

“Balanced aggregation – “snow man” shaped or tripod-like (fumed) particles that allow for better fixation on toner resin surfaces”

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Abstract

The aggregates for two types of fumed silica are compared with each other and with colloidal silica similar to one used as a spacer additive for toner. These examples of fumed silica differ in that one is made up of very large (sub-micron) sized primary particles with a low degree of aggregation while the second fumed silica example has a much higher, balanced, degree of aggregation. The aggregates of both forms of fumed silica disperse on a toner surface to result in effective particle diameters larger than the colloidal silica particle. Also, because of their fractal morphology, these dispersed aggregates are more likely to remain fixed on the toner surface as compared to the colloidal-based additives.

1. Introduction

In order to meet current trends in laser printing (“eco-printing”, “green” toners) external additives designed to function as spacers between toner particles are increasingly important to the toner formulator. The basic design concept behind spacers is that by anchoring very large silica particles on the toner surface a barrier is created that keeps toner-toner impact from embedding other surface additives (those needed to control powder free-flow and help obtain and maintain charge) – it might be imagined that the very large silica particles act as “bumpers” between impacting toner particles. Until most recently, the source of these spacer silicas has been from wet-process colloidal silica – subsequently hydrophobized and dried. Such silica has the attractive characteristic that the technology to grow large, spherical silica cores is well understood and the silica itself should be easy to disperse on the toner particle. As the interest in colloidal silica additives has grown, it has generally been thought that for spacers: “largest is best.” However, one key word in the earlier description is that the very large silica particles need to be “anchored” to the toner surface. This is not necessarily something that these high sphericity particles can guarantee – their water-based origin also leads to other potential weaknesses [1]. In this paper we examine the idea that aggregated particles would provide a better anchoring mechanism and if the aggregates possess sufficient effective volume on the toner surface they would also act efficiently as spacers. This concept is schematically illustrated in Figures 1 & 2.

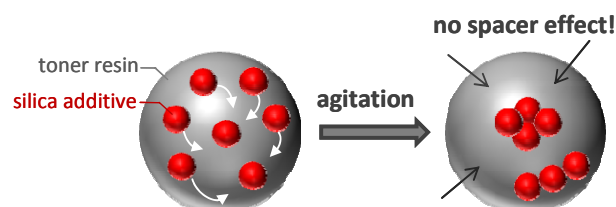


Fig. 1: Poor fixation of spherical silica particles on toner resin surface

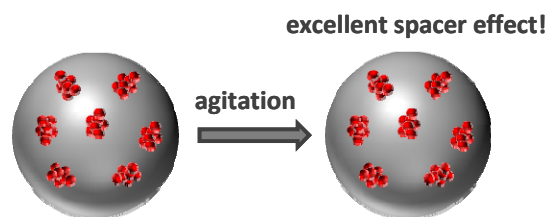


Fig. 2: Good fixation of snow man like silica particles on toner resin surface

2. Experimental procedures

2.1. Materials

Syntheses of the pyrogenic silicon dioxide examples featured in this paper have been described previously [2-4].

2.2. Methods

2.2.1 TEM investigation

Transmission Electron Microscopy (TEM teknolab.JEM-1011) studies were performed to ascertain average particle size and degree of aggregation for the untreated silica example materials.

2.2.2 Particle Size – Effective Aggregate Diameter

An indirect means was used to measure the effective aggregate diameter – an approximation of the aggregated particle size dispersed on the toner surface [5]. In this method a sample of the additive powder, Example 1, is mixed in ethanol for ten minutes with a 300W Ultrasonic homogenizer and the particle size distribution is measured (Horiba Dynamic Scattering Particle Size Distribution Analyzer LB-500). A sample of Example 2 was prepared in

a similar way (measured using laser scattering Horiba LA920) to examine its effective aggregate volume.

3. Results and discussions

Pyrogenic silicon dioxide has played an essential role in toner formulation for over 40 years. The first patented demonstration of the use of organic surface modified fumed silica to promote toner powder flow and stabilize triboelectric charge under environmental extremes was published in 1973 by Chatterji et al. [6]. Since then diverse particle type, size, and surface modifications have been employed throughout toner technology.

Control over the pyrogenic process is affected by several parameters: flame composition and raw material concentration being the most important. By exploring the far limits of these parameters two distinct pyrogenic silicas have been prepared, details of which are summarized in Table 1 and in TEM micrographs (Figures 3 & 4).

Table 1 – Spacer Silica Examples

	Example 1 “Fumed Sub-micron Silica”	Example 2 “Snow Man Particle”	Colloidal Example
Production Process	Pyrogenic Silica	Pyrogenic Silica	Wet-Process Silica
Structural Feature	Very Large 1° Particle/Low Aggregation	Large 1° Particle/ Very High Aggregation	Very Large, Spherical Silica Particle
Surface Area (BET) [m²/g]	40 ± 20	200 ± 50	20 ± 10
Average 1° Particle Size [nm]	80 - 100	40	110
Effective Particle Diameter [nm]	250	300	110
Approximate Aggregate Number	4 - 5	10	1

For Example 1 (Figure 3), conditions are chosen such that the primary particle size is maximized while as a consequence dramatically reducing the primary particle aggregation. The average primary particle size, as estimated through TEM imaging, is between 80 – 100 nm. Examination of powder dispersion and slurry dynamic scattering reveals that the aggregate is approximately 250

nm in diameter and thus on average consisting of 4 – 5 primary particles.

Under a different set of flame conditions an entirely different particle nature is achieved for Example 2 as shown in Figure 4. Here conditions are such that the degree of aggregation grows at the expense of primary particle size. As seen in the micrograph, the necking between primary particles is pronounced and, as is detailed elsewhere [4], there is a high degree of micro-porosity, unusual for fumed silica. The TEM images, suggesting a “Snow Man” or tripod shape, clearly indicate that the aggregates are bulky and would perform well as spacers on the toner surface.

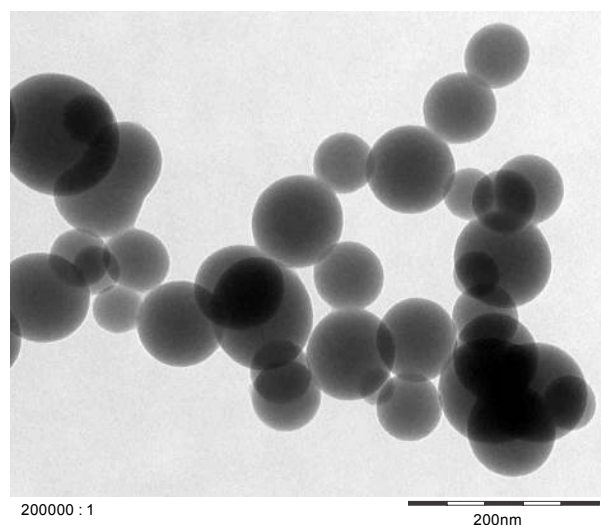


Fig. 3: TEM image of spherical, submicron-size fumed silica particles

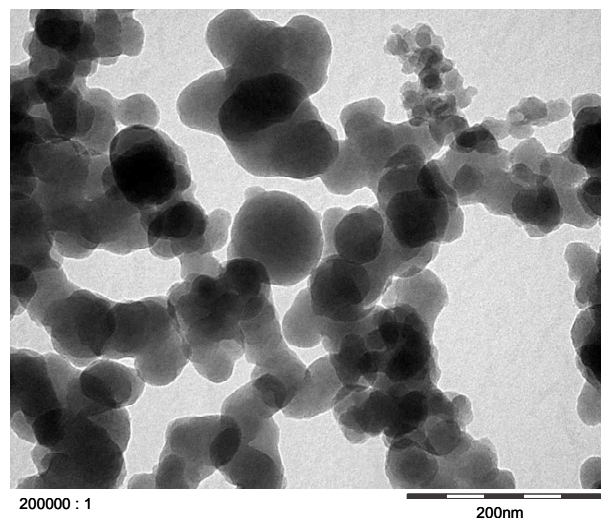


Fig. 4: TEM image of non-spherical, submicron-size fumed silica particles

3.1. Spacer effect

In order to investigate aggregate diameter in detail, particle size analyses were performed on slurries of the two types of fumed silica [7]. This slurry method approximates the process by which silica is dispersed on the toner surface and as seen in Table 1 the effective particle diameter is quite large – approximately 250 nm in Example 1 and 300 nm in Example 2. These values illustrate an important point: fumed silica, although frequently characterized by its primary particle size, is an aggregated material. It is well documented that break-down of these aggregates ultimately reaches limits dictated by achievable shear energies. Typically, the average aggregate size limit for most fumed silica grades is roughly 100 nm, although under special high energy processing this might be pushed somewhat lower – the important point is that primary particles exist only under very **unusual** circumstances. However, in the examples examined here the aggregates are truly sub-micron in dimension and in fact surpass the particle size for the Colloidal Example.

As a brief explanation, the Colloidal Example was chosen because it is similar to a frequently encountered commercial spacer additive. In Figure 5 a TEM image for similar sized wet-process colloidal silica is presented. In the figure both the very large primary particle diameter and the lack of aggregation are apparent.

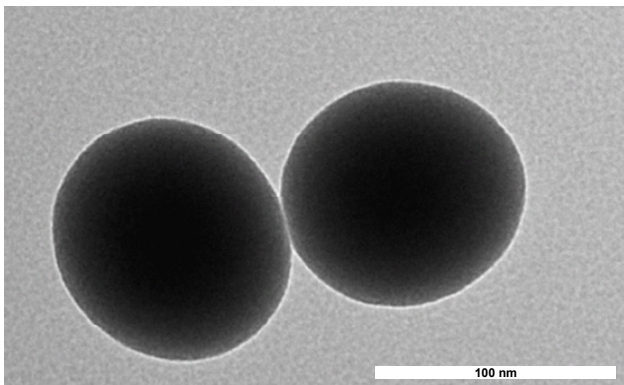


Fig. 5: TEM image spherical colloidal silica particle (note: scale is twice as small as Figures 3 & 4)

From this discussion it can be seen that to properly understand the effective particle size for fumed silica on a toner surface, one must consider the aggregate size. In the cases of Examples 1 & 2, this effective particle size is in actuality larger than the common commercial wet-process spacer silica. And as follows, surface modified grades of the “fumed sub-micron silica” have been prepared and tested successfully as a spacer additive [1]. Surface modification of Example 2 fumed silica has not been made available, yet it would be expected to perform well as a spacer additive.

Additive adhesion

Surface modified colloidal silica has been used as a spacer additive for well over a decade [8]. In that time toner formulators have learned to work with the additive’s strengths and weaknesses. Foremost among strengths: colloidal silica based additives perform well in extended print runs or with toner systems designed for lower fusing temperatures – they demonstrate the spacer effect for impacting or soft toner particles.

The low aggregation and high sphericity of the particles also means that the additive, generally, is easy to disperse. The downside of the dispersion ease can be however poor adhesion. Thus the particles can under tribo-mechanical conditions detach from the surface or migrate on the surface and aggregate with themselves – in both cases leading to less effective performance. The fumed silica particles, on the other hand, have an inherent fractal nature that means when dispersed on the toner surface have several points of contact – thus resisting detachment from the surface or migration across the surface (Figure 6). It would be expected that both spacer effect fumed silicas, Examples 1 & 2, would more firmly anchor to the toner surface and provide more robust performance vs. a colloidal-based system.

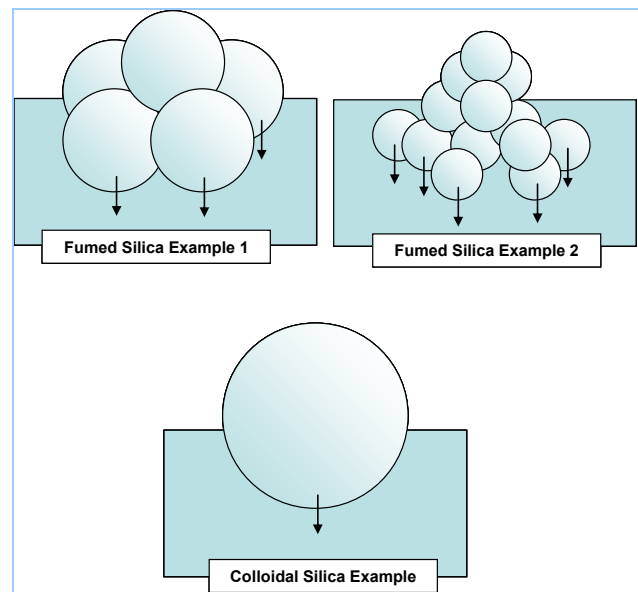


Fig. 6: Schematic illustration of the points of adhesion for the Spacer Silica Examples

4. Conclusions

Two fumed silica types, designed for their spacer effect, have been shown to have aggregate sizes well over 100 nm. Their effective particle sizes therefore are larger than that for a commercial colloidal-based grade frequently used as spacer additive for toners. The fractal nature of the fumed spacer grades also lead to the expectation that their adhesion to the toner surface would be greater than that for the

colloidal material – thereby providing greater robustness for toner treated with such additives.

5. References

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