Treated Metal Oxide Additives for Toner Tribocharge Control

Joachim K. Floess, Cabot Corporation, 700 E. US Highway 36, Tuscola, IL 61953, Dmitry Fomitchev, Hairuo Tu, Jinsong Liu, Alyson Christopher, and William Williams, Cabot Corporation, Business and Technology Center, 157 Concord Road, Billerica, MA 01821

Abstract

The tribo-charge performance of treated silicas made from a selection of different aqueous colloidal silicas and treated with several different silanes is shown to be principally a function of the logarithm of the water partial pressure during development. However, no correlation between the tribo-charge behavior and the silica surface water concentration was found. Surface treatment with silanes containing certain ionizable functional groups can have a dramatic impact on tribo-charge behavior that differs significantly from treatment with only simple alkane-type silanes. A series of SEM micrographs is also presented, which show that the treated colloidal silicas fully retain their original size and shape and that the silica particles have excellent dispersibility and adhesion to the toner particle.

Introduction

Treated metal oxide particles are used in toner formulations to improve free flow, provide anti-blocking, and as a release aid. In addition, the oxide particles can substantially affect the tribo-charging characteristics of the toner. Of particular interest to formulators is the ability to adjust the charge level, deliver rapid and uniform charge development, and for the charge to be minimally affected by environmental temperature and humidity conditions. This list of requirements presents a significant set of challenges to additive manufacturers, particularly given that the physics both of free flow and tribo-charging remains poorly understood. These topics have been long standing research problems. Schein [1] has summarized the current understanding of several mechanistic features of the tribo-charge process; however, it is still not possible to relate tribo-charge performance to the material properties of the toner and carrier. Even less understood is the role of additives on the tribo-charge characteristics of the toner. Schein did not address this 'three body problem,' but studies by other investigators [2] have attempted to correlate the tribo-charging of silica-toner mixtures with the moisture content of the (treated) silica additive.

Recently, Cabot Corporation has introduced a new series of treated colloidal silica particles [3, 4] that provide a much wider range of particle sizes, particle morphologies, and treatment chemistries than have been available previously. In this paper, we present the results of several analytical measurements that we have made in an effort to elucidate new insights into the principal factors that may impact the tribo-charge behavior and performance of this new class of silica additives. We show that the tribo-charge performance can be correlated in a fairly simple way and that it is determined principally by the water partial pressure during development. We also show that it is possible to make additives that are less humidity sensitive through surface treatment with silanes having ionizable functional groups.

In particular, this study attempted to address the following questions:

1. Is there a relationship between tribo-charge performance and the silica surface moisture? What is the affect of the surface moisture concentration on tribo-charge? How do the type of surface treatment and the particle surface area affect tribo-charge?
2. How is the additive distributed on the toner particle, and what is the history of the additive as it is blended with toner, charged, and separated from the carrier?

Experimental

Tribo-charge measurements were done using a Vertex T-150 blow-off tribo-charger. Samples were prepared by mixing 4 wt% of the treated colloidal silica with a 9 µm pulverized styrene-acrylic toner. The additive loading was held constant independent of the additive size. (At 4 wt% loading, 55 µm spherical particles will give a theoretical coverage of 100%.) No other additive was used. The additive and toner were mixed for 3 minutes using a householder blender that was pulsed at 5 s intervals, so as to avoid overheating the toner. The toner/silica mixture was then rolled for 1 hr. A sample of the rolled toner was put in a glass jar containing a Cu-Zn ferrite carrier coated with a silicone resin at 2 wt% toner loading. The jar was placed in a humidity chamber overnight. HH conditioning was done at 30 ºC and 80% RH; HL at 27 ºC and 20% RH; and LL at 18 ºC and 20% RH. After conditioning, the sample jar was closed with a plastic cap and rolled for 30 minutes. The samples were tested immediately after rolling.

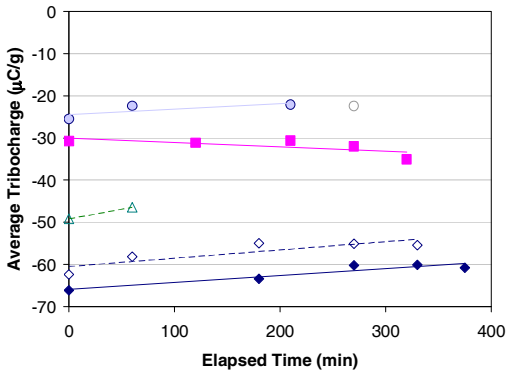

Figure 1. *Change in tribocharge with time; ◊ -LL; □ -HH; Δ -NN; o -bare toner at NN. Open symbol – open grounded pan; closed symbol – closed jar.*

For the bare toner and for one silica (HMDZ treated, 75 m^2/g type 1colloidal silica) - toner mixture, a subsequent series of tribo-charge measurements were made, over a 6 h period, to determine

the rate of charge loss. Between measurements, the toner/carrier mixture was kept in the original jar with the cap closed and at ambient conditions. In addition, a portion of the LL conditioned toner/carrier mixture was placed on a grounded aluminum plate and left exposed to the ambient laboratory atmosphere (23 ºC and 53% RH). The results are presented in Figure 1 and show that the original toner charge dissipates only very slowly. In fact, the charge loss rate is practically the same for the toner-additive mixture, the bare toner, and the sample held in contact with the grounded plate and exposed to ambient conditions. The initial charge on the toner is determined by the humidity level during development but thereafter changes at practically the same rate under a range of environmental conditions.

Water adsorption isotherms for the silica particles (without toner) were measured at 25 ºC using a dynamic vapor sorption balance from Surface Measurement Systems. All samples were outgassed at 125 ºC for several hours before measurement.

SEM images of the toner-additive mixture, after blending, after development, and after blow-off, were obtained using an Elionix field emission scanning electron microscope operated at 10 or 15 kV potential. All samples were mounted on aluminum stubs using double-backed tape and sputter-coated with platinum in a Hummer VI Sputter-coater. The time lag between sample mounting and sputter coating was typically a few minutes.

Results

The water adsorption isotherms at 25º C for various colloidal silicas and for a treated fumed silica are presented in Figure 2. The amount of water adsorbed was normalized with respect to the surface area of the silica and is given as the number of water molecules/nm^2. The surface areas were determined using N_2 adsorption and the BET equation. The water partial pressure is given on a logarithmic scale so as to allow easier comparison to the HH and LL tribo-charge data to be presented later. The adsorption isotherms differ substantially among the various kinds of colloidal silicas, and for any particular type of colloidal silica the adsorption isotherms are largely independent of the treatment chemistry. For example, the isotherms for the CS- type 2 silica (52 m^2/g) with three different types of silane treatments (HMDZ, octlytriethoxysilane, or a cyclic aza-silane) are practically identical and are significantly different from the isotherms for the same treatment on different silicas. The amount of adsorbed water is determined primarily by the type of base silica and is only slightly influenced by the type of surface treatment. Furthermore, the amount of water adsorbed by different types of colloidal silica varies widely. Some treated colloidal silicas absorb small amounts of water – similar to that of a treated fumed silica - while in other cases, the water adsorption capacity is very high and nearly identical to that of an untreated silica. Secondly, the shape of the adsorption isotherms differs sharply among the various colloidal silicas. Some silicas exhibit a dominant multi-layer region, whereas in other cases the silica exhibits a strong Henry's law adsorption regime and less pronounced multi-layer adsorption. In general, the difference in water sorption capacity at both high and low humidity conditions tend to differ by over an order of magnitude among the various samples. Furthermore, several of the silicas show only a small difference in water adsorption relative to the untreated silica, particularly at low humidity conditions.

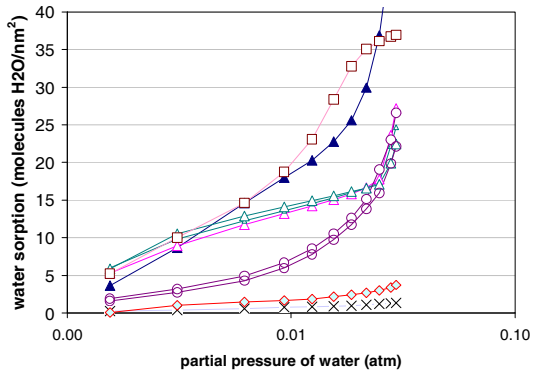

Figure 2. *Water adsorption isotherms at 25º C. □ - HMDZ treated type 1 (75 m^2/g) CS; Δ - type 2 (52 m^2/g) CS – various treatments; ◊ - HMDZ treated type 3 (43 m^2/g) CS; o - HMDZ and cyclic aza-silane treated type 4 (39 m^2/g) CS; x - cyclic aza-silane treated fumed silica (95 m^2/g); closed symbol – untreated silica*

Figures 3-5 present tribo-charge data for the formulated toner. Figure 3 presents the data for the bare toner, the toner with a standard fumed silica additive (Cabot TG-810 - HMDZ treated, 300 m^2/g silica) at 0.5 wt% silica loading, and the toner with two HMDZ treated colloidal silicas. The toner charge shows an excellent correlation with respect to the water partial pressure at which the toner was conditioned and developed and is independent of the conditioning temperature. The temperature at which conditioning was done is given above the data points. However, during the development step, the toner/carrier mixture probably equilibrates to a temperature a few degrees above ambient.

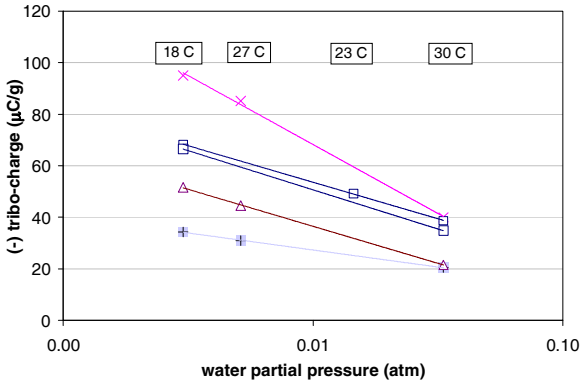

Figure 3. Toner tribo-charge as a function of developer humidity: □ - type 1 CS with HMDZ treatment; Δ - type 2 CS with HMDZ treatment; x – TG-810 fumed silica; + - bare toner.

At the high humidity condition, the water partial pressure extends into the condensation region of the isotherms shown in Figure 2 because the temperature at which the isotherms were

measured is slightly lower than the temperature used for HH conditioning.

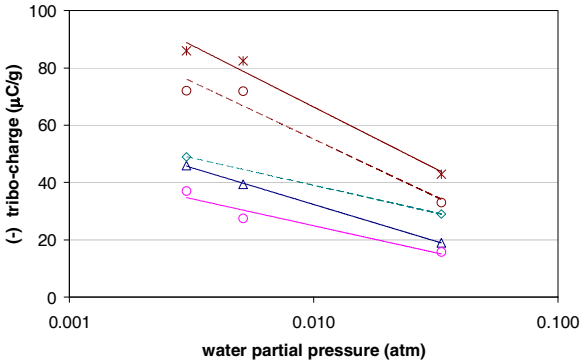

Figure 4. *Toner tribocharge as a function of developer humidity: Δ octlytriethoxysilane treated -type 2 CS; o -dual HMDZ and octyltriethoxysilane (upper) and octyltriethoxysilane only (lower) treated type 3 CS; ◊ -dual HMDZ and octyltriethoxysilane treated type 4 CS; · - HMDZ treated 65 m²/g CS.*

Additional tribo-charge data are presented in Figure 4, where the tribo-charge performance of various colloidal silicas shows little or no correlation with respect to the silica surface area or the treatment chemistry. In fact, appropriate combinations of silica type and surface treatment can yield tribo-charge values similar to that obtained with a treated fumed silica, but with particles of larger size and lower surface area. Consequently, it is possible to provide improved anti-blocking without any loss of tribo-charge capability.

The colloidal silica tribo-charge lines all have about the same slope with respect to water partial pressure. They are unlike the silica water adsorption isotherms, which exhibit widely different shapes and magnitudes.

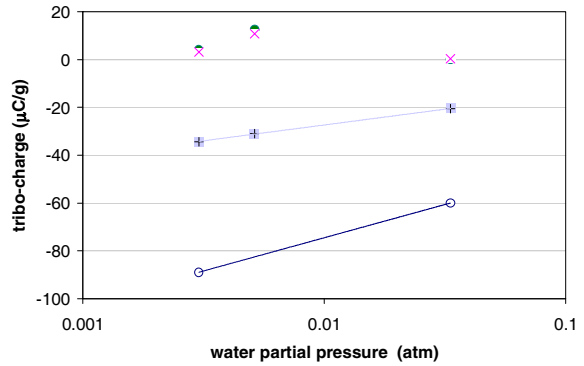

Figure 5. *Tribocharge as a function of developer humidity: o -type 2 CS treated with two different functionalized silanes; x =95 m2/g fumed silica treated with a functionalized silane; + - bare toner*

Figure 5 presents the tribo-charge results for a fumed and a colloidal silica treated with functionalized silanes. In this case the silicas were silylated with silanes that in one case included a secondary amine and in the other case a strong electron withdrawing group. These functionalized silanes not only provide a dramatic shift in the tribo-charge, but also result in a weaker humidity dependence than silicas treated with simple alkane silanes.

SEM Micrographs

A series of electron micrographs were made with the objective of following the history of the additive particles during blending with the toner, tribo-charge development, and after blow-off of the toner from the carrier. Micrographs are shown for two HMDZ treated type 1 colloidal silicas, whose tribo-charge data were presented in Figure 3. The two colloidal silicas are identical in nearly all aspects, except particle shape – one silica has slightly aggregated particles, whereas the other particle is unaggregated and spherical. The objective of the study was to determine how the additive-toner particle interaction changes during charging and what physical features of the additive/toner system may be important in the charging behavior of the composite system.

Figure 6 shows a close-up of a toner particle with additive after the blending step. The micrographs show excellent dispersion of the particles on the surface and also show that the treated particles fully retain the size and shape of the original colloidal silica. Surface coverage of the additives on the toner is

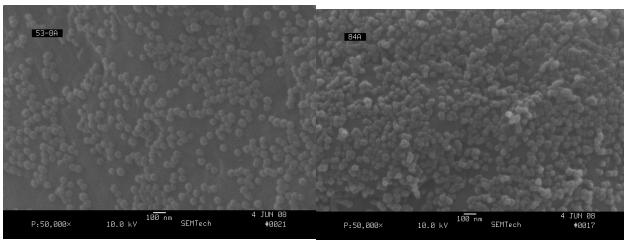

Figure 6. Type 1 CS on a toner particle after blending. Left photo: spherical particle; right photo: aggregated particle

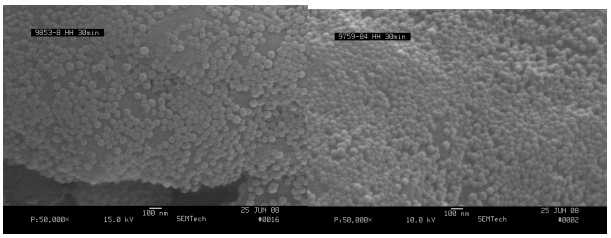

Figure 7*. Type 1 CS on a toner particle after development at HH conditions. Left photo – spherical particle; right photo – aggregated particle. At LL development conditions, the micrographs were similar.*

estimated at approximately 60% for the spherical particles and up to 90% for the aggregated particles. (This coverage was estimated visually from individual images and is not a true statistical value.)

The aggregated particles show distinct regions of multi-layer coverage, which is not seen with the spherical particles.

Figure 7 shows images of the particles after development with the carrier. Overall, there is little change in the features of the additive on the toner particle after tribo-charging. We observed no substantial transfer of the additive to the carrier, and the carrier surface before and after blow-off contains nearly identical amounts of silica. Figure 8 is a micrograph of a toner particle after blow-off and again there is little difference compared to the micrograph of the original blended toner. Once blended with the toner, the silica additive remains with the toner particle throughout the individual tribo-mechanical operations; there is no evidence that the silica particles themselves retain individual charges that would result in a separation of the additive from the toner and attachment to the carrier. Instead, the toner-additive composite acts as single charged dielectric particle.

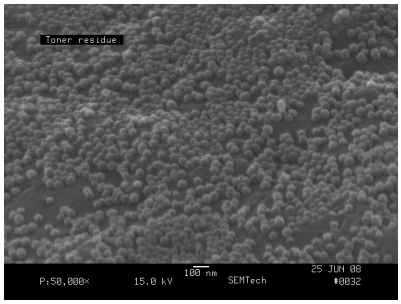

Figure 8. *Type 1 CS on a toner particle after blow-off. Spherical colloidal silica particles.*

Discussion and Conclusions

Cabot Corporation has developed a series of new treated colloidal silica additives for use in dry toner formulations. After treatment and drying, these additives fully retain the original size and shape of the base colloidal silica particle as shown by the electron micrographs presented above. The availability of colloidal silicas in a broad range of sizes and shapes allows the manufacture of treated silica particles having a wide range of physical and chemical characteristics.

In this paper we have attempted to show several relationships between tribo-charge performance and particle characteristics. Additional work is currently underway to further understand these complex phenomena. The principal conclusions are:

1. For simply hydrophobized silica particles, the magnitude of the charge correlates approximately linearly with the logarithm of the partial pressure of water present during conditioning just prior to development of the toner. Interestingly, however, we did not observe any clear correlation between the number of water molecules on the silica surface and the tribo-charge performance for different types of colloidal silicas. As was shown in Figure 2, the moisture content of different treated silicas varies widely from 2 to over 15 molecules/nm^2 (at a water partial pressure of 0.006 atm). The water content of the silica is determined by the base silica and is not appreciably influenced by the treatment chemistry. Furthermore, we did not observe any clear correlations between tribo-charge performance and the type of surface treatment (absent any functional groups) or the silica particle size

2. The charge generated on the toner particle during development is not readily dissipated from the particle and the toner charge remains reasonably constant with time. The rate of loss of charge is the same for particles on a grounded plate and exposed to ambient conditions as for particles kept in a closed container.

3. The use of silanes that add a functional group to the silica surface allows for the most dramatic control of the tribo-charge behavior. The presence of certain ionizable groups on the silica particle seems to fully over-ride the inherent tribo-charge characteristics of a toner-silica mixture when the silica particles are only hydrophobized with simple alkane-type silanes. Silica particles having ionizable functional groups also show a decreased tribo-charge dependence on humidity. Further work is on-going to better understand the tribo-charge performance of metal oxide particles treated with silanes having an ionizable functional group.

4. SEM micrographs show that the treated colloidal silicas have excellent dispersibilty and fully retain their original size and shape after treatment and drying. The additive remains tightly bound to the toner particle throughout the charging and carrier separation steps. It is believed that the silica/toner composite particle acts as a single dielectric particle over which the charge is distributed in some manner. For the example shown, the level of tribo-charge was not affected by the degree of surface coverage of the additive on the toner surface.

References

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