plot: 0.5 wt% into 4 wt%).The plots show the peak **q/d** positions for the added and incumbent toner populations. The inset plots show the corresponding charge spectra envelope.*

Finally, for production level full-color xerographic printing, within-print image uniformity remains as a problem that requires ultimate stability from both xerographic materials and marking technologies. For donor roll-based imaging systems, the creation and maintenance of a uniformly-toned donor roll is a critical requirement since control strategies cannot sense or correct for point-to-point imaging variability.

Summary

As outlined in the present review, toner aging has largely replaced carrier aging as the most critical problem for designers of xerographic materials, especially for high-quality digital printing applications. From the patent literature, it is clear that present progress is focused on a continual invention of innovative mixtures of complex external toner additives designed to reduce toner aging. At present, from a toner viewpoint, base resin selection still appears to be chiefly driven by fusing performance requirements, cost and manufacturability (especially for chemical toners), despite evidence that base resins differ in their tendency for toner aging.

For the future, the transition from conventionally-processed to chemically-produced toners will pose an additional challenge —— preliminary studies indicate that the physics and chemistry of chemical toners will mandate a new set of charging and aging design rules for robust marking materials.

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