The Effects of Fumed Silica Structure on Toner Properties

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Abstract

The majority of today's electro-photographic toners incorporate an external additive(s) to fine tune their desired performance attributes. One of the key additives found to be effective at influencing powder flow, charging behavior, and charge stability of conventionally milled or chemically produced toners is fumed silica and more so if the silica has been rendered hydrophobic.

Fumed silica is produced via a pyrogenic process and results in primary particles coalescing, fusing and sintering to form particles with an aggregated structure. This secondary particle has a size ranging from approximately 100 – 200 nm depending on the process conditions for the specific silica grade. These aggregates form hydrogen bonds via the silanol groups and also become mechanically intertwined forming a tertiary structure called agglomerates. The size of these agglomerates can span from several microns to several hundred microns. Due to the much larger size and irregularities associated with an agglomerated particle, more aggressive shear conditions would be required to distribute the silica more uniformly on the toner surface. Such conditions could lead to silica becoming embedded and affect the toner itself. In the end, the structure and size of the agglomerate results in particle dispersibility unto the toner being compromised. Poor dispersibility of the external additive can lead to non-uniform behavior with respect to the toner's flow, charge and stability leading to sub-standard print performance and longevity.

In an earlier paper we presented a study comparing structure modified de-agglomerated fumed silica to that of traditional fumed silica[1]. The conclusion then was that de-agglomerated silica dispersed more efficiently and thereby led to improvements in toner flow, charging characteristics and charge stability. In this study, the work is a continuation and extension of the effects structure modification has on performance.

1. Introduction

Fumed silica is generally characterized by three distinct parameters: 1) particle size and distribution, 2) surface chemistry/treatment and 3) structure. When speaking of silica structure, there are two "forms" we will refer to: the aggregate and the agglomerate. The aggregate structure is a fusion of primary particles held together with strong forces that is not divisible by ordinary means. The agglomerate is a collection of these aggregates which are held together by weak forces and mechanical entanglement and will break down to aggregates with sufficient application of shear forces.

Typically, the smaller agglomerated structures (aggregate clusters) will require more intense shearing to break down to the aggregate structure. Furthermore, the surface treatment employed can affect the agglomerate's "stability". The poly-dimethylsiloxane (PDMS) treatment tends to result in an agglomerate which is more resistant to shear as compared to a dimethyldichlorosilane (DDS) treatment due to the adhesive/cohesive differences. To achieve a uniform mass distribution of a small, adhesive external additive on the toner particle will require more energy and as a byproduct of this process, result in more heat being generated.

As the market shifts to raw toners with lower glass transition temperatures (Tg), the incidence of toner deformation, additive embedding and particle-particle adhesion will increase. Another aspect of a lower Tg, chemically produced toner (CPT) to be considered is the adhesive surface presented to the silica agglomerate. When the agglomerate initially adheres to the tackier toner surface, the agglomerate can require more energy and time to break down to the smaller aggregates - if it isn't embedded into the toner first.

A conventionally milled toner due to its irregular shape would help break down silica agglomerates somewhat better in a mixing process than a chemically produced toner (CPT) which has a more spherical shape. This rounder shape of the CPT exerts less shear on the silica agglomerate during mixing.

One potential remedy is the development of external silica-based additives that can disperse rapidly and uniformly on the toner surface with a minimal amount of shear. Reducing shear force also minimizes heat generation from the process, which is advantageous for the lower Tg toners. Structure modified silica have been shown to disperse quickly, efficiently and cover the toner surface more uniformly[1].

This paper will explore the de-agglomeration of silica types that vary based on surface treatment, structure modification and particle size in order to enhance the dispersibility of silica in terms of rate and coverage on a toner particle.

2. Experimental Procedures

2.1. Materials

2.1.1 Core materials

The fumed silicas used in this work were supplied by Evonik Industries AG and NIPPON AEROSIL CO., LTD. and produced by established processes previously described[2]. The pyrogenic process to make fumed silica has great versatility to produce average primary particle sizes ranging from 7 to approximately 100 nm[3], encompass a variety of hydrophobic treatments and structure modifications.

2.1.2 Structure modification

Two distinct processes have been used to alter the agglomerate structure of the silica particles of interest. The process details are beyond the scope of this paper. However, one of the obvious effects, which are dependent on the agglomerate altering process employed, is the change in bulk density. A standard silica would typically have a bulk density in the range of ~40 – 50 g/l.

The high energy process (herein called **structure modification**) used to produce the AEROSIL® R 9200 (sample “D4”) material yielded a bulk density of 171 g/l. This process substantially increases bulk density over the starting core powder. Employing a lower energy process (herein called **de-agglomeration,**), on AEROSIL® RY 300 (sample “L3”), R 974 (sample “L4”) and R 972 (sample “L2”), reduced bulk density. The decrease in bulk density values, between the standard (samples designated with an “A” prefix) and de-agglomerated version (samples designated with the “L” prefix), is as little as 23% for the AEROSIL® R 972 (sample A2 vs L2), 35% for the AEROSIL® R 974 (sample A4 vs L4) and as much as 57% for the AEROSIL® RY 300 (sample A3 vs L3). Particle size and surface treatment are two other distinct variables contained in this work as defined in Table 1.

Table 1: General characterization of fumed silica samples

Sample ID	BET (m^2/g)	1° Particle Size (nm)	Surface Treatment	Bulk Density (g/l)
A3	300	7	PDMS	51
L3	300	7	PDMS	22
A4	200	12	DDS	49
L4	200	12	DDS	32
D4	200	12	DDS	171
A2	130	16	DDS	52
L2	130	16	DDS	40

Fumed silica is commonly treated with a hydrophobic reagent to affect the flow, charge behavior and stability of the toner. While there are a variety of silanes that are used to modify the silica surface[4], for this study PDMS and DDS treated silicas were selected.

2.1.3 Toner formulations

The toner used for this investigation was an 8 µm polyester negative-type black toner. In all cases, the amount of silica on toner is 1.00 ± 0.01% (wt/wt). Using a commercial lab blender, the toner and additive were first pre-mixed for 3 intervals of 10 seconds (with a 10 second cool down period between each interval) at an intermediate speed setting of 3. The samples were then sieved through a 300 µm screen. The material which passed through the screen was collected and placed in an environmental chamber at 25°C and 50% relative humidity for 24 hours minimum.

After conditioning, 2 grams of the specific toner-silica mixture was added to 48 grams of non-coated ferrite carrier (PowderTech Co. F150).

2.2. Methods

2.2.1 SEM analysis of toner mixtures

SEM images were taken of the toner particle with the various silicas to see the quantity and quality differences of silica coverage.

2.2.2 Dispersibility (particle size distribution)

In order to compare the dispersibility of members of a class of similar silica external additives, an indirect technique, earlier described[1], was used. In this method the silica’s particle size distribution is measured (Horiba Particle Size Analyzer LA-950) in ethanol while applying set amounts of shear through sonication. Through careful control of time and shear conditions, the relative dispersibility of the silica can be ascertained.

2.2.3 Tribo-electrostatic charge (T-ESC)

T-ESC was measured using a blow-off type electrostatic charge meter (Vertex T150). A sample of toner (2 g) was combined with a non-coated ferrite carrier (48 g) and agitated with a Turbula mixer. All sample preparation and measurement was carried out in a constant temperature/constant humidity room.

2.2.4 Charge distribution

The charge distribution was determined with a q-test (Epping GmbH). The toner formulation was agitated with a non-coated ferrite carrier using a Turbula mixer before measurement.

3. Results and Discussion

3.1. SEM analysis of toner mixture

Figure 1 shows the SEM images of the PDMS treated silica (A3 and L3) after blending for a 10 second interval 3 times (total = 30 seconds) on a commercial lab blender. These images show the same effect as seen from previous work with AEROSIL® RY 200[1]. A greater quantity of the de-agglomerated silica version (sample L3) can clearly be seen on the toner particle’s surface and it is distributed more uniformly as compared to the standard sample A3.

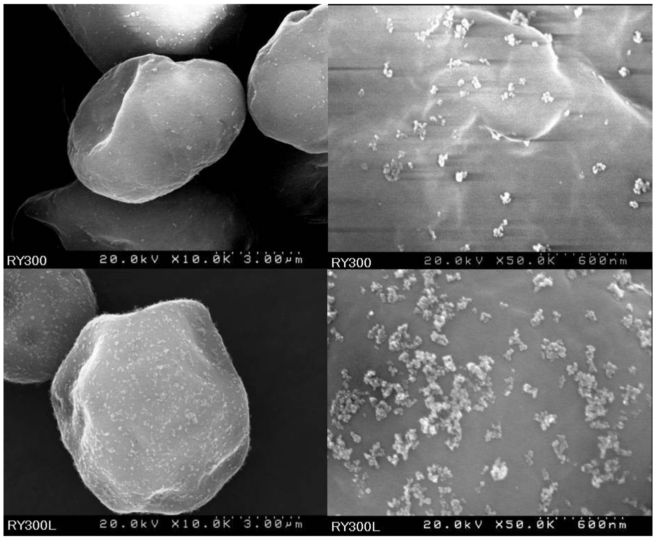

***Figure 1**. SEM images of AEROSIL® RY 300 (A3 - top) and RY 300 L (L3 - bottom) on the toner particle’s surface (agitation time is 1 minute)*

In contrast to the PDMS treated silica without the benefit of a de-agglomeration process (sample A3), the three DDS treated silicas covered the toner surface better qualitatively and quantitatively [Figure 2]. The de-agglomerated silica (sample L4) dispersed onto the toner surface in a greater quantity than the structured modified silica (sample D4). Under these shear conditions we see slight differences between the standard structure A3 sample and the de-agglomerated L4 sample. In Figure 2, it appears that the standard structure silica (sample A4) exhibits large clumps compared to the evenly distributed de-agglomerated silica (sample L4). This difference is subtle however and its impact on toner performance requires further testing.

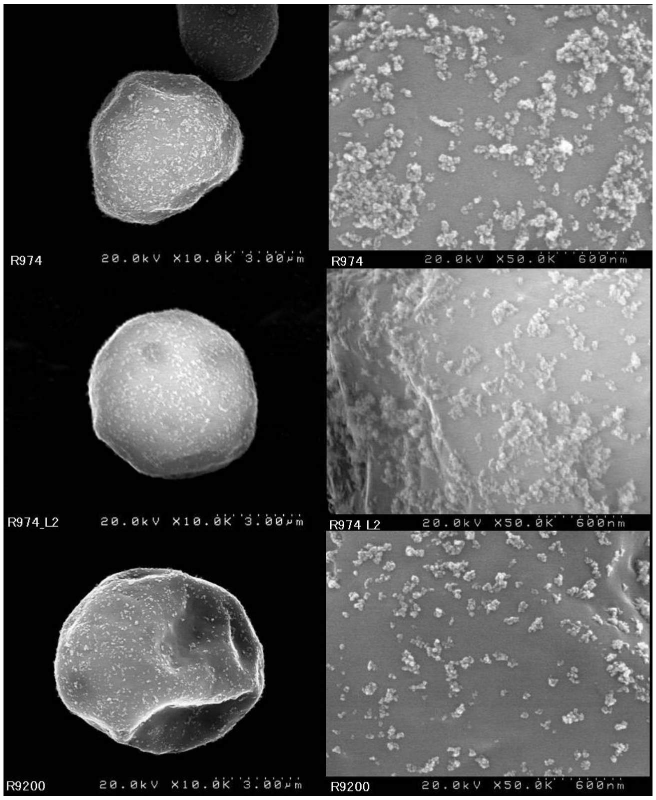

Figure 2*. SEM images of DDS treated silicas with different structuring processes:A4 – Standard, L4 – Low Energy and D4 – High Energy.*

3.2. Dispersibility

Using our indirect technique to characterize dispersibility, the initial particle size was measured on the various samples. The samples were then sonicated with the time required to achieve a particle size of less than 1 µm and the particle's size at breakdown being recorded [Table 2]. The methanol wettability values are an indication of silica surface's hydrophobicity. The PDMS treated samples (A3 and L3) have more hydrophobic character than the remaining DDS treated samples. Also note that the de-agglomeration process does not affect the silica's hydrophobicity.

Table 2: Methanol dispersibility of study samples

Sample ID	MeOH Wettability (%)	Initial Particle Size (µm)	Time To Breakdown (sec)	Size at Breakdown (µm)
A3	80%	84.03	>480	n/a
L3	75%	14.46	60	0.23
A2	55%	63.7	240	0.18
L2	50%	0.29	Immed.	n/a
A4	45%	65.55	240	0.41
L4	45%	0.29	Immed.	n/a
D4	50%	25.16	>480	n/a

From the above table, samples L2 and L4 did not require sonication to achieve a sub-micron particle size. While the L3 sample required 60 seconds, the remaining samples did not achieve a particle of less than 1 micron after sonicating for 480 seconds.

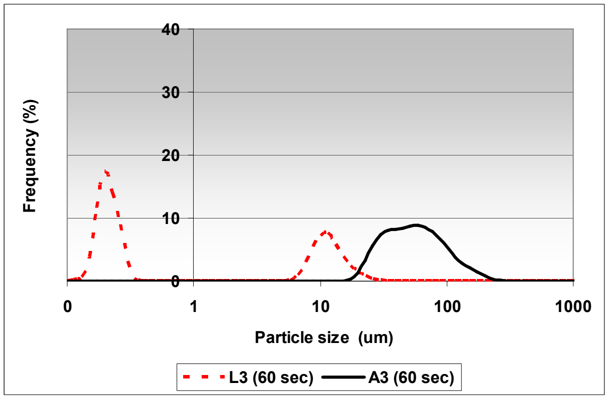

Figure 3*. Particle size distribution of samples L3 and A3*

Figure 3, above, shows the particle size distribution of sample A3 and the de-agglomerated version, sample L3 in ethanol after 60 seconds of sonication. The graph clearly shows the particle size distribution has shifted into the sub-micron region and indicates the de-agglomeration process enables the silica particles to be dispersed more readily than silica without the benefit of this process.

A similar observation is made when sample A4 undergoes the de-agglomeration process. However, the transition to the narrower, sharper distribution of the agglomerate structure does not occur for the material processed via the structure modification process (sample D4).

In comparing the two graphs [Figures 3 and 4], the de-agglomerated sample L4 has a near unimodal distribution, in contrast to the A3, L3 sample series or the structure modified D4 sample.

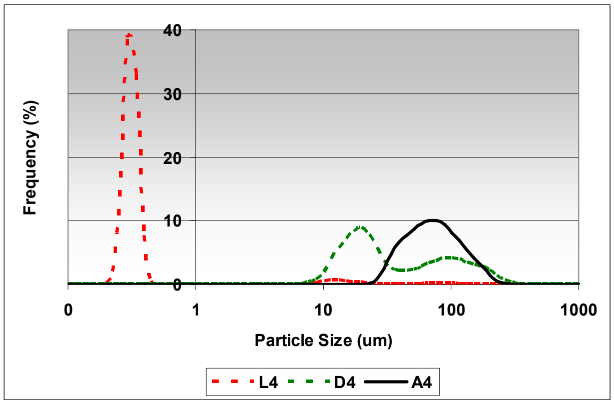

Figure 4. *Particle size distribution of DDS treated silicas*

3.3. Charge strength and charge distribution

Charge strength and charge distribution of the samples were measured as a function of mixing time. The results show the charge strength of the toner, without benefit of an external additive, and the effect silica addition has on the toner's charge behavior. The silica was incorporated with toner using a Turbula mixer rotating at 24 rpm for the time specified on the graph's x axis. Silica addition consistently increased the magnitude of the charge on the toner [Figure 5] as expected. The de-agglomerated, PDMS treated silica (sample L3) charges up faster than the standard A3 silica and is in agreement with previous work [1]. In the comparison between A4 and the de-agglomerated version, L4, it was surprisingly to see the responses are nearly identical. The high energy structure modified silica, D4, shows a quick charge-up followed by a level response with additional mixing time.

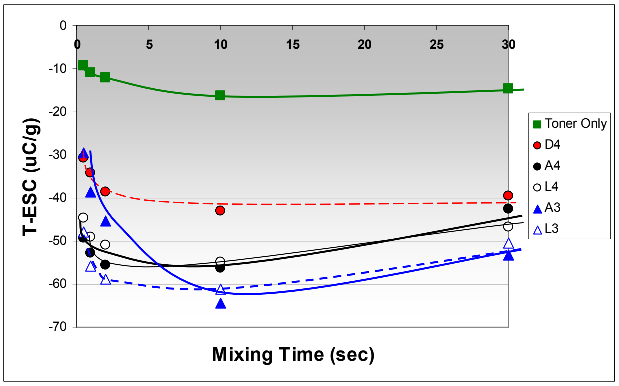

Figure 5. *Charge strength of toner:silica mixtures and response to mixing*

When the external additive has been uniformly dispersed on the toner surface, changes in charge distribution should be small. As seen in Figure 6, the de-agglomeration process has enabled the toner to have a consistent response after 5 and 30 minutes of mixing.

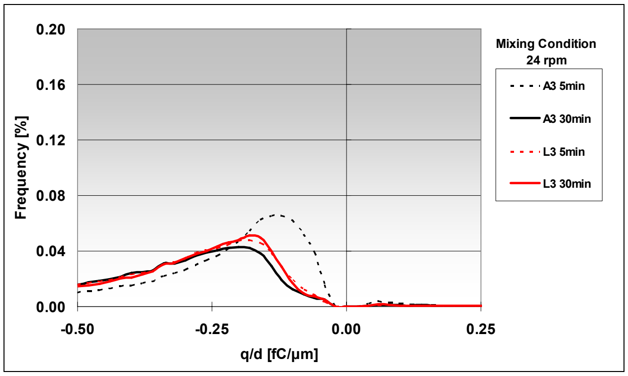

Figure 6. *Charge distribution of toner:silica mixtures and response to mixing*

In Figure 7, the charge distribution curves for DDS treated silicas are presented. The three DDS treated samples have comparable charge and distribution, relative to each other, after 5 minutes of mixing, indicative of the rapid and uniform dispersal of silica on the toner.

The distribution curves are sharper and narrower as compared to the AEROSIL® RY 300 series in Figure 6 (samples A3 and L3). After 30 minutes of mixing, the structure modified and de-agglomerated samples still have a narrow distribution yet both are broader slightly relative to the standard sample A4.

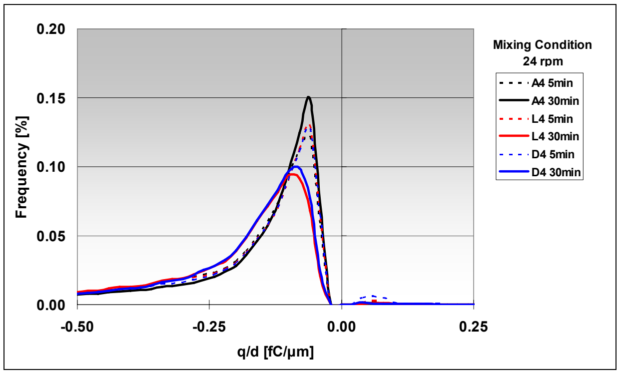

Figure 7. *Charge distributiion of toner: silica mixtures and response to mixing*

4. Conclusions

The treatment of the particles with a low energy de-agglomeration process consistently results in a fumed silica particle which disperses more readily and uniformly as seen in this work and a previous study[1]. The benefit of the de-agglomeration process does not appear dependent on the specific surface treatment (hydrophobicity) or surface area (particle size).

The de-agglomeration process as applied to the AEROSIL® R 972 and R 974 samples (sample L2 and L4) resulted in charge behavior characteristics similar to the standard sample in spite of observable differences in dispersibility. It is suspected that the mixing regimen was too aggressive resulting in potential differences in charge behavior being negated. A less aggressive incorporation method for the silica-toner mixtures will be investigated.

Of continued interest is the development of this low energy process and its implications on low Tg toners where the mixing regimen must impart minimal shear (and heat) to prevent toner deformation and silica embedding.

References

[1] Y. Amano, et al.; Comparison between de-agglomerated and traditional fumed silica external additives and their performance in toner formulations, NIP 25 (2009)

[2] Technical Bulletin Fine Particles, No. 11, 4th edition, "Basic Characteristics of AEROSIL® Fumed Silica", Degussa (2006).

[3] Paul Brandl, et. al., 24th International Conference on Digital Printing Technologies, Society for Imaging Science and Technology, pg. 1 (2008)

[4] Technical Information No 1222 "AEROSIL® Fumed Silica and AEROXIDE® Fumed Metal Oxides for Toner", Degussa (2006)

Author Biography

Leo Nelli is a scientist at Evonik Degussa within the Technology Solutions group. His work is focused on developing new approaches using fumed metal oxides, precipitated silica, colloidal silica and dispersions for multiple applications with an emphasis on the paper and printing industries. Leo has over 20 years experience in the paper and print industry, has been granted three US patents, 1 China patent and has additional applications pending.