External Additives for Toners: Characteristics of Fumed Silica, Colloidal Silica, and Next Generation Materials

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Abstract

Demand for higher print resolution and reduced energy consumption is driving development of smaller and softer toners. Embedding of external additives into soft toners during the development and deterioration of properties such as cohesion and tribocharge is one of the major problems that toner formulators face. In order to protect small particles on the toner surface from being embedded, large particle silica is often used as a spacer particle. Over the last ten years, spacer additives have become a crucial component of modern formulations. Cabot has recently significantly extended its portfolio of external additives for toners with an emphasis on large particle silica. In particular, several new grades based on 60 m^2/g fumed silica, and colloidal silicas with particle sizes between 40 and 200 nm have been introduced. In this paper, we present performance data for a set of fumed and colloidal silicas that illustrates the effect of different surface treatments. In addition, Cabot has developed novel silica-polymer composite particles that show promise as spacer additives. These materials show reduced drop off from the toner surface compared to colloidal silica of similar size, potentially allowing formulators to use larger size spacer particles.

Introduction

In electrophotography, the ability of toner particles to flow, charge, and transfer is critical. Modern toners would not be able to function without the presence of external additives that provide improved flow properties and contribute to the toner's charging behavior [1, 2]. In the last decade there have been several major trends in the printing industry. One of these is the ongoing shift to toners with lower fusing temperature, which is in turn driven by industry requirements for faster printing speed and reduced energy consumption. These new toners have presented challenges for toner formulators who need to adapt their additive packages to meet freeflow and charging requirements but also provide toner that is more durable in stressful high-speed print environments.

These trends have increased the importance of silica additives with large primary particle sizes that are still able to provide tribocharge and freeflow benefits to the toner. Cabot has expanded its portfolio of products to include both fumed and colloidal additives with a range of surface chemistries and particle sizes to cover these new industry needs. Previous publications have discussed these developments in detail [3, 4].

In the first part of this paper we will compare the performance of small particle size fumed silica (~200 m^2/g), large particle size fumed silica (~60 m^2/g), and colloidal silica with ~110 nm size with a range of surface treatments. These results show that while there are differences between the classes of material in terms of their relative tribocharge and freeflow performance, the impact of different surface treatment types is generally consistent.

In the second part of this paper, we introduce a new class of materials that are under development at Cabot: silica-polymer composite particles. These particles have been developed to address the need for improved spacing and anti-blocking performance required with smaller, lower melting toners that are being developed today. Ideally, larger size colloidal silica (150-300 nm) could provide improved spacing performance, but additive drop-off becomes increasingly problematic as the size of the colloidal silica increases from 100-300 nm. The new silica-polymer composite particles show reduced drop-off, while also providing tribocharge and freeflow similar to colloidal silica.

Materials

Commercial and developmental additives were selected for evaluation in this study. Figure 1 compares the particle morphology of the different materials. Images A and B in Figure 1 show a representative transmission electron microscope (TEM) image of Cab-O-Sil™ fumed small particle silica (SPS) and fumed large particle silica (LPS). Fumed silica is an amorphous fluffy white powder that consists of 7 to 50 nm primary particles that are fused into branched-chain three-dimensional aggregates with sizes from 100 to 400 nm. The surface area of fumed SPS is typically in the range of 200-350 m^2/g, while fumed LPS is typically in the range of 50-90 m2/g. Image C in Figure 1 shows a representative TEM image of Cab-O-Sil™ colloidal silica. Colloidal silica is a different form of amorphous silica which is produced in aqueous solution. The particle size of colloidal silica generally is in the range between 5 and 500 nm. Typically, colloidal silica exists as a dispersion of discrete particles which do not form branched aggregates (although aggregated colloidal silica can be produced).

In order to render the silicas more hydrophobic and improve the tribocharging and freeflow properties, the fumed and colloidal silicas were surface treated with various hydrophobizing agents, such as hexamethyldisilazane (HMDZ), polydimethylsiloxane (PDMS) oil, octyltriethoxy silane (OTES), or octyltrimethoxy silane (OTMS). Further details on the additives selected for the study and their characteristics are given in the Results section.

Image D in Figure 1 shows a representative TEM image of silica-polymer composite particles. These particles are made via a proprietary process, resulting in spherical silica domains that are fused to the exterior of a polymeric core. The size of the silica domains as well as the overall composite particle size can be tuned via control of the synthetic process. Additional details on the composite particles is given in the Results section below.

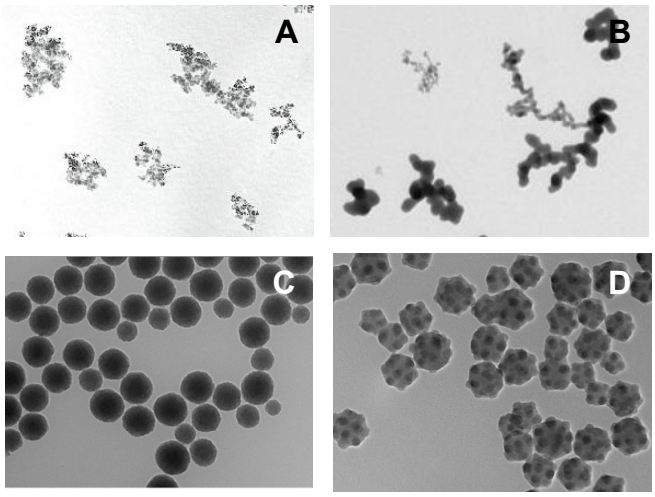

***Figure 1**. TEM images showing particle morphology for fumed SPS (A), fumed LPS (B), colloidal LPS (C), and silica-polymer composite particles (D)*

Experimental

Additive Characterization

Surface area of the additives was determined using the standard BET method. Helium pycnometry was used to measure the specific gravity. The measurements were performed in Micromeritics analytical laboratory. Particle size distributions of the composite particles and treated colloidal silica were measured by dispersing in methyl ethyl ketone (MEK) and then measuring with dynamic light scattering using a Nanotrac 250™ instrument. Concentrations of particles in MEK were on the order of 1-3 wt%.

Preparation of Toners and Developers

Universal mill IKA M20 was used to mix the toner additives with a commercial 9 μm black polyester chemical toner containing no other external additives. Loading of the additive was the same for all materials in a given classs (Fumed SPS, etc.), but was varied between classes to keep the toner surface coverage approximately equal. More specifically, Fumed SPS: 1%; Fumed LPS: 2%; and Colloidal LPS and Composite Particles: 4% on toner. To prevent toner from overheating and melting, mixing was performed in three 15 sec pulses separated by 15 sec cooling intervals. Developers were prepared by mixing the formulated toners with a Cu-Zn ferrite carrier coated with a silicone resin (carrier particle size 60-90 μm; Powdertech Co., Ltd.). The developers contained 2 wt% of toner and 98 wt% of carrier. Before the measurements of triboelectric charge, the developers were conditioned for several hours in controlled temperature and humidity chambers at 18 °C/20 %RH (further in the text abbreviated as LL) or 30 °C /80 %RH (further in the text abbreviated as HH) conditions.

Measurement of Toner Performance

After conditioning in controlled humidity chambers, the developers were placed in glass jars and charged by rolling for 30 min at 185 rpm on a roll mill. Triboelectric charge measurements were then performed using the blow off method (on a Vertex T-150 instrument). Approximately 1 g of charged developer was placed inside a Faraday cage and a high pressure air jet was used to blow off toner from the carrier. The carrier remained in the cage and its charge was measured with an electrometer inside the Vertex T-150 tester. The amount of blown off toner was determined by weighing the cage with the developer before and after the measurement. Each measurement was repeated three times.

Cohesion measurements were performed using a Hosokawa powder tester. 2 g of toner mixed with an additive was paced on an upper sieve of a stack of three sieves (mesh 100, 200, and 325) and the sieves were allowed to vibrate for 50 seconds with the amplitude of 0.5 mm and frequency of 50-60 Hz. The cohesion was calculated according to the formula: Cohesion% = $50\times Mt+30\times Mm+20\times Mb$, where M_t, M_m ,and M_b are the weights of toner remaining on the top, middle, and bottom sieves, respectively, when the vibration stopped.

Additive drop-off was measured by taking a 5 g sample of toner mixed with an additive and dispersing it in 100-130 mL of deionized water containing 1 wt% of Triton X-100 surfactant. The dispersion was subjected to sonication for 60 seconds and then it was filtered through #1 Whatman filter paper. The filter cake was dried overnight at 40 °C and then for 1 h at 70 °C. Approximately 1 g samples of the dried toner were placed in ceramic crucibles and then burned in a furnace for 2 h at 700 °C. The amount of an external additive remaining on toner after the ultrasonic treatment was determined from the difference between the weights before and after the exposure to 700 °C. Two dispersions in water were prepared for each toner/additive mixture, subjected to ultrasound treatment, filtered, dried, and burned. The results were calculated as an average of two measurements.

Results and Discussion – Part 1: Comparison of Fumed and Colloidal Silica

Fumed SPS, fumed LPS, and colloidal LPS additives with different surface treatments were formulated with toner and evaluated as described in the Experimental section. A summary of the additive material properties is given in Table 1. If the additive is a commercial product, the grade name is also given.

Table 1: Properties of Treated Fumed and Colloidal Silica

Additive	Base Silica Surface Area (m^2/g)	Surface Treatment
FSPS-1	200	HMDZ
FSPS-2	200	OTMS
FSPS-3 *(TG-308F)*	200	PDMS
FLPS-1 *(TG-5110)*	60	HMDZ
FLPS-2	60	OTMS
FLPS-3 *(TG-5180)*	60	PDMS
CLPS-1 *(EP-C110)*	30	HDMZ
CLPS-2 *(TG-C190)*	30	OTES

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Results of the toner performance testing are shown in Figures 2, 3, and 4.

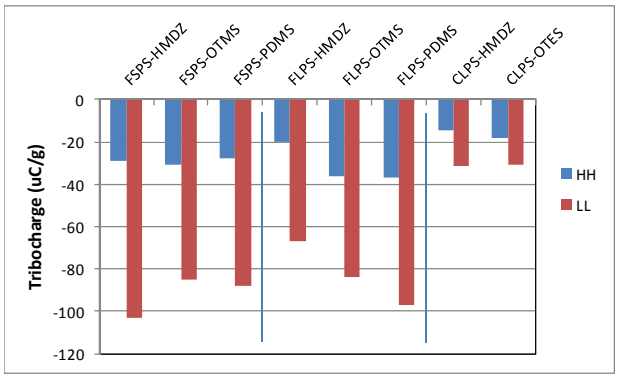

Figure 2. *Results of tribocharge measurements for toners conditioned at different humidity levels*

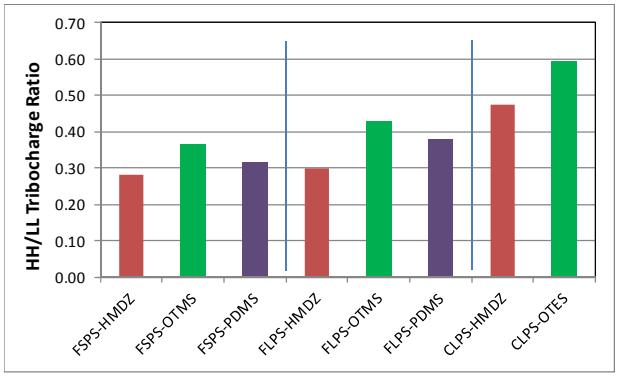

Figure 3*. Humidity resistance of tribocharge*

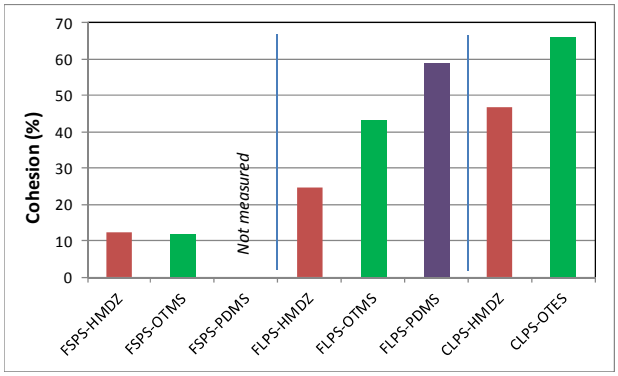

Figure 4*. Cohesion of toner (lower equals better toner freeflow)*

Figure 2 shows a comparison of the tribocharging performance of polyester toner formulated with the different additives. One clear observation is that the colloidal resulted in significantly lower (absolute) charge, regardless of the treatment. For the fumed SPS, there are no major differences between the additives, although the HDMZ treated 200 m^2/g silica shows a higher charge at LL conditions. Interestingly, for the 60 m^2/g fumed silicas, the HMDZ treated silica actually charges lower. Therefore there may be advantages to PMDS or OTMS treated fumed LPS for higher charging. As was noted in the Experimental section, the SPS fumed silicas were formulated at 1% loading, as compared to 2% loading for the LPS fumed silicas. The fumed SPS silicas are therefore more effective at increasing tribocharge.

Figure 3 (tribocharge humidity resistance) shows more clear trends with treatment. In all three categories, the alkyl silane treatment (OTMS or OTES) shows improved humidity resistance compared to HMDZ. PDMS treatment provides a humidity resistance that is intermediate between HDMZ and alkyl silane. The overall humidity resistance of colloidal silica is higher, but this is tempered by the lower absolute tribocharge (see Figure 2).

Toner freeflow (Figure 4) also shows clear trends with both the size of the silica and treatment type. Fumed SPS provides excellent freeflow (lower Cohesion values) compared to LPS. For the large particle silicas, HMDZ treatment provides superior freeflow performance. OTMS treated silica provides worse freeflow performance than HDMZ, but is better than PDMS.

These results demonstrate that additive selection and toner formulation involves balancing performance tradeoffs. Fumed SPS (200-350 m^2/g) is very effective at delivering high tribocharge and good toner freeflow at low loadings. However, to prevent embedding, large particle silica must usually be used. Colloidal silica is an effective spacer but the tribocharging effect is weak and toner freeflow can be negatively affected. Surface treatment of the LPS is a therefore a handle to balance cohesion and tribocharging. Alkoxy-silane treatment provides a good balance of excellent humidity resistance with reasonably good cohesion.

Results and Discussion – Part 2: Composite Particles

While tribocharge and freeflow of spacer particles like colloidal silica are important, the primary function of a spacer additive is to improve the durability of the toner during extended printing. If the spacer particle is not strongly adhered to the toner surface, it can drop-off of the toner during development. Tendency for spacer drop-off increases with the increase in spacer particle size, making drop-off a major limiting factor that often prevents the use of spacers larger than 100 nm.

To alleviate the problem of spacer drop-off, a new type of material, silica-polymer composite particles, has recently been proposed by Cabot. A proprietary synthesis method of silica-polymer composite particles allows tuning of the mean particle size in the range between 50 and 500 nm. The width of the particle size distribution for the composite particles is close to that of colloidal silica.

To understand how the performance of composite particles compares to colloidal silica, two composite particle samples were prepared that had a mean diameter of 112 and 130 nm. For comparative purposes, these were compared against two colloidal silicas: TG-C190 (110 nm treated with OTES, as described in Part 1) and TG-C6020N, which is a non-spherical (slightly aggregated) colloidal silica with mean diameter of 190 nm treated with HMDZ.

The ”liquid phase” drop-off test described in the experimental section was conducted on toner formulated with these four additives; the results are presented in Figure 5.

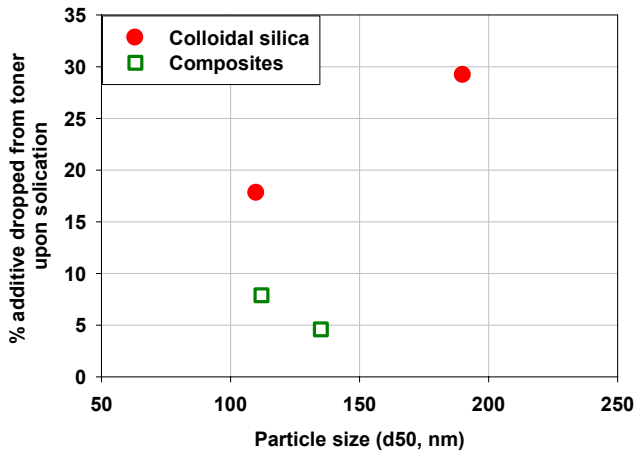

Figure 5. *Additive drop-off of colloidal silica (shown as circles) and silica-polymer composite particles (shown as squares).*

Data in Figure 5 illustrate that drop-off of colloidal silica increases significantly with the increase in particle size from 110 nm to 190 nm. One possible explanation for this increase is that for spherical or nearly spherical particles, mass and the detachment force increase significantly with the increase in particle size while the adhesive force remains relatively constant, as it is related to the additive-toner contact area. Composite particles were developed to address this problem. According to the results of helium pycnometry, composites have density 10-30% lower than density of silica (the polymer core has density close to 1 g/cm^3 while silica has density near 2.2 g/cm^3). It is also likely that bumpy shape of these particles, with silica protruding from the particle surface, allows for multiple points of contact with the toner surface and therefore greater adhesive force than colloidal silica. It is anticipated that the difference in drop off between colloidal silica and composites will increase further with increase in the particle size.

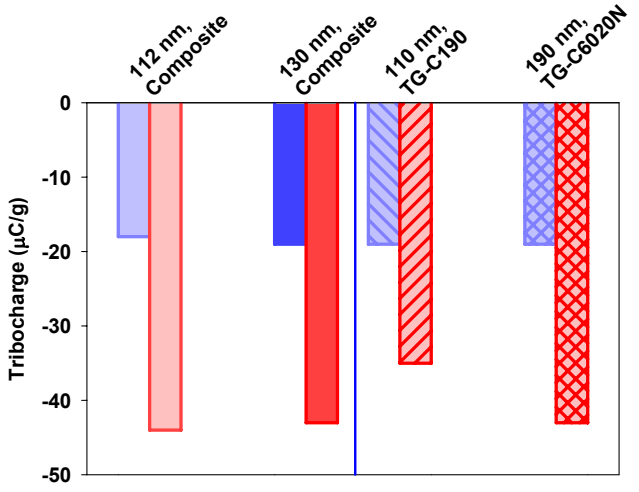

Figure 6. *Tribocharge data for model toner formulated with colloidal silica and composite particles. Data at HH conditions are the shorter bars.*

Results of model toner tribocharging with colloidal silica and composite particles are shown in Figure 6 and Figure 7. These results show that the triboelectric charging characteristics of composite particles are very similar to that of colloidal silica.

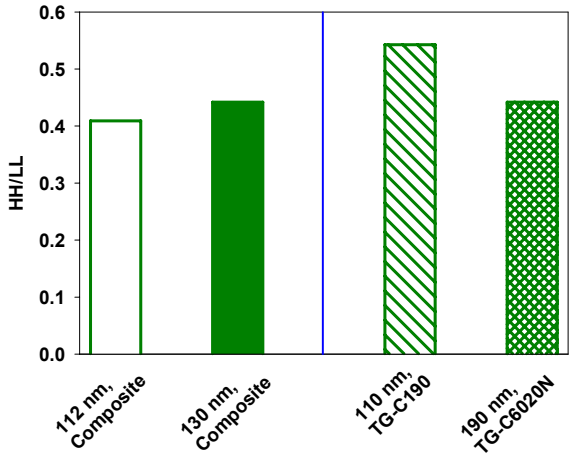

Figure 7. Humidity resistance for toners with composites and colloidal silica

Conclusions

In this paper, we have shown that toner additives based on fumed and colloidal silica can be used to tune toner tribocharge and freeflow. While LPS silicas generally charge lower and are not as effective at providing freeflow, the relative effect of different surface treatments is similar for LPS and SPS silicas.

It has also been demonstrated that silica-polymer composite particles present a new class of materials that can be used as spacer particles in modern toner formulations. These particles may provide significant performance advantages over colloidal additives due to reduced drop-off from the toner. It is likely that by using composite spacers, the accessible range of spacer sizes will be extended beyond 100 nm to 200 or even 300 nm.

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Author Biography

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