Colloidal Silica Particles for Toners: Treatment Chemistry

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Abstract

Treated colloidal silica particles represent a new, prominent class of toner formulation additives, which have recently become commercially available. Many of the performance aspects of these particles are determined principally by the particle surface chemistry. We have found that by careful control and manipulation of the surface treatments, we can control the magnitude of the tribo-charge and manufacture additives with either a negative or a positive tribo-charge.

In this paper we present tribo-charge results for a class of silica powders manufactured from aqueous colloidal silica dispersions. Surface treatments are done using various mono- and tri-functional organosilane treating agents. Analysis of these silicas using magic angle spinning cross polarization NMR provides detailed information on the chemical moieties present on the surface and allows us to better understand how these moieties impact the performance properties of the additive.

Introduction

The treatment of colloidal particles with organosilanes in the liquid phase has made available a range of new treated particles having widely different particle size, particle shape, and surface treatment. Liquid phase treatment allows one to use a variety of treating agents, and process conditions which permit the development of additives with performance characteristics that can be tailored to the needs of various formulations.

Unlike fumed oxides, colloidal metal oxides are available in sizes from <10 to >200 nm. Typically, the particles are unaggregated and have a near spherical shape, but colloidal dispersions having structured particles (e.g., Cab-O-Sperse™) are also commercially available. The key factor in the treatment of these aqueous dispersions is to provide sufficient surface treatment of the particles so that agglomeration does not occur when the dispersion is dried and converted to a dry powder. We have previously reported [1] that by careful control of the liquid-phase treatment chemistry, one can obtain a particle that retains the size and shape of the original colloid.

In this study, we extend our surface chemistry to include treatment with amine functionalized organosilanes that yields a silica additive that can provide the toner with a positive tribo-charge. Colloidal silicas with different particle sizes were treated with mono-functional, tri-functional or with a mixture of mono and tri-functional silanes directly in the liquid phase. (This silane functionality is with respect to hydrolysis and gives the reactive groups that link with the silanol groups on the silica surface.) Some of these silanes contain amino groups, which provide the positive tribo-charge. Results are given for surface treatments performed at two distinct reaction conditions (#1 and #2). In general, however, the processing conditions and solution chemistry can be varied over a wide range of conditions to yield particles with different levels of treatment, extent of cross-linking, and surface functionality.

The objectives of this study were to determine the effects of reaction conditions, type of treating agents, and particle size on tribo-charge performance of the silica additive in a standard toner formulation. In addition, solid state ^{29}Si, ^{13}C, and ^{1}H NMR were used to determine the surface functionality, which provide an understanding of the relationship between surface chemistry and tribo-charge characteristics.

Experimental

Several colloidal silicas with different mean particle sizes were treated with either a mono-functional trimethyl silane, a tri-functional silane, or with mixed functional silanes directly in the liquid phase. After treatment, the dispersion was dried to yield a fine white powder. The powder is composed of loosely agglomerated individual colloidal silica particles that can be readily re-dispersed back to the original colloidal silica particles.

The treated silicas were analyzed for surface area, total carbon content, and particle size distribution. In addition, selected samples were also analyzed by solid state ^{1}H, ^{29}Si, and ^{13}C NMR.

Solid state NMR spectra were recorded using a Bruker Avance II NMR spectrometer with ^{1}H, ^{29}Si, and ^{13}C resonance frequencies at 400.19, 79.49, and 100.62 MHz, respectively. ^{1}H magic-angle spining (MAS) NMR spectra were collected with direct polarization at a MAS rate of 14 kHz. Both ^{29}Si and ^{13}C NMR were measured using the cross-polarization magic-angle spining (CP/MAS) technique with MAS rates at 8 kHz and 12 kHz, respectively. Linear ramp of proton channel RF amplitude from 70% to 100% during the cross-polarization contact time was used for achieving good and stable Hartmann-Hahn matching condition at the high magic angle spinning speeds. The contact time for ^{29}Si CP/MAS measurements were set as 10 ms, while ^{13}C CP/MAS used a contact time of 1.5 ms. High power composite pulse proton decoupling (TPPM) was applied during the data acquisition period. All of the NMR measurements were performed at room temperature. The ^{1}H, ^{29}Si, and ^{13}C NMR chemical shifts were referenced to tetramethylsilane using an external standard of tris(trimethylsilyl)silane.

Tribo-charge measurements were done using a Vertex T-150 blow-off tribocharger. Samples were prepared by mixing in a laboratory blender 4 wt. % of the treated colloidal silica with a pulverized styene-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 toners were developed by rolling toner (2 wt. %)/carrier (98 wt. %) mixture for 30 min in glass jars. The carrier is a 70 µm Cu-Zn ferrite coated with silicone resin. Before measurements, 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.

Results

Treatment with mono- and tri-functional alkyl silanes.

Results of tribo-charge measurements for a colloidal silica with a mean particle size of 85 nm treated with three different or mixed organosilanes at reaction conditions #1 and #2 are summarized in Table 1.

The data illustrate the pronounced effect that the different treating agents can have on the tribo-charge performance of these additives in a toner formulation. Depending on treatment, tribo-charge varies over 30 µC/g range at HH and over 67 µC/g at LL conditions.

Table 1. Tribocharge data for a series of samples treated with different silanes at two reaction conditions.

#	Treatment	HH (µC/g)	LL (µC/g)
1	Mono-functional amino silane and tri-functional alkyl silane	-4	+9
2	Tri-functional silane, Condition #1	-14	-29
3	Mono-functional silane, Condition #1	-21	-51
4	Tri-functional silane, Condition #2	-19	-52
5	Mono-functional silane, Condition #2	-27	-68
6	Mono-functional/ Tri-functional silane, Condition #2	-34	-58

In fact, the use of amino-functional treating agents can yield a fully positive tribo-charging additive, and extend the tribo-charge range even further than shown in Table 1. Amino silane treatment of colloidal silica, such as example **1**, will be discussed in the next section of this paper.

In this section, we will focus attention on the NMR results for negative charging additives, as illustrated by samples **2**-**6**, which were treated with mono- and tri-functional alkyl silanes at two processing conditions, designated as conditions #1 and #2.

SEM photograph of conventional toner particle covered with treated colloidal silica **6**, is shown in Figure 1.

^{29}Si CP MAS NMR spectra of **2** and **4** as well as the spectrum of the untreated base silica are shown in Figure 2. Peaks Q2 and Q3 in these spectra are due to the silicon atoms of the surface that are bonded only to oxygen atoms and having one and two OH groups attached, respectively [2].

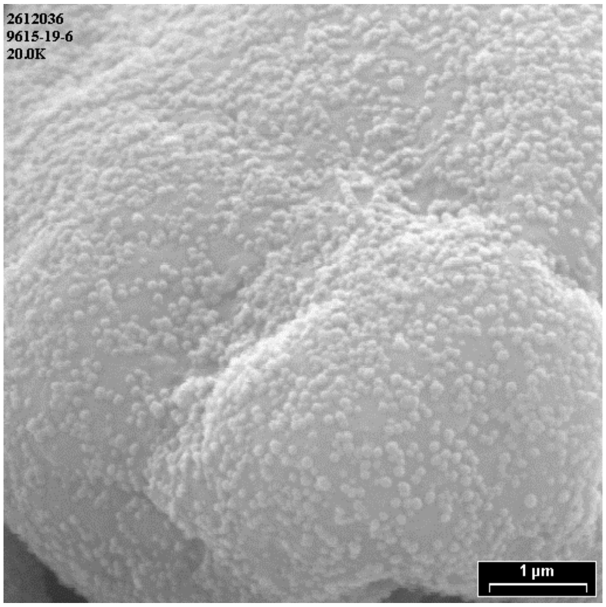

*Figure 1. SEM photograph of **6** on the surface of conventional toner particle. Loading of **6** is 4 wt %.*

Comparison of the relative intensities of Q2 and Q3 before and after the treatment suggest that more treating agent was attached to silica surface at condition #1 than at condition #2.

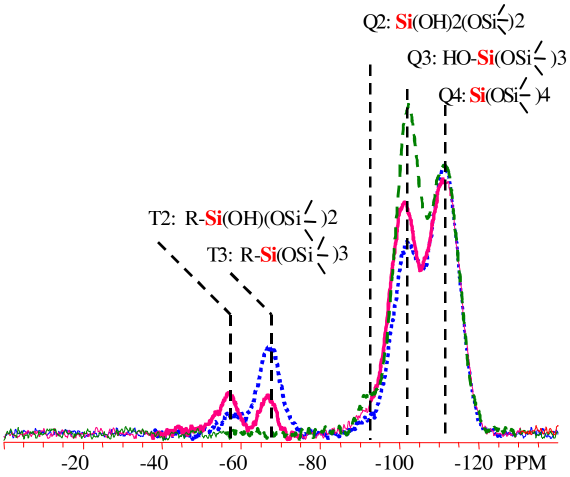

*Figure 2. ^{29}Si CP/MAS NMR spectra of untreated silica (dashed line), sample **2** (dotted line), and sample **4** (solid line).*

Peaks T2 and T3 are due to the silicon atoms that are bonded to three oxygen atoms and one carbon atom of alkyl group, and having one uncondensed hydroxyl and no uncondensed hydroxyl, respectively [2]. These signals appear only in the spectra of organosilane treated particles and do not appear in the spectra of untreated silica. Relative intensities of T2 and T3 suggest that the treating agent is significantly more cross-linked when the reaction is conducted at condition #2 rather than at condition #1. For both T2 and T3, it is difficult to differentiate between a siloxane bond to the silica surface and a siloxane bond that is a cross-link to another treating agent. Based on steric considerations, we believe that a silane is typically attached to one or two surface sites, and T3 is mostly due to the surface attached silane that is corss-linked to at least one other silane molecule.

Samples **3** and **5** were treated with mono-functional silane at conditions #1 and #2, respectively. Comparison of tribo-charge data for **2** and **4** as well as for **3** and **5** indicates that treatment at condition #2 systematically affords samples with higher tribo-charge than treatment at condition #1.

Sample **6** was treated with a combination of mono- and tri-functional silanes. We have observed that dual treatment at condition #2 affords samples with the highest tribo-charge that also possess a good balance of other properties such as good free flow and more constant tribo-charging over a range of HH to LL conditions.

It has been previously reported [3, 4] that tribocharge is strongly influenced by the humidity of the environment and presence of water molecules on particle surface. ^{1}H MAS NMR allows one to probe treated silica for the presence of water molecules attached to the surface via hydrogen bonding as well as bulk water layers present on the surface. Figure 3 shows the ^{1}H MAS NMR spectra of **6** after drying from the aqueous dispersion together with the spectrum of the same material after it was extracted with an organic solvent. The intense peak at 5 ppm is due to multi-layer or bulk water on the particle surface. This water may be located at the silica surface in regions below the hydrophobic organic surface or in the pores between the particles. Somewhat surprisingly, extracted samples, from which unattached silanes have been removed, do not exhibit the bulk water peak but only show a broad water peak around 3 ppm. This peak is indicative of the presence of a monolayer of water attached to the surface via hydrogen bonding. Further studies of the effect of bulk and hydrogen bonded surface water on tribocharging are currently underway.

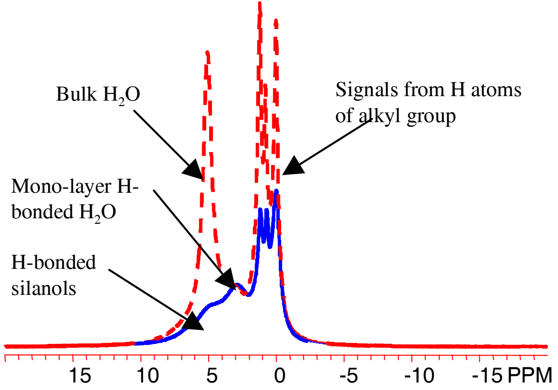

Figure 3. *^{1}H MAS NMR spectra of **6** dried from aqueous dispersion (dashed line), and extracted with an organic solvent (solid line).*

Treatment with mono-functional silane containing amino group. Unlike particles treated only with surface hydrophobizing reagents such as alkyl silanes, colloidal silicas treated with silane containing an amino group show a direct correlation of tribo-charge with the amount of amino silane on the surface and with particle surface area. Alkyl silane treated particles do not show a direct dependence of tribo-charge on carbon loading or a significant dependence on surface area in the 20 – 60 m^2/g range. The relationship between the tribo-charge and the amino silane loading is illustrated in Figure 4.

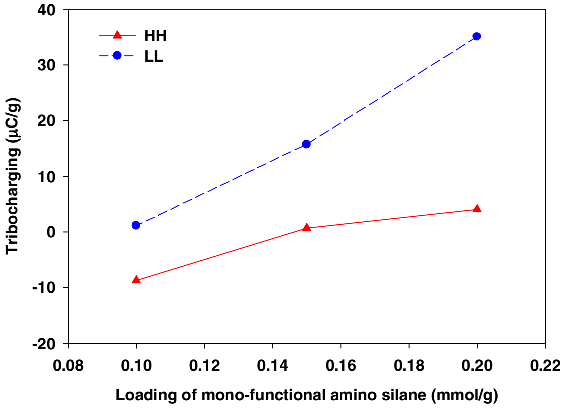

Figure 4. *Tribocharge as a function amino silane loading for colloidal silicas treated with amino silane and tri-functional alkyl silane.*

The dependence of tribo-charge on surface area (particle size) is shown in Figures 5 and 6. The same linear correlation between the tribo-charge at HH and LL conditions and surface area of the sample is observed for both types of surface treatment, as is the magnitude of the charge. This suggests that the magnitude of the tribo-charge is determined by the amount of amino silane present on the surface.

The alkyl silane also plays an important role because it provides essential hydrophobic characteristic not existing on surfaces treated with amino silane alone. Absence of hydrophobizing co-treatment diminishes the magnitude of the positive tribo-charge. This is shown by the solid state ^{1}H NMR data in Figure 7 and tribo-charge data summarized in Table 2. Samples **7** and **8** have the same amount of amino silane attached (carbon content after treatment with amino silane is 0.85 % for both materials). But as shown by the NMR spectra, application of the second level of surface treatment clearly reduced the amount of bulk water on the surface.

More detailed studies of the effect of hydrophobic treatment on tribo-charge of amino silane treated colloidal silica are currently underway.

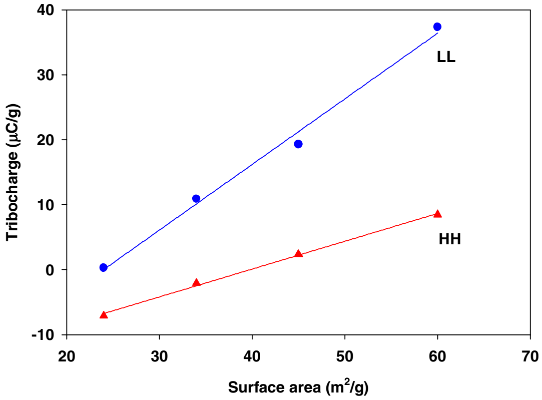

Figure 5. *Tribocharge as a function of surface area for particles treated with mono-functional amino silane and tri-functional silane.*

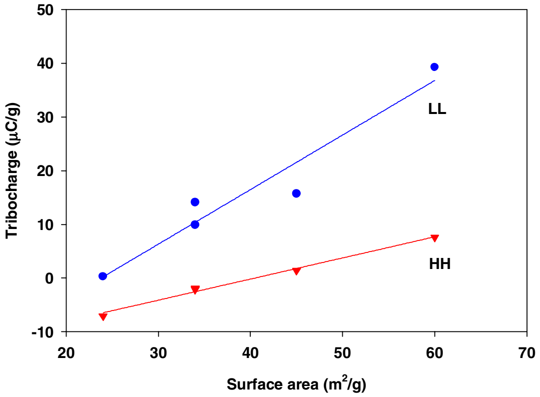

Figure 6. *Tribocharge as a function of surface area for particles treated with a mono-functional amino silane and a mono-functional alkyl silane.*

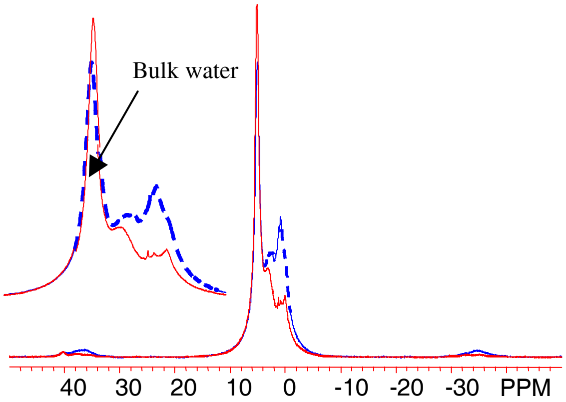

Figure 7. *^{1}H MAS NMR spectra of **7** (solid line) and **8** (dashed line). **7** contains significantly more bulk water as illustrated by intensity of the peak at ~5 ppm. Insert on the left is magnified part of the spectrum between 15 and –5 ppm.*

Table 2. Tribocharge data for mono-functional amino silane treated silicas.

#	Treatment	HH (μC/g)	LL (μC/g)
7	Amino silane only	-9	-13
8	Amino silane and alkyl silane	-2	+11

^{13}C CP/MAS NMR spectra of two samples treated with 0.05 and 0.15 mmol/g of a mixture of amino silane and alkyl silane are shown in Figure 8. Signals from the carbon atoms of the amino silane chain are identified on the spectra. As expected, the signal intensity correlates with the amount of treating agent used. The relative intensities and width of peaks associated with different carbon atom positions in the chain can be interpreted in terms of the relative mobility of the atoms on the surface and position of the organic chain with respect to the surface.

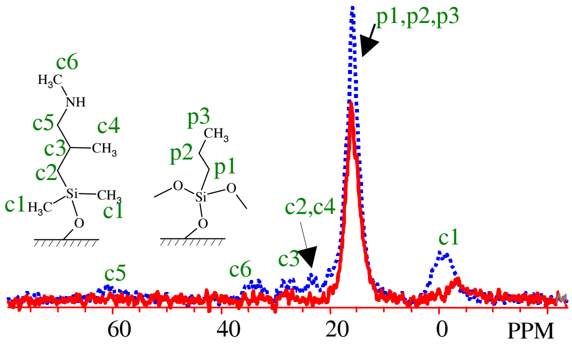

Figure 8. *^{13}C CP/MAS NMR spectra of silica treated with 0.05 mmol/g (solid line) and with 0.15 mmol/g (dotted line) of amino-silane and with tri-functional alkyl sialne.*

Conclusions

Data presented in this paper demonstrate that by changing silane treating agents and treatment conditions we can alter the tribo-charge performance of a model toner formulation over a wide range.

We have also found that solid state NMR spectroscopy is a very powerful tool for characterization of the functional groups on the silica surface. By combining solid state ^{1}H, ^{13}C, and ^{29}Si NMR, we can begin to develop semi-quantitative correlations between surface functionality and tribo-charge performance. The work to date has primarily focused on identification of the principal surface groups and determining which groups may have the most significant influence on tribo-charge behavior.

References

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