

# A Conceptual Model of Toner Charge Admixing

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## Abstract

During xerographic development, charged toner particles are removed from the developer by the latent electrostatic image, and are replaced by uncharged dispensed toner particles. As a result, the total toner population in a developer contains charged incumbent particles and uncharged added particles. To maintain image quality, the latter toner particles must rapidly charge-equilibrate with the already-charged toner particles in the developer. As outlined in the present paper, a conceptual charge-admix model based on a direct graphical analysis can provide a clear picture of toner-carrier and toner-toner charge-admix-exchange processes. The model starts with the "perfect" charge admix case, and this is then used as a base for the development of a model for atypical charge admix processes. The model also describes toner charging performance from the initial developer charge-up step through the charge spectra of the final toner admix step. In this paper, predictions from the conceptual model are also reviewed for various levels of developer mixing and aging.

## Introduction

In recent years, informative but complex theoretical models have been published for triboelectric charging<sup>1</sup> and charge admixing<sup>2</sup>. A series of detailed experimental studies has also been published<sup>3-20</sup>, and a simplified version of the theoretical triboelectric charging model has been used as a conceptual framework to provide a mechanistic understanding of triboelectric charging<sup>6</sup>. In this present report, the conceptual-based toner charging model is extended to include charge-admixing phenomena.

## Theory

### Toner Triboelectric Charging

For a well-mixed two-component xerographic developer, the toner triboelectric charge (toner charge to mass ratio,  $q/m$ ) can be related to toner concentration,  $C$ , by<sup>1</sup>:

$$q/m = (A'/(C + C_o)) \cdot (\phi_{toner} - \phi_{carrier}) \quad (1)$$

where  $A'$  and  $C_o$  are constants, and  $\phi_{toner}$ ,  $\phi_{carrier}$  represent the charging tendency of the toner and carrier particles.

For an external additive toner, Eqn. 1 becomes:

$$q/m = (A'/(C + C_o)) \cdot (\theta \cdot (\mu_{additive} - \mu_{toner}) + \mu_{toner} - \phi_{carrier}) \quad (2)$$

where  $\theta$  is the additive surface coverage, and  $\mu_{additive}$  and  $\mu_{toner}$  are the intrinsic charging tendencies of the additive and the base toner<sup>6</sup>. (Toner aging frequently reflects a decline in  $\theta$  with toner use).

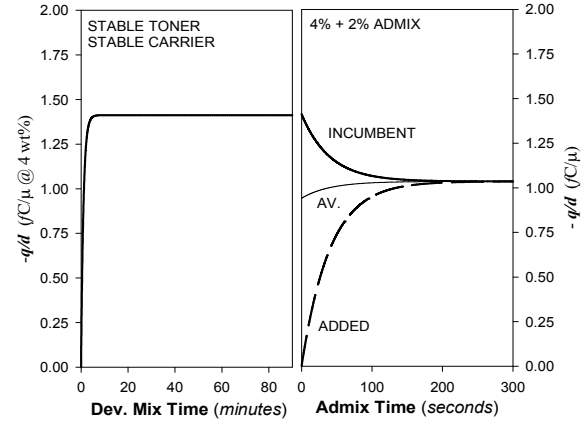


Figure 1: Perfect  $q/d$  response.  
(identical incumbent and added toner).

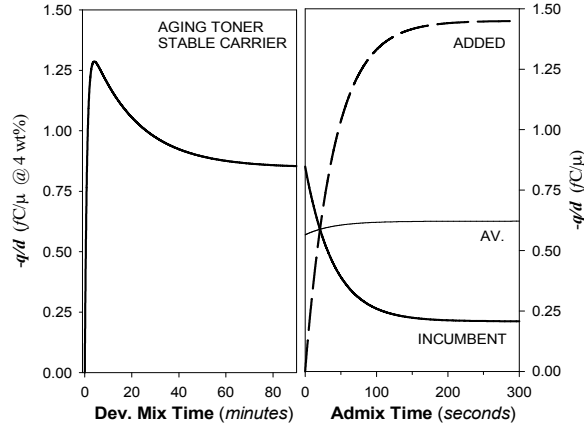
### Toner-Toner Charge-Admixing

Normally, the addition of uncharged toner particles to a charged developer reduces the toner charge-to-mass ratio,  $q/m$ . For example, for an increase in  $C$  from 4 wt% to 6 wt%, Eqn. 1 predicts that the final reduced  $q/m$  value will be:

$$q/m_{6\%} = q/m_{4\%} \cdot ((4 + C_o)/(6 + C_o)) \quad (3)$$

During a perfect admix event (identical added and incumbent toner particles), the added toner particles gain charge and the incumbent toner particles lose charge until both toner populations reach a common charge level<sup>4</sup>. The change in toner charge with admix time, can be conveniently illustrated using charging plots based on reasonable values for the parameters of Eqn. 2. For example, for a negative polarity toner (7 $\mu$  diameter, 1.1 g/cc density), mixed with a 65 $\mu$  steel carrier,  $A' = 110 \mu C/g \cdot wt\% \cdot eV^{-1}$  and  $C_o = 1.5 wt\%$ . For  $\theta = 0.8$ , a typical negative toner polarity can be generated using  $\mu_{add} = 0 eV$ ,  $\mu_{toner} = 2.5 eV$  and  $\phi_{carrier} = 3.0 eV$  as model values. From these values,  $q/m = -50 \mu C/g$  at  $C = 4 wt\%$ , and  $-36.7 \mu C/g$  at  $C = 6 wt\%$ .

While the average  $q/m$  value of a toner can be readily measured via a total blow-off tribo charge procedure, the results of charge admix experiments are best understood in terms of the entire toner charge spectrum. From the spectrum, the individual charge contributions (toner charge-to-diameter,  $q/d$ ) from the added and incumbent toner populations can be assessed and monitored as a function of admix time. For the example shown in Fig. 1, the initially-uncharged added toner particles gain charge, and the incumbent toner particles lose charge during a perfect admix event, until both toner populations reach a common  $q/d$  level of  $-1.04 fC/\mu$  (i.e.,  $-36.7/35.4$  where 35.4 is the  $q/m:q/d$  conversion factor for a 7  $\mu$  toner with a density of 1.1 g/cc).



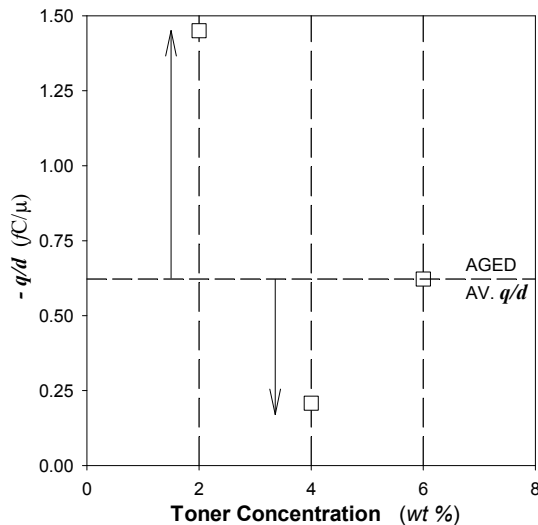
**Figure 2:** Atypical  $q/d$  response.  
(aged incumbent and fresh added toner).

By contrast, if the charging properties of the incumbent toner particles become degraded during the initial developer mixing step, then charge-sharing between unaged, added toner particles and degraded, incumbent toner particles will produce an equilibrium bimodal charge spectrum. For example, Fig. 2 shows the admix result for a model toner that has lost 50% of its initial surface additive. In this figure, the fresh, added toner gains a high negative charge and the charge of the aged, incumbent toner falls to a low negative value. The root cause of this effect is the mismatch between the  $\phi_{\text{toner}}$  values for the added toner ( $\phi_{\text{added toner}} = 0.5$  eV) and the incumbent toner ( $\phi_{\text{incumbent toner}} = 1.5$  eV).

For the above examples, the  $q/d$  admix responses were calculated using a simple model, as described in the following section.

## Model Formulation

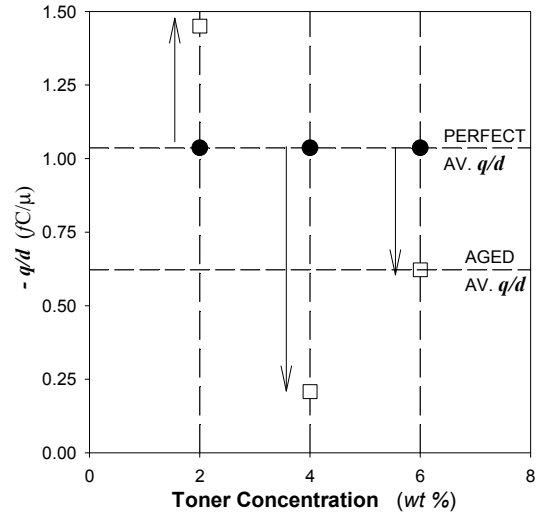
To illustrate the charge admix process between fresh and aged toner particles, nominal numerical values will be used for the key parameters. In this way, the charge-admixing relationships between incumbent and added toner populations (of identical



**Figure 3:** Atypical  $q/d$  response of added and incumbent toner, referenced against the average  $q/d$ .

particle size) can be directly displayed in a simple graphical form, and these relationships can then be used to develop deterministic equations for the charge admix process. In particular, the model relationships for the perfect admix case can be extended to include the effects of an atypical admix process.

Fig. 3 shows the  $q/d$  responses for the case of an atypical charge admix created by an age-induced increase in  $\phi_{\text{incumbent toner}}$ . In this plot, the post-admix  $q/d$  value of  $-0.62$  fC/ $\mu$  at 6 wt% is the weighted sum of  $-1.45$  fC/ $\mu$  at 2 wt% and  $-0.20$  fC/ $\mu$  at 4 wt%. As expected for a charge redistribution between 4 wt% of charged toner and 2 wt% of uncharged toner, the increase in  $q/d_{\text{added}}$  is twice the decrease for  $q/d_{\text{incumbent}}$  (with the changes measured with respect to the aged toner admix  $q/d_{\text{weight average}}$  value).



**Figure 4:** Atypical  $q/d$  response of added and incumbent toner, referenced against the average  $q/d$  for perfect admix.

Fig. 4 shows the relationship between long-term, atypical admix  $q/d$  values (open square symbols). In this figure, the  $q/d_{\text{weight average}}$  value for perfect admix is taken as the reference value. The plot shows that the total change in  $q/d_{\text{added}}$  for atypical admix can be graphically viewed as the sum of a contribution for perfect admix (i.e., from an initial 0 fC/ $\mu$  to  $-1.04$  fC/ $\mu$ ) and an added toner-toner charge-sharing contribution (from  $-1.04$  fC/ $\mu$  to  $-1.45$  fC/ $\mu$ ).

With a reference value of the perfect admix  $q/d_{\text{weight average}}$ , Figure 4 also shows (in a negative toner sense) that the toner-toner charge-sharing increase in  $q/d_{\text{added}}$  is equal in magnitude to the decrease in the  $q/d_{\text{weight average}}$  value at the total toner concentration of 6 wt%. Thus, increases in  $q/d_{\text{added}}$  can be expressed in terms of equivalent decreases in  $q/d_{\text{weight average}}$ , and this is a useful result since changes in  $q/d_{\text{weight average}}$  can be directly expressed in terms of key parameters such as  $\phi_{\text{toner}}$  and  $\phi_{\text{carrier}}$ . For example, the long-term, perfect admix weight average  $q/d_{\text{weight average}}$  can be calculated as:

$$q/d_{\text{weight average},\infty} = \frac{A^*}{(C_{\text{incumbent}} + C_{\text{added}} + C_0)} \cdot (\phi_{\text{toner,new}} - \phi_{\text{carrier}}) \quad (4)$$

where  $A^* = A/35.4$  (for the  $q/m$  to  $q/d$  conversion).

and for the example shown in Fig. 1, Eqn. 4 gives a value of  $-1.04 \text{ fC}/\mu$ . By definition, for the perfect admix case, this is also the value of  $q/d_{\text{added},\infty}$  and  $q/d_{\text{incumbent},\infty}$ .

At the total toner concentration of 6 wt%, the change  $\Delta$  in the  $q/d_{\text{weight average},\infty}$  value from the perfect admix to the atypical admix case will be driven by a charge exchange between the aged incumbent toner and the fresh added toner:

$$\Delta = \frac{A^*}{(C_{\text{incumbent}} + C_{\text{added}} + C_o)} \cdot (\phi_{\text{toner,new}} - \phi_{\text{toner,aged}}) \quad (5)$$

Thus, from the graphical symmetry shown in Figure 4, the  $q/d_{\text{atypical, weight average},\infty}$  and  $q/d_{\text{atypical, added},\infty}$  values for the atypical admix case will be:

$$q/d_{\text{atypical, weight average},\infty} = \text{PF} - \Delta \quad (6)$$

and

$$q/d_{\text{atypical, added},\infty} = \text{PF} + \Delta \quad (7)$$

where **PF** is the  $q/d_{\text{weight average},\infty}$  for perfect admix, as given by Eqn. 4.

After extended charge admixing,  $q/d_{\text{weight average},\infty}$  will be given by the weight-average sum of contributions from the incumbent and added toner populations:

$$q/d_{\text{weight average},\infty} = \frac{C_{\text{added}}}{C_{\text{sum}}} \cdot q/d_{\text{added},\infty} + \frac{C_{\text{incumbent}}}{C_{\text{sum}}} \cdot q/d_{\text{incumbent},\infty} \quad (8)$$

where  $C_{\text{added}}$ ,  $C_{\text{incumbent}}$  and  $C_{\text{sum}}$  are the toner concentrations of the added toner, the incumbent toner and the total toner population, respectively.

From Eqn. 8,  $q/d_{\text{incumbent},\infty}$  can be deduced from the calculated  $q/d_{\text{weight average},\infty}$  and  $q/d_{\text{added},\infty}$  values:

$$q/d_{\text{incumbent},\infty} = \left( \frac{C_{\text{sum}}}{C_{\text{incumbent}}} \cdot q/d_{\text{weight average},\infty} \right) - \left( \frac{C_{\text{added}}}{C_{\text{sum}}} \cdot q/d_{\text{added},\infty} \right) \quad (9)$$

If Eqn. 9 is rewritten in terms of the relationships listed in Eqns. 6 and 7, then the result is as shown in Eqn. 10:

$$\begin{aligned} q/d_{\text{incumbent},\infty} &= \left( (\text{PF} - \Delta) \cdot \frac{C_{\text{sum}}}{C_{\text{incumbent}}} \right) - \left( (\text{PF} + \Delta) \cdot \frac{C_{\text{added}}}{C_{\text{incumbent}}} \right) \\ &= \left( \text{PF} - \Delta \cdot \left( \frac{C_{\text{sum}} + C_{\text{added}}}{C_{\text{incumbent}}} \right) \right) \\ &= (\text{PF} - \Delta \cdot \beta) \end{aligned} \quad (10)$$

and values of the  $\beta$  factor in Eqn. 10 are listed in Table 1 for various values of  $C_{\text{add}}$  and  $C_{\text{incumbent}}$ .

**Table 1**

$C_{\text{add}}$	$C_{\text{incumbent}}$	$\beta$
1	4	1.5
2	4	2.0
3	4	2.5
4	4	3.0

From a mechanistic viewpoint, it is useful to expand the parameters of Eqns. 6, 7 and 10 into their component factors. For example, the expression for  $q/d_{\text{atypical, weight average},\infty}$  that is given in Eqn. 6 expands to:

$$q/d_{\text{atypical, weight average},\infty} = \left( \frac{A^*}{(C_{\text{sum}} + C_o)} \right) \cdot (\phi_{\text{toner,aged}} - \phi_{\text{carrier}}) \quad (11)$$

For  $q/d_{\text{atypical, add},\infty}$ , the expanded expression is:

$$q/d_{\text{atypical, add},\infty} = \left( \frac{A^*}{(C_{\text{sum}} + C_o)} \right) \cdot \left( \begin{aligned} &(\phi_{\text{toner,new}} - \phi_{\text{toner,aged}}) \\ &+ (\phi_{\text{toner,new}} - \phi_{\text{carrier}}) \end{aligned} \right) \quad (12)$$

For  $q/d_{\text{incumbent},\infty}$ , the expanded expression is:

$$q/d_{\text{atypical, incumbent},\infty} = \left( \frac{A^*}{(C_{\text{sum}} + C_o)} \right) \cdot \left( \begin{aligned} &(\phi_{\text{toner,new}} - \phi_{\text{carrier}}) \\ &- \left( \frac{C_{\text{sum}} + C_{\text{added}}}{C_{\text{incumbent}}} \right) \cdot (\phi_{\text{toner,new}} - \phi_{\text{toner,aged}}) \end{aligned} \right) \quad (13)$$

As shown in Fig. 2, the added and incumbent toner populations rapidly reach an initial common  $q/d$  value when the admix is atypical; by contrast, Fig.1 shows that the charge admix is slower when the process is perfect, even if the charge-sharing rate constant,  $r$ , is assumed to be identical for both types of admixing. This observation indicates that a mismatch between the added and incumbent toner particles can actually be beneficial from a short-term, charge admix viewpoint. However, the initial common  $q/d$  value for atypical charge admix is not an equilibrium value, and the  $q/d_{\text{atypical, incumbent}}$  and  $q/d_{\text{atypical, added}}$  values continue to diverge beyond this initial common  $q/d$  value, eventually reaching separate plateau values. Therefore, in practice, only a small degree of mismatch can be tolerated if the overall admix charge spectrum is to remain unimodal.

Table 2 gives representative values for  $t_{\text{crossover}}$  (atypical charge admix) and  $t_{\text{add}}$  (perfect admix) for model toners with  $\phi_{\text{new}} = 0.5\text{eV}$ , and  $\phi_{\text{aged}} = 1.5\text{eV}$ . ( $\phi_{\text{carrier}} = 3.0\text{eV}$ ,  $A^* = 3.11$ ,  $C_{\text{incumbent}} = 4 \text{ wt\%}$ ,  $C_{\text{add}} = 2 \text{ wt\%}$ ,  $C_o = 1.5$ ).

**Table 2**

ADMIX RATE CONSTANT	ATYPICAL ADMIX	PERFECT ADMIX
$r \text{ (sec}^{-1}\text{)}$	$t_{\text{crossover}} \text{ (sec.)}$	$t_{\text{add}} \text{ (sec.)}$
0.01	52	685
0.02	26	343
0.05	10	137
0.10	5	69
0.20	3	34

## Sample Model Predictions

The expressions in equations 11-13 can be used to model a wide range of possible toner charge admix scenarios. For this present report, a limited number of illustrative examples will be presented. In each model plot, the dashed line represents  $q/d_{added}$ , the solid line  $q/d_{incumbent}$ , and the thin line  $q/d_{weight\ average}$ .

### External Additive and CCA Effects

While the loss of a surface additive can create toner aging, the magnitude of this type of toner aging will also be governed by the relative magnitudes of the  $\mu_{additive}$  and  $\mu_{base\ toner}$  terms, and this can have a large effect on the subsequent charge admix process.

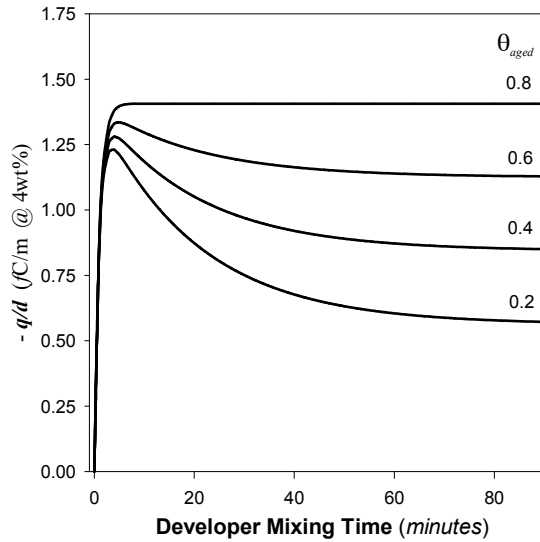


Figure 5: Toner  $q/d$  aging response for a low-charging base toner.

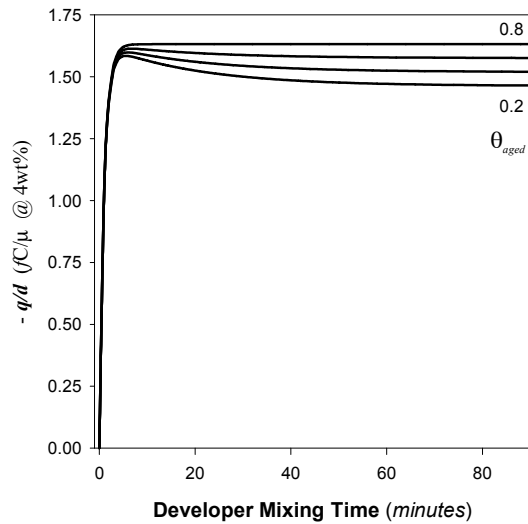


Figure 6: Toner  $q/d$  aging response for a high-charging base toner.

For example, Figs. 5 and 6 show the predicted developer  $q/d$  response for toners that differ in their charge sensitivity to surface additive loss. Both figures show a range of additive loss from 0% to 75%, but  $(\mu_{additive} - \mu_{base\ toner}) = (0 - 2.5) \text{ eV} = -2.5 \text{ eV}$  in Fig. 5, and  $(\mu_{additive} - \mu_{base\ toner}) = (0 - 0.5) \text{ eV} = -0.5 \text{ eV}$  in Fig. 6. As a result, the pre-admix developer mixing process in Fig. 5 produces a large decrease in  $q/d_{incumbent}$ , and this creates a large divergence between the  $q/d_{incumbent}$  and  $q/d_{added}$  values during a subsequent 2 wt% into 4 wt% toner admix step. For a 75% loss of surface additive,  $q/d_{incumbent}$  is actually driven wrong-sign, as shown in Fig. 7.

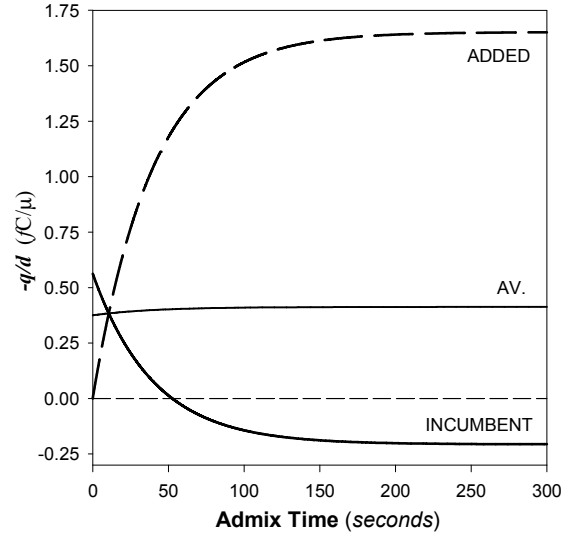


Figure 7: Charge admix response after 75% loss of external additive from a low-charge base toner.

By contrast, Fig. 6 shows only a minor decline in  $q/d_{incumbent}$  during the developer mixing step (even for cases where there is a large loss of surface additive), and a 2 wt% into 4 wt% admix step shows only a minor difference between  $q/d_{incumbent}$  and  $q/d_{added}$  even for a 75% loss of surface additive (Fig. 8).

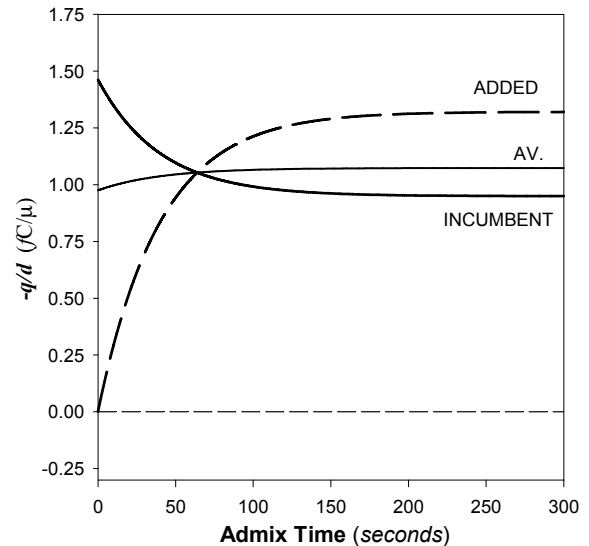


Figure 8: Charge admix response after 75% loss of external additive from a high-charge base toner.

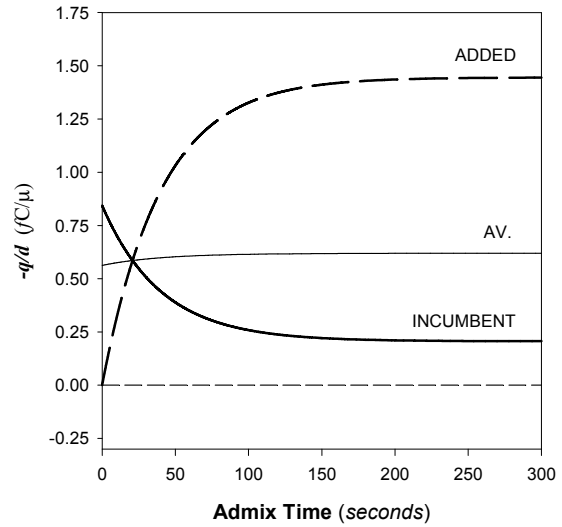
The model toner shown in Fig. 5 is strongly dependent on the surface additive for its negative charge ( $\mu_{base\ toner} \gg \mu_{additive}$ ), so that  $\phi_{toner, aged} > \phi_{toner, new}$  as a result of surface additive loss during the developer mixing process. For the model toner shown in Figure 6,  $\mu_{base\ toner} \equiv \mu_{additive}$  so that any loss of surface additive during the developer mixing step will have only a small effect on  $q/d_{incumbent}$ . (Of course, other toner properties such as powder flow, cohesivity, etc. will be affected by the loss of the surface additive).

A difference between  $\phi_{incumbent\ toner}$  and  $\phi_{added\ toner}$  can also be caused by batch-to-batch errors during the additive blending step of the toner production process (e.g., an incorrect weight or omission of the additive), or by use of a 3rd-party toner in place of an OEM toner. If an additive-free base toner is added to an additive toner, the added toner can be driven wrong-sign, and  $q/d_{added} \neq q/d_{incumbent}$  at all admix times. (If surface additive is transferred to the additive-free toner during the charge admix step, then the overall response will be more complex). When an additive toner is added to an additive-free toner, the added toner will be driven to a highly negative state, and the incumbent toner to a wrong-sign state. When a low additive toner is added to a very low additive toner,  $q/d_{added} \neq q/d_{incumbent}$  at all admix times, but with the added toner at a low right-sign charge level.

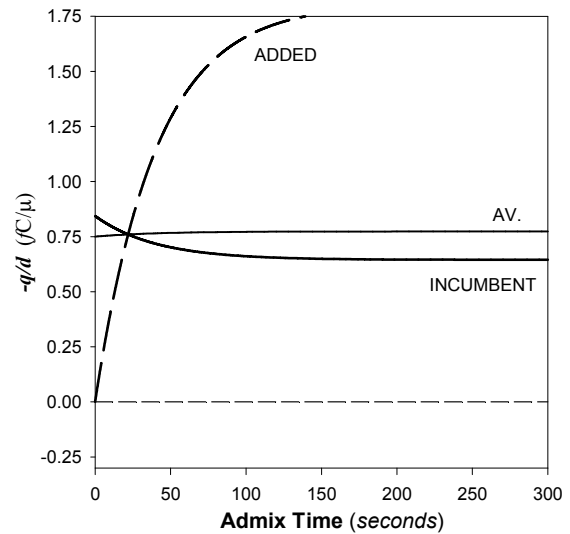
In theory, the addition of a charge-enhancing charge control agent, CCA, to a base toner should reduce the mismatch between  $\mu_{base\ toner}$  and  $\mu_{additive}$ , and hence reduce the level of atypical charge admix for toners based on unstable external particulate additives. Additionally, CCA additives can also produce toner (and carrier) aging via CCA transfer between the toner and carrier particles, so that it is possible that CCA's may also enhance the charge-admix process by creating a small mismatch between  $\phi_{toner, aged}$  and  $\phi_{toner, new}$ . Finally, the electrical conductivity of CCA particles has also been hypothesized as mechanism for CCA-enabled toner charging<sup>21</sup>, so that CCA's might also be expected to facilitate toner-toner admix charging. (While the **potential** for atypical charge admix is set by the mismatch between the toner terms,  $\phi_{incumbent}$  and  $\phi_{added}$ , the **rate** of toner-toner charge admix will be influenced by toner surface species that facilitate charge transfer (e.g., conductive or semiconductive species such as pigments, CCA's, metal oxides, metal salts, adsorbed/absorbed water, etc.).

### Admix Toner Concentration Effects

Since the charge admix of fresh and aged toner particles involves toner-toner charge-sharing, the ratio of the added toner concentration to the incumbent toner concentration will have a strong effect on the overall process. This effect is illustrated in Figs. 9-10, where 2 wt% and 0.5 wt% of toner are added to an aged toner. Note that the long-term  $q/d_{incumbent}$  value approaches the  $q/d_{weight\ average}$  value as the added toner concentration decreases — i.e., even an aged toner can give a normal charge admix response (in terms of  $q/d_{incumbent}$ ) if the added toner concentration is kept at a low value (e.g., via uniform, well-dispersed and efficient toner dispensing/in-blending).



**Figure 9:** Addition of 2 wt% of fresh toner into a developer with 4 wt% of aged toner (50% loss of external additive).



**Figure 10:** Addition of 0.5 wt% of fresh toner into a developer with 4 wt% of aged toner (50% loss of external additive).

### Conclusions

While the aging of xerographic carrier beads is normally a long-term process, toner aging can occur on a much shorter print interval time scale. Besides the toner-based aging mechanisms outlined in this present report, other important toner aging factors include excessive mechanical forces within a development housing, and variable printing modes (e.g., abrupt transitions between text and pictorial images).

From a toner viewpoint, the major design challenge is the creation of a robust toner that functions in all modules of a xerographic printer (i.e., development, transfer, fusing and cleaning). While charge exchange is a key element in triboelectric charging, perhaps a materials-based solution to atypical charge admix will involve toner additives/components that moderate the rate of charge transfer from aged toner particles.

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## Author 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 was an expatriate at Fuji Xerox, Takematsu, Japan. He now consults on topics from xerographic materials to cross-cultural interactions with Japan. 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.*