

Treated Colloidal Silica Particles for Toner Formulations

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Abstract

Surface modified silica particles are used as external additives to toners to improve free flow, to reduce agglomeration of toner particles, and to modify the tribo-charging characteristics of the final toner formulation. In many of the new toner formulations, large diameter spherical silica particles, rather than the traditional aggregated fumed silicas, are needed to give the required performance characteristics to the toner. In fact, large (order 100 nm) spherical silica particles have been cited as an essential additive in preventing agglomeration in new toner formulations [1].

The manufacture of large treated spherical silica particles presents a variety of chemistry and processing challenges. Both the reaction and drying conditions during manufacture must be carefully controlled to produce powders with uniform treatment and minimal aggregation. In this paper, we shall discuss the effects of the treatment chemistry and the base silica particle size on toner tribo-charging and humidity stability and toner free flow for a model toner system.

Introduction

The development of new and smaller toner particles made by direct polymerization processing has led to a need for next generation free flow and anti-blocking additives. Traditionally, surface treated (hydrophobic) fumed silica has been widely used as the principal free flow and tribo-charge additive. However, because these new toner particles have a smaller size, and therefore a higher surface area per unit mass, greater inter-particle spacing is required than in standard toners to reduce the interaction energies, per unit mass, to acceptable levels. Consequently, new metal oxide additives are needed to supply the requisite free flow, anti-blocking, and tribo-charge performance that these smaller and more uniform polymerization toners require. Ideally, these new additives should also possess a narrow size distribution as very fine particles will tend to be impacted into the toner surface while large particles will adhere poorly to the toner surface.

We have attempted to address these needs by developing a series of fully treated colloidal silica particles. Unlike fumed silica, liquid phase colloidal silicas can be manufactured and processed to give a broad range of particle sizes, narrow size distributions, and a range of particle morphologies. A more spherical particle morphology and a narrow size distribution can provide improved anti-blocking and free flow performance compared to fumed silica, while different particle sizes allow us to optimize the inter-particle spacing. Furthermore, by controlling the subsequent treatment chemistry and drying conditions, we can vary both the tribo-charging and free flow performance of the additive.

This ability to de-couple the physical shape and size characteristics of the particle from the subsequent treatment chemistry gives us a highly versatile manufacturing approach and allows us to deliver a wide range of additives that can be tailored to the needs of a specific formulation.

Experimental

Stable colloidal silica dispersions can be made or are commercially available at silica concentrations of up to 40 wt% (and even higher) and with a mean particle size of less than 10 nm to over 120 nm. Dispersions having a quite narrow size distribution – with a geometric standard deviation, σ_g , as low as 1.2 – can be obtained. Particle shape ranges from almost spherical to irregular spherical (‘potato-like’ shape). Dispersions of rod-shaped and chain-like aggregates of silica particles are also available. Typical size distributions are shown in Figure 1 for several colloidal silicas of different average size.

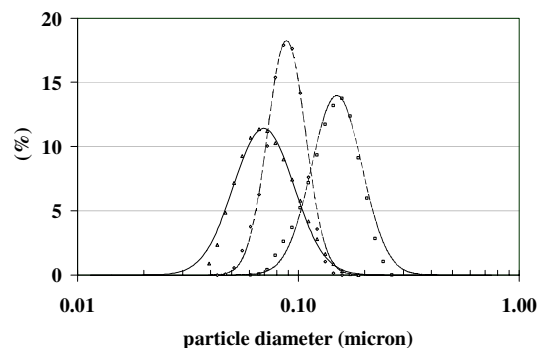


Figure 1. Particle size distributions for a series of ‘irregular spherical’ colloidal silicas measured by dynamic light scattering. Curves are best-fit log-normal distributions.

We have chosen to characterize the colloidal silicas by dynamic light scattering (Microtrac UPA Analyzer). Traditionally, colloidal silicas are characterized by a particle diameter calculated from surface area measurement on the dried colloidal silica:

$$d_{p,ave} = 6000/(\rho \cdot SA) \quad (1)$$

where d_p is the particle diameter in nm, SA is the surface area in m^2/g , and ρ is the density of the solid in g/cc . The average particle size obtained by dynamic light scattering measurements tends to be substantially higher than the particle size calculated from surface

area measurements even after taking into account the volume-average to surface area-average correction [2], which is small for distributions with small σ_g values (approx. 7% at $\sigma_g = 1.3$). For comparative purposes, the corresponding average surface areas (calculated by eq. 1) for the distributions shown in Figure 1 are: 19.0, 30.8, and 38.1 m²/g.

Commercial colloidal silicas are made by aggregation of sodium silicate sols at basic pH and under hydrothermal conditions. However, Stöber-type colloidal silicas made from TEOS are also commercially available as are colloidal silicas made with fumed silica particles (e.g., Cab-O-SperseTM, Cabot Corp.).

The colloidal silicas were treated with either a mono-functional trimethyl silane, a tri-functional C₈ (n-alkane) silane, or with mixed functional silanes directly in the liquid phase. The treatment reactions were done at two distinct treatment conditions. The treating agents, solution chemistry, and processing conditions can all be varied to yield particles having different levels of treatment, cross-linking of the treating agents, and surface functionality.

After treatment, the dispersion is dried to yield a fine white powder. The powder is composed of loosely agglomerated individual colloidal silica particles that can be readily re-dispersed as described below.

All of the samples were manufactured in a pilot plant facility at multi-kilogram scale.

The treated silicas were characterized for carbon loading, surface area, and particle size. In addition, both proton and ²⁹Si NMR were used to determine the loss of surface silanols and to characterize the functionality of the surface treatment.

The toner was formulated by mixing 4 wt% of the treated colloidal silica in a laboratory blender with a pulverized styrene-acrylate toner (average diameter = 9 μm) free of any external additives. Theoretical toner coverage is 60% for the 90 nm colloidal silica. The silica loading was held constant in all of the tests.

The toner was developed by rolling for 30 min at 2% loading in glass jars. The carrier is a 70 μm Cu-Zn ferrite coated with silicone resin. Samples were conditioned in a standard humidity chamber at HH (35° C and 80% RH) and at LL (18° C and 15% RH) conditions overnight. The tribo-charge was measured in a Vertex T-150 blow-off tribo-charger.

Free flow was measured using an in-house made perforated roll tube by measuring the amount of toner discharged from the tube after 30 rotations. The roll tube is 25 mm in diameter and has seven 0.5 mm discharge holes. It is rotated at 30 rpm. The initial charge to the tube is 40 g.

The objective of these experiments was to determine the effect of the additive particle size, the treating agent, the treatment methodology and process conditions on the tribo-charging and free

flow performance of the silica particles when used in a dual component toner formulation.

Results

We are able to treat various colloidal silica dispersions directly in the liquid phase using several different process conditions. The treated, dried particles retain their original size and shape and can be redispersed either in a solvent or by admixing with toner particles. As an example, Figure 2 shows the particle size distribution of the treated, dried powder after re-dispersion in a solvent (THF) with sonication relative to the original colloidal silica particle size distribution. Aside from a small secondary peak – presumably consisting of particle agglomerates – the particle size distribution is recovered nearly intact.

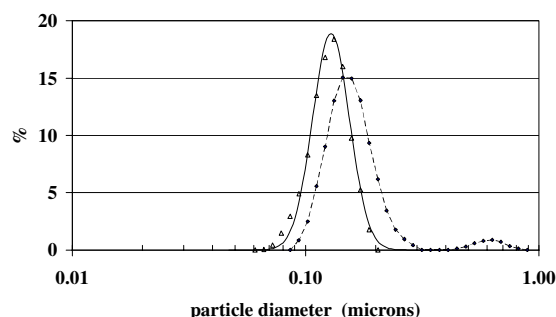


Figure 2. Particle size distribution of the original colloidal silica (—Δ—) compared to the particle size distribution of the treated powder (---◇---). Powder redispersed in THF and sonicated.

When admixed with toner particles, the silica shows excellent dispersion and good adhesion to the toner particle. This is shown by the electron micrograph in Figure 3.

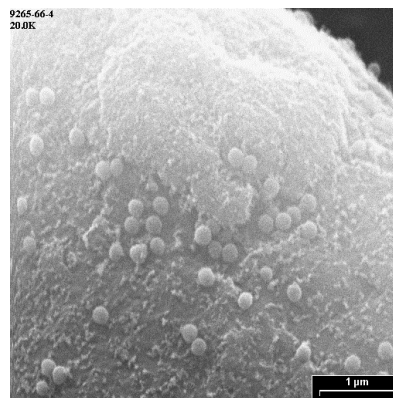


Figure 3. SEM image of treated colloidal silica particles dispersed on a styrene-acrylate toner particle

The tribo-charge performance of the treated colloidal silicas is shown in Figure 4. Here the HH tribo-charge data are presented as a function of the average particle diameter for all three of the treating agents and for two treatment conditions. Particles made at process condition 2 clearly have a higher tribo-charge than those made at condition 1. Surprisingly, there is no effect of particle size for the 90 and 130 nm particles. With smaller particles, a trend towards increasing tribo-charge is noted, although the number of data points is small.

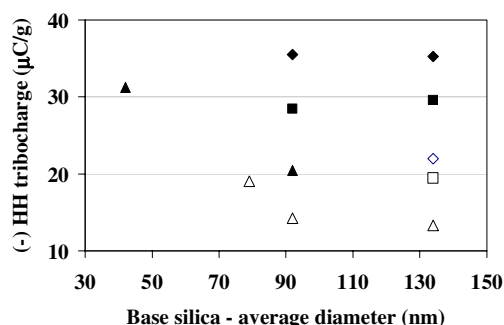


Figure 4. The (-) HH tribo-charge of the toner as a function of the base-silica particle diameter. Open symbols are process condition 1; closed symbols are process condition 2; □: mono-functional treating agent; △: tri-functional treating agent; ◇: mixed functional treating agent.

Treatment with mixed functional silanes gives the highest level of tribo-charging. Through modification of the process conditions and by changing the treating agent, it is possible to move the tribo-charge over a fairly broad range of values. For the two large particle sizes that were extensively studied in this project, no effect of size on tribo-charging was noted. This implies

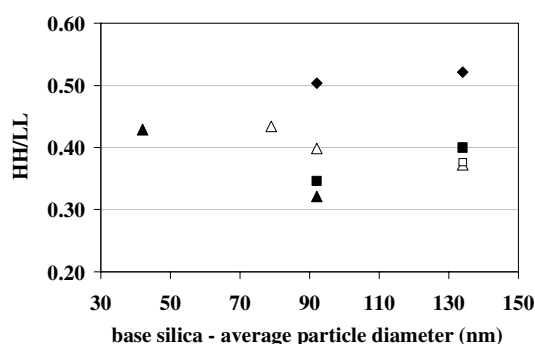


Figure 5. The HH/LL humidity sensitivity ratio as a function of the average diameter of the base silica. Symbols are as in Figure 4.

that, with this particular toner formulation, it is possible to change the additive size within this range without affecting the tribo-charge performance.

Figure 5 shows the ratio of the tribo-charge at HH to LL conditions as a function of the average particle diameter. Although the mixed functional silane again gives the best HH/LL ratio, the differences between the other treating agents and the two process conditions are no longer as pronounced.

Figure 6 shows the toner fluidity as measured by the amount discharged from the roller device. The data are plotted as a function of the additive diameter. Free flow is optimized with surface treatment using the mono-functional silane. The choice of processing conditions seems to be less important. No effect of particle size was noted over the entire size range except for the case of the mono-functional treating agent.

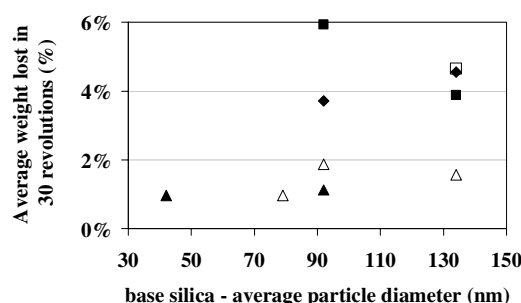


Figure 6. Free flow data as a function of the average diameter of the base silica. Symbols are as in Figure 4.

Discussion

By changing the reaction conditions and treating agent, one can produce additives with a broad range of tribo-charging and free-flow characteristics. The performance attributes shown above are a function of the model formulation used in this study; other toner formulations will probably give somewhat different response characteristics. For this toner system, the size of the additive, in the range of 90 – 130 nm, had little effect on the tribo-charge and free flow performance. Nonetheless, the ability to choose particle size and treatment chemistry independently gives a substantial degree of flexibility to the manufacturing process.

Mixed and mono-functional treating agents were found to give the best tribo-charge and free-flow performance. The reaction of mono-functional silanes with the silica surface is believed to be straightforward in that the silane bonds directly to a silanol site [3]. The reaction is site specific, and the surface area of the silica determines the carbon loading. For a trimethyl group, the theoretical sterically limited surface coverage is 2.7 groups/nm² (8.1 C-atoms/nm²) [4] and such a treating agent will give a nearly uniform hydrophobic umbrella over the surface of

the silica. Sterically, this configuration provides sufficient space for water molecules to sit beneath the organic umbrella and hydrogen bond with residual surface silanols since only 1/2 to 2/3 of the available surface silanols are directly reacted. It is known that greater quantities of carbon than the theoretical limit can be added to the surface presumably through reaction at locally catalyzed surface sites, where Si-O-Si bonds are cleaved and more complex silsesquioxane-like and polymeric structures can form [5]. Carbon measurements showed that the actual trimethyl coverage is typically between 3 and 6 trimethyl groups/nm², or up to 2x the theoretical limit.

In comparison, tri-functional treating agents can react with silanol groups on the silica surface as well as cross-link with each other either at the surface or in the liquid phase prior to reaching the surface. Multiple layers of carbon can be put on the oxide surface in a non-specific manner. Total carbon loading is determined by the amount of treating agent that is added to the system as no vapor phase route exists for removal of the treating agent once cross-linking takes place. Furthermore, by altering the reaction conditions, one can influence the reaction pathways by impacting the relative rates of the hydrolysis, cross-linking, and direct surface reactions. The intent of reaction conditions 1 and 2 was to provide an environment where the relative rates of these reaction pathways are quite different. This was indeed the case as was shown by subsequent ²⁹Si NMR analysis of samples made at the two different reaction conditions. However, reaction condition 2 yields particles with a higher tribo-charge that cannot be explained only by variations in the relative extent of cross-linking and surface bonding.

Mixed functional treating agents were tried so as to obtain both an increase in carbon coverage beyond the amount possible with mono-functional silanes alone and to decrease the silanol content of both the silica surface and that occur as a result of incomplete cross-linking of the tri-functional silane. NMR measurements show that the cross-linked trifunctional silanes contain a substantial number of hydroxyl groups. While the use of mixed functional silanes did not eliminate these silanols completely, it decreased their number significantly.

Although we believe to have some understanding of the silane chemistry at the silica surface, the connection between surface treatment chemistry and tribo-charging remains elusive. This is an area of considerable study. A recent paper by Veregin et al. [6] has shown that the tribo-charge of the metal oxide additive can be predicted on the basis of the ratio of the acid to base – electron acceptor to electron donor – sites on the additive particles. However, what remains unknown is how the various surface treatments will affect this ratio.

Conclusions

Fully hydrophobic silica particles of different sizes and shape morphologies can be made by surface treating colloidal silicas with organosilanes. We have shown that the size distribution of the treated silica is practically the same as the original base colloid so that it is possible to independently vary particle size and surface treatment.

Both tribo-charge and free flow performance is strongly influenced by reaction conditions and the type of treating agent. Tribo-charge can be maximized through the use of mixed functional silanes. Particle size – in the range of 90 to 130 nm – does not have an effect on the tribo-charging characteristics of the toner.

The results presented here are for a model toner system. For other developers and formulations, the performance characteristics of the additive may be substantially different. As a result, we believe that it is imperative to develop a flexible and versatile manufacturing process that can make additives having a wide range of particle size and surface treatments, which can be tailored to the needs of a specific toner formulation.

References

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