

# New Submicron Silica Produced by the Fumed Process

Naohiro Naito<sup>1</sup>, Yuki Amano<sup>1</sup>, Yusuke Tosaki<sup>1</sup>, Robert Johnson<sup>2</sup>, Andreas Hille<sup>3</sup>; <sup>1</sup>NIPPON AEROSIL CO., LTD., Yokkaichi Mie Japan, <sup>2</sup>Evonik Degussa Corporation, Piscataway, NJ, USA, <sup>3</sup>Evonik Industries AG, Rheinfelden Germany,

## Abstract

Submicron silicas produced by fumed processes and their corresponding surface-modified counterparts are compared with respect to their applicability as external additives for electrophotographic toners. The principal metric for comparison is tribo-electrostatic charge (T-ESC) stability under extended activation periods. Experimental samples are surface-modified submicron silicas produced by a fumed process. These materials have sufficient hydrophobicity and can work as spacer particles to prevent the embedding of small particle size external additives. This spacer-attribute thereby eliminates problems with charge stability and flowability, especially under extreme environmental conditions, that can impact toner performance.

## 1. Introduction

For several decades, nano-structured fumed silica has been an essential external toner additive. Originally, the hydrophobicity and charge control of such additives were the primary benefits, but as technology has evolved another attribute became important: the spacer effect of surface-adherent silica particles has been found to be of critical importance. During the early decades, the average primary particle size of fumed silica available to the commercial formulator was in the range of 7-40 nm.

In this paper, a newly developed submicron silica (average primary particle size is ca. 80-100 nm) produced by a flame process is described. A unique feature of these large-particle additives is that they can be surface-modified with a broad variety of reagents, such as Hexamethyldisilazane (HMDS) or Polydimethylsiloxane (PDMS), among others. In the current study the properties and application data of fumed submicron silica will be presented.

## 2. Experimental procedures

### 2.1. Materials

#### 2.1.1 Core materials

The surface modified fumed silica used, supplied by Evonik Industries AG and NIPPON AEROSIL CO., LTD., was produced by established processes previously described [1]. The flame - or pyrogenic - process to make fumed silica has great versatility and can produce average primary particle sizes ranging from 7 to approximately 100 nm [2]. In this study the average primary particle size is 80-100 nm in diameter [Table 1].

**Table 1: BET and Particle size of fumed silica**

Sample designation	BET surface area [m <sup>2</sup> /g]	Average primary particle size [nm]
A12	200	12
A100	40	80-100

#### 2.1.2 Surface Modification Agent

Surface modified fumed silicas have long been used as toner external additives. In earlier technology, the surface-modified silica provided hydrophobicity to the toner particle and thereby ensured good powder flow. It soon became apparent that surface modification also greatly influenced the nature, speed, and stability of triboelectric charging for toner and therefore a variety of reagents have been employed [3]. Of the three most commonly encountered: DDS (dimethyldichlorosilane), HMDS (hexamethyldisilazane), and PDMS (poly-dimethylsiloxane) we will focus in this study on the HMDS and PDMS treatments. Additives with HMDS treatment are of interest because they impart high flowability for the toner and those with a PDMS treatment are utilized because of their high hydrophobicity.

**Table 2: Surface treated external additives used in this investigation**

	AEROSIL <sup>®</sup> RX 200	Sample A	Sample B
Core material/ Surface Treatment	A12/ HMDS	A100/ HMDS	A100/ PDMS
BET [m <sup>2</sup> /g]	140	30	18
Bulk Density [g/l]	ca. 40	ca. 130	ca. 120
Carbon Content [wt%]	2.0-3.0	0.1-1.0	3.0-4.0
Hydrophobicity [%]	> 98	> 98	> 98

#### 2.1.3 Toner formulations

The toner used for this investigation was a polyester negative-type black toner (8 micron average particle size). Three toner samples were prepared as summarized in table 3. Using a Henschel-type mixer, the toner and additive were pre-mixed for one minute at 600 rpm and followed with a second mixing step for three minutes at 3,000 rpm. For the B2 and B3 preparations, the submicron silicas, Sample A and Sample B, were pre-mixed with the toner alone and in the second, full-mix step the AEROSIL<sup>®</sup> RX

**Table 3: Composition of toner samples investigated in this paper**

Toner sample designation	Additive Amount (wt%)		
	AEROSIL <sup>®</sup> RX 200	Sample A	Sample B
B1	1.0	2.0	-
B2	1.0	-	2.0
B3	1.0	-	-

200 was added. This was done to prevent embedding of the small primary particle size silica, AEROSIL® RX 200 into the surface of the toner particle.

## 2.2. Methods

### 2.2.1 TEM investigation of core material of Sample A and Sample B

In order to check the average primary particle size and aggregation of fumed silica, Transmission Electron Microscopy (TEM) studies were performed.

### 2.2.2 FE-SEM analysis of toner mixture

A Field Emission-Scanning Electron Microscopy (FE-SEM) image was used to check dispersibility and embedding of fumed silica aggregates into the toner particle (Hitachi SEM S4100). Two samples were prepared. In the first, toner (2 g) was combined with a non-coated ferrite carrier (48 g) and agitated with a Turbula mixer for 1min. The second sample was mixed for 30min.

### 2.2.3 Dispersibility (particle size distribution)

The particle size distribution of the dispersed external additive on a toner particle surface is notoriously difficult to measure. We sought an indirect method that could approximate especially the dynamic process of additive dispersion.

In this method the particle size distribution is measured (Horiba Laser Scattering Particle Size Distribution Analyzer LA-920) for the external additive by itself in a liquid medium such as ethanol. Through careful control of time and shear conditions, the relative dispersibility of the silica can be ascertained.

### 2.2.4 Tribo-Electrostatic charge (T-ESC)

T-ESC was measured using a blow-off type electrostatic charge meter (Kyocera Chemical TB-220). 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 non-coated ferrite carrier by Turbula mixer before measurement.

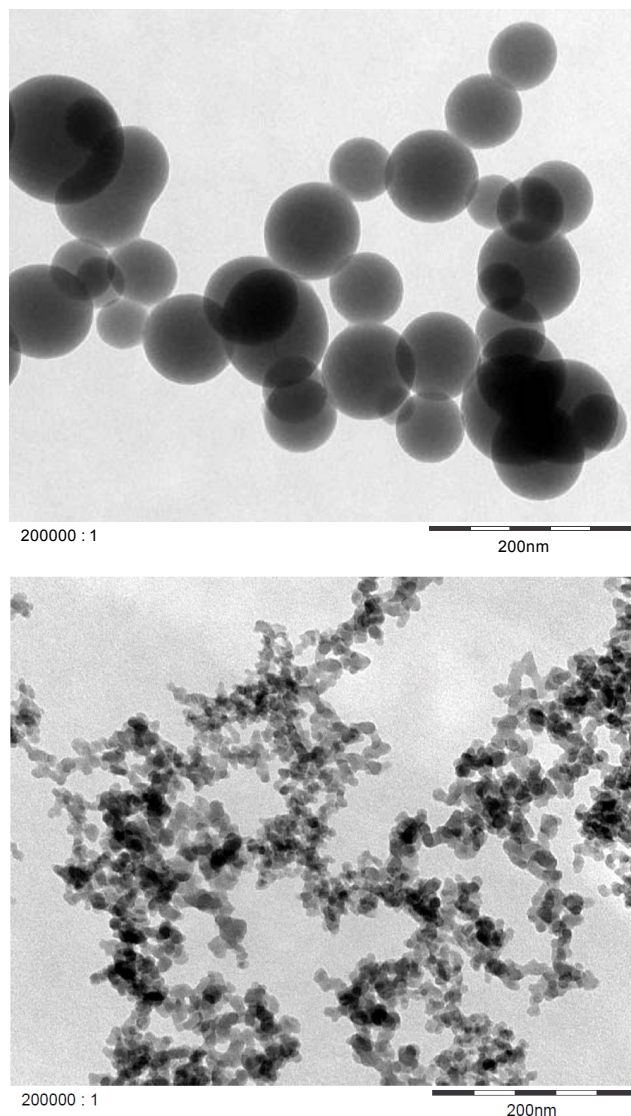
## 3. Results and discussions

### 3.1. TEM investigation

Figure 1 shows the TEM images of the core material for Sample A and Sample B, i.e. the hydrophilic silica prior to surface modification and contrasts that with the hydrophilic silica precursor for AEROSIL® RX 200.

The core material for Sample A and Sample B was evaluated using TEM and based on this optical determination the primary particle size was estimated as between 80-100 nm. In addition, we confirmed that this core material is aggregated to a much lower degree than other fumed silica external additives, such as AEROSIL® RX 200. Indeed, the core material for the submicron fumed silicas shows far less necking between primary particles

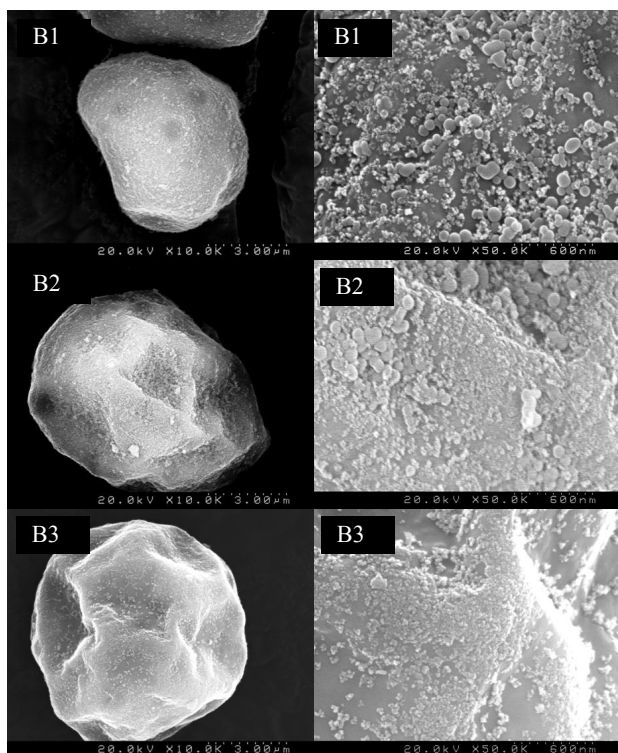
within the small aggregates than is commonly found, indicating that Sample A and Sample B should readily disperse on the toner surface.



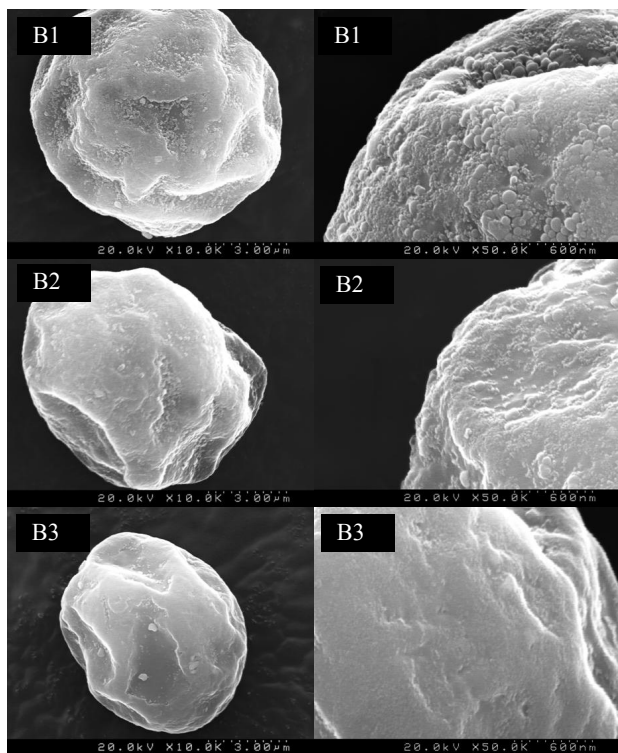
**Figure 1.** TEM images of core material of Sample A and Sample B vs. the core material for AEROSIL® RX 200.

### 3.2. FE-SEM analysis of toner mixture

Figure 2 shows the SEM images of the various silica combinations on the toner (B1, B2, & B3) after a short period of mixing (agitation time is 1min). The good dispersibility of all silicas is evident in the figure. Close examination of images for B1 and B2 shows the submicron silica mixed amongst a background of the widely dispersed small primary particle silica, AEROSIL® RX 200.



**Figure 2.** SEM images of B1 (Sample A + AEROSIL® RX 200), B2 (Sample B + AEROSIL® RX 200) and B3 (AEROSIL® RX 200) on the toner (agitation time is 1min)

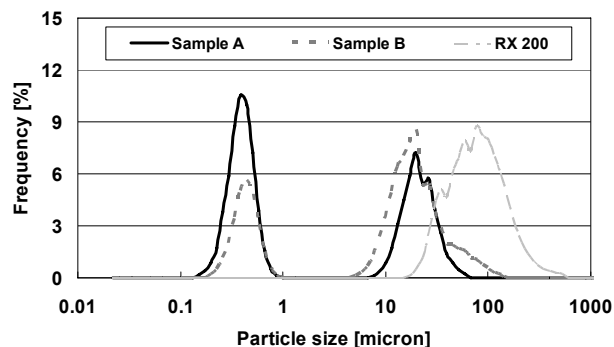


**Figure 3.** SEM images of B1 (Sample A + AEROSIL® RX 200), B2 (Sample B + AEROSIL® RX 200) and B3 (AEROSIL® RX 200) on the toner (agitation time is 30min)

The impact of greater shear on the toner is illustrated in the SEM images of Figure 3. After an agitation of 30 minutes the silica additives are still clearly visible in images B1 and B2 while in image B3, the smooth toner surface indicates that small fumed silica alone will be embedded under these mixing conditions. This microscopic evidence is a good indicator of the spacer-attribute possessed by that both submicron fumed silicas, Sample A and Sample B.

### 3.3. Dispersibility

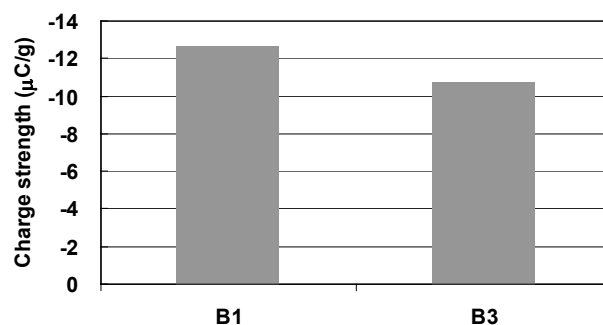
Using our indirect technique to characterize dispersibility, we measured the particle size distribution of Sample A and Sample B in ethanol vs. that of AEROSIL® RX 200 [Figure 4]. The combined data plot clearly shows that Sample A and Sample B can be dispersed more readily than AEROSIL® RX 200. Note that the regular grade shows a significant fraction of agglomerated silica (i.e. particle fraction between 10 and 80 micron) even after sonication.



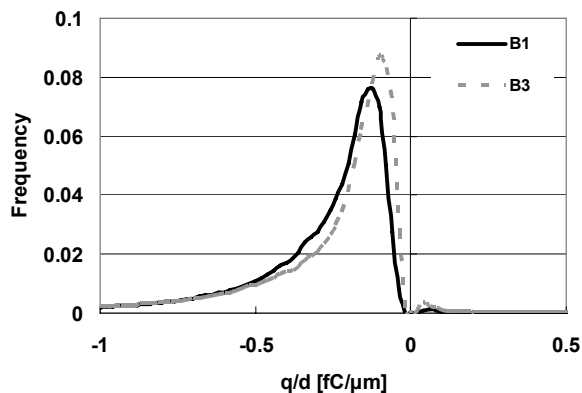
**Figure 4.** Particle size distribution of Sample A, Sample B and AEROSIL® RX 200

### 3.4. Charge strength and charge distribution

Charge strength and distribution of B1 and B3 were measured by tribo charge meter [Figure 5] and q-test [Figure 6]. These results show that Sample A increases charge strength for the toner to a relatively small extent and that the majority of the surface charge is regulated by the widely dispersed small silica additive, AEROSIL® RX 200.



**Figure 5.** Charge strength of B1 (Sample A + AEROSIL® RX 200) and B3 (AEROSIL® RX 200)



**Figure 6.** Charge distribution of B1 (Sample A + AEROSIL® RX 200) and B3 (AEROSIL® RX 200)

#### 4. Conclusions

Submicron fumed silica additives, Sample A and Sample B, both display a good spacer attribute. The function of these materials as spacers between toner particles was confirmed by

SEM studies under short and long mixing conditions. Both additives demonstrated an ability to ensure stability for charge characteristics, i.e. charge strength and charge distribution, under extensive shear conditions similar to those commonly encountered in commercial electrophotographic printing.

#### References

- [1] Technical Bulletin Fine Particles, No. 11, 4<sup>th</sup> edition, "Basic characteristics of AEROSIL® fumed silica", EVONIK (2006).
- [2] Paul Brandl, et al., 24th International Conference on Digital Printing Technologies, Society for Imaging Science and Technology (IS&T), pg. 1, (2008)
- [3] Technical Information No. 1222 "AEROSIL® Fumed Silica and AEROXIDE® Fumed Metal Oxides for Toner", EVONIK (2011).

#### Author Biography

*Naohiro Naito received his Masters degree in Materials Science and Engineering from Nagoya Institute of Technology (Japan) in 2003. He joined Lion Corporation in the same year. Since 2008, he has worked for NIPPON AEROSIL Co., Ltd. (Japan). His work has focused on research of fumed silica / fumed metal oxides and their application as external additives for toner.*