# Comparison of Fumed and Colloidal External Additives for Toner

***Angelos Kyrlidis, Dmitry Fomitchev, Alyson Christopher, Holly White; Cabot Corporation; Billerica, MA 01821, USA***

## Abstract

*External additives play a very important role in the performance of toner. They were originally used to adjust the toner freeflow and fine-tune its tribocharging performance. Recent trends towards color chemically produced toner have brought changes in the toner particle size and its composition. These changes have put even higher performance demands on the additives. For example, larger contribution to the tribocharging control for both positive and negative charging toner, requirements for spacing and durability for dual component toner, control of surface energy for more efficient toner transfer. Cabot offers a portfolio of modified silica additives that cover a unique range of morphologies, particle sizes and surface chemistries. In this paper we will compare the performance of treated silica additives with similar surface chemistries and different morphologies to explore some of the similarities and differences of colloidal and fumed silica-based products. Coverage, tribocharging, and freeflow are the key functions that are studied for dual component negative toner systems.*

## Introduction

In electrophotography the ability of toner particles to flow, charge, and transfer is critical. This performance is practically impossible in the absence of external additives that provide improved flow properties and contribute to the toner's charging behavior [1]. In the last decade there have been several major trends in the printing industry: improved print quality at lower cost, faster printing speed, and the increasing use of color. These trends have in turn driven some of the key developments in toner, namely the shift towards chemically produced toner (CPT) with smaller particle sizes, the shift to polyester resins for improved fusing, and the need to be able to fine-tune charging across all four subtractive (CMYK) color toners. These new needs have developed challenges for the toner formulators who need to adapt their additive packages to meet both the traditional freeflow and charging requirements but also provide toner that is more durable in the stressful high-speed print environments and that can transfer efficiently in multiple steps until it is finally fused on paper.

These trends have increased the importance of silica additives with large primary particle sizes that can provide performance comparable to that of the 'conventional' silica additives. Cabot has expanded its portfolio of products to include colloidal additives with the full range of surface chemistries that enable negative or positive tribocharging at a broad range of particle sizes to cover these new industry needs. Previous publications have discussed these developments in detail [2].

In this paper we will compare the performance of colloidal silica additives with the performance of fumed silicas with similar primary particle sizes. We will first describe the morphological differences between the two particles, and then illustrate the similarities and differences in performance for the two main functions of the particles, namely tribocharging and freeflow.

## Characteristics of Fumed and Colloidal Silicas

Although they are both amorphous silicas, the two types of particles have significant differences in their morphologies that impact their performance in toner systems.

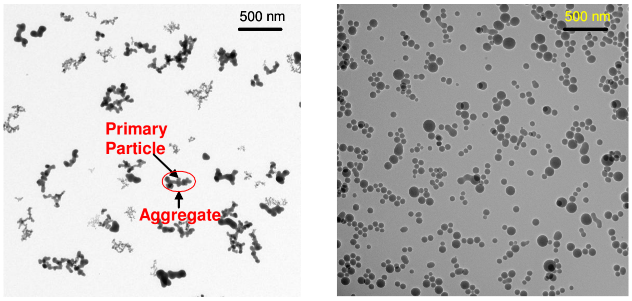
### *Fumed silica*

Fumed silica is an amorphous fluffy white powder which is produced by flame hydrolysis of silicon tetrachloride or other silanes. It consists of 7 to 50 nm primary particles which are fused into branched-chain three-dimensional aggregates with sizes from 100 to 400 nm. The primary particle size and the aggregate size are controlled by the conditions of the flame hydrolysis process. The surface area of commercially produced fumed silica is typically in the range between 50 and 350 $m^2/g$. Due to high temperature synthesis conditions, fumed silica has silanol density of only 2-4/$nm^2$. A transmission electron microscopy (TEM) image of fumed silica with a surface area of 60 $m^2/g$ is shown in Figure 1.

### *Colloidal silica*

Colloidal silica is a different form of amorphous silica which is produced in aqueous solution. The particles form and grow due to polymerization of silicic acid. The particle size and shape depend on the polymerization conditions such as temperature, pressure, polymerization time and pH. The particle size of colloidal silica generally is in the range between 5 and 500 nm. Unlike fumed silica, colloidal silica exists as a dispersion of discrete particles which do not form branched aggregates. Silanol density on the surface of colloidal silica is significantly higher than on the surface of fumed silica and is about 7-9/$nm^2$. The drying of colloidal silica dispersions usually leads to formation of a glass-like solid which is not possible to disperse back to primary particles. In order to produce hydrophobic free flowing powder dispersible back to primary particles, colloidal silica has to be surface treated prior to drying. A TEM image of a colloidal silica with surface area of 60 $m^2/g$ is also shown in Figure 1.

Both fumed and colloidal silicas can be surface modified with a range of treating agents to impart hydrophobicity and to allow the control of the charging and freeflow behavior [3].



60 m$^2$/g fumed silica  60 m$^2$/g colloidal silica

***Figure 1.** Comparison of morphologies of fumed and colloidal silicas.*

## Experimental Testing Protocols

### *Selection of additives*

Both fumed and colloidal silicas discussed in this paper have a surface area of 60 m$^2$/g. The corresponding average primary particle size for these materials is 40-50 nm, and the average aggregate size of the fumed silica is 190 nm. For comparison purposes, a fumed silica with a surface area of 325 m$^2$/g is also used as a reference. This fumed silica has an average primary particle size of 8 nm and an average aggregate size of 140 nm. All silicas were hydrophobized by surface modification with hexamethyldisilazane (HMDZ) and are either commercially available or developmental products.

### *Preparation of developers and tribocharge measurements*

The toner was formulated by blending 50 g of 9 µm polyester chemical toner and the calculated amount of an external additive using a high intensity 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 on a roll mill.

0.8 g of toner/additive mixture was placed into a glass jar and 40 g of carrier (75 µm silicone coated Cu-Zn ferrite, purchased from Powdertech Co., Ltd.) was added. The jar was closed and the mixture was shaken 10 times by hand.

The developer was conditioned in a humidity chamber at 30ºC and 80% RH (HH–conditions); and 18ºC and 15% RH (LL–conditions) for at least 4 h. After conditioning, the sample jar was closed and the toner was developed by rolling the jar for 30 min at 185 rpm. Samples were tested for tribocharge immediately after removal from the roll mil.

Tribocharge measurements were done using a Vertex T-150 blow-off tribocharger. Blow-off was done using several bursts of 20 psig air for 60 sec. Each measurement was repeated three times and the average is reported.

### *Free flow measurements*

Free flow measurements were performed using two different techniques:

a) An in-house built flow tester: The tester consists of a horizontally mounted 350 mm long hollow stainless steel tube with an inner diameter of 50 mm. Seven evenly spaced 3 mm holes are drilled along one side of the tube. The tube is rotated at 4 rpm around the horizontal axis and the amount of toner discharged through the holes after 60, 90, and 120 revolutions is measured. Initial toner charge to the tube is 40 g. It is assumed that the larger weight loss means higher free flow.

b) A Schulze RST-XS ring shear tester: This technique measures the cohesive strength and bulk density of each tested toner formulation at different consolidation pressures. Our tests were conducted at 25 $^{o}$C and 50% relative humidity. In general, powders with good flowability are those having low cohesive strength and high bulk density [4].

### *SEM imaging*

SEM images of the toner-additive mixtures were obtained using an Amray 3300FE field emission scanning electron microscope. All samples were mounted on aluminum stubs using double-backed tape and sputter-coated with platinum in a Hummer VI Sputter-coater.

## Results

### *Coverage*

High surface area fumed silica is used traditionally as an external additive in toners in combination with other additives to enhance the freeflow properties and contribute to the tribocharging of the toner. Typical loadings are in the 1% range which ensure good coverage of the toner surface. A chemical toner loaded with 2 wt% of fumed silica with a surface area of 325 m$^2$/g is shown in Figure 2. The silica appears to be uniformly distributed on the toner surface.

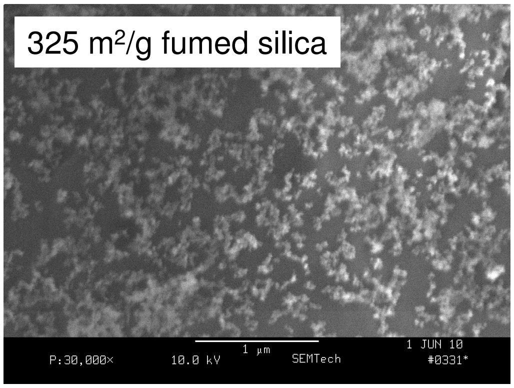


***Figure 2**. SEM images of toner loaded with 2 wt% fumed silicas with surface area of 325 m$^2$/g*

Colloidal and fumed silicas with lower surface areas are typically used as external additives in dual component toners designed for high speed office and commercial printers. The larger primary particle sizes of these additives (40-50 nm) allows the toner to retain its tribocharging and freeflow performance without degradation, which usually occurs by embedding of the external additives into the surface of the toner through collisions with the carrier beads. Because of their lower surface areas, typically higher loadings of these additives are required to cover the toner surface.

In Figure 3, we compare the coverage of the toner surface by fumed and colloidal silicas with similar primary particle sizes at 2 wt% loadings. From the SEM images it is apparent that the aggregated morphology of the fumed silica manifests itself in lower coverage of the toner surface. The colloidal silica in contrast is unagglomerated and easily dispersed on the surface of the toner. Its coverage is more uniform than the comparative fumed silica and approaches the level of coverage obtained by the high surface area fumed silica.

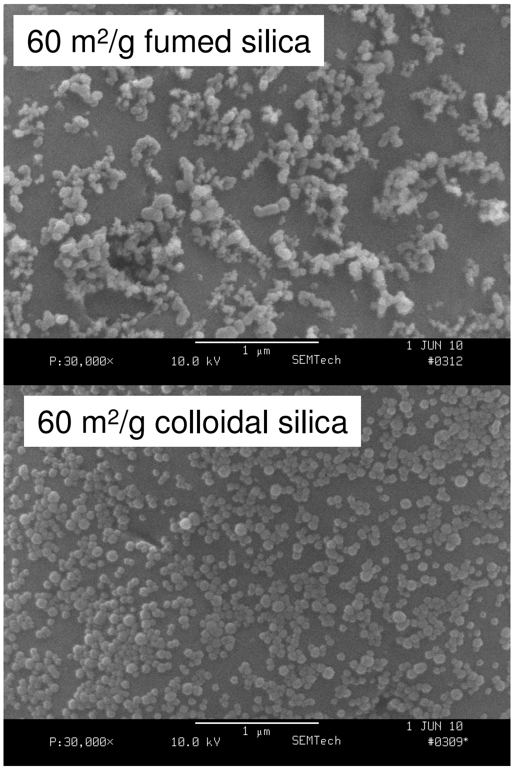


***Figure 3**. Comparison of SEM images of toner loaded with 2 wt% colloidal and fumed silicas with 40-50 nm primary particle size.*

## *Tribocharging*

The tribocharging performance of silicas in toner is primarily a function of their surface chemistry and their surface area. Usually, high surface area silicas contribute significantly to the total charge build up, which in some cases restricts the total amount that can be used to control freeflow. This can be seen in Figure 4, where toner formulated with fumed silica with 325 $m^2/g$ surface area that is HMDZ modified is shown to reach charges of > 100 µC/g at loadings greater than 1 wt%. Fumed silicas with 60 $m^2/g$ surface areas modified with HMDZ have lower tribocharge, as is shown in Figure 5.

In Figure 5, we also compare the tribocharging of a 60 $m^2/g$ colloidal silica treated with HMDZ. Its tribocharging is at similar levels as the corresponding fumed silica at equivalent loadings. This comparison can be made at both of the environmental conditions that were tested. We can therefore conclude that despite different material synthesis conditions, colloidal and fumed silica show similar tribocharge properties. It is well known that fumed or colloidal silicas treated with HMDZ, PDMS, and alkoxysilane treatments charge toner negatively, whereas amine-containing surface groups are required to make the silicas charge toner positively, when combined with the appropriately coated carrier particle, which also has a significant effect on the tribocharging of the silica [5].

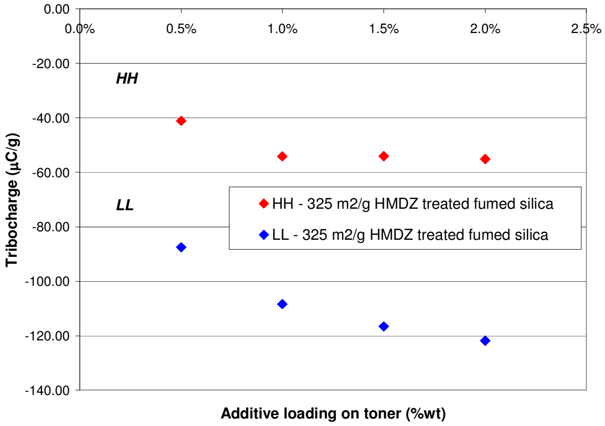


***Figure 4**. Tribocharging as a function of additive loading for 325 $m^2/g$ HMDZ treated fumed silica.*

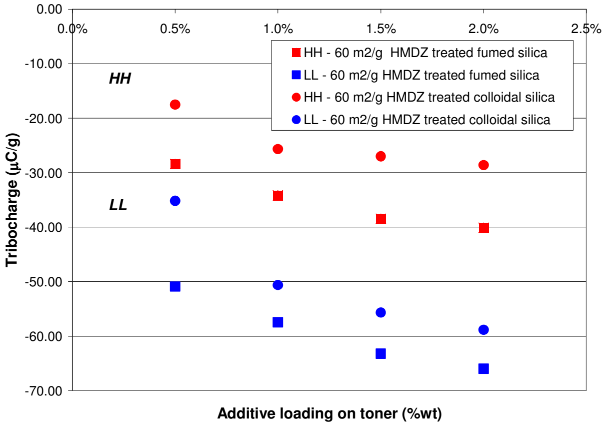


***Figure 5.** Comparison of tribocharging as a function of loading of fumed and colloidal silicas under HH (30 °C and 80% RH) and LL (18 °C and 15 % RH) conditions.*

## *Freeflow*

The freeflow performance of silicas in toner is also determined by their surface chemistry and surface area. The treated high surface area fumed silicas have been historically used as additives to reduce toner cohesion which is required for the toner to be able to dispense and transfer effectively. In Figure 6 we compare toner freeflow performance using our in-house apparatus. The as-is (bare) toner shows the worst performance, as expected. The addition of 2 wt% colloidal silica gives the best performance which is better than that of both fumed silicas considered in this paper. The improved performance of the colloidal silica can be partially explained by the very good coverage (as was shown in

Figure 3). It is unclear why the high surface area fumed silica which had similar coverage had inferior performance. It is hypothesized that the aggregated and fractal structure of fumed particles can lead to 'entanglement' which would in turn lead to inferior flow performance. The tested loading of 2 wt% for the high area silica is on the high end of typical toner formulations, so the optimal loading for freeflow may be lower.

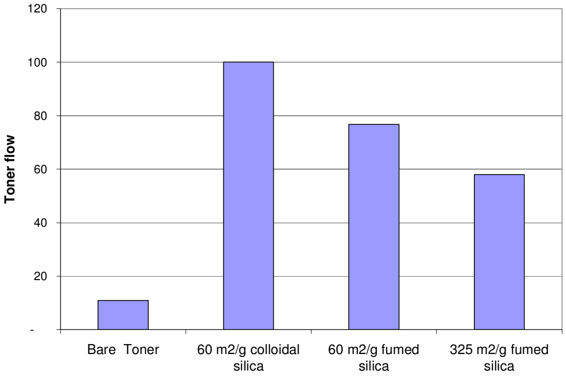


***Figure 6.*** *Comparison of relative freeflow (amount collected) for toner formulated with 2 wt% colloidal and fumed silica using in-house testing apparatus.*

The results from the in-house testing were also comparable and in agreement with the more rigorous ring shear testing that was conducted under controlled environmental conditions. The bare toner is found to have substantially higher cohesion strength and a more pronounced effect of consolidation pressure. In the absence of external additives, toner will cake and not be able to flow properly. As shown in Figure 7, with the addition of silicas the cohesive strength is reduced significantly. The colloidal additives have the most pronounced effect, while both low and high surface area fumed silicas have comparable effects on the cohesion strength of the toner.

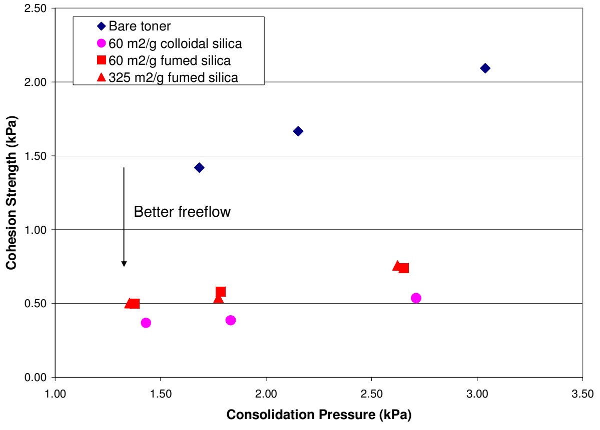


***Figure 7.*** *Comparison of cohesion strength for toner formulated with 2 wt% colloidal and fumed silica measured using a ring shear tester.*

These similarities of the two fumed silicas can also be observed in Figure 8 where the bulk densities of the various toners are compared. The bare toner has the lowest bulk density because of its high cohesive strength. The toners formulated with treated silica external additives have higher bulk densities. The toner formulated with the colloidal silica has the highest bulk density, as expected based on the other results.

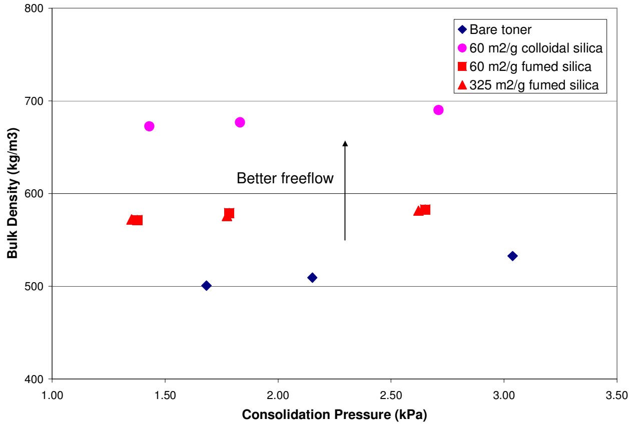


***Figure 8.*** *Comparison of bulk density for toner formulated with 2 wt% colloidal and fumed silica measured using a ring shear tester.*

## Conclusions

The trend towards color chemical toner based on polyester resins has necessitated the use of additives with larger primary particles to ensure durable performance. In comparisons of coverage, tribocharge, and freeflow of colloidal and fumed silicas with the same surface area and correspondingly same average primary particle size we find that the colloidal silicas can provide similar tribocharging performance with enhanced freeflow, which can be attributed to their ease of dispersion and unaggregated morphology which leads to better coverage of the toner surface.

This study has focused on toners formulated with a single additive. In real formulations, multiple additives are needed to provide the right balanced performance. Both fumed and colloidal treated silicas should be considered in the optimization of the formulations.

## References

[1] A. S. Diamond, "Handbook of Imaging Materials", Marcel Dekker (1991).
[2] D. Fomitchev et al., Tribocharge Performance of Colloidal Silica Additives in a Dual Component Developer, NIP 25 (2009).
[3] J. Liu, et al., External Additives for Toners: Treatment with Functional Silanes for Active Triboelectrostatic Charge Control, NIP 25 (2009)
[4] G. Mehos, S. Clement, Prevent Caking and Unintended Agglomeration, Chemical Engineering, 55, August, (2008)
[5] L. B. Schein, "Electrophotography and Development Physics", Laplacian Press (1996)