

A Model Analysis of the Triboelectric Charging of Fumed Silicas

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Abstract

Nano-sized (e.g., 7nm primary particle size) fumed silica particles typically exhibit an ultra-high negative triboelectric charge-to-mass ratio (q/m) when agitated with micron-sized (e.g., 50 to 100 μ diameter) carrier beads. Micron-sized toner particles (e.g. 5 to 9 μ diameter) also exhibit an increasingly negative charge when fumed silica particles are applied as external additives to their surface.

In this present report, a quantitative analysis of triboelectric charging data from mixtures of fumed silica particles and carrier beads is presented, based on a mechanistic model for triboelectric charge generation. The model is also used to illustrate the connection between the triboelectric charging properties of fumed nano-sized silica particles and the charge level of external additive micron-sized toners

Introduction

Conventional fumed silica particles typically impart a high negative polarity to micron-sized toner particles. Since such fumed silica particles intrinsically charge to an extremely high negative level, the increase in the measured blow-off triboelectric charge of surface-additive toner particles might merely reflect independent contributions from toner and silica particles. However, complementary charge spectra measurements indicate that the intrinsic negative charge level of toner particles is increased when nano-sized fumed silica particles are blended onto the surface of the toner particles — the toner charge spectrum shows a single narrow peak that moves to an increased negative charge level for the toner particles that are coated with surface additives [1]. Essentially, therefore, fumed silica additives act as particulate sources of negative charge at the toner surface, thereby increasing the overall negative charge of the toner particles.

Theory

The triboelectric model of Gutman and Hartmann [2] provides a useful mechanistic description in terms of both the physics and chemistry of charging, and has been successfully used to analyze a wide variety of experimental triboelectric charging data [2-12].

For a stable well-mixed, two-component toner/carrier developer mixture, the model indicates that the equilibrium toner charge to mass ratio q/m , in units of $\mu\text{C/g}$, will be given by:

$$q/m = \left(\frac{A'}{(C + C_0)} \right) \cdot (\phi_{\text{toner}} - \phi_{\text{carrier}}) \quad (1)$$

where ϕ_{toner} and ϕ_{carrier} are the characteristic charging energy factors for the toner particles and carrier beads, respectively, in units of eV, and C is the weight percent toner concentration (i.e., 100· (toner weight / carrier weight)).

For any particular xerographic carrier bead, the pre-factor constant A' can be approximated in units of $\mu\text{C}\cdot\text{g}^{-1}\cdot\text{eV}^{-1}$ as:

$$A' = \left(\frac{4\pi R^2 \epsilon_0}{\text{Med}} \right) = \frac{3\epsilon_0}{ed\rho R} \quad (2)$$

where R is the carrier bead radius, ρ is the carrier bead density, ϵ_0 is the permittivity of free space, M is the mass of a carrier bead, e is the electronic charge, and d is the tunneling distance for charge exchange.

For any particular toner/carrier pair, C_0 is a weight percent constant, given approximately by:

$$C_0 = \left(\frac{\rho_{\text{toner}} \cdot r_{\text{toner}}}{\rho_{\text{carrier}} \cdot R_{\text{carrier}}} \right) \cdot 100 \quad (3)$$

where ρ_{toner} and ρ_{carrier} are the toner and carrier densities in g/cc, and r_{toner} is the toner particle radius.

Thus, the A' constant in Equation 1 is a function of carrier bead size and density, while the C_0 term is a function of the size and density of both the carrier beads and toner particles.

For a two-component xerographic developer based on iron carrier beads having a density of 7.8 g/cc and toner particles having a density of 1.2 g/cc, Table 1 lists the A' and C_0 values calculated from Equations 2 and 3 for typical carrier and toner sizes, and Table 2 gives these values for xerographic developers based on ferrite carrier beads with a density of 4.98 g/cc. Note that ferrite carrier beads are predicted to give higher A' and C_0 values than iron carrier beads, for any particular size combination of carrier bead and toner particles.

Carrier Dia. (μ)	A' ($\mu\text{C}\cdot\text{g}^{-1}\cdot\text{eV}^{-1}$)	C_0 (wt%)		
		9 μ toner	7 μ toner	5 μ toner
100	70	1.4	1.1	0.8
65	110	2.1	1.7	1.2
35	200	4.0	3.1	2.2

Table 1. Calculated A' and C_0 values for xerographic developers based on iron carrier beads ($\rho=7.8$ g/cc) and polyester toner particles ($\rho=1.2$ g/cc).

Carrier Dia. (μ)	A' (μC.g ⁻¹ .eV ⁻¹)	C ₀ (wt%)		
		9 μ toner	7 μ toner	5 μ toner
100	110	2.2	1.7	1.2
65	170	3.3	2.6	1.9
35	315	6.2	4.8	3.4

Table 2. Calculated A' and C₀ values for xerographic developers based on ferrite carrier beads (ρ=4.98 g/cc) and polyester toner particles (ρ=1.2 g/cc).

While the above triboelectric charging model calculations are based on conventionally-sized toner/carrier two-component xerographic developers, the charging model has general applicability. For example, the model can also be used to analyze the triboelectric charging performance of nano-sized particulate external toner additives, as illustrated in the following sections of this present report.

Experimental

A Technical Information Report, TI 1222, published by Nippon Aerosil Co., Ltd., lists the physical and triboelectric properties of a wide range of hydrophobic fumed silica particles [13]. (See also [14–16]).

For the triboelectric charge evaluations listed in the TI 1222 report, 0.1g samples of fumed silica were mixed in a Turbula mixer (e.g., for 30 seconds, at 25°C/45% relative humidity) with 50g of iron and ferrite-based carrier beads, and Table 3 lists representative results:

#	AEROSIL® grade	q/m iron (μC/g)	q/m ferrite (μC/g)	Surf. Ctg.	size (nm)
1	R972	-1340	-857	DDS	16
2	R974	-1351	-825	DDS	12
3	RY50	-371	-253	DMPS	40
4	NY50	-867	-526	DMPS	30
5	RY200S	-1266	-951	DMPS	16
6	RY200	-1079	-668	DMPS	12
7	R202	-1518	-1041	DMPS	16
8	RX50	-838	-516	HMDS	40
9	NAX50	-1109	-781	HMDS	30
10	RX200	-1434	-796	HMDS	12
11	R8200	-839	-393	HMDS	12
12	RX300	-1450	-892	HMDS	7
13	R812	-1651	-1203	HMDS	7
14	R812S	-1478	-905	HMDS	7
15	R805	-1145	-653	RS	12
16	R104	-1373	-657	D ₄	12
17	R106	-1530	-794	D ₄	7

Table 3. Experimental triboelectric charge values for a range of fumed silicas charged against iron and ferrite-based carrier beads (data from report TI 1222). The surface treatments are:

DDS = dimethyldichlorosilane; DMPS = dimethylpolysiloxane;

HMDS = hexamethyldisilazane; RS = alkylsilane;

D₄ = octamethylcyclotetrasiloxane

Clearly, the *q/m* values obtained when fumed silica particles are used as “toners” in a two-component xerographic developer are one hundred times higher than the *q/m* values typically generated by conventional toner/carrier pairs. However, since fumed silica particles have surface areas of 50 to 300 m²/g (cf. toner particles with surface areas of 1 m²/g or less), the fumed silica charge behavior is actually not excessive when expressed in terms of charge per unit area. For example, a *q/m* of −30 μC/g for a 7μ toner (geometric surface area = 0.7m²/g) translates to about 3.10¹⁰ electrons/cm², while a *q/m* value of −1478 μC/g for the R812S fumed silica (geometric surface area = 390 m²/g) translates to about 2.10⁹ electrons/cm², and a *q/m* value of −371 μC/g for the RY50 fumed silica (geometric surface area = 70 m²/g) translates to about 3.10⁹ electrons/cm².

Data Analysis

Triboelectric Charging of Fumed Silica

For nano-sized silica particles on micron-sized carrier beads, Equation 3 predicts a zero value for the C₀ term in Equation 1. Therefore, for any individual sample of SiO₂, the triboelectric charge generated from 0.1g of SiO₂ agitated with 50g of iron carrier beads will be:

$$q/m_{\text{silica/iron}} = \left(\frac{A'_{\text{iron}}}{\frac{0.1}{50} \cdot 100} \right) \cdot (\phi_{\text{silica}} - \phi_{\text{iron}}) \quad (4)$$

Similarly, for the same SiO₂ sample, the triboelectric charge generated from 0.1g of SiO₂ agitated with 50g of ferrite carrier beads will be:

$$q/m_{\text{silica/ferrite}} = \left(\frac{A'_{\text{ferrite}}}{\frac{0.1}{50} \cdot 100} \right) \cdot (\phi_{\text{silica}} - \phi_{\text{ferrite}}) \quad (5)$$

Eliminating the ϕ_{silica} term from between these two equations, yields:

$$q/m_{\text{silica/ferrite}} = \left(\frac{A'_{\text{ferrite}}}{A'_{\text{iron}}} \right) \cdot q/m_{\text{silica/iron}} - \left(\frac{A'_{\text{ferrite}}}{\frac{0.1}{50} \cdot 100} \right) \cdot (\phi_{\text{ferrite}} - \phi_{\text{iron}}) \quad (6)$$

Figure 1, (see next page) is a plot of ferrite-charged versus iron-charged *q/m* values for each individual SiO₂ sample listed in Table 3, and the zero intercept value indicates that $\phi_{\text{ferrite}} = \phi_{\text{steel}}$ for the data set. As a result,

$$\frac{q/m_{\text{silica/ferrite}}}{q/m_{\text{silica/iron}}} = \frac{A'_{\text{ferrite}}}{A'_{\text{iron}}} = \left(\frac{\rho_{\text{iron}}}{\rho_{\text{ferrite}}} \cdot \frac{R_{\text{iron}}}{R_{\text{ferrite}}} \right) \quad (7)$$

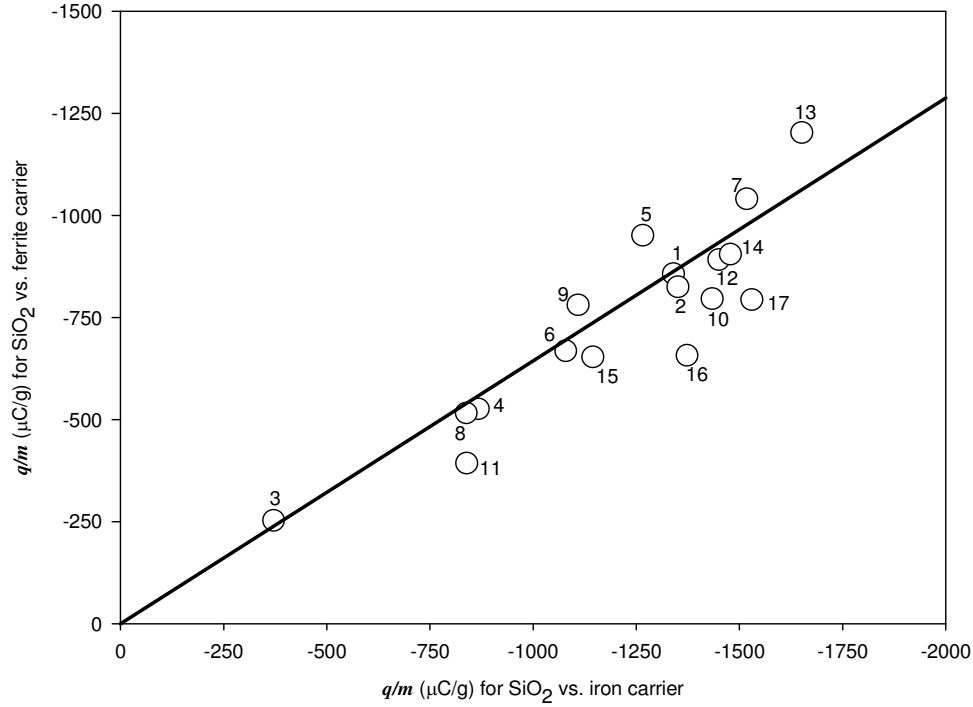


Figure 1. Ferrite-charged versus iron-charged q/m values for each individual SiO_2 sample listed in Table 3. The number labels correspond to the sample numbers listed in Table 3.

With assumed values of $\rho_{\text{iron}} = 7.8 \text{ g/cc}$ and $\rho_{\text{ferrite}} = 4.98 \text{ g/cc}$, a slope value of 0.644 for the data plot indicates a $R_{\text{iron}}/R_{\text{ferrite}}$ ratio of 0.41, i.e., if the test iron carrier has a diameter of 50μ then the test ferrite carrier diameter (assuming equivalent spherical morphology) is predicted to be 122μ . (The predicted carrier size ratio, of course, is dependent on the assumed carrier density values — for a low density atomized or sponge iron carrier/ferrite carrier combination, the predicted size ratio will be closer to 1).

In general, for comparison with experimental SiO_2 :carrier triboelectric charging data, Equations 4 and 5 cannot provide a unique theoretical prediction for q/m since they contain two unknown factors, namely ϕ_{silica} and ϕ_{carrier} . However, as shown in Table 3, R812S generates an exceptionally high negative charge, and it is therefore convenient to assign a reference value of 0 eV to ϕ_{R812S} , so that factors such as ϕ_{carrier} and ϕ_{silica} can be deduced from experimental q/m values.

For example, based on an assumed reference value of 0 eV for ϕ_{R812S} , and an experimentally-determined q/m of $-1478 \mu\text{C/g}$ for a 0.2wt% mixture of R812S and a 50μ iron carrier:

$$-1478 = \left(\frac{140}{(0.2 + 0)} \right) \cdot (0 - \phi_{\text{iron}})$$

which yields $\phi_{\text{iron}} = 2.1 \text{ eV}$.

Similarly, from a q/m of $-905 \mu\text{C/g}$, determined experimentally for a 0.2wt% mixture of R812S and a 122μ ferrite carrier:

$$-905 = \left(\frac{90}{(0.2 + 0)} \right) \cdot (0 - \phi_{\text{ferrite}})$$

which yields $\phi_{\text{ferrite}} = 2.0 \text{ eV}$.

Accordingly, $\phi_{\text{carrier}} = 2 \text{ eV}$ can be used for the entire present experimental data set (coupled with assumed carrier sizes of 50 and 122μ , and 7.8 and 4.98g/cc densities).

Triboelectric Charging of Toners with External Additives

For toners coated with external particulate additives such as fumed silica, the ϕ_{toner} term in Equation 1 can be expressed in terms of area-weighted contributions from the base toner material and from the external additive coating [3-4]. For a fractional additive coverage, Θ , the ϕ_{toner} term becomes:

$$\begin{aligned} \phi_{\text{toner}} &= \mu_{\text{silica}} \cdot \Theta + \mu_{\text{base toner}} \cdot (1 - \Theta) \\ &= \Theta \cdot (\mu_{\text{silica}} - \mu_{\text{base toner}}) + \mu_{\text{base toner}} \end{aligned} \quad (8)$$

where μ_{silica} and $\mu_{\text{base toner}}$ are characteristic charging factors for the respective surface types.

For toners based on external additives, then, Equation 1 becomes:

$$q/m = \left(\frac{A'}{(C+C_0)} \right) \cdot (\theta \cdot (\mu_{\text{silica}} - \mu_{\text{base toner}}) + \mu_{\text{base toner}} - \phi_{\text{carrier}}) \quad (9)$$

If $\mu_{\text{silica}} < \mu_{\text{base toner}}$, then the surface additive will reduce the ϕ_{toner} term, thereby changing q/m to a more negative value.

For a toner coated with a **monolayer** of SiO_2 additive, Equation 9 becomes:

$$q/m = \left(\frac{A'}{(C+C_0)} \right) \cdot (\mu_{\text{silica}} - \phi_{\text{carrier}}) \quad (10)$$

For the case of a toner totally coated with a highly-negative SiO_2 such as R812S, the q/m value can be used to deduce ϕ_{carrier} , using $\mu_{\text{R812S}} = 0$ eV as a defined reference value. (Note: while this is the same strategy as that used in the analysis of the silica/carrier charging data set, the $(C+C_0)$ term in Equation 10 will reduce the q/m value for the additive-coated toner greatly below that given by an equivalent silica/carrier pair).

Using the deduced value for ϕ_{carrier} obtained from an external additive toner/carrier test, the q/m value of base additive-free toner particles mixed with carrier beads can then be used to deduce a value for $\mu_{\text{base toner}}$:

$$q/m = \left(\frac{A'}{(C+C_0)} \right) \cdot (\mu_{\text{base toner}} - \phi_{\text{carrier}})$$

so that:

$$\phi_{\text{base toner}} = \mu_{\text{base toner}} = q/m \cdot \left(\frac{(C+C_0)}{A'} \right) + \phi_{\text{carrier}} \quad (11)$$

For 7μ toner particles triboelectrically charged against 50μ iron carrier beads at a 3wt% toner concentration, typical parameters are:

$$A' = 140 \mu\text{C} \cdot \text{g}^{-1} \cdot \text{eV}^{-1} \quad C_0 = 2.2 \text{ wt\%} \quad C = 3 \text{ wt\%} \\ \phi_{\text{toner}} = 1.5 \text{ eV} \quad \phi_{\text{carrier}} = 2.0 \text{ eV}$$

and q/m for the additive-free toner particles becomes:

$$q/m = \left(\frac{140}{(3+2.2)} \right) \cdot (1.5 - 2.0) \\ = -13.5 \mu\text{C/g}$$

By contrast, if a **monolayer** of highly-negative SiO_2 (e.g. R812S) is applied to the toner particles, then $\phi_{\text{toner}} = 0$ eV, and the q/m value of the surface-treated toner particles becomes:

$$q/m = \left(\frac{140}{(3+2.2)} \right) \cdot (0 - 2.0) \\ = -54 \mu\text{C/g}$$

i.e., the negative toner charge is increased by a factor of 4.

Unfortunately, the above strategy for increasing the negative charge level of a toner can lead to an unstable loss of charge. For example, mechanical stresses in a xerographic development module can lead to a usage-induced “burial” of particulate external additives into the sub-surface of toner particles, and thereby produce a reduction in the overall triboelectric charging ability of toner particles (effectively, the toner charge properties decline towards that of the base toner). This can be a particularly critical problem for high-speed xerographic printers, where the toner residence time in the development module can vary widely in response to the type of image being printed — a transition from long-term text prints to full-pictorial prints can be a stress condition, with unaged dispensed toner being abruptly added to a developer that contains “aged” toner. Typically, usage-induced “loss” of toner surface additives is a first-order kinetic process, so that the highest rate of additive loss occurs during the initial time of toner “aging”, i.e., at any toner “aging” time t , the effective additive surface coverage θ_t will be given by:

$$\theta_t = \theta_0 \cdot (1 - F \cdot (1 - \exp\{-k \cdot t\})) \quad (12)$$

where θ_0 is the time-zero additive coverage, F is the long-term fractional loss of additive and k is the rate constant for the loss process.

As shown in Equation 8, the effect of additive “loss” on q/m can be minimized via a reduction in the mismatch between the μ_{silica} and $\mu_{\text{base toner}}$ values. For example, the data in Table 3 indicate that the RY50 fumed silica is less triboelectrically-active than the highly negative R812S silica. In terms of μ_{silica} , the deduced value for μ_{RY50} is 1.46 eV, based on an assumed value of 0 eV for μ_{R812S} .

Accordingly, for 7μ toner particles charged against a 50μ iron carrier at a 3 wt% toner concentration:

$$q/m = \left(\frac{140}{(3+2.2)} \right) \cdot (1 \cdot (1.46 - 1.5) + 1.5 - 2.0) \\ = -14.5 \mu\text{C/g}$$

for toner particles coated with a **monolayer** of RY50 silica, and this value is close to the $-13.5 \mu\text{C/g}$ predicted for an additive-free toner.

Similarly, for 7μ toner particles charged against a 122μ ferrite carrier at a 3 wt% toner concentration:

$$q/m = \left(\frac{90}{(3+1.38)} \right) \cdot (1 \cdot (1.46 - 1.5) + 1.5 - 2.0) \\ = -11.1 \mu\text{C/g}$$

for toner particles coated with a **monolayer** of RY50 silica, and this is close to the $-10.3 \mu\text{C/g}$ value predicted for additive-free toner.

As evident from the above calculations, the choice of SiO_2 -type can greatly affect the overall triboelectric charge level and charge stability of toner particles based on external additives. It must be noted, however, that the present results are not universally applicable. For example, toner charge enhancement created via external additives is governed by the surface coverage θ of any particular additive **and** by the term $(\mu_{\text{silica}} - \mu_{\text{base toner}})$. Accordingly,

a change in the value of $\mu_{\text{base toner}}$ (e.g., via a change in the toner binder-resin type, in colorant type or level, or by the addition of an internal charge control agent) can also affect the triboelectric charge level and charge stability of a toner based on an external additive. Likewise, extrinsic effects such as a change in the ambient humidity may also affect toner charging by altering the values of key intrinsic xerographic developer properties such as μ_{silica} , $\phi_{\text{base toner}}$ and ϕ_{carrier} .

In general, of course, an external toner additive can be applied at a sub-monolayer coverage, in order to reduce the overall toner charge level and the absolute magnitude of any usage-induced decrease in charging performance. In this regard, since the primary particle size of the RY50 silica is 40 nm and is 7 nm for the R812S silica, a monolayer of these silicas on a 7 μ toner particle will require an additive level of 3.8 wt% and 0.67 wt%, respectively.

Finally, a stable external additive toner based on the highly-negative R812S silica can be achieved if the base toner is highly-negative. For example, if $\mu_{\text{base toner}}$ is set at 0.1 eV (e.g., via the addition of a negative charge control agent to the toner bulk), then the q/m value for 7 μ toner particles charged against a 50 μ iron carrier at a 3 wt% toner concentration will be:

$$q/m = \left(\frac{140}{(3 + 2.2)} \right) \cdot (0.1 - 2.0) \\ = -51 \mu\text{C/g}$$

for base toner particles, and this value is close to the $-54 \mu\text{C/g}$ predicted for toner particles coated with a **monolayer** of R812S silica. For this highly-negative toner, therefore, q/m will be maintained even if there is a usage-induced “loss” of surface SiO_2 .

Similarly, a high value of toner q/m created via an increased value for μ_{carrier} — e.g., via the use of a N- based carrier coating — will partially stabilize toner q/m by moderating the effect of the Θ , $\mu_{\text{base toner}}$ and μ_{silica} terms on the expression:

$$(\Theta \cdot (\mu_{\text{silica}} - \mu_{\text{base toner}}) \pm \mu_{\text{base toner}} - \mu_{\text{carrier}})$$

Conclusion

As demonstrated in this present report, a simple mechanistic model for the triboelectrification of a two-component xerographic developer can provide an internally-consistent, quantitative analysis of the effect of external additives on toner charging. Beyond the experimental data cited in this present report, the model is applicable to a wide range of toner charging processes, and could be profitably used to provide a quantitative analysis of the many qualitative experimental studies that are presented at NIP conferences.

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Biography

Robert Nash received his Ph.D. in Physical Chemistry from the University of Bristol, England. He joined the Xerox Corporation in 1970. From 1998 until the end of 2000 he 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.