The Effect of Toner Resin on Triboelectric Aging

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Abstract

The base resin for a xerographic toner is typically selected on the basis of its melt rheological properties, especially for high-speed printer applications where imaging fusing performance requires a "low-melt" toner. However, a base resin may also strongly affect the triboelectric aging performance of a xerographic developer. For example, the interaction of a toner charge control additive (CCA) with toner and carrier surfaces will depend on CCA / toner base resin compatibility. Similarly, residual chemical species from the resin polymerization process may act as carrier "poisons" (and thereby degrade or enhance the tribo-charging ability of a carrier). Additionally, a toner base resin can also affect xerographic image performance (via the image density: image development potential relationship), and thereby affect imaging latitude and imaging process control.

Introduction

Charge control agents (CCAs) are typically melt-mixed into a toner base resin to control the polarity and magnitude of the charge-to-mass ratio (***q/m***) of a xerographic toner. As shown in many past studies [1-8], the CCA surface concentration on toners can strongly affect ***q/m*** performance. As a result, CCA effects on toner charging and on developer aging can be functions of CCA level, CCA type, resin/CCA compatibility, and on toner manufacturing melt-mix conditions. In this paper, experimental triboelectric aging data are presented and analyzed for CCA-based toners that differ only in their base resin. From image density scans taken during the aging tests, the effect of resin type on xerographic image development performance is also evaluated.

Theory

For a well-mixed two-component xerographic developer, the toner ***q/m*** can be simply related to toner and carrier charge properties by:

$$\boldsymbol{q/m} = A / (C + C_0) \tag{1}$$

where C is the toner concentration (i.e., toner mass/carrier mass wt.%), and C_0 is an offset constant term that is a function of the diameter and density of both the toner particles and the carrier beads. [9]

The A term in Eq. (1) can be expanded as

$$A = A' \cdot (\phi_{toner} - \phi_{carrier}) \tag{2}$$

The A' term is a constant, controlled by the diameter and density of the carrier beads, and the ϕ_{toner} and $\phi_{carrier}$ charge terms are functions of the toner and carrier chemistry, respectively. [10,11]

The ϕ terms can be expressed in terms of surface-weighted contributions $\mathbf{P}_i$, $\mathbf{P}_j$, etc.:

$$\phi = \mathbf{P}_i.\mu_i + \mathbf{P}_j.\mu_j + \ldots. \tag{3}$$

where the **P** terms sum to unity, and the μ terms represent the characteristic charging factors for the various surface species. (For toner, the species will include the base resin, colorants, CCAs, external additives, etc.; for carrier, the species will include the core surface, the coating, and "contaminants" such as components transferred from the toner particles. For both toner and carrier, changes in ambient humidity can also affect the μ terms).

Age-induced changes in the charging performance of a xerographic developer reflect changes in the toner and carrier **P** terms, and thence the A term of Eq. 1. Accordingly, at any aging time, t, the A term can be conveniently used as a charging metric, based on the measured ***q/m*** and C values:

$$A_t = \boldsymbol{q/m}_t \cdot (C_t + C_0) \tag{4}$$

For an extended print run, where fresh toner is continually added to the working developer, changes in A_t normally reflect age-induced changes in the carrier **P** terms. For developers based on simple toners, the main triboelectric aging mechanism is the build-up of a thin film of toner on the carrier surface [9] (the so-called "impacted toner" or "scum"), thereby creating an exponential decline in A_t:

$$A_t = (A_0 - A_{II}) \cdot exp\{-k \cdot t\} + A_{II} \tag{5}$$

where A_0 is the time-zero value, A_{II} is the long-term final value of A, and k is the rate constant for the toner film build-up process. (For an extensive toner film build-up, the value of A_{II} can approach zero).

By contrast, the A_t aging profile for developers based on CCA-containing toners, can follow a complex pathway between several intermediate charge states, as a result of CCA transfer between the toner and carrier particles[1]:

$$A_0 \xrightarrow{k_1} A_I \xleftarrow{k_2/k_3} A_{II} \tag{6}$$

and for this type of aging process, the A_t response will be[1]:

$$\begin{aligned} A_t = {} & (k_2/(k_2 + k_3)) \cdot (A_I - A_{II}) \cdot exp\{-(k_2 + k_3) \cdot t\} \\ & -(A_I - A_0) \cdot exp\{-k_1 \cdot t\} + (k_3/(k_2 + k_3)) \cdot A_I \\ & +(k_2/(k_2 + k_3)) \cdot A_{II} \end{aligned} \tag{7}$$

If the final A_{II} state is assumed to be zero-charging, then Eq. (7) simplifies to:

$$A_t = (k_2/(k_2 + k_3)) \cdot (A_I) \cdot exp\{-(k_2 + k_3) \cdot t\} - (A_I - A_0) \cdot exp\{-k_1 \cdot t\} + (k_3/(k_2 + k_3)) \cdot A_I \quad (8)$$

From a mechanistic viewpoint, the transition from the initial A_0 developer state to the "aged" A_I and A_{II} states can be driven by changes in the charging properties of both toner and carrier particles, but the A_t values only reflect the overall effects. For a detailed analysis, therefore, certain assumptions must be taken in order to reduce the number of unknown variables. For tests on CCA toners, it is convenient to take a CCA-free toner as the reference material, i.e., assume that $\phi_{base\ toner} = 0$ eV, so that $\phi_{carrier}$ can be deduced via:

$$\phi_{carrier} = \phi_{base\ toner} - \boldsymbol{q/m} \cdot (C + C_0)/ A' \quad (9)$$

From bench charging tests of fresh carrier beads and beads totally coated with CCA, values for $\mu_{carrier}$ and μ_{CCA} can be similarly deduced [4], all based on the initial assumption of $\phi_{toner} = 0$ eV. These values can then be used to deduce the value of the various **P** terms in the charging equation, with the triboelectric charge aging data being used to follow age-induced changes in the **P** terms.

Experimental Procedure

Black, positive polarity 9 μ diameter toners were prepared via conventional melt-mixing / jetting /classification, based on styrene-butadiene (Sty-Bu) and polyester base resins containing about 0.25 wt % of a positive CCA. For reference, CCA-free toners were also examined.

Steel 130μ diameter carrier beads, powder-coated with an acrylate/fluoropolymer mixture were used to create test developers at a toner concentration of 3 wt%.

The test developers were aged in a computer-controlled imaging fixture, operated in an insulative development mode. A single development roll, biased cyclically at +300 volts dc and –100 volts dc, was operated against a grounded organic photoreceptor to produce a 5% solid-area coverage at a target density of 1.4 o.d. The toner usage rate was about 100 g/hr., and one hour of fixture operation was equivalent to about 10K prints in a high-speed digital printer.

At set time intervals, small samples of developer were taken for total blow-off ***q/m*** measurements. For xerographic evaluations, the developed toner mass per unit area and solid-area optical density values of images on the photoreceptor were taken for a range of biases applied to the development roll.

Results and Discussion

Triboelectric Aging

Figure 1 shows the A_t aging profiles for the CCA-based Sty-Bu toner, the CCA-based polyester toner, and a CCA-free polyester toner. While the CCA Sty-Bu toner gave excellent long-term A_t stability, the polyester-based toners gave rapid A_t degradation both with and without CCA.

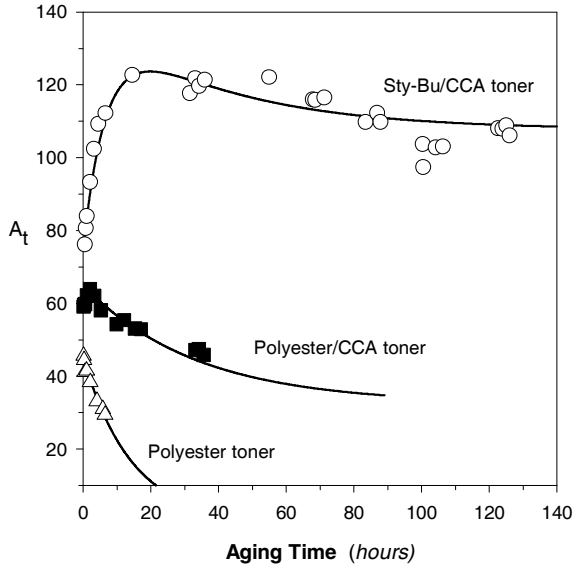

Figure 1. *A_t tribo aging profiles for the three test toners.*

The lines through the data points in Figure 1 were drawn according to Eq. 8, using the values listed in Table 1, with A_{III} assumed to be zero.

Table 1

Toner	A_I	A_{II}	A_{III}	k_1	k_2	k_3
Sty-Bu CCA	75	140	0	0.15	0.02	0.006
Polyester CCA	60	65	0	1.0	0.015	0.015
Polyester no CCA	45	45	0	0	0.07	0

The data from the CCA-based toners indicate that the triboelectric aging performance of a single toner design can be strongly affected by the base toner resin. While the data from the CCA-based toners reflect differences in CCA/resin compatibility, the data from the CCA-free polyester toner indicates that rapid triboelectric aging can occur even in the absence of a CCA.

If the observed ***q/m*** aging is associated with a "poisoning" of the carrier surface, then the effect on $\phi_{carrier}$ will be a function of the level of carrier surface contamination, $\theta_{carrier,\ poison}$, and the μ value of the "poison":

$$\phi_{carrier} = \theta_{carrier,\ poison} \cdot (\mu_{poison} - \mu_{carrier}) + \mu_{carrier} \quad (10)$$

As a result, $\phi_{carrier}$ will vary if $\theta_{carrier,\ poison}$ changes with aging time, e.g. if the carrier contamination is assumed to increase with aging time to a maximum level, then:

$$\theta_{carrier,\ poison} = \theta_{carrier,\ maximum} \cdot (1 - exp\{-k.t\}) \quad (11)$$

Finally, for a positive polarity toner, a normal toner impaction process will slowly increase $\mu_{carrier}$ and thereby create a slow decrease in ***q/m***, so that the $\mu_{carrier}$ term should be modified as:

$$\mu_{carrier,imp} = \mu_{carrier,0} \cdot exp\{+k_{imp} \cdot t\} \quad (12)$$

Xerographic Development Response

Figure 2 shows the ***q/m***:C operating points for an output image density of 1.4 o.d. for the aging tests on the three toners.

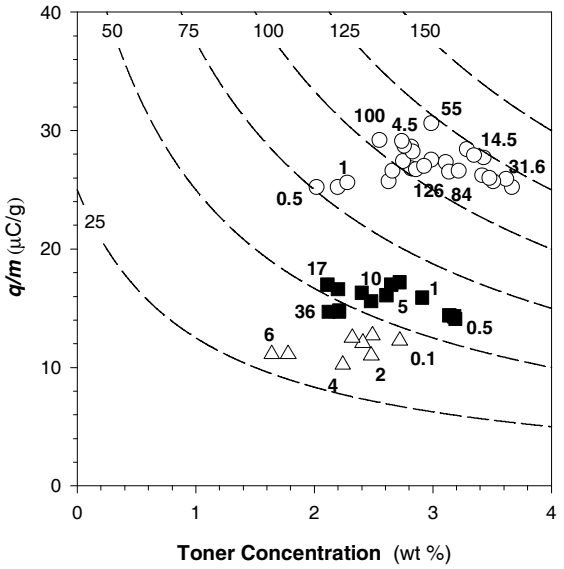

Figure 2. ***q/m***:*C aging tracks for the three test toners.*
○:Sty-Bu/CCA toner, ■: Polyester/CCA toner, △:Polyester/no CCA. The bold numbers are for selected aging times. The dotted curves are for A_t values ranging from 25 to 150.

For the Sty-Bu/CCA toner test, the xerographic set point starts at C = 2 wt% at A_t = 75, and rises rapidly to a maximum at C = 3.5 wt% at A_t = 125. Thereafter, the operating point decreases slowly to C = 3 wt% at an A_t of 100. For the polyester/CCA toner test, the set point decreases rapidly from C = 3.2 wt% to 2.2 wt%, and A_t declines from 60 to 45. For the polyester base toner test, the set point decreases extremely rapidly from C = 2.8 wt% to 1.5 wt%, and A_t declines from 45 to 30.

In each test, the developer essentially produces a fixed output solid image density at a characteristic constant value of ***q/m***. This imaging response is typical of insulative development operation at a low development potential with a single development roll. For such a case, the initial development will be given by[12]:

$$DMA = \boldsymbol{K} \cdot (V_{DEV} - V_{D,0})/(\boldsymbol{q/m}) \quad (13)$$

or

$$SAD = \boldsymbol{K'} \cdot (V_{DEV} - V_{D,0})/(\boldsymbol{q/m}) \quad (14)$$

where DMA is the developed toner mass per unit area, SAD is the optical density of the developed solid image patch, V_{DEV} is the development potential (in normal xerographic operation, $V_{DEV} = V_{image} - V_{bias}$, where V_{image} is the potential of the electrostatic image on the photoreceptor, and V_{bias} is the background-suppression bias applied to the development roll), $V_{D,0}$ is an offset, threshold potential triboelectrically created in the development zone during imaging, and ***K***, ***K'*** are constants for any particular development system. In the present tests, the Sty-Bu and polyester toners gave a common, linear SAD:DMA relationship:

$$SAD = 2.86 \cdot DMA \quad (15)$$

An unusual feature of the data in Figure 2 is that each developer operates at a characteristic ***q/m*** value — for the Sty-Bu/CCA toner, the run ***q/m*** at all developer ages is about 27 μC/g, for the polyester/CCA toner it is about 16 μC/g, and for the CCA-free polyester toner it is about 12 μC/g (the CCA-free toner was aged at a bias of 225 volts, hence the low run ***q/m*** value). From an image development viewpoint, therefore, the Sty-Bu/CCA toner has the highest efficiency since it generates the target image density at the highest ***q/m*** value.

Discussion

Triboelectric Aging

In prior bench test studies on CCA-containing and CCA-free toners [4], a CCA-free Sty-Bu toner with the test carrier was shown to give a highly-negative toner polarity, and with A' and C_0 calculated as 70 and 1.0 respectively, and with μ_{resin} defined as 0 eV, the bench test data indicate $\phi_{carrier}$ = 1.15 eV and μ_{CCA} = 4.50 eV. With $\mu_{carrier}$ = 1.15 eV applied to the time-zero Sty-Bu/CCA data of the present tests, the value of ϕ_{toner} is predicted to be 2.25 eV, and the toner and CCA μ values predict a 50% coverage of CCA on the toner surface, as calculated from:

$$\phi_{toner} = 2.25eV = \theta_{toner,CCA} \cdot (\mu_{CCA} - \mu_{resin}) + \mu_{resin}) \quad (16)$$

For the developer based on a CCA-free polyester toner, a time-zero $\phi_{carrier}$ value of 1.15 eV (as deduced from the Sty-Bu/CCA test) gives a time-zero μ_{resin} value of 1.80 eV for the polyester base toner.

For the polyester/CCA toner, the time-zero ***q/m*** value gives 2.07 eV for ϕ_{toner} (based on $\phi_{carrier}$ = 1.15 eV), and since the base toner test gave μ_{resin} = 1.80 eV, the surface CCA coverage for the polyester/CCA toner is deduced to be 10%.

Thus, for the CCA-containing toners, the deduced surface CCA concentration is 50% for the Sty-Bu/CCA toner and only 10% for the polyester/CCA toner, even though both toners have a common recipe — a clear base toner resin effect on CCA surface accessibility.

The triboelectric aging data for all three test toners show rapid initial transients that appear characteristic of "carrier poisoning" effects rather than normal long-term "toner impaction" effects. For the Sty-Bu/CCA toner, the deduced value of μ_{poison} is 0.25 eV at a final carrier surface coverage of 75%. These values indicate a CCA surface exposure of only about 10%, if the "poison" is a toner film. The net effect is an initial decrease in $\phi_{carrier}$ from 1.15 eV to 0.50 eV, thus producing an increase in A_t

Table 2

Toner	k	$\theta_{carrier,max}$	$\theta_{toner,CCA}$	μ_{poison}	μ_{CCA}	μ_{resin}	ϕ_{toner}	$\phi_{carrier}$	k_{imp}
Sty-Bu/CCA	0.25	0.75	0.50	0.25	4.50	0	2.25	1.15	0.005
PE/CCA	0.025	0.05	0.10	2.07	4.50	1.80	2.07	1.15	0.006
PE/ no CCA	0.070	0.80	-	1.80	-	1.80	1.80	1.15	0.008

from 77 to 122. (By contrast, aging simulations based on $\mu_{poison} = \mu_{toner} = 2.25$ eV, or on $\mu_{poison} = \mu_{CCA} = 4.50$ eV predict a rapid decrease in A_t even for low levels of poison on the carrier surface).

For the polyester/CCA toner, a value of $\mu_{poison} = \mu_{CCA} = 4.50$ eV predicts a final carrier surface coverage of 1%, while $\mu_{poison} = \mu_{toner} = 2.07$ eV predicts a final carrier surface coverage of 5 %. In both cases, the predicted initial effect on $\phi_{carrier}$ is only a 4% increase, with an attendant initial decrease in A_t from 64 to 60.

The difference in aging performance between the two CCA-based toners reflects the relative values of the μ_{toner}, $\mu_{carrier}$, μ_{poison} and $\theta_{carrier,\ poison}$ terms, as controlled by the compatibility of the CCA for the two base resins — for the Sty-Bu/CCA toner, carrier poisoning effectively increases the positive charge level of the toner; however, for the developer based on the polyester/CCA toner, carrier poisoning decreases the toner charge.

For the CCA-free polyester toner, a value of $\mu_{poison} = \mu_{toner} = 1.80$ eV predicts a final carrier surface coverage of 35 %. The predicted initial effect on $\phi_{carrier}$ is a 20% increase, with an attendant initial decrease in A_t from 46 to 29. Again, the poor aging performance is driven by the lack of a mechanism to increase A_t by a decrease in $\phi_{carrier}$

For reference, the deduced parameters for the three test developers are listed in Table 2.

Xerographic Development Response

Representative image density:development potential scans for the Sty-Bu/CCA and a polyester/CCA toner are shown in Figures 3 and 4 (in these tests, $V_{DEV} = V_{bias}$ since the photoreceptor was kept at ground potential). From the initial linear development data, the two test toners show a common ***K*** factor of about 0.11.

However, from the density plots, the $V_{D,0}$ value for the Sty-Bu/CCA toner is 20 volts and is 85 volts for the polyester/CCA toner. As a result, at any development potential and ***q/m*** value, the Sty-Bu/CCA toner produces a higher image density than the polyester/CCA toner, and this accounts for the ability of the Sty-Bu/CCA toner to produce a target density of 1.4 o.d. at ***q/m*** = 27μC/g vs. ***q/m*** = 16 μC/g for the polyester/CCA toner during the present aging fixture tests.

For well-toned developers, the offset bias $V_{D,0}$ is generated via an in-situ triboelectric interaction in the development zone between toner particles and the surface of the photoreceptor. The present tests indicate that the base resin of a CCA-based toner can affect the value of this offset parameter, and thence xerographic development efficiency.

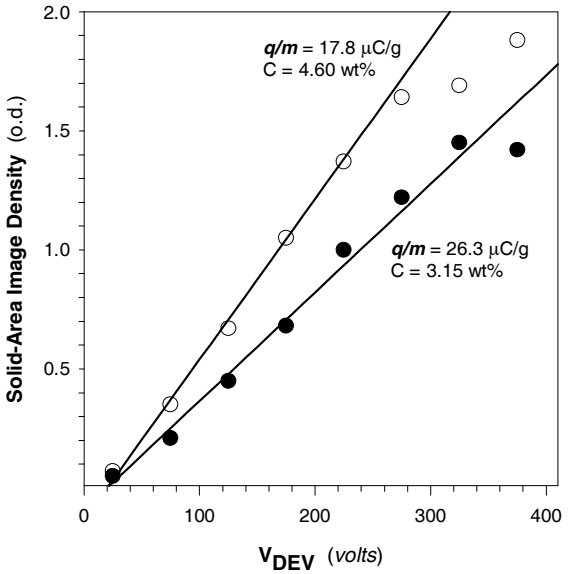

Figure 3*. SAD vs. Dev. Potential for Sty-Bu/CCA toner.*

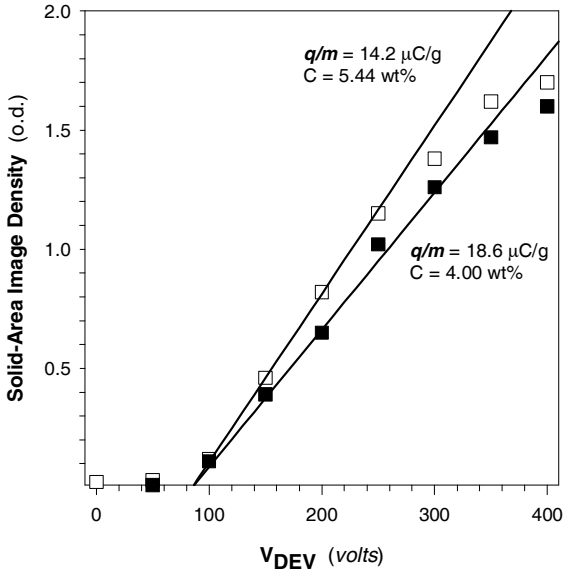

Figure 4. *SAD vs. Dev. Potential for Polyester/CCA toner.*

Conclusions

The rate and mode of triboelectric aging of developers based on CCA-toners can be strongly influenced by the toner resin, as a result of differences in resin/CCA interactions. Therefore, a CCA-based toner design may require reformulation if the toner resin is changed, or if the scale or mode of toner production is altered.

From a process control viewpoint, a change in toner resin will also affect the overall xerographic development latitude, if the toner/photoreceptor triboelectric charging interaction alters the development efficiency. Similarly, general changes in toner design, such as the type and concentration of colorants, additives, etc., may also have a similar effect on xerographic development. As a result, an imaging process adjustment (e.g., a change in image potential or bias) may be necessary to maintain a target level of development at a desired developer set-point (i.e., at a specified value of ***q/m*** and toner concentration), if a toner recipe is changed.

In summary, the present experimental data demonstrate that a change in toner resin to provide improved toner fusing performance may create new modes of developer failure from both a triboelectric aging and xerographic image development viewpoint.

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