Tribocharge Performance of Colloidal Silica Additives in a Dual Component Developer

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Abstract

Cabot has recently introduced a new series of treated colloidal silica additives for toner applications. Because of their larger size, narrower size distribution, and more spherical shape these additives can provide improved anti-blocking and free flow in toner formulations. Colloidal silica based additives are available in a wide range of particle sizes and with different shape characteristics, which provide the formulator much latitude in matching the additive to the needs of the toner. These colloidal silicas are available with tribocharging characteristics from positive to highly negative.

In this paper, we present a study of the tribocharge performance of this new class of additives. We have investigated the effects of particle size, coverage, and moisture content on tribocharge performance and have investigated the rate of charge build-up and charge stability with time in a model dual component system.

Introduction

Toner additives provide a broad range of performance functions to the toner. These include providing free flow and anti-blocking to the toner, improving toner transfer from the drum to the paper, assisting in the uniform and consistent charging of the toner, and improving toner removal during the cleaning cycle. In order to achieve these multiple performance objectives, one desires particles that are uniform in size, that will adhere but not imbed into a toner particle during development – i.e., have good durability - and that can provide an appropriate and uniform tribo-charge to the toner. Historically, various treated fumed silicas have been used to enhance toner performance. However the demands of recent, newer classes of toner that use lower T_g polymers, have more regular shapes, and may comprise a core-shell type structure require additives having performance characteristics that extend beyond those obtainable from traditional fumed silica additives [1]. To achieve the performance goals of these new toners requires a silica additive that has good dispersibility, is available in selectable particle sizes and has a narrow size distribution, provides the required durability, and gives consistent as well as selectable tribocharge performance.

Cabot Corporation has recently introduced the Cab-O-Sil™ TG-C series of treated colloidal silicas to provide a new type of additive for next generation toner formulations. Through the direct treatment and recovery of non-agglomerated powders from colloidal silica dispersions, we can provide additives that have a broad range of physical properties and surface treatments. Particles sizes from 50-200 nm are available and with shape characteristics from nearly spherical to aggregated or structured. Tribocharge performance spans the range from slightly positive to highly negative. These features give the formulator much flexibility in selecting an optimum particles size, tribocharge capability, and surface chemistry for any given formulation.

In this paper, we report on the size characteristics and moisture adsorption behavior of these colloidal silica additives since it is thought that these factors can have a significant impact on tribocharge performance. In addition, we have studied the charge-up rate and durability of several of the additives in a model dual component developer. Electron microscopy was used to determine changes in additive coverage and distribution on the toner particle and on the carrier as a function of time.

Experimental

Additive loading and fractional surface coverage

Toners were formulated using a 9 µm polyester chemical toner. In all cases, the additive mass loading was kept constant at 4 wt%. As a result for different size additives, the surface coverage will vary. Surface coverage as a function of the average additive particle size can be calculated from the following equation assuming smooth spherical particles:

$$\text{Fractional coverage} = \text{wt\%}/(1-\text{wt\%})(d_t\rho_t/d_a\rho_a)\ (\alpha/\pi)$$

where the subscripts *t* and *a* refer to the toner and additive, respectively, *d* and *ρ* are the particle diameter and density and α is the packing factor. Table 1 summarizes the coverage factors for different size additives and a packing factor, α, of 1:

Table 1. Additive coverage on toner and carrier surfaces.

additive size (nm)	at 4% additive loading; 2% toner loading in developer		
	% coverage additive on toner	% coverage additive on carrier	% coverage toner on carrier
200	36%	30%	26%
110	66%	54%	26%
85	86%	70%	26%
60	122%	99%	26%

Toner preparation and tribocharge measurement

The toner was prepared by blending 50 g of toner and additive using a kitchen blender. To avoid overheating the toner, the blender was pulsed at 5 s intervals for 3 minutes; after blending, the toner-additive mixture was rolled an additional 1 h. The toner was added to the carrier - a 75 µm silicone coated Cu-Zn ferrite - at 2 wt% loading. Samples of the carrier-toner mixture were placed in glass jars and put in a humidity chamber for conditioning. HH conditioning was done at 30 ºC and 80% RH; NN conditioning was 25 ºC and 50% RH; and LL conditioning was 18 ºC and 15% RH. After conditioning, the sample jar was closed with a plastic cap. The toner was developed either by rolling or shaking. Shaking was done using a Turbula Shaker and gave a more intense agitation process than rolling. At a specified development time, the jar was removed from the roller or shaker and a small amount of sample taken out. The jar was then returned to the shaker or roller for further development. Samples were tested for tribocharge immediately after removal from the jar.

Tribocharge measurements were done using a Vertex T-150 blow-off tribocharger. Blow-off was done using several bursts of 20 psig air for 30 or 60 sec.

Moisture content

The moisture content of the additives was determined from weight loss measurements by TGA. In the TGA analysis, the samples were initially heated to 30 ºC and held at this temperature for 30 min. The temperature was then ramped at 4 C/min to 120 ºC and held at 120 ºC for 30 min. Finally, the temperature was raised to 220 ºC at 4 ºC/min and held at 220 for 30 min. Sweep gas was dry air at 130 cc/min. Independent head space analysis of the off-gases showed that practically all of the weight loss is due to water. Prior to analysis, the samples were allowed to equilibrate at ambient laboratory conditions (water partial pressure = ~0.006 atm) before analysis. Water sorption measurements – reported previously [2] – showed that the water uptake over the range of temperatures and relative humidity conditions typical of a laboratory environment does not change appreciably.

Hydrophobicity was not determined as we believe that water adsorption capacity is the correct characterization method for additives used in dry systems such as toners. Hydrophobicity [3] measures wetting capability and is not directly related to the adsorption capacity of the surface.

Particle Size Analysis

Particle size analysis was done using a Nanotrac UPA model NPA-252 dynamic light scattering instrument. Samples were prepared by dispersing the treated silica in an aqueous surfactant solution and sonicating the solution.

SEM analysis

SEM images of the toner-additive mixture, at various development times were obtained using an Elionix field emission scanning electron microscope operated at a 10 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 and Discussion

Tribocharging

Figure 1 summarizes the tribocharging ability of Cabot's Cab-O-Sil^{TM} TG-C treated colloidal silica. The reported tribocharge is a weighted average of the tribocharge at HH and LL conditions and approximately corresponds to the NN tribocharge. The data are presented as a function of the additive grade and the available surface treatments. The average particle size for each of the TG-C series grades is given in the Figure; particle sizes range from 60 – 200 nm. Highest levels of tribocharging are available with either the 60 or 85 nm particle sizes. The 70 nm grade provides a medium level of tribocharge at a particle size comparable to the 60 and 85 nm grades. The larger particles all provide a moderate level of tribocharge. The 200 nm grade is an aggregated colloidal silica, whereas the other particle sizes all have a spherical or nearly spherical shape.

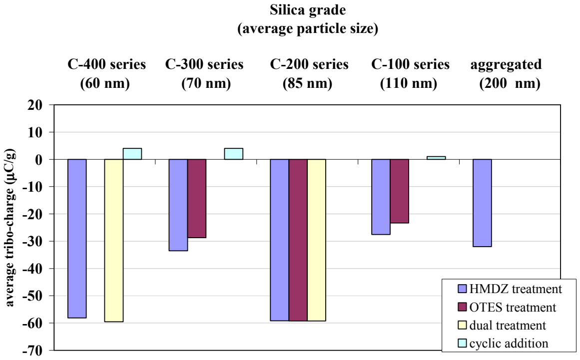

Figure 1. Tribocharging characteristics of various colloidal silicas as a function of particle size. The average tribocharge is calculated from the tribocharge values at HH and LL , which are weighted so as to approximately give the tribo-charge at NN conditions. Tribocharge is for a model toner formulation at 4 wt% additive loading with rolling. The 200 nm particle is an aggregated particle.

Surface treatments are available with hexamethydisilazane (HMDZ), octyltriethoxysilane (OTES), combined HMDZ and OTES treatment, or with HMDZ and a cyclic-azasilane. The cyclic treatment affords a neutral or a slightly positive charging additive. Aside from the cyclic silazane treated silicas, the other surface treatments do not have a substantial effect on tribocharge performance within a given size class of particles. Tribocharge capability is most closely related to the class of particles, but particle size itself does not show a direct correlation to tribocharge capability as might have been expected. Similarly, coverage is also not the principal factor controlling tribocharge as the 70 and 200 nm particles impart about the same tribocharge but at very different levels of surface coverage (see Table 1). Nonetheless, it is likely that high tribocharge levels can be more easily achieved with smaller than with large, low surface area particles at least at reasonable loading levels.

Other treatment and size variations are possible based on Cabot's proprietary treatment chemistries.

Particle size distribution

Typical particle size distributions are presented for the 60, 85, 110, and 200 nm particle sizes in Figure 2. The distributions tend to be narrow having geometric standard deviations between 1.2 and 1.4. The curves drawn through the data points are visual best fit log-normal functions. (The area under curve of the log-normal function was adjusted in some cases so as to give an improved visual fit to the data points.) The narrowness of the particle size distributions allows optimizing the toner particle separation so as to maximize free flow and durability performance of the toner.

Moisture content

Figure 3 shows the moisture content for a number of treated colloidal silicas. Prior to analysis, the samples were allowed to equilibrate at ambient laboratory RH conditions. However, in a number of cases, the samples were pre-dried at 120 °C for 30 min and then re-equilibrated at ambient laboratory conditions overnight before analysis. The pre-heated samples gave identical weight loss curves as the original sample. This implies that the amount of adsorbed water is an equilibrium quantity that is a function of the partial pressure of water to which the additive is exposed.

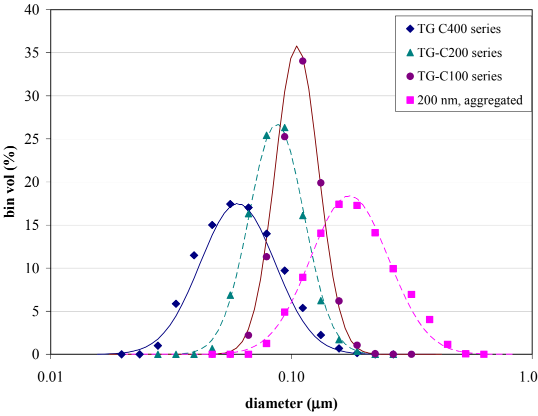

Figure 2. Particle size distribution for treated colloidal silicas. Curves through data points are visual best fit log-normal functions.

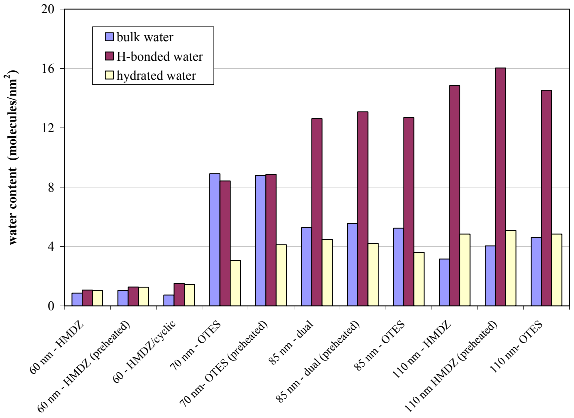

Figure 3. Water loss from treated colloidal silica samples. Different forms of water were assigned on the basis of the temperature at which water loss occurred.

The water content and its distribution shows significant differences between the 60, 70, and 85 nm size classes but less so between the 85 and 110 nm classes. The water content is given in terms of molecules per nm^2 so as to take into account differences in surface areas.

Water content is divided into contributions from bulk water, hydrogen bonded water, and hydrated water that are present on the silica. These forms of water were determined from the TGA analysis, where the weight loss at each isothermal step of the temperature profile tended to approach an asymptotic value. The weight loss at 30 °C was assigned to bulk water present on the surface. This water is a direct function of the ambient relative humidity. The weight loss at 120 °C is assumed to be H-bonded water because of the higher temperature required for its removal, and water loss at 220 °C is assumed to be hydrated water resulting from silanol condensation in the base silica

There is no direct correlation between water content (in any of its forms) and tribocharge capability. On the other hand, as mentioned previously, the tribocharge level is determined by the size class and is presumably due to differences in the base silica caused by differences in growth conditions and the ionic composition at the surface of the particle.

Durability tests

Toner tribocharge as a function of shaking time of the toner-carrier mixture is presented in Figure 4. Data are presented for the bare toner and the toner formulated with three different HMDZ treated silicas: TG-C110 (110 nm particle), TG-C413 (60 nm particle), and a 50 m^2/g fumed silica.

The data demonstrate that TG-C110 doesn't significantly enhance the toner tribocharge, whereas both fumed silica and TG-C-413 increase toner charge substantially. Interestingly, the colloidal silica (C-413) increases the charge considerably more than fumed silica. After 30 min development time, the difference in tribocharge level between fumed silica and C-413 is close to 40%

SEM micrographs (Figure 5) of the C-110 additive show that the additive is well dispersed on the toner surface and gives a uniform surface coverage. The additives exhibit a tendency to accumulate in cracks and surface depressions as development time increases. The ability of silica particles to accumulate in groups suggests that any charge on the additive or toner surfaces must distribute itself in a way to allow development of particle

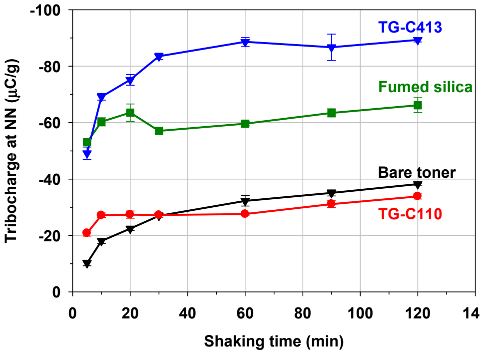

Figure 4. Tribocharge at NN conditions as a function of development time (Turbula Shaker) for bare toner, and toner formulated with TG-C110, TG-C413, and low surface area fumed silica. Error bars in many cases are of a size of the markers and thus could not be clearly seen.

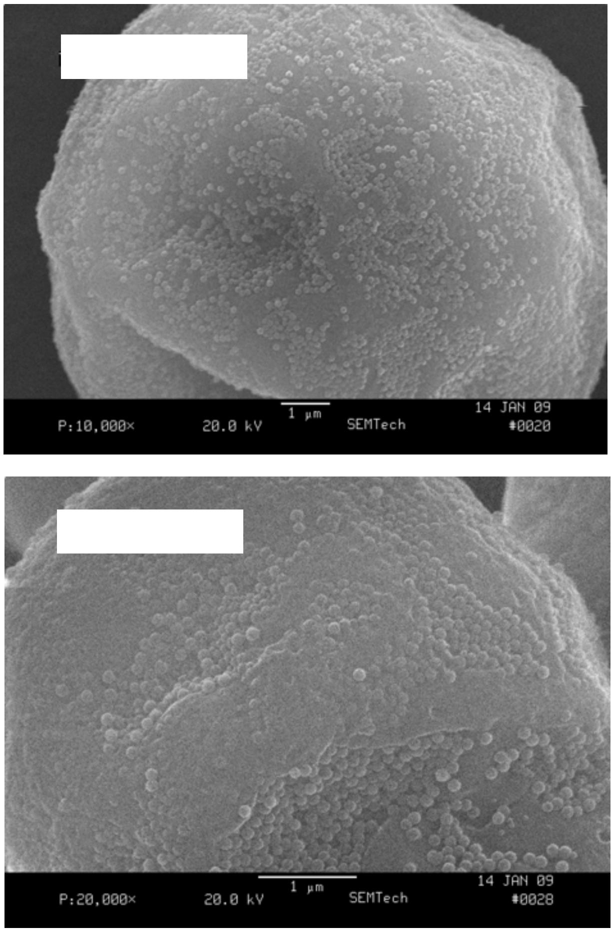

Figure 5. FE-SEM images of toner formulated with TG-C110 colloidal silica in the Turbula Shaker - after 10 min (top) and 30 min (bottom). Loading of C-110 is 4 wt%.

assemblies. However, no drop-off in tribocharge performance is observed, as was shown by the data in Figure 4. This behavior is similar to what was observed in the control experiment conduced with the low surface area fumed silica (Figure 6). Close examination of SEM images showed that silica aggregates also move on toner surface and have tendency to accumulate in surface depressions. Comparable surface coverage is obtained with fumed silica and the C-110 grade even though tribocharge effects are significantly different.

Figure 7 shows the 200 nm colloidal silica additive, which is an aggregated particle of irregular shape, after 10 and 30 min of durability testing. This particle was designed to provide different level of spacing and to minimize drop-off of silica particles. This additive can provide greater spacing than the low surface area fumed silica as can be seen by comparing the micrographs of Figures 6 and 7.

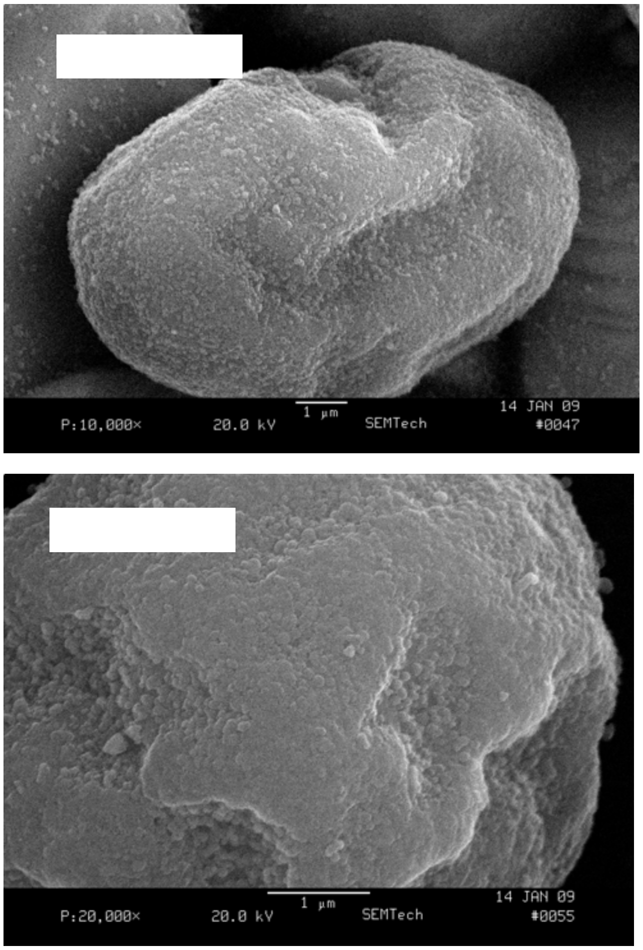

Figure 6. FE-SEM images of toner formulated with low surface area fumed silica in the Turbula Shaker - after 10 min (top) and 30 min (bottom). Loading is 4 wt%.

Summary and Conclusions

Treated colloidal silica additives, because of their low structure, have excellent dispersibility and give uniform coverage on the toner surface. Their narrow size distributions provides uniform toner spacing and the availability of different size particles gives one the ability to optimize anti-blocking for both black and color formulations.

The current product line of TG-C grade silicas covers a size range from 50 to 200 nm and includes individual spherical, aggregated, and structured particles. The product line could be extended to smaller and larger particles of various shapes to meet the needs of the toner industry.

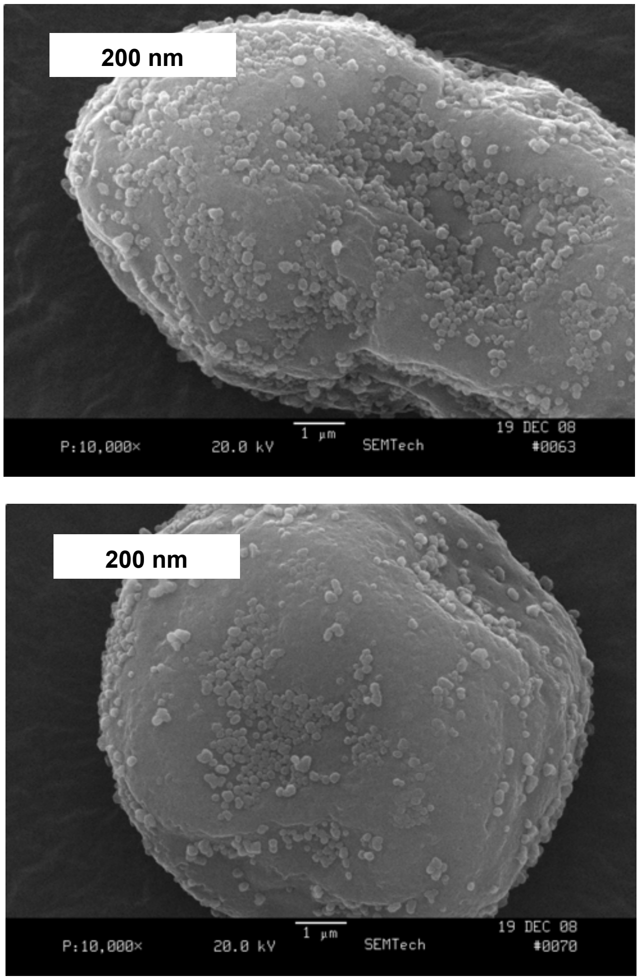

Figure 7. FE-SEM images of toner formulated with aggregated 200 nm colloidal silica additive in the Turbula Shaker - after 10 min (top) and 30 min (bottom). Loading is 4 wt%.

Similar levels of tribocharge are obtained with particles of widely different size and at different levels of coverage. We do not observe a quantitative trend in tribocharge performance with respect to particle size.

We also did not observe a quantitative correlation of tribocharge with either the water content of the particle – the water content of the C-400 series is close to that of low surface area HMDZ treated fumed silica – or the type of surface treatment. Within a size class, tribocharge performance was often very similar for the different surface treatments (aside from treatment with the cyclic aza-silane) used to hydrophobize the silica.

An important factor in determining the tribocharge performance appears to be the nature of the base silicas. The different particle size groups (i.e., TG-C100, TG-C200, TG-C300, and TG-C400) coincide with silica particles that have been subjected to differences in particle growth history and ionic compositions of the surface.

In the context of an ion-transfer model [4] for tribocharging, it is believed that surface water plays a crucial role in facilitating the movement of a mobile ion from one surface to another. As such both the adsorbed water and residual surface silanol concentration were thought to be important factors in determining the tribocharge performance of these additives. However, simple correlations between water in its various forms or the silanol content have not been successful in providing a relationship to tribocharge performance.

Nonetheless, by treating colloidal silicas, one can obtain a broad palette of silica additives of different sizes each having a fairly narrow size distribution and with a range of possible surface treatments. The different grades possess a range of charging characteristics and can provide the requisite free flow, anti-blocking, and transferability characteristics needed in modern toner formulations.

References

[1] Kambara, H., “External Additives,” In Advanced Technology and Application of Toner;,Takeuchi, M., Oguchi, T., eds.; CMC Publishing: Tokyo, Japan, 2009; pp 99-106

[2] J. K. Floess, D. Fomitchev, H. Tu, J. Liu, A. Christopher, and W. Williams, Proceedings of the 24th International Conf. on Digital Processing Technologies, IS&T, Pittsburgh, PA, 59, 2008.

[3] Adamson, A. W., “Physical Chemistry of Surfaces,” John Wiley, New York, 1976.

[4] McCarthy, L. S. and Whitesides, G. M., Angew. Chem., Int. Ed., 47, 2188, 2008.

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