Development of a Consistent Triboelectric Charging Series Based on Fumed SiO$_2$ as a Reference Probe Material

Robert J. Nash and Richard N. Muller
Xerox Corporation, Webster, New York

Abstract

The triboelectric charging series concept has been explored using a series of negative and positive polarity developers based on two toners and three carriers. The toner charging properties have been systematically modified via the addition of a "negative" fumed silica at five weight % concentrations. The triboelectric impact of the silica additive has been used to unify the experimental data taken with negative and positive polarity developers, and the key features of the triboelectric charging series concept have been illustrated using the overall data set. With the fumed silica set as the arbitrary zero of the charging series, the component carrier and toner charging values have been deconvoluted from the observed difference q/m measurements.

Introduction

As is well-known, the component materials of typical xerographic developers can be arranged to form a triboelectric charging series—that is, a series where materials are ranked according to their charging tendencies.[1-6] This type of series is broadly valid—the extremes of "positive" and "negative" toner charging can be represented by toners containing quaternary ammonium salts[7,8] and metal organic acid salts[9-11] or metal azo dyes[12] respectively, and by fluoropolymer[13,14] and acrylate[15,16] carrier coatings. Indeed, in broad practical applications, the available range of charging behavior from "positive" to "negative" is frequently used to provide a "tunable" charge level via an appropriate mixture of positive and negative materials. Such applications include mixtures of toner resins,[5] mixtures of external additives,[17] and mixtures of carrier coating polymers.[10,18,19] However, at a detailed level, a comprehensive triboelectric series typically contains anomalies and apparent exceptions—e.g., when paired with a variety of triboelectrically-effective materials, a particular material may generate triboelectric charging responses that appear consistent with a variety of ranking locations in an overall triboelectric series.

Such ranking problems may merely reflect experimental difficulties with respect to sample-to-sample reproducibility. However, an additional key problem with triboelectric charge generation is that it involves charge exchange between triboelectrically-dissimilar materials and thus reflects a differential process. Besides being a potential source of variability, this latter differential aspect means that an absolute ranking can only be given in terms of some specified "reference" material. For screening and evaluation purposes, specific "reference" carriers or toners are often used, and even single-component toners[20,21] and external toner additives[22,23] can be ranked against a surrogate carrier. However, this approach lacks general applicability, since industrial research and development groups typically utilize "reference" materials appropriate to their particular intended commercial applications.

Ideally, a universal reference material must be reproducible and generally available, and should preferably be usable with both positive and negative xerographic developer designs. Fumed "negative" SiO$_2$ particles, applied as an external additive to toner surfaces appear capable of acting as a functional reference probe material, since such particles create well-defined changes in the charging level of a xerographic developer when incrementally applied to the surface of toner particles.[24-27] For "negative" SiO$_2$'s, this effect appears largely independent of silica surface chemistry,[25] and is a simple direct inverse function of SiO$_2$ particle size. Conventional fumed SiO$_2$ particles also offer the advantage of being much more "negative" than typical xerographic toners or carrier coatings, and thus naturally form a boundary "benchmark" for negative charging.

In the present study, this concept of using "reference" SiO$_2$ particles will be illustrated via an analysis of experimental triboelectric charging data from developers based on cross-mixtures of a variety of "positive" and "negative" toners and carriers, with the charge-modifying effect of added SiO$_2$ particles being used to provide a common charging link between the various developers. The experimental charging data will also be used to illustrate some key features and problems with the general concept of a triboelectric charging series.

Theory

The toner charge-to-mass value, *q/m*, generated by any particular toner-carrier combination as a function of mixing time t can be simply expressed as[28]:

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

where *A'* is a characteristic constant dependent on electrostatic and physical constants (such as carrier and toner size and density), *C* is the concentration of toner in the developer expressed as a weight percentage of the carrier, C_0 is a characteristic constant based on carrier and toner physical

properties, ϕ_{toner} and $\phi_{carrier}$ represent the charging tendency of the toner and carrier, respectively, expressed in eV, and the $(1 - exp\{-\gamma \cdot t\})$ term accounts for the charging rate profile.

Generally, xerographic toners and carriers are based on several distinct components, and conceptually ϕ_{toner} and $\phi_{carrier}$ can be expressed in terms of surface-weighted sums of contributions from these components, e.g.:

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

where the fractional weights $\mathbf{P}_i$, $\mathbf{P}_j$ etc., add to unity, and the parameters μ_i and μ_j, etc. are charging factors for the various surface components.

According to Equation (1), for toners and carriers of fixed size and constant toner concentration, the q/m values for a series of toners measured against a series of carriers should show parallel responses, with offsets governed by the magnitude of the respective $(\phi_{toner} - \phi_{carrier})$ differences. As an example, the *ith* and *jth* components in Equation (2) may be viewed as dissimilar carrier coating components such as PMMA and PVF, and for such a case q/m might be expected to become increasingly negative with an increasing proportion of the carrier coating as PMMA. However, while q/m is generally found to be a monotonically decreasing function of carrier PMMA, an experimental plot of q/m versus PMMA wt% is usually somewhat non-linear.[29] This result, then, suggests a variability in the carrier coating surface coverage: weight concentration relationship, and this is a typical complication in triboelectric charging series tests. By contrast, the addition of fixed increments of "negative" SiO2 as an external additive to toners frequently generates a strictly proportional negative response in q/m,[24] suggesting that SiO2 can be used as a probe to alter q/m by controlled linear amounts. Such a strategy can be outlined as follows:

In general, components i, j etc. represent toner resin, carbon black, carrier coating polymer, etc. For the particular case of a toner plus external additive such as fumed SiO2, it is convenient to express ϕ_{toner} in terms of a single consolidated "toner" term, μ_{toner} (containing contributions from binder resin, colorant, etc.) and an additive term μ_{SiO2}, e.g.:[24]

$$\phi_{toner} = \mathbf{P}_{toner} \cdot \mu_{toner} + \mathbf{P}_{SiO2} \cdot \mu_{SiO2} \qquad (3)$$

or,

$$\phi_{toner} = \mathbf{P}_{SiO2} \cdot (\mu_{SiO2} - \mu_{toner}) + \mu_{toner} \qquad (4)$$

For the case where $\mu_{toner} > \mu_{SiO2}$, Equation (4) predicts that ϕ_{toner} (and hence q/m) will linearly decrease (i.e., become increasingly more negative) as SiO2 weight concentration on the toner (or, proportionately, SiO2 surface coverage) increases, with a response governed by the magnitude of the difference term $(\mu_{SiO2} - \mu_{toner})$.

In general, then, the triboelectric charging response of a developer containing SiO2 as an external toner additive will be:

$$q/m = (A'/(C + C_0)) \cdot [\mathbf{P}_{SiO2} \cdot (\mu_{SiO2} - \mu_{toner})$$
$$+ (\mu_{toner} - \mu_{carrier})] \cdot (1 - exp\{-\gamma \cdot t\}) \qquad (5)$$

Thus, from a series of triboelectric charging data taken over a range of toner SiO2 levels, it should be possible to deduce the values of the difference terms $(\mu_{SiO2} - \mu_{toner})$ and $(\mu_{toner} -$

$\mu_{carrier})$ given assumed values for terms such as A', C_0 and $\mathbf{P}_{SiO2}$. Additionally, an assumed value of μ_{SiO2} would allow an absolute value to be assigned to μ_{toner} and thence to $\mu_{carrier}$, and given the extreme negative charging tendency of normal fumed SiO2, it is convenient to set μ_{SiO2} as the reference zero for a triboelectric charging series. This strategy has been used in the present experimental study, and illustrative examples are discussed in the Results and Discussion sections of the present report.

Experimental

Steel carriers, coated with PVF/PMMA mixtures having nominal proportions of 0:100, 50:50 and 70:30 (carriers N, M with about 125 µm diameter, and P with about 95µm diameter respectively), were used to provide a range of carrier charging performance from negative to positive (with respect to the effect on toner charge). Two simple model toners (about 9 µm volume median diameter), based on two polymers and a single carbon black (toners TL and TH), were combined with the coated carriers to produce six two-component developers spanning the range from highly positive q/m to highly negative q/m. A hydrophobic 8nm "negative" fumed SiO2 was blended at 0, 0.1, 0.2, 0.4 and 0.6 wt% with the test toners to provide a wide range of additive coverage. (The SiO2 additive was applied to the toner via roll-milling in the presence of small steel mixing balls for 30 minutes. For toner TL, the test q/m data indicated effective additives levels of 0, 0.1, 0.2, 0.4 and 0.5 wt%; for toner TH, the effective levels were 0, 0.15, 0.25, 0.4 and 0.55 wt%).

The triboelectric charging performance of the 30 test developers was monitored via conventional total-blowoff q/m measurements taken during paint-shaker agitation of the samples. For all q/m tests, the toner concentration was set at 3 wt%, and the developers were conditioned at 16ºC/ 20% relative humidity overnight prior to agitation.
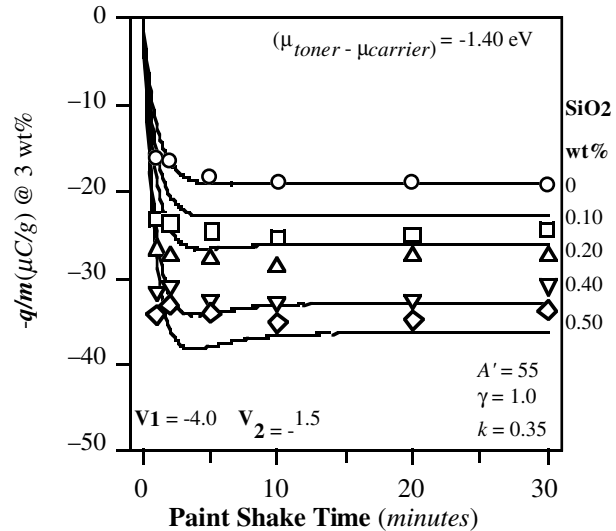

Figure 1. q/m @ 3wt%, for toner TL + carrier N at five levels of SiO2.

Results

Figures 1, 2 and 3 show typical data from toner TL with carriers N, M and P respectively. From the data taken with

the SiO_2-free base toner/carrier combinations, it is clear that q/m decreases monotonically as the PMMA content of the carrier coating increases. To a first-order, the data also show that toner TL is approximately triboelectrically "equivalent" to carrier M, since the developer based on this latter carrier generates a q/m value close to zero with toner TL.
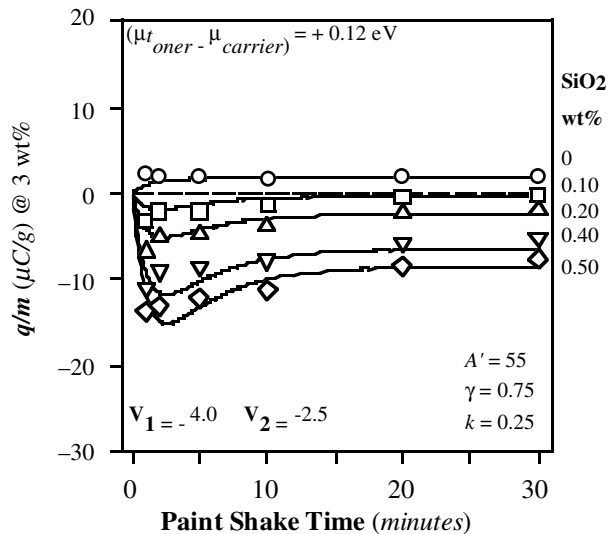

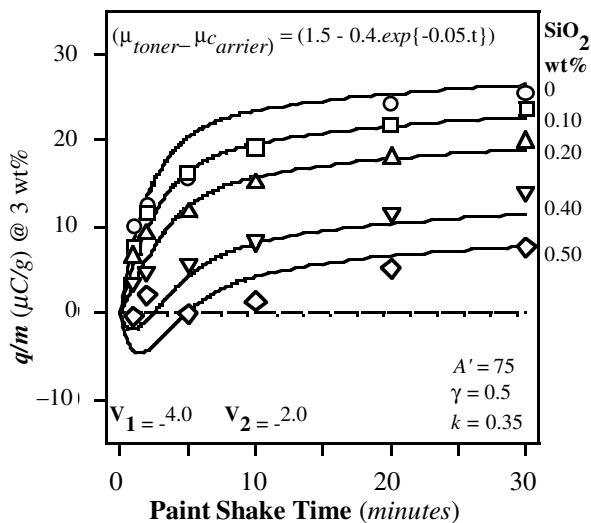Figure 2. q/m @ 3wt%, for toner TL + carrier M at five levels of SiO_2.

Figure 3. q/m @ 3wt%, for toner TL + carrier P at five levels of SiO_2.

As noted in the earlier Theory section, it should be possible to extend the data analysis through an application of Equation (5) to the entire data set. However, the actual experimental data show a more complex response to SiO_2 content than that predicted by Equation (5), and as discussed in an earlier report[24] the actual data can be viewed as the result of a progressive mixing-induced "loss" of tribo-electrically-effective SiO_2 from the surface of the test toners during the q/m-generating step. With this view, the factor P_{SiO2} decreases exponentially from an initial surface coverage Θ according to a relationship of the form:

$$P_{SiO2} = \Theta \cdot [1 - F \cdot (1 - exp\{-k \cdot t\})] \qquad (6)$$

where F is the fraction of SiO_2 "lost" after extended mixing, and k is the rate constant for the "loss" process. For a dispersed layer of SiO_2 on a toner surface, Θ will be a direct function of SiO_2 wt % content, and for the present materials, a direct geometric calculation based on the sizes and densities of the toner and SiO_2 yields:

$$\Theta = 1.7 \cdot SiO_2 \text{ wt\%} \qquad (7)$$

With Equations (6) and (7) substituted into Equation (5), the overall result can be expressed parametrically as:

$$
\begin{aligned}
q/m = &(A'/(C + C_0)) \\
&\cdot [V_1 \cdot \text{wt\%} - V_2 \cdot \text{wt\%} \cdot (1 - exp\{-k \cdot t\}) + V_3] \\
&\cdot (1 - exp\{-\gamma \cdot t\})
\end{aligned} \qquad (8)
$$

where

$$V_1 = 1.7 \cdot (\mu_{SiO2} - \mu_{toner}) \qquad (9)$$

$$V_2 = 1.7 \cdot (\mu_{SiO2} - \mu_{toner}) \cdot F \qquad (10)$$

and

$$V_3 = (\mu_{toner} - \mu_{carrier}) \qquad (11)$$

i.e., the q/m response of a toner plus SiO_2 can be viewed as a sum of a linear response with respect to SiO_2 level, a time-dependent response weighted by the SiO_2 level, and a base toner/carrier response.

From the physical properties of the present experimental carriers, $A' = 55$ for carriers N and M, $A' = 75$ for carrier P, and for the 9 µm test toners $C_0 \approx 1$. Using these assumed values, the five SiO_2 data sets for each charging experiment can be analyzed as a common set according to the parametric Equation (8).

For cases where $\gamma \gg k$, the analysis is fairly constrained with the initial q/m response being driven chiefly by V_1, V_3 and γ, and the long-time response being governed by k and V_2. However, for cases where the two rate constants are similar in magnitude, a range of parameter values can produce an excellent agreement between actual and predicted q/m values for all mixing times and all SiO_2 levels. Since small values of V_1 will underestimate the q/m-depressing effect of SiO_2, the non-linear curve-fitting procedure was arbitrarily set to find the lowest adequate value of V_1. (V_3, of course, is not a free variable since it is unambiguously given by the q/m value of the carrier + toner-only experiment. Note, also, that some of the test developers did not show a single saturating exponential q/m: mixing time response in the carrier + toner-only tests, and for these developers the ($\mu_{toner} - \mu_{carrier}$) term was given a mixing time-dependency of the form [$q_1 - q_2 \cdot exp\{-\delta \cdot t\}$]). From the deduced values of V_1, the assumption of $\mu_{SiO2} = 0$ was used to produce a deduced value for μ_{TL} and thence carrier values of μ_N, μ_M and μ_P.

For the data shown in Figures 1, 2 and 3 a common value of $V_1 = -4.0$ eV · wt%$^{-1}$ was found, and this leads to a common value of $\mu_{TL} = -(4.0/1.7) = +2.35$ eV, on a scale where μ_{SiO2} has been taken as zero. (This value of μ_{toner}, plus the $\mu_{carrier}$ values deduced from the carrier + toner-only tests was used to draw the predicted curves in Figures (1)-(3), with a single equation being used for each entire data set). By definition from Equation 1, a common value of μ_{toner} will produce a plot of ($\mu_{toner} - \mu_{carrier}$) vs. the corresponding deduced $\mu_{carrier}$ values with a linear slope of -1

and an intercept value of μ_{toner} on both ordinate and abscissa. The solid line in Figure 4 shows such a plot for the data from Figures 1, 2 and 3, and while this plot contains no new information it can be viewed as a simple geometric illustration of the concepts of a triboelectric series. For example, a "more positive" second toner, (e.g., toner TH), should produce a response parallel to that given by toner LT, with an intercept offset of ($\mu_{TH} - \mu_{TL}$). If the experimental data form a self-consistent triboelectric series, then this second prediction can be made in two ways: (a) values of μ_N, μ_M and μ_P obtained from the initial experiment with toner LT can be used to calculate a value of μ_{TH} from each value of ($\mu_{TH} - \mu_N$), ($\mu_{TH} - \mu_M$) and ($\mu_{TH} - \mu_P$) respectively, and the result should be a common value of μ_{TH}; (b) the new data can be analyzed (again using the assumption of $\mu_{SiO2} = 0$) to produce values of μ_{TH}, μ_N, μ_M and μ_P, with the expectation that the analysis will produce a common value for μ_{TH} from the three data sets, and carrier μ values that match those deduced in the initial experiments with toner TL.

Figures (5)-(7) show the experimental data taken with the second toner, TH along with the curves predicted from an analysis according to strategy (b). For this data set taken with toner TH, the analysis yields a common value of V_1 of -6.0 eV $\cdot$ wt%$^{-1}$. The deduced value of μ_{TH} is thus $-(-6/1.7)$ $= +3.53$ eV, as indicated by the upper dashed line in Figure (4), and subtraction of the ($\mu_{TH} - \mu_{carrier}$) values from the second set of experiments from μ_{TH} produces a new set of predicted mcarrier values, as indicated on the dashed line.
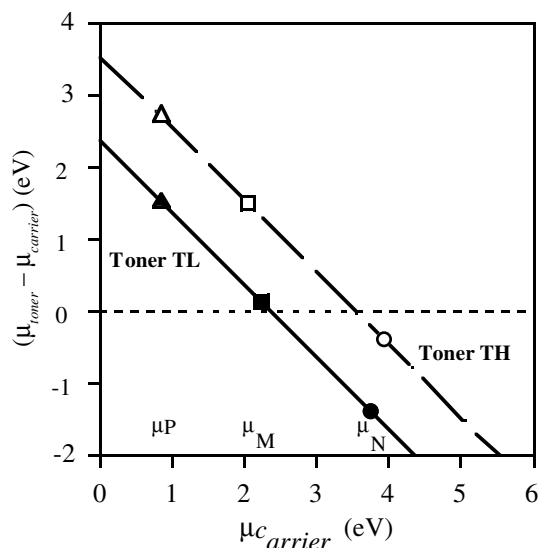

Figure 4. ($\mu_{toner} - \mu_{carrier}$): $\mu_{carrier}$, for toners TL and TH with three carriers N, M and P.

Discussion

As can be seen from Figure 4, the values of $\mu_{carrier}$ deduced from the two sets of data agree within 5 to 10% for any particular carrier, and each test toner gives an internally consistent data set (as judged by the common deduced values for μ_{toner}). Thus, in principle, it should be possible to predict the q/m value of any combination of toner and carrier in the present set, at any fixed concentration of SiO$_2$. However, in practice, the individual mixing time depen-

dencies create complex q/m: mixing time responses, and these non-linear q/m responses tend to obscure the basic similarities of the various test results. At long-mixing times, however, most of the mixing-induced changes have decayed to zero, so that at long mixing times q/m can be predicted to be a simple direct function of SiO$_2$ wt%, according to:

$$q/m = V_1 \cdot (1 - F) \cdot \text{wt\%} \qquad (12)$$

It might be assumed, therefore, that the effect of SiO$_2$ on q/m might be most readily gauged from single-point q/m data taken after extended mixing. However, such limited data will contain a "hidden" $(1 - F)$ factor, so that q/m: SiO$_2$ dependencies deduced from such single-point data will actually be an unknown fraction of the actual dependency. (Conceptually, single-point q/m measurements taken at short mixing times should more accurately reflect the magnitude of the toner/SiO$_2$ interactions, but since these data can also be affected by opposing "charging-up" and "SiO$_2$-loss" factors, they may also yield a "modified" q/m: SiO$_2$ relationship).
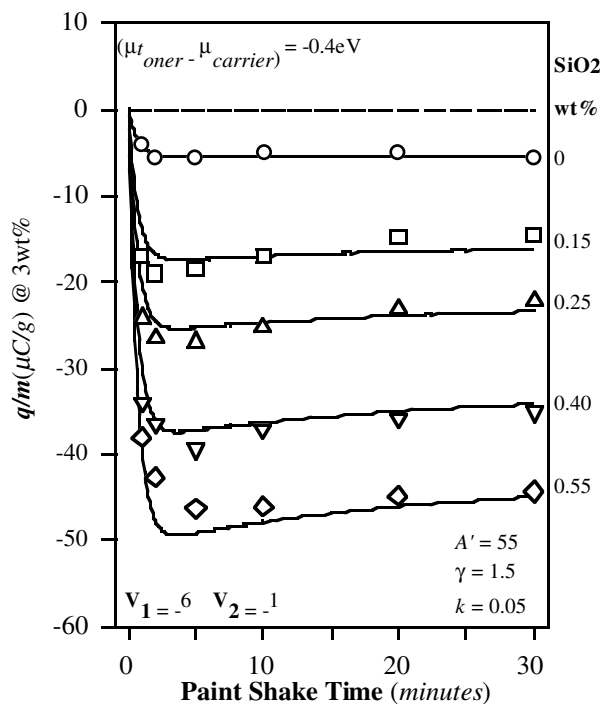

Figure 5. q/m @ 3wt%, for toner TL + carrier N at five levels of SiO$_2$.

The data taken after extended mixing do, however, provide a convenient visual demonstration of the concepts of a triboelectric charging series. For example, while the data in Figures 5 and 6 are from a negative and positive developer, respectively, the q/m data taken after 30 minutes of mixing over a range of SiO$_2$ content can be brought into coincidence by a simple linear "shift" in the q/m values. For example, if 25 μC/g is subtracted from each "30 minute" q/m value in Figure 6, then the "shifted" data set matches that of Figure 5. For these two sets of data, the 25 μC/g value reflects the difference between the $\mu_{carrier}$ values of the two carriers. In fact, since the data in Figures 5 and 6 follow a similar non-linear response to mixing (i.e., similar values for γ, k and F), the data can also be shifted into

coincidence at any particular mixing time—when the carrier + toner-only data are matched, the carrier + toner/SiO$_2$ data (at all SiO$_2$ levels) will also be brought into coincidence. This illustrates that the toner/SiO$_2$ interaction is independent of carrier type and developer polarity for the present test materials.
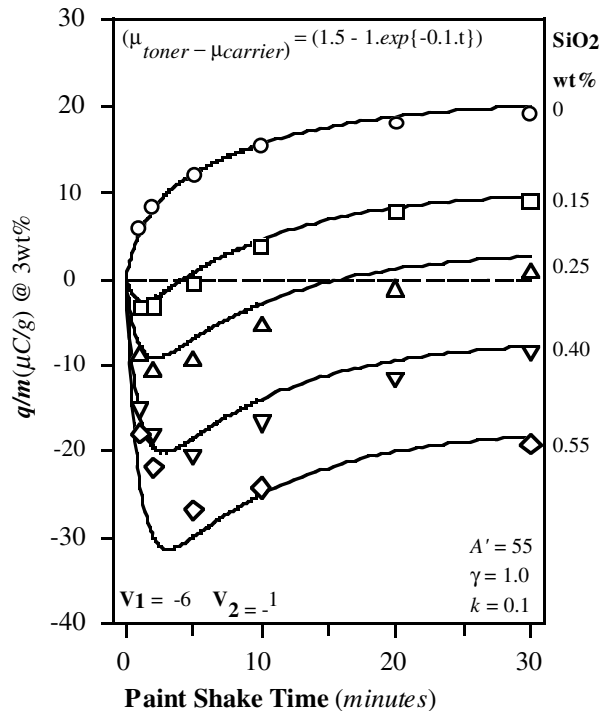

Figure 6. q/m @ 3wt%, for toner TL + carrier M at five levels of SiO$_2$.

The experimental data shown in Figures 1-3 and 5-7 graphically show the increased sensitivity of *q/m* to SiO$_2$ content driven by the high value of $(\mu_{SiO2} - \mu_{toner})$ for toner TH. Additionally, analysis of the data shows that toner TH is largely free of any SiO$_2$ "loss" process—the observed non-linear *q/m* data for developers based on this toner plus SiO$_2$ actually appear to reflect non-linearizes in the charging-up behavior of the base carrier + toner-only developer).

With regard to carrier effects, the data from carriers N,M and P illustrate a subtle effect of carrier size on developer properties. Thus, the slightly reduced size of carrier P creates an increase in the *A'* factor from 55 to 75, so that the *q/m* values generated with carrier P all reflect Δμ terms multiplied by a pre-factor of 75 instead of the 55 value characteristic of carriers N and M. Thus, the *q/m*: SiO$_2$ responses shown in Figures 3 and 7 are somewhat larger than would be expected based on data taken with carriers N and M.

The above results, then, illustrate some of the experimental difficulties present in all *q/m* measurements, with especial emphasis on their relevance to the generation of a triboelectric charging series based on *q/m* measurements. Some additional potential problems include:

- Multiple external and/or internal additives, or mobile additives: Clearly, the *q/m* response of a complex developer design[17] will reflect multiple interactions, and the resultant *q/m* values may appear inconsistent with any simple triboelectric series concept.
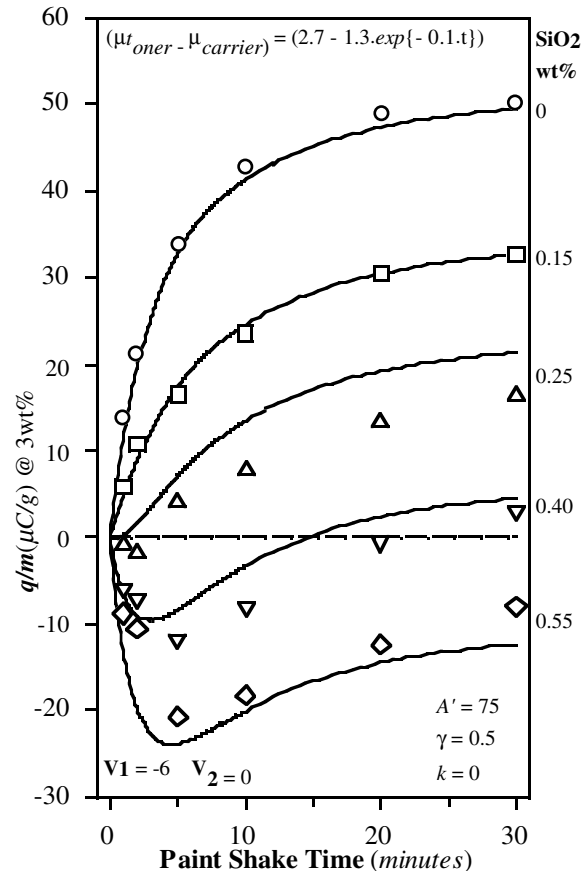

Figure 7. q/m @ 3wt%, for toner TL + carrier P at five levels of SiO$_2$.

Also, the transfer of charge control species or filming external additive from a toner to a carrier can create highly complex *q/m* relationships,[24] and the effect may differ as carrier type is varied.[30] In a related manner, if the charging properties of external additives are altered by chemical treatments (e.g., "positive" SiO$_2$'s),[22] then mixing-induced carrier contamination will occur if the surface treatments are somewhat labile. For such cases, the "as measured" *q/m* data can show great apparent anomalies e.g., "reversals" in *q/m*:toner concentration or *q/m*: SiO$_2$ content relationships.

- Ambient effects: The *q/m* values of many xerographic developers show a marked response to changes in ambient humidity, and data taken under variable conditions will show poor reproducibility.
- Carrier effects: Xerographic carriers can be obtained with a wide range of sizes, surface textures, and coatings. While such differences can be creatively used to "adjust" the triboelectric properties of a developer, they can be potential sources of confusion for any test of triboelectric charging theories.

In summary, deconvoluted of the present experimental data set allowed the data to be described in terms of a self-consistent triboelectric charging series. The data also provided a comprehensive assessment of the effect of "negative" SiO$_2$ on the *q/m* properties of a wide range of

developers, and showed that both positive and negative polarity developers share a common response. The concept of using a negative polarity SiO$_2$ as a reference probe in q/m studies appears to have great merit in careful charging studies; for casual "single-point" q/m measurements, however, the potential q/m variability as a function of mixing dynamics make SiO$_2$-based toners a poor choice for systematic studies. Additionally, because of various counterbalancing charging effects, as evident in charging equations such as Equation 8, a "goodness-of-fit" criterion does not necessarily indicate "correctness-of-fit"—any single set of experimental data can be fitted by several possible values for the sets of controlling factors. As a corollary, it is clear that experimental q/m values can be significantly altered by small changes in key factors.

Finally, while triboelectric charging theories are almost invariably limited to an analysis of average q/m values, the functional performance of commercial xerographic developers is often affected more by the distribution of toner charging properties rather than any average value. In particular, the rate at which a charged developer can provide charge to added uncharged toner (the so-called "admix rate") can strongly affect the level of development of xerographic background particles, and while the q/m level and polarity of a toner can be simply adjusted via changes in carrier coating chemistry, these changes may adversely affect the admix rate of the resultant developers.[31]

References

1. J. Lowell and A. C. Rose-Innis, *Adv. Phys.*, **29**, 947, (1980).
2. P. C. Julien, in *Carbon Black-Polymer Composites*, ed. E. K. Sichel (Marcel Dekker, NY), p. 189, (1982).
3. J. Henniker, *Nature*, **196**, 474, (1962).
4. D. M. Pai and B. E. Springett, *Rev. Mod. Phys.*, **63**, (1), 163, (1993).
5. US Patent 5,314,777.
6. US Patent 5,379,097.
7. US Patent 3,893,935.
8. US Patent 5,069,994.
9. US Patent 4,206,064.
10. US Patent 4,985,327.
11. US Patent 4,762,763.
12. US Patent 5,483,327.
13. US Patent 5,480,757.
14. US Patent 4,737,435.
15. US Patent 5,376,493.
16. US Patent 5,478,687.
17. US Patent 5,120,631.
18. US Patent 4,929,528.
19. US Patent 5,340,677.
20. US Patent 4,989,044.
21. US Patent 5,464,720.
22. US Patent 4,902,570.
23. US Patent 5,024,915.
24. R. J. Nash, S. M. Silence and D. N. Muller, *10th. Intl. Cong. on Adv. in Non-Impact Printing Technol.*, A. Melnyk, ed., IS&T, Springfield VA, 95, (1994); (see page 169, this publication).
25. A. Stubbe, *7th. Intl. Cong. on Adv. in Non-Impact Printing Technol.*, K. Pietrowski, ed., IS&T, Springfield VA, 241, (1991).
26. A. R. Gutierrez, H. J. Nguyen and A. F. Diaz, *8th. Intl. Cong. on Adv. in Non-Impact Printing Technol.*, E. Hanson, ed., IS&T, Springfield VA, 122, (1992).
27. A. C-M. Yang and C-Yu Chou, *11th. Intl. Cong. on Adv. in Non-Impact Printing Technol.*, J. Anderson ed., IS&T, Springfield VA, 130, (1995); (see page 230, this publication).
28. E. J. Gutman and G. C. Hartmann, *J. Imaging Sci. and Technol.*, **36**, (4), 335, (1992).
29. J. H. Anderson, *J. Imaging Sci and Technol.*, **38**, (4), 378, (1994); (see page 189, this publication).
30. US Patent 4,789,614.
31. P. C. Julien, *8th. Intl. Cong. on Adv. in Non-Impact Printing Technol.*, E. Hanson, ed., IS&T, Springfield VA, 102, (1992).