# The charge properties and durability of new submicron silica

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## Abstract

*Submicron silicas produced by hybrid process and their corresponding surface-modified counterparts are compared with respect to their applicability as external additives for electro-photographic 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 hybrid process. The hybrid materials have sufficient hydrophobicity and can work as spacer particles to prevent the embedding of small particle size external additives. Further characteristics and advantages for this new external additive type will be presented. The surface modification improves charge stability and the spacer effect, especially under extreme environmental conditions, that can impact toner performance.*

## 1. Introduction

In a previous study [cf. NIP29 proceedings][1] we discussed a type silica as external additive for toner, which is produced by a hybrid process, that combines the particle characteristics of the colloidal silica process (i.e. mono-disperse submicron particles with high sphericity) with the surface modification flexibility of flame-pyrolysis produced silica. It was shown that because these materials exhibit strong hydrophobicity and function well as spacer particles to prevent the embedding of smaller particles, they can be considered valuable tools for toner formulators.

It was also shown that the hybrid process silica, while displaying an excellent "spacer effect" like standard colloidal-type silica, surpasses those materials with its superior hydrophobicity and resistance to moisture pick-up.

In this paper it is described, how charge modification of hybrid silica affects the durability and fixation on the toner surface. A unique feature of this hybrid silica is the flexibility to apply a broad variety of surface-modification reagents, such as Hexamethyldisilazane (HMDS) or Polydimethylsiloxane (PDMS), combined with amino-silane and others. In the underlying study the effect of charge control on the charge properties and durability of hybrid silica will be presented.

## 2. Experimental procedures

### *2.1. Materials*

#### *2.1.1 Core materials*

The core materials used in this study were produced by well-known techniques of the previously outlined sol-gel process (here called "hybrid-process"). We further distinguish the wet process samples by their modes of surface modification: for the hybrid case, techniques similar to those applied to fumed silica were employed. However, the final product contains higher levels of residual moisture.

**Table 1: Characteristics of hybrid process silica**

| Item | Characteristics of Hybrid process silica |
|---|---|
| Core material process | Sol-gel |
| Surface modification | Variety |
| Residual moisture content | Low |
| Particle size distribution | Narrow |
| Ease of dispersion | Good |
| Primary particle size [nm] | 110±30 |

#### *2.1.2 Surface Modification Agent*

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 tribo-electric charging for toner and therefore a variety of reagents has been employed. [2] In this study we will focus on the HMDS (hexamethyldisilazane) and PDMS (poly-dimethylsiloxane) 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]

**Table 2: Physicochemical properties of hybrid process silica**

| | Hybrid-Process Sample | |
|---|---|---|
| Surface Treatment | HMDS | PDMS |
| BET [$m^2$/g] | 15-30 | 15-25 |
| Bulk Density [g/l] | ca. 400 | ca. 500 |
| Carbon Content [wt%] | 0.3-0.6 | 1.0-1.5 |
| Hydrophobicity [%] | > 70 | > 90 |
| Moisture [%] | < 0.5 | < 0.5 |

Moreover, in this study, to achieve stable charge strength and durability, we applied amino-silane with a surface treatment modifier (ex. HMDS and PDMS). Adding amino-silane further promotes better charge control properties compared to using only a single surface modification agent. [Table 3.]


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**Table 3: Properties exerted by the surface treatment modifier**

| Surface treatment | Silica's Properties |
|---|---|
| HMDS<br>+<br>Amino-silane | Flow-ability, Hydrophobicity<br>+<br>Charge control |
| PDMS<br>+<br>Amino-silane | Cleaning, Hydrophobicity<br>+<br>Charge control |

#### *2.1.3 Toner formulations*

The toner used for this investigation was a polyester negative-type black toner (8 micron average particle size). Samples were prepared by mixing silica (3g) and toner (97g) using a Henschel-type mixer. Using a Henschel-type mixer, the toner and additive were pre-mixed for one minute at 600 rpm and subsequently mixed again for three minutes at 3,000 rpm.

### *2.2. Methods*

#### *2.2.1 TEM investigation of core material of hybrid process silica*

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

#### *2.2.2 Particle size distribution (Dispersibility)*

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 of the silica is measured by Horiba Dynamic Light-Scattering Particle Size Analyzer (LB-500). LB-500 calculates the particle size distribution from the frequency intensity distribution of light by projecting a laser beam to the particles dispersed in a liquid, which is scattered by the particles. It is based on the so-called dynamic light scattering theory. In liquid the particles are moving irregularly 3nm ~ 6 μm (Brownian motion).

Irradiating a laser beam having a constant frequency in the particle and observing the scattered light from the particles, Evaluation liquid was prepared mixing silica (1g) and water (99g) using a homogenizer (Premix Co.,Ltd.) for 10 minutes at 3000rpm.

#### *2.2.3 Tribo-Electrostatic charge (T-ESC)*

T-ESC was measured using a blow-off type electrostatic charge meter (Kyocera Chemical TB-220). Each surface treated silica sample (0.1 g) was combined with a non-coated ferrite carrier (50 g) and agitated with a Turbula mixer from 5 to 30 minutes. All sample preparation and measurements were carried out in a constant temperature/constant humidity room.

#### *2.2.4 FE-SEM analysis of toner mixture with hybrid process silica*

A Field Emission-Scanning Electron Microscopy (FE-SEM, Hitachi SEM 4100) image was used to check dispersibility and embedding of fumed silica aggregates into the toner particle.

Samples were prepared by combining toner with hybrid submicron silicas (3wt %). [See. 2.1.3 formulation]

As a confirmation method of silica fixation and durability on the toner surface, a second mixing step performed, varying from 3 min to 60 min.

## 3. Results and discussions

### *3.1. TEM investigation*

Figure 1 shows a TEM image of the core silica with a relatively large primary particle size, which was used to prepare the hybrid-process material. The core is not aggregated as the typical fumed silica. Through optical analysis of the TEM image, the average primary particle size was estimated at approximately 110 nm. In addition, we confirmed that this hybrid-process submicron silica is aggregated to a much lower degree than the commercially available colloidal submicron silica. As final details, the hybrid-process core appears similarly spherical, mono-disperse, and with equivalent average primary particle size (approximately 110 nm) indicating that both samples should be easily dispersible on the toner surface.

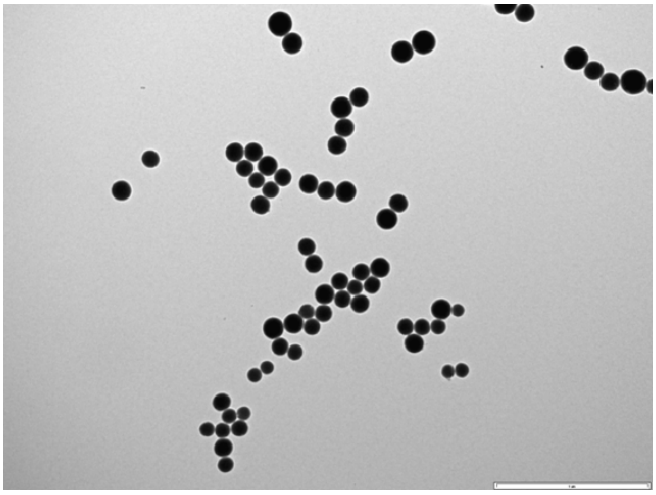

***Figure 1**. TEM images of hybrid process silica.*

### *3.2. Dispersibility*

To confirm the primary particle size of our TEM observation, we measured the particle size distribution of hybrid process silica by using particle evaluation equipment [2.2.2] [Figure 2]. The combined data plot clearly shows that hybrid process silica can be dispersed more effectively. And this result shows that hybrid process silica exists as a primary particle or two and three particle aggregated.

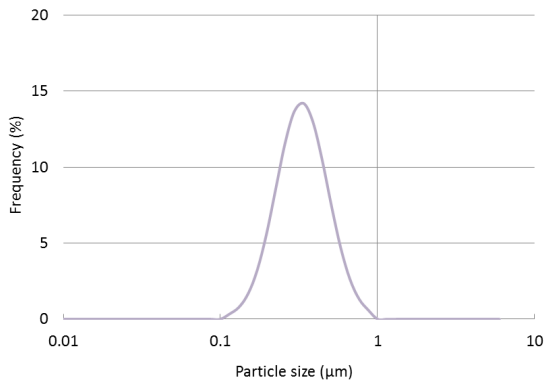


***Figure 2**. Particle size distribution of hybrid process silica.*

### 3.3. Physicochemical properties of samples

**Table 4: Physicochemical properties of hybrid process silica in this investigation**

| Surface Treatment | HMDS | HMDS + Amino-silane | PDMS | PDMS + Amino-silane |
|---|---|---|---|---|
| BET [$m^2/g$] | 30 | 15-30 | 25 | 15-25 |
| Carbon Content [wt%] | 0.3-0.6 | 0.3-0.8 | 1.0-1.5 | 1.5-2.5 |
| Hydrophobicity [%] | > 70 | > 60 | > 90 | > 70 |
| Moisture [%] | < 0.5 | < 0.5 | < 0.5 | < 0.5 |

The added amino-silane does not drastically change the carbon content. The Hydrophobicity is reduced slightly. Loss in drying remains on same level as without amino-silane. In conclusion the addition of amino-silane, does not alter the physicochemical properties of these hybrid process silica significantly.

### 3.4. Charge strength and charge stability

Charge strength of hybrid silica were measured by a tribo charge meter [Figure 3]. These results show that the charge strength of hybrid silica can be controlled by changing the reagent. As expected surface modification with HMDS or PDMS show a dramatic influence on the charge characteristics, enhancing adhesion to the toner surface.

We can widely control the charge characteristics by application of various surface modification agents. As expected, surface modification has a strong impact on the additive charge and, clearly, surface modification brings an important charge capability to spacer-effect silica.

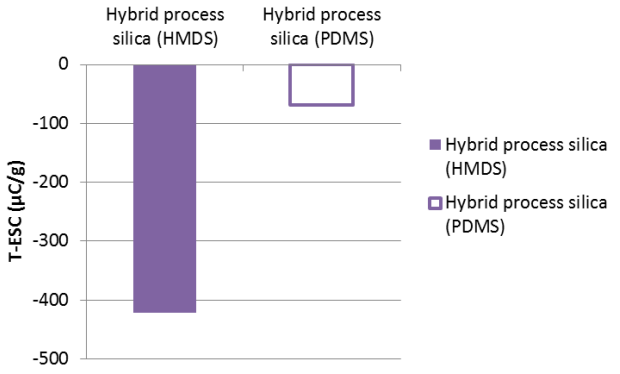


***Figure 3**. Charge strength (T-ESC value) of hybrid process silica treated by HMDS and PDMS*

T-ESC value of hybrid silica treated by HMDS showed strong negative charge, and that of hybrid silica treated by PDMS showed low negative charge. By changing the surface modification agent, the charge value can be controlled between strong negative charge and low negative charge.

Moreover, in this study, the charge value can be controlled widely from high negative to high positive value by combining amino-silane with HMDS or PDMS. The charge value depends on the quantity of amino-silane additive used [Figure 4]. Various charge characteristics can be achieved by applying different ratios of surface modification agents.

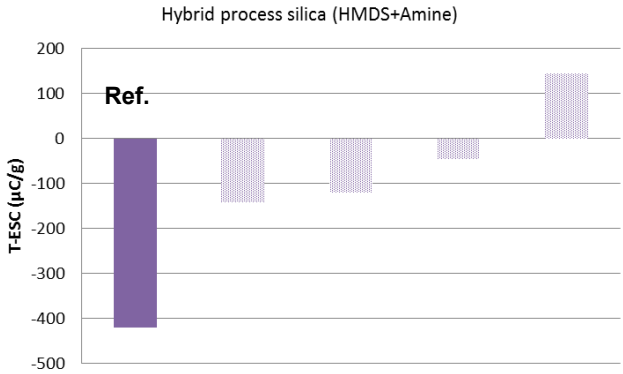


***Figure 4**. Charge strength (T-ESC value) trends of hybrid process silica treated by HMDS with adding each amino-silane.*

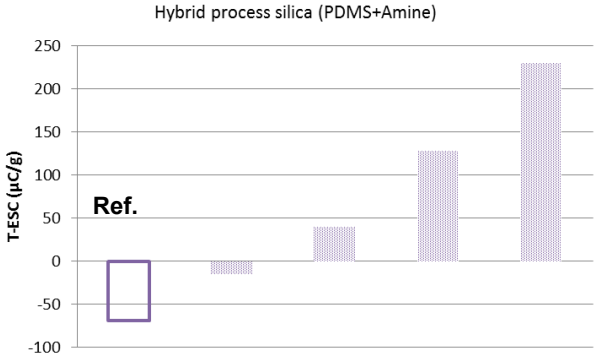


***Figure 5**. Charge strength (T-ESC value) trends of hybrid process silica treated by PDMS with adding each amino-silane.*


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The charge durability of hybrid silica treated with HMDS and amino-silane was shown. The charge value (T-ESC) was analyzed after mixing of silica and carrier for 5 min, 10 min and 30 min [Figure 6]. The results confirm that the charge remains almost constant for hybrid silica treated with HMDS and amino-silane.

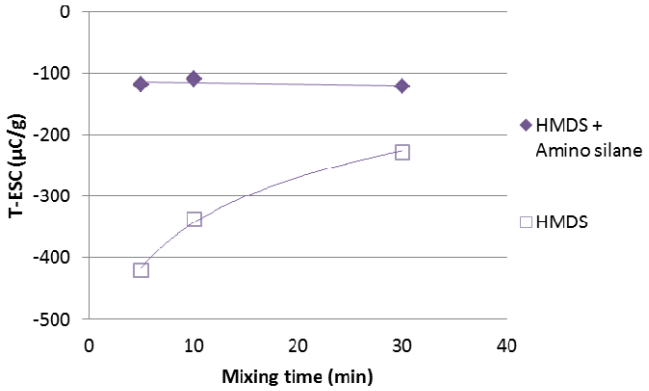


***Figure 6**. Charge durability of hybrid silica treated by HMDS with Amino-silane from 5 min to 30 min.*

### 3.5 FE-SEM analysis of toner mixture

Figure 7 shows the SEM images of hybrid silica dispersibility on the toner surface after a short period of mixing (agitation time is 4min). It is particularly evident in this SEM picture that hybrid submicron silica can function well as spacer. Because of hybrid process silica size, even after mixing, hybrid process silica can work as a spacer, and this spacing keeps the smaller silica from embedding beneath the toner surface even under shearing conditions. The good dispersibility of all silicas is evident in the figure.

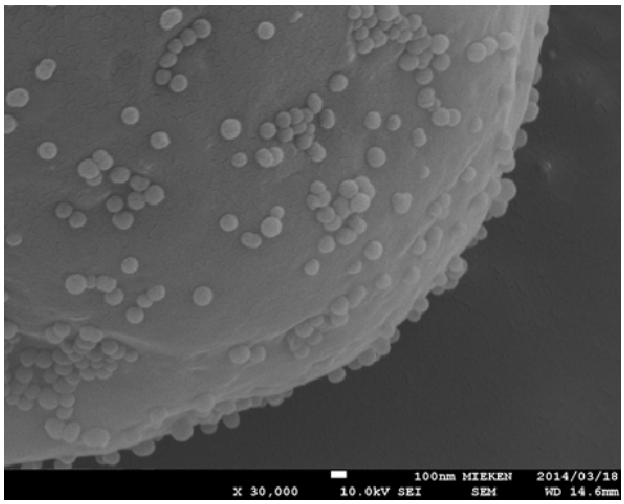


***Figure 7**. SEM images of hybrid silica on the toner (agitation time: 4 min)*

### 3.6. Silica adhesion durability on toner surface after agitation

Further evidence of good dispersiblity and adhesion durability on the toner surface (not embed into toner resin) of the hybrid submicron silica is shown in Figure 8. Several images of Fig.8 were taken for silica/toner samples after a short period of mixing [agitation time: (A 3min), (B 10min), (C 30 min), (D 60 min).]

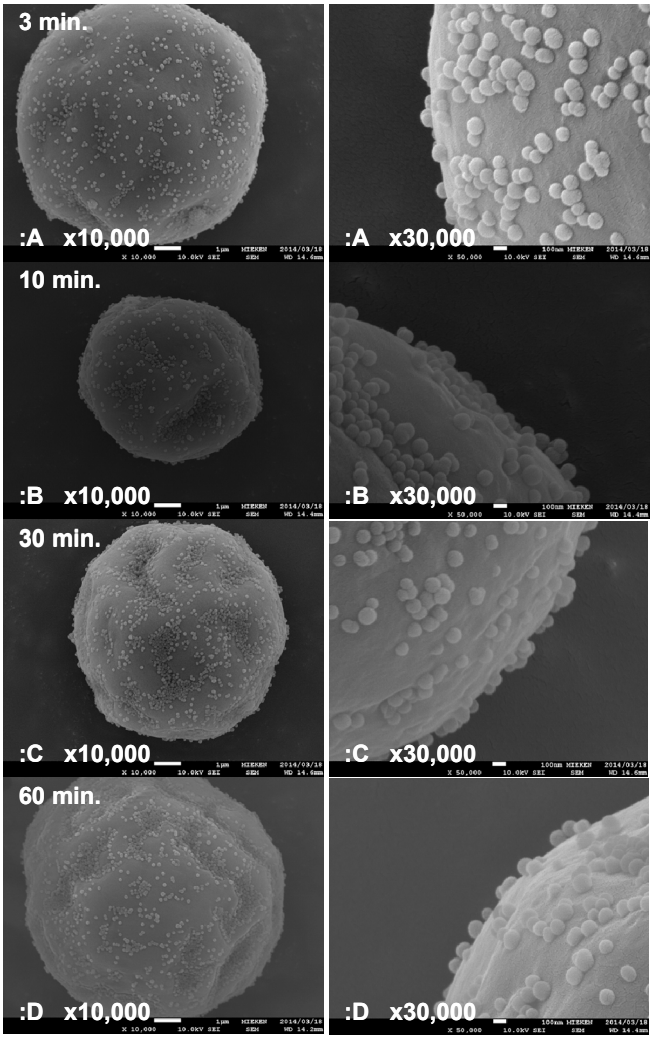


***Figure 8**. SEM images of durability of hybrid process silica on the toner (agitation time is from 3min (A) to 60min (D))*

The impact of greater shear on the toner is illustrated in the SEM images of Figure 8. After an agitation time of 60 minutes (image D) the hybrid silica still adheres to the toner surface, which is clearly visible in image D. The evaluation results are a good indicator of the spacer effect exhibited by the hybrid silica on the toner surface after some time of agitation. Because hybrid process silica is not prone to embedding into the toner after mixing, the characteristics of hybrid silica on toner do not change much over time after agitation.

## 4. Conclusions

Hybrid silica additives showed a good spacer effect on the toner surface. Moreover the good spacer effect can be maintained for even after long agitation time. The function of this hybrid silica as spacers between toner particles was confirmed by SEM observation for short and long agitation conditions. Hybrid process silica treated with HMDS or PDMS together with amino-silane demonstrated a very good stability of charge characteristics, i.e. charge strength (T-ESC value) and charge durability. The charge characteristics can be controlled even under extensive shear conditions similar to those commonly encountered in commercial electro-photographic printing.

## References


[1] Yusuke Tosaki, et al., 29th International Conference on Digital Printing Technologies, Society for Imaging Science and Technology (IS&T)

[2] Technical Information No. 1222 "AEROSIL® Fumed Silica and AEROXIDE® Fumed Metal Oxides for Toner", EVONIK (2011).

[3] Naohiro Naito, et al., 28th International Conference on Digital Printing Technologies, Society for Imaging Science and Technology (IS&T)

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## Author Biography

*Yusuke Tosaki received his Master degree in Materials Science and Engineering from Gifu University (Japan) in 2005. He joined AICA Kogyo Co.,Ltd. in the same year. Since 2007, he has worked for NIPPON AEROSIL Co., Ltd. (Japan). His work has focused on research of fumed silica and hybrid silica / fumed metal oxides and their application as external additives for toner ant others.*


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